Book of Abstracts

LYON - FRANCE

MAY 30TH - JUNE 3RD 2010

WELCOME FROM THE CHAIR

Formerly known as the Natural Gas Conversion Symposium (NGCS), the triennial Novel Gas Conversion Symposium has brought together the world's leaders in synthesis gas production and utilisation since 1987 to share information on the latest trends in research and technology development in these fields. The ninth edition of the Novel Gas Conversion Symposium ("NGCS 9") takes place in Lyon, France from May 30th to June 3rd, 2010, in the prestigious "Cité des Congrès" along the Rhone river. With more than 450 scientists, researchers, and industry executives from over 40 countries participating, NGCS 9 continues the tradition of high quality academic, industry, and technical interaction for which the symposia series is well known.

Lyon has a rich historical and cultural heritage, with its 2000 year-old historic centre recognised as a UNESCO World Heritage Site. Today, this brilliant city is also fully immersed in 21st century modernity. In this respect, the choice of Lyon to host the NGCS 9 was largely motivated by its dense and dynamic industrial surroundings with large refineries, petrochemical, chemical and gas industries, strongly networked with high level public and private research centres. This is perfectly illustrated by the three co-organizers of the event, IRCELYON-CNRS-UCBL for academia, IFP for public and private research centres and Total for large companies.

This Symposium Book of Abstracts includes the short abstracts of 5 plenaries lectures, 19 keynotes lectures, 115 oral presentations and 364 posters, which have been peer reviewed before selection. The extended abstracts are presented in the USB memory stick. These documents reflect the extreme interest of our worldwide scientific community for the topics encompassed by the symposium:

1. Natural gas and biogas purification (filtration, CH_4/CO_2 separation, sulfur and nitrogen removal, etc.)
2. Production of synthesis gas from natural gas, coal, biomass or waste; clean coal; syngas chemistry: purification, water gas shift (WGS), reverse WGS and synthetic natural gas (SNG)
3. Synfuels: Fischer-Tropsch synthesis, gas to liquids, coal to liquids, biomass to liquids, methanol, higher alcohols and DME
4. Direct-indirect conversion of methane to oxygenates, olefins, aromatics; C_1-C_3 intermediates to chemicals
5. Energy (IGCC, catalytic combustion, hydrogen production from C_1-C_4 gases) and novel concepts for feedstock activation (plasma, dense membrane, etc.)
6. Technical-economical studies, technology demonstration, industrial processes and plant operation

Following the excellence requirements of all the NGCS events, particular care has been taken to balance academia and industrial participation, as well as to offer the opportunity to participate to high quality scientists from all over the world (28 countries are represented for oral presentations).

We would like to gratefully acknowledge here the efficient help of the NGCB, the ISAB, the scientific and local committees and all the institutions and companies which have supported the symposium.

We wish all the participants a brilliant meeting and do hope that science and friendship will merge again to continue the strong tradition of the NGCS series.

Claude Mirodatos (IRCELYON-CNRS-UCBL)
Francis Luck (Total)
Slavik Kasztelan (IFP)

NGCS 9 Chairmen

SYMPOSIUM COMMITTEES

Local Organising Committee

Claude Mirodatos (IRCELYON, CNRS-UCBL, FR) - Chairman
Francis Luck (TOTAL, FR) - Chairman
Slavik Kasztelan (IFP, FR) - Chairman
Yves Schuurman (IRCELYON, CNRS-UCBL, FR) - Vice-Chairman
Marta Bausach (IRCELYON, CNRS-UCBL, FR) - Vice-Chairman and Conference Secretariat
Michel Lacroix (IRCELYON, CNRS-UCBL, FR)

Natural Gas Conversion Board (NGCB)

Ad Punt (Shell, NL) - Chairman
Anders Holmen (Norwegian University of Science & Technology, NO) - Vice-Chairman
Per Bakkerud (Haldor Topsøe, DK) - Secretary
Theo Fleisch (Fuel Conversion Solutions, USA) - Treasurer
Gordon Kelly (Johnson Matthey Catalysts, UK) - Chairman - IFC
Enrique Iglesia (University of California at Berkeley, USA) - Chairman - ISAB
Carlos Apesteguia (INCAPE, AR)
Xinhe Bao (Dalian Institute of Chemical Physics, CN)
Alex Bell (University of California at Berkeley, USA)
Krijn de Jong (University of Utrecht, NL)
Jay Labinger (California Institute of Technology, USA)
Claude Mirodatos (IRCELYON, CNRS-UCBL, FR)
Rob Motal (Chevron, USA)
Sebastian Muschelknautz (Linde, DE)
Jens Rostrup-Nielsen (Haldor Topsøe, DK)
Domenico Sanfilippo (IT)
Lanny Schmidt (University of Minnesota, USA)
David Trimm (CSIRO, AU)
Wataru Ueda (Hokkaido University, JP)
Steve Venables (Sasol, SA)

Programme Committee (topics coordinators)

David Farrusseng (IRCELYON, CNRS-UCBL, FR)
Marco Tagliabue (ENI S.p.A, IT)
Anders Holmen (Norwegian Univ. of Science and Technology, NO)
Yves Schuurman (IRCELYON, CNRS-UCBL, FR)
Andrei Khodakov (UCCS, Univ. des Sciences et Technologies de Lille, FR)
Jean-Luc Duplan (IFP Lyon, FR)
Alain Kiennemann (Univ. Louis Pasteur, Ecole Chimie Polymeres et Materiaux, FR)
Mikhail Yu Sinev (Semenov Institute of Chemical Physics, Russian Academy of Sciences, RU)
Daniel Duprez (LACCO, CNRS, Poitiers, FR)
Narcis Homs (Faculty of Chemistry, Univ. of Barcelona, ES)
Cristina Maretto (Total, FR)
Robert Motal (Chevron, USA)
Arend Hoek (Shell, NL)

INDEX

NGCS
LYON
2010
9

Novel Gas Conversion Symposium

C1-C4 chemistry: from fossil to bio resources

INDEX ACCORDING TO NGCS 9 SESSIONS

AWARD RECIPIENT

PLENARY LECTURES

KEYNOTE PRESENTATIONS

ORAL PRESENTATIONS

Session I - Natural gas and biogas purification (filtration, CH_4/CO_2 separation, sulfur and nitrogen removal, etc)

Session II - Production of synthesis gas from natural gas, coal, biomass or waste; clean coal; syngas chemistry: purification, water gas shift (WGS), reverse WGS and synthetic natural gas (SNG)

Session III - Synfuels: Fischer-Tropsch synthesis, gas to liquids, coal to liquids, biomass to liquids, methanol, higher alcohols and DME

Session IV - Direct-indirect conversion of methane to oxygenates, olefins, aromatics; C_1-C_3 intermediates to chemicals

Session V - Energy (IGCC, catalytic combustion, hydrogen production from C_1-C_4 gases) and novel concepts for feedstock activation (plasma, dense membrane, etc)

Session VI - Technical-economical studies, technology demonstration, industrial processes and plant operation

Session VII - FP7 EU projects

POSTER PRESENTATIONS

Session I - Natural gas and biogas purification (filtration, CH_4/CO_2 separation, sulfur and nitrogen removal, etc)

Session II - Production of synthesis gas from natural gas, coal, biomass or waste; clean coal; syngas chemistry: purification, water gas shift (WGS), reverse WGS and synthetic natural gas (SNG)

Session III - Synfuels: Fischer-Tropsch synthesis, gas to liquids, coal to liquids, biomass to liquids, methanol, higher alcohols and DME

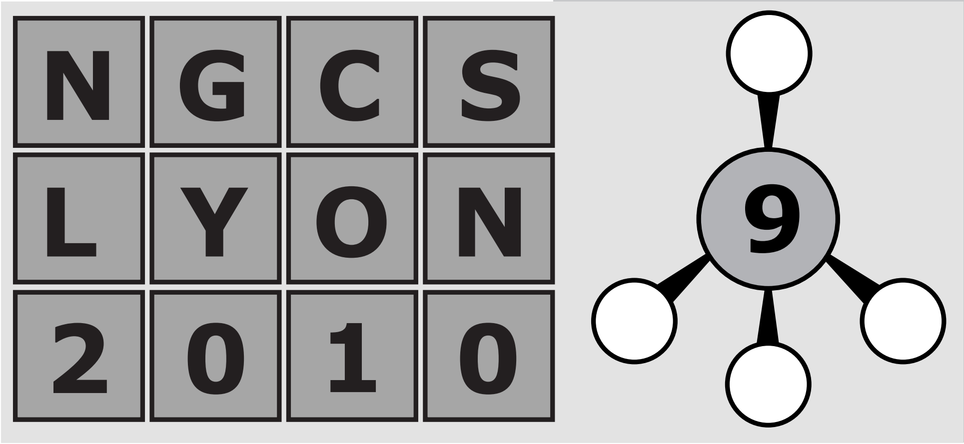
Session IV - Direct-indirect conversion of methane to oxygenates, olefins, aromatics; C_1-C_3 intermediates to chemicals

Session V - Energy (IGCC, catalytic combustion, hydrogen production from C_1-C_4 gases) and novel concepts for feedstock activation (plasma, dense membrane, etc)

Session VI - Technical-economical studies, technology demonstration, industrial processes and plant operation

AUTHORS INDEX

PLENARIES, KEYNOTES, ORAL AND POSTERS INDEX



Novel Gas Conversion Symposium

C1-C4 chemistry: from fossil to bio resources

AWARD RECIPIENT

Supported Cobalt Catalysts for Fischer-Tropsch Synthesis

Anders Holmen
Department of Chemical Engineering, Norwegian University of Science & Technology (NTNU),
Sem Saelands vei 4, NO-7491 Trondheim, Norway. *holmen@chemeng.ntnu.no*

At specific process condions, the support, promoters and the size and structure of the metal particles determine the performance of Co-based FTS catalysts. Some recent results obtained in our laboratory of these effects on alumina supported Co catalysts and on model catalysts such as Co supported on carbon nanofibers will be reported. For most Co catalysts the turnover rate is constant and independent of the system provided that the Co particle size is larger than a certain value. The catalyst design, however, has a large influence on the C_5^+ selectivity. Recent advances in catalyst characterization have made *in situ* techniques an important tool for studies of the FT Synthesis.

NGCS
LYON
2010
9

Novel Gas Conversion Symposium
C1-C4 chemistry: from fossil to bio resources

PLENARY LECTURES

PL1

Structure sensitivity of methane and CO activation

R.A. van Santen
Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, P.O. Box 513, 5600 MB Eindhoven,
The Netherlands. *r.a.v.santen@tue.nl*

Methane activation of importance as one of the elementary reaction steps in the steam reforming reaction. CO activation is essential to hydrocarbon chain formation reactions as the Fischer-Tropsch reaction. Detailed information is becoming available on the particle size dependence of these reactions.

Whereas the rate of the methane reforming reaction uniformily increases with decreasing transition metal catalyst particle size, activity as well as selectivity of the Fischer-Tropsch reaction steeply decreases below a particular nanoscale particle size.

We will argue that the unique particle size dependence of the methane reforming reaction is specifically due to the fast elementary rate of the surface reaction that forms CO. The size dependence of the Fischer-Tropsch reaction relates to the need for CO activation to be fast compared to the chain growth and chain termination reaction steps. These two reactions will be used to illustrate a general theory of transition metal structure sensitive and insensitive catalytic reactions [1].

Due to the access of computational catalysis to transition state structures and corresponding free energies it has become clear that structure dependence in transition metal catalysis has an intrinsic relation with the nature of the chemical bonds to be activated.

[1] R.A. van Santen, M. Neurock, S.G. Shetty, Chem. Rev. 2010, 110, 2005–2048.

PL2

NGCS 9 – Extended abstract template
Direct Methane Conversion Routes to Chemicals and Fuels

J.L.G. Fierro
Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie 2, Cantoblanco, 28049 Madrid, Spain - *jlgfierro@icp.csic.es*

Abstract

Methane is particularly attractive C-containing source because of the large reserves of natural gas, but the technology for their conversion to chemicals and liquid fuels remains elusive due to the extremely high stability of C-H bonds of the CH_4 molecule. The control of methane chemistry would provide chemicals and liquid fuels, bringing an alternative to petroleum and enabling the use of plentiful, though often remote, natural gas that today is uneconomical to transport to market. In addition, It could also reduce the tremendous green house effect of CH_4 (23 times higher than equivalent volume of CO_2) or flaring of gas associated with petroleum production and might even provide a means to upgrade landfill gas.

Many concepts have been developed for improving the industrial processes which convert methane into olefins, higher hydrocarbons and gasoline by both indirect and direct conversion processes. However, these industrial processes involve expensive separation steps and/or require high temperatures, usually above 600ºC, with the subsequent consumption of energy. Direct methane conversion eliminates the need, and consequently improves the economy of the process. However, reactions of methane generally have high activation energy and, once activated, it is difficult to stop the reaction from going further than desired products [1-3]. On the other hand, the non-favourable thermodynamics for methane self-interaction reactions indicates that without strong oxidants, it would difficult to convert methane into higher hydrocarbons at moderate temperatures using conventional catalytic approaches.

Currently, two large-scale, viable approaches for converting methane to liquid hydrocarbons are being used: the methanol-to-gasoline (MTG) route, and the Fischer-Tropsch (FT) route. Both of these processes begin with the production of synthesis gas from methane, which is a high-temperature, endothermic, costly operation. Concepts for directly converting methane to a liquid hydrocarbon fuel without reforming methane to synthesis gas conceptually appear attractive. A few have reached the stage where a preliminary evaluation directed at understanding the critical process factor is possible. Conceptually, direct methods should have a distinct economic advantage over indirect methods, but to date, no direct processes have been reached a commercial stage. Product yields are generally small [4] while operating in a single-pass mode, which makes separations difficult and costly.

This lecture covers alternatives developed along last two decades aimed to convert methane into valuable products by avoiding the highly energy demanding steam reforming process. The methane decomposition is firstly considered as a way to produce COx-free hydrogen to be used in fuel cells. Thermal cracking, oxidative coupling, selective partial oxidation, conversion of methane to aromatics, methane activation and functionalization via homogeneous catalysts, halogenation/oxyhalogenation and biomimetic conversion routes are briefly examined.

Each alternative has its own set of limitations. However, economical separation of useful products is common to all with the most important issues being the separation of oxygen from air in that processes which require C-H bond activation with oxygen. Extensive utilization of methane for the production of fuels and chemicals appears to be near, but current economic uncertainties limit the amount of research activity and the implementation of emerging technologies is expected to come.

Although oxidative routes based on the use of dioxygen, if successful, would be of enormous industrial significance, it appears that a suitable active and selective catalyst has yet to be designed. Conversions involving selective chlorination are more attractive as far as activity and selectivity are concerned, but the problems associated with the use of highly corrosive environments remain. Methane coupling to unsaturated hydrocarbons may be useful provided that more active and selective catalysts can be discovered, but, of course, a plentiful source of such unsaturated feed is required in order to exploit this approach.

Recent patents on plasma-assisted methane conversion processes appear quite promising to obtain simultaneously acetylene and liquid fuels. Notable projections emerge when looking at the combined processes in which one endothermic reaction is coupled with an endothermic one. Proper management of the heat may result in overall autothermal operation, thus offering economical incentives for process development.

In summary, many recent attempts have shown promise but the challenge of designing suitable selective and active catalysts remains.

References

[1] Tabata, K.; Teng, Y.; Takemoto, T; Suzuki, E.; Banares, M.A.; Pena, M.A.; Fierro, J.L.G., *Catal. Rev.-Sci. Eng.* **2002**, 44, 1.
[2] Xu, Y.; Bao, X.; Lin, L., *J. Catal.* **2003**, 216, 386.
[3] Choudhary, T.V.; Aksoylu, E.; Goodman, D.W., *Catal. Rev.-Sci. Eng.* **2003**, 45, 151.
[4] Lunsford, J.H., *Catal. Today* **2000**, 63, 165.

PL3

Research on Thermochemical Conversion of Biomass at the National Renewable Energy Laboratory

Robert M. Baldwin
National Bioenergy Center, National Renewable Energy Laboratory, Golden CO USA
Robert.baldwin@nrel.gov

Introduction

The thermochemical platform at the National Bioenergy Center, National Renewable Energy Laboratory (NREL) is primarily concerned with research on conversion of biomass to transportation fuels using non-biological techniques. Research is conducted in the following five areas relating to thermochemical conversion:
1) Biomass gasification
2) Syngas cleaning
3) Syngas conversion to transportation fuels
4) Biomass pyrolysis
5) Upgrading of pyrolysis liquids

In addition, the Platform supports activities in both technoeconomic and sustainability analysis for thermochemical conversion processes.

Research on biomass gasification focuses on applications of low-temperature atmospheric pressure technologies using both steam and recycle gas as the fluidizing medium. The work is primarily carried out in NREL's 20 kg/h process development unit; a schematic of the system is shown in Figure 1.

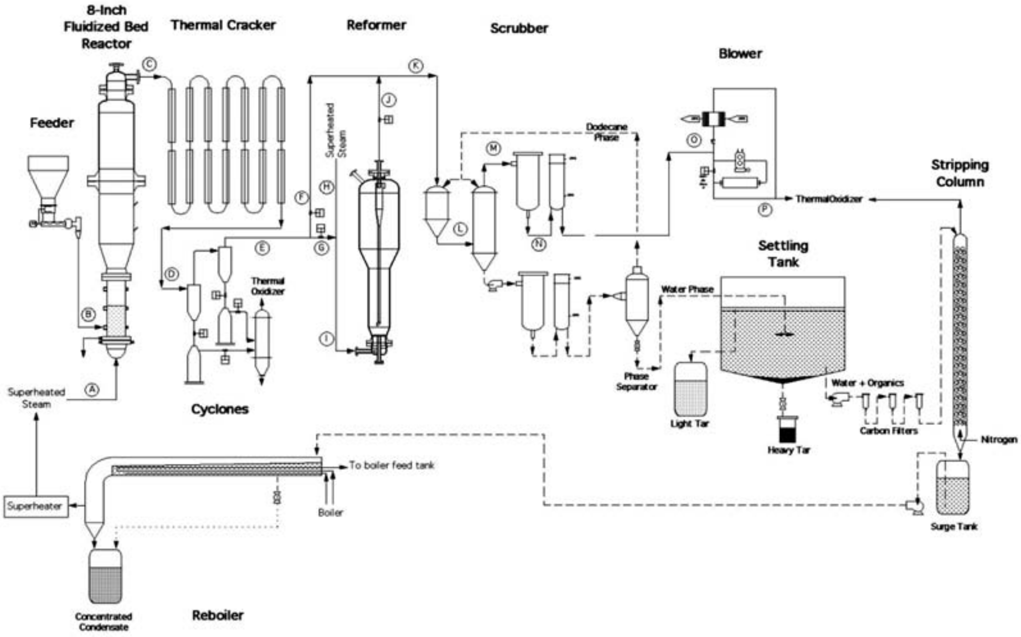


Figure 1: Process Development Unit

The PDU is very flexible, and can be used for studies of both gasification and pyrolysis in either the fluidized bed or entrained-flow mode of operation. Research on syngas cleaning has focused on development of a novel fluidizable tar reforming catalyst. This catalyst has shown to be very effective in destroying tars (>99%) and reforming methane (>90%) in a high-sulfur environment. Research on development of high-temperature sulfur sorbents is also underway at NREL. A novel manganese-based sorbent that removes H_2S from 1,000 to 1 ppmv in simulated syngas has been developed and tested on biomass-derived syngas in the PDU. Syngas conversion research is currently aimed at improving catalysts for one step conversion of biomass-derived gas to ethanol. Work on improving sulfide catalysts and rhodium based materials is in progress using simulated syngas and authentic biomass-derived syngas from the PDU. Future work will investigate other fuels with an emphasis on high-density infrastructure-compatible materials – specifically hydrocarbons.

Research on biomass pyrolysis is aimed at catalytic pyrolysis with the goal of improving pyrolysis yields and improving the quality of the primary liquid products. These studies are being carried out in batch microreactors, and in bench-scale semi-continuous units as well. Investigations of upgrading pyrolysis vapors by catalytic and non-catalytic means is underway. Use of zeolites to deoxygenate pyrolysis vapors and manufacture transportation-range hydrocarbon fuel molecules from fractionated biomass is currently in progress. Work on stabilization of pyrolysis oil by hot-gas filtration of the primary pyrolysis vapors is also underway.

Research on upgrading of pyrolysis liquids is primarily focused on the examination of mild hydrotreating to reduce oxygen and TAN in order to create an acceptable refinery feedstock and/or blendstock. Work is also underway to investigate the integration of biomass-derived pyrolysis oils and fractions of hydrotreated oils with the petroleum refining infrastructure.

Laboratory research is supported by detailed work on technoeconomic and sustainability analyses for alternative biomass-to-fuels strategies. Detailed process models are developed using the best available material and energy balance information and unit operations models created at NREL and elsewhere. These models are used to identify cost drivers which then form the basis for research programs aimed at reducing costs and improving process efficiency while maintaining sustainability and an overall net reduction in greenhouse gases.

PL4

Award lecture

Supported Cobalt Catalysts for Fischer-Tropsch Synthesis

Anders Holmen

Department of Chemical Engineering, Norwegian University of Science & Technology (NTNU),
Sem Saelands vei 4, NO-7491 Trondheim, Norway. *holmen@chemeng.ntnu.no*

At specific process condions, the support, promoters and the size and structure of the metal particles determine the performance of Co-based FTS catalysts. Some recent results obtained in our laboratoty of these effects on alumina supported Co catalysts and on model catalysts such as Co supported on carbon nanofibers will be reported. For most Co catalysts the turnover rate is constant and independent of the system provided that the Co particle size is larger than a certain value. The catalyst design, however, has a large influence on the C_5^+ selectivity. Recent advances in catalyst characterization have made *in situ* techniques an important tool for studies of the FT Synthesis.

PL5

Enabling small scale GTL

Jan J. Lerou[1]
[1]Velocys, Inc., 7950 Corporate Blvd., Plain City, Ohio, USA, *lerou@velocys.com*

1. Introduction

Microchannel process technology offers process intensification, in the form of enhanced heat and mass transfer, to a wide range of chemical reactions. This paper discusses the application of microchannel technology to the production of ultra-clean synthetic fuels. These fuels, which are one-to-one replacements for petroleum derived fuels, are produced by passing synthesis gas (syn-gas), a mixture of carbon monoxide and hydrogen, over a cobalt or iron catalyst; a process known as Fischer-Tropsch (FT) synthesis for its German inventors. The most efficient path to syn-gas isthe conversion of natural gas via steam methane reforming (SMR). Both the SMR and FT benefit from the process intensification offered by microchannel technology, resulting in smaller, less costly processing hardware; thus, enabling cost effective production of synthetic fuels from smaller facilities, appropriate for stranded and associated gas resources, both on and offshore. The products from FT processes can be upgraded into diesel or synthetic paraffinic kerosene, or simply blended with crude oil for transport to the world market. Leading companies in this field included Velocys, Inc. (USA), Compact GTL (UK), and Chart Industries (USA).

2. Experimental

In 2008, a Velocys pilot scale microchannel FT reactor, utilizing an advanced catalyst supplied by Oxford Catalysts (UK), exceeded 4,000 hours time on stream. This reactor operated steadily, achieved over 70% carbon monoxide (CO) conversion, and showed minimal catalyst deactivation after thousands of hours of operation.Throughout the run, counterproductive methane make stayed below 10%, which is comparable with commercial FT processes. At the writing of this abstract, final preparations are being made for the start-up of a demonstration scale 100 liter per day microchannel FT reactor at a biomass gasification plant in Austria [1].

Microchannel process technology has also been shown to intensify SMR. Current industrial reforming box furnaces operate with contact times around 1 second. Reforming in microchannel architecture allows this to be reduced to about 5 milliseconds, 200 times faster. Microchannel SMR has been scaled up to a pilot reactor with a capacity of 235 Nm^3/hour. This unit operated successfully for over 500 hours with excellent performance on the process side, and no carbon build-up inside the microchannels.

3. Results

Compared to conventional tube style reactors, the reaction passages in microchannel FT have orders of magnitude smaller characteristic dimensions, which greatly improve heat and mass transfer. This allows optimal temperature control across the catalyst bed, which maximizes catalyst activity and life, and leads to far higher reactor productivity. A comparison of productivity, defined as barrels/day of FT product per tonne of reactor mass, is shown in Figure 1 [2,3,4]. Microchannel SMR offers similar advantages, reducing reactor size by up to 90%.

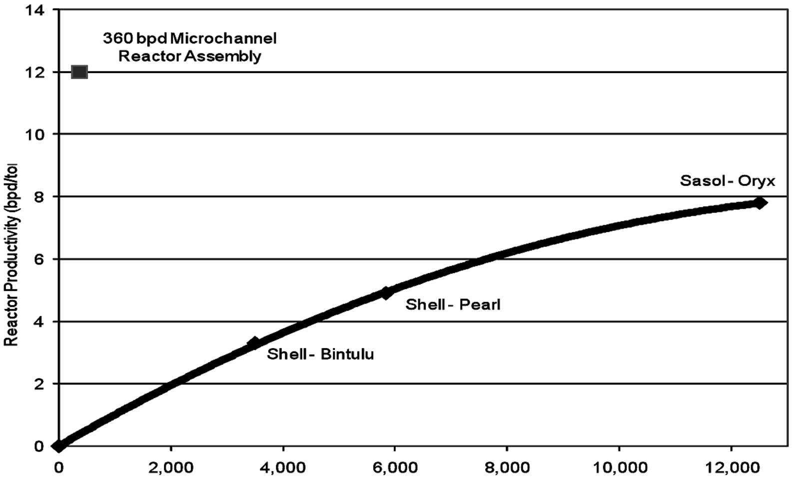


Figure 1- Microchannel FT improves reactor productivity and achieves economy of scale at lower capacity

4.Discussion

Due to improved volumetric and catalytic productivity, micro-channel SMR and FT enables lower capital and operating costs compared to conventional gas-to-liquids (GTL) processes. Because conventional GTL technologies are not economically viable at small scale, the current focus is on large, land-based natural gas fields, such as those in Qatar. However, only about 6% of the world's gas fields are large enough to sustain a GTL plants with 10,000 bpd or greater capacity. Reducing the production rate to 2,000 bpd makes approximately 40% of gas fields viable sources. Microchannel technology permits economic production at this smaller scale [5].

In addition to SMR and FT, microchannel processing technology is being applied to the final step of a synthetic fuel process – hydrocracking. At Velocys, a development program funded by U.S. Department of Agriculture and others is currently underway and producing encouraging results, including demonstrating 30 times higher reactor and catalyst productivity.

5. Conclusion

Due to a number of factors, including volatile oil prices, and concern about global climate change, alternative fuels are receiving an unprecedented level of attention. These include FT based processes that can convert abundant natural gas into synthetic crude, which can be blended and shipped with crude oil. Furthermore, the application of microchannel technology to SMR and FT enables cost effective production at the smaller-scales appropriate for both onshore and offshore GTL facilities for stranded and associated gas reserves.

As noted above, a field demonstration of Velocys microchannel FT, utilizing a slipstream of biomass derived syngas will begin operations in May 2010 in Austria. A second demonstration of Velocys technology, slated for 2011 in Brazil, will be of an integrated GTL process, which includes both microchannel FT and microchannel SMR [6]. Compact GTL is also nearing commercialization, and is on schedule to deliver a GTL pilot plant to Petrobras in 2010 [7].

6. References

[1] Microchannel reactors: Demonstrating the future for distributed biofuels production, Velocys, November 2, 2009

[2] K. T. Jarosch, A. L. Tonkovich, S. T. Perry, D. Kuhlmann, Y. Wang, Reactors for Intensifying Gas-to-Liquid Technology, in Microreactor Technology and Process Intensification, ACS Symposium Series n 914, September 2005.

[3] R.L. Espinoza, A.P. Steynberg, B. Jager, A.C. Vosloo, Applied Catalysis A: General 186 (1999) 13–26

[4] Font Freide, Joep J. H. M.; Collins, John P.; Nay, Barry; Sharp, Chris, American Chemical Society, Division of Petroleum Chemistry, Preprints, v 50, n 2, March, 2005, p 149-151

[5] N. Jones, T. Tveitnes, "The M-flex LNG Carrier Design", GASTECH 2008, Bangkok, Thailand

[6] GTL Agreement with Petrobras and Partners, Velocys, February 9, 2010

[7] CompactGTL on schedule to deliver Petrobras pilot plant in 2010, Compact GTL, January 2010

Novel Gas Conversion Symposium

C1-C4 chemistry: from fossil to bio resources

KEYNOTES PRESENTATIONS

KN1

Catalytic activation and functionalization of methane and ethane

Johannes A. Lercher
Technische Universität München, Department of Chemistry and Catalysis Research Institute
Lichtenbergstrasse 4 85748 Garching Germany, *johannes.lercher@ch.tum.de*

Options to activate the C-H bonds in methane and ethane will be compared using two successful approaches activating the C-H bond of methane and functionalizing the molecule, i.e., the oxidative chlorination of methane to methyl chloride and the conversion of methane to methanol. The two routes take opposite approaches to introduce a functional group. For the generation of methyl chloride, chlorine is introduced via electrophilic substitution, while for the methanol case the formed methoxy groups is reacted with an OH- in a nucleophilic elimination step. The reactivity of methane and ethane will be compared on other chloride and oxide based catalysts.

KN2

Core-shell-like Capsule Catalyst for One-Step Synthesis from Syngas: Spatial-Confined Effect and Shape Selectivity

Noritatsu TSUBAKI, Yoshiharu YONEYAMA, Jun BAO, Xingang LI
Email: tsubaki@eng.u-toyama.ac.jp

This keynote speech proposed a new concept of multiple functional catalyst with core-shell structure developed by our group. Syngas firstly passes through zeolite shell membrane to reach inner core catalyst, forming normal paraffins. Before leaving catalyst, all these linear hydrocarbons must be isomerized at acidic sites of zeolite.The prepared capsule catalysts show excellent performance for the direct synthesis of isoparaffins based on the FTS reaction.

KN3

C-H Bond Activation on Isolated Metal Centre on Oxide Surfaces

Christophe Copéret
Université de Lyon, Institut de Chimie de Lyon, C2P2 – Equipe COMS (CNRS – CPE –UCBL) 43 Bd du 11 Novembre 1918 69616 Villeurbanne Cedex, France, *E-mail : coperet@cpe.fr*

The conversion and the functionalisation of alkanes are important processes in chemistry, because the main source of carbons is still petroleum, and reducing the number of steps is an important objective within the context of sustainable development. Here, we will discuss the low temperature C-H activation of alkanes on isolated metal centres of surfaces on oxide materials leading to organometallic species and/or intermediates as a key step for alkane conversion processes such as hydrogenolysis, alkane metathesis including methane cross-metathesis and the non-oxidative coupling of methane.

KN4

Novel Catalysts for Low steam to Carbon Ratio (S:C) Applications

Sam French, Martin Fowles, Peter W Farnell and Richard J. Oldman[a]
Johnson Matthey Catalysts, Belasis Ave., Billingham, Cleveland TS23 1LB, UK.
[a] University College London, Dept. of Chemistry, 20 Gordon Street, London, WC1H 0AJ
sam.french@matthey.com

Understanding and generating catalytic solutions that allow the adoption of the optimal process flowsheet conditions is a major driver for industrial catalytic R&D. The business incentives to provide the best reactor and best catalyst combination for the given problem have resulted in novel engineering designs and led to materials being produced. In this paper Gas Heated Reforming technology for the production of syn gas at low S/C ratio will be discussed. The financial and environmental benefits of this technology are outlined. Examples will be presented where technical targets have been identified and solutions addressed using fundamental research techniques.

KN5

Recent developments in the Fischer-Tropsch synthesis over supported cobalt catalysts

Edd A. Blekkan
Dep. of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway,
edd.blekkan@chemeng.ntnu.nor

The talk will address some fundamental and applied issues linked with supported cobalt catalysts and their application in the Fischer-Tropsch synthesis (FTS). The main emphasis will be on natural gas as a feedstock, but issues specific to the conversion of syngas from biomass gasification will also be touched upon. The ambition is to describe the state of the art in selected areas. The fundamental issues include the mechanism, particle size effects, and the influence of water on rate and selectivity. Finally some applied aspects of the FTS will be introduced, especially focusing on BTL, including syngas issues and introducing microstructured reactors.

KN6

Cobalt particle size effects on catalytic performance for the production of synthesis gas from ethanol steam reforming – Smaller is better.

A.L. Macedo, L.V. Mattos, J.P. den Breejen, J.H. Bitter, K.P. de Jong, **F.B. Noronha**
Instituto Nacional de Tecnologia -, Av. Venezuela 82, CEP 20081-312, Rio de Janeiro - Brazil, Tel. (55-21) 2123 1177;
e-mail: fabio.bellot@int.gov.br

The aim of this work was to study the influence of cobalt particle size on the performance of carbon nanofibers (CNF) supported Co catalysts on SR of ethanol. A significant effect of the Co particle size on the SR of ethanol over Co/CNF was observed. The TOF increased with decreasing Co particle size, which was ascribed to the increasing number of unsaturated cobalt surface atoms. Moreover, the smallest Co particle sizes showed the lowest catalyst deactivation, which was due to a lower amount of carbon deposition and less sintering.

KN7

Deactivation and regeneration of cobalt based Fischer-Tropsch synthesis catalysts

J. van de Loosdrecht[1], I.M. Ciobica[2], M.M. Hauman[1], J.M. Maloka[1], D.J. Moodley[1], A.M. Saib[1], B.H. Sigwebela[1], R.A. van Santen[2], C.J. Weststrate[2], J.W. Niemantsverdriet[2]
[1]Sasol Technology (Pty) Ltd, PO Box 1, Sasolburg 1947, South Africa, *Jan.vandeLoosdrecht@sasol.com*
[2]Schuit Institute of catalysis, Eindhoven University of technology, Postbus 513, Eindhoven 5600 MB, The Netherlands

Cobalt based Fischer-Tropsch synthesis (FTS) catalysts are at the heart of the Gas-To-Liquids (GTL) process. Due to the cost of both cobalt and noble metals, which are often used as promoters, extended catalyst life is required to make the process economically feasible. Typically, all cobalt-based FTS catalysts exhibit deactivation with time-on-stream. A fundamental understanding of the deactivation mechanisms at play during FTS is key to extending catalyst lifetime. A three step regeneration process, i.e. (1) dewaxing (2) oxidation and (3) reduction was found to adequately reverse these deactivation mechanisms resulting in a significant increase in catalyst life

---

KN8

Emerging technologies for olefins production from non-conventional feedstock's: MTO/OCP technology demonstration

W. Vermeiren
Total Petrochemicals, Rue d'industrie 52, B-1040 Brussels, Belgium
walter.vermeiren@total.com

Due to depleting petroleum feedstock and increasing cost for its production, the industry needs new technologies to transform non-conventional feedstock into light olefins, like ethylene and propylene. Many of these technological steps are new for the olefin-producing industry and invoke a game-changing way of thinking. The different ways to obtain light olefins from non-conventional feedstock will be reviewed and in particular the one using methanol. Total Petrochemicals and UOP are currently demonstrating in a fully integrated semi-commercial demonstration plant, the conversion of methanol into light olefins by means of MTO and OCP process and subsequent polymerisation into polyethylene and polypropylene.

KN9

CH_4/CO_2 separations for gas upgrading by adsorption and membranes processes

A. Méthivier, G. Pirngruber
IFP Lyon, Rond Point de l'Echangeur de Solaize, BP 3, 69360 Solaize, *alain.methivier@ifp.fr*

Natural gas, syngas or biogas need to be upgraded in order to fulfil the market and CO_2 emissions specifications.
Regarding these new challenges, the CH_4/CO_2 separation is very important and the appearance of new materials offers the opportunity for introducing breakthrough in adsorption and membrane processes. New research strategies and methodologies have to be used. Our presentation focuses on examples of advanced methodologies used in order to establish a link between process specifications and adsorbent properties for their customization for CH_4/CO_2 separation.

KN10

Pearl GTL, Development of an Integrated World Scale Complex in Qatar

Rob Overtoom, Pearl Technology Mgr
Qatar Shell Service Company W.L.L, PO Box 3747 Doha Qatar, e-mail: *Rob.R.M.Overtoom@shell.com*

Pearl GTL is a 140,000 bbl/d fully integrated upstream/downstream GTL complex under construction in Qatar. The presentation will highlight the design philosophy for technology scale-up of the complex; touch base on project execution with multiple contractors through construction to commissioning and start-up. Subsequently, insight will be given into engineering challenges related start-up and operation of a such fully integrated complex.

KN11

Bridging the gap between lab and practice in ethane oxidative dehydrogenation

Angeliki A. Lemonidou
Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus, 54124 Thessaloniki, Greece,
e-mail: *alemonidou@cheng.auth.gr*

Catalytic oxidative dehydrogenation (ODH) of ethane is an attractive alternative route for ethylene production. The catalytic properties of NiO in ethane ODH can be tuned with doping, according to the nature of the dopant in Me-promoted NiO catalysts. The dopants can increase or decrease the unselective excess electrophilic oxygen species of NiO, leading to respectively reduced or enhanced activity in the selective conversion of ethane to ethylene. Ni-Nb-O mixed metal oxide catalysts have been proved promising for further scale-up, exhibiting an ethylene yield of 46% at 400°C for the catalyst with Nb/Ni ratio of 0.176 ($Ni_{0.85}Nb_{0.15}$).

KN12

Natural gas: removal of main impurities and mercaptans

Alberto de Angelis
Eni refining and marketing division, via Maritano 26, S. Donato Milanese, Italy, *e-mail: alberto.de.angelis@eni.it*

The composition of natural gas as extracted from wells is variable and may be present large quantities of contaminants, which have to be removed before its commercialization. The most common impurities are: light alkanes, carbon dioxide, nitrogen, water, and compounds containing sulphur (i.e. hydrogen sulphide, mercaptans and sulphur itself).

In this key note industrial methods for natural gas impurities elimination will be illustrated with a peculiar attention to commercial and new methods for mercaptans removal from natural gas and light hydrocarbons.

KN13

Bio-Syngas via CHOREN's gasification technology - Operation of BTL Demo plant and future prospects -

Matthias Rudloff
CHOREN Industries GmbH, Frauensteiner Straße 59, 09599 Freiberg, Germany. *matthias.rudloff@choren.com*

Gasification of biomass offers a smart option for biomass utilization as a broad range of different feedstock can be converted into high flexibility synthesis gas. CHOREN's different entrained flow gasifiers offer excellent syngas quality for large scale industrial applications. The hot commissioning of the 45 MW gasifier (Beta plant) started in November 2009. Already in December 2009, several days of continuous operation of the gasifier could be demonstrated. Encouraged by this success, the development of several international projects speeded up significantly.

KN14

Oxidative Coupling of Methane: Thirty Years of Studies. What We Learned?

Mikhail Sinev
Semenov Institute of Chemical Physics, R. A. S., 4 Kosygin street, Moscow 119991, Russia, *sinev@chph.ras.ru*

A lapse of thirty years after the first publications on transformation of methane to higher hydrocarbons, first of all to ethane and ethylene, known as oxidative coupling of methane (OCM) allows one to analyze the novelty that this process has brought to the understanding of catalytic chemistry of light alkanes. In particular, the interplay between the reactions of free radicals and thermochemical properties of oxide catalyst and their importance for efficient formation of OCM products are revealed. The main principles of kinetic modeling and optimization of OCM and related processes are discussed.

KN15

The Impact of Markets on the Economic Viability of Gas Conversion Technology

Rob Motal, Michael Speltz, Nancy Tsai
Chevron Energy Technology Company, 6100 Bollinger Canyon, San Ramon, CA 94583, *robmotal@chevron.com*

Markets are difficult to predict, always changing and often misinterpreted. Too often promising gas conversion research is met with a dramatically different economic view than when it started. Financial support frequently dries up and scaleup stops. Some of the simple economic valuations used in initiating research are examined including their limitations. A global free agent-based economic model was prepared with an emphasis on competition from oil products, coal as well as gas. Insights from this model are presented to better understand the fundamental driving forces that impact the markets and the economic viability of gas conversion technology.

KN16

Gaining insight into the short contact time CPO of methane through advanced experimental and modelling techniques

A. Beretta
LCCP-Laboratory of Catalysis and Catalytic Processes, Dipartimento di Energia, Politecnico di Milano,
piazza Leonardo da Vinci 32, 20133 Milano, Italy. *alessandra.beretta@polimi.it*

This work reviews the study of CH_4-CPO on Rh catalysts, performed in the recent years by LCCP at Politecnico di Milano, in cooperation with leader research groups. The contribution focuses on the use of advanced experimental and modelling tools to gain insight into the kinetics of CH_4 activation on Rh in the presence of O_2, H_2O and CO_2 and to rationalize the performance and thermal behaviour of autothermal reformers. This, in turn, provides with guidelines for the optimal design of the short contact time CPO-reformer.

KN17

From functionalised alkanes to hydrocarbons – MTO, MTG and beyond

Unni Olsbye, Stian Svelle, Karl-Petter Lillerud
in GAP Centre of Research-Based Innovation, Dept. of Chemistry, University of Oslo, Oslo, Norway. *unni.olsbye@kjemi.uio.no*

Conversion of functionalised alkanes, mainly methanol, into higher hydrocarbons is a process which is gaining increasing commercial importance for the conversion of coal, natural gas and biomass into valuable chemicals and fuels. The reaction proceeds over acidic catalysts, and a prevailing question is to which extent product selectivity and catalyst stability may be tuned by changing the density and strength of acid sites, as well as the channel, cavity and crystal dimensions in the case where microporous catalysts are used. This lecture will review recent findings on such correlations, based on state-of-the-art mechanistic insight.

KN18

Selective oxidative activation of short alkanes using structured reactor concepts

A.C. van Veen[1,2]
[1] Ruhr-University Bochum, Lab. of industrial Chemistry, Universitätsstr. 150, 44780 Bochum, Germany; *andre.vanveen@rub.de*
[2] IRCELYON, UMR 5256 CNRS - Université de Lyon, 2, av. A. Einstein, 69626 Villeurbanne cedex, France

The activation of short alkanes has potentially a large impact on industrial chemistry however presenting the challenge that products are more reactive than reactants. Applying here the attractive oxidation catalysis was widely investigated but yields remained limited in conventional fixed bed reactors. Structured reactors may enable higher yields, lead to safer operation and allow the cost cutting use of air as oxidizer when a separation function is included in the reactor. The present work will give an overview over the benefit and the limitations employing structured reactors presenting selected examples for the selective oxidative activation of methane and ethane.

KN19

A novel process with CO_2 mitigation in plan

Zhongxue Gan
Hua Xiang road, Economic an Technology development zone, Lang Fang Hebei, China 065001, *ganzhongxue@enn.cn*

NGCS
LYON
2010
9

Novel Gas Conversion Symposium
C1-C4 chemistry: from fossil to bio resources

ORAL PRESENTATIONS

Session I - Natural gas and biogas purification

(filtration, CH_4/CO_2 separation, sulfur and nitrogen removal, etc)

O 36
(114)

Kinetics and mechanisms of ZnO sulfidation reaction: A microstructural approach

L. Neveux[1,2] D. Chiche[1],D. Bazer-Bachi[1], M. Pijolat[2], L. Favergeon[2]
[1] IFP Lyon, 69360 Solaize BP3, France, *laure.neveux@ifp.fr*
[2]Centre SPIN, URA CNRS 2021, Ecole nationale supérieure des Mines, 158 Cours Fauriel, 42023 Saint-Etienne cedex 2

Among the second generation biofuels, BTL processes (BiomassTo Liquid) aim at turning the agricultural wastes into fuel. BTL processes comprise a first step of biomass gasification into syngas. The deep desulfurization of syngas can be achieved with zinc oxide according to the reaction: $ZnO_{(s)}+H_2S_{(g)} \rightarrow ZnS_{(s)}+H2O_{(g)}$. The aim of this work is to model the different elementary steps involved in the solid-gas reaction at a microscopic scale, by proposing mechanisms for this solid state transformation, as this cannot be found in the literature. The sulfidation reaction is studied through thermogravimetric measurements to focus on the kinetics of the solid transformation.

O 37
(282)

Tuning the polarity of Metal-Open Frameworks for CO_2 capture from Natural Gas

S. Aguado, U. Ravon, J. Canivet, C. Mirodatos, **D. Farrusseng**, M. Tabliabue, C. Rizzo
Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS -
Université de Lyon, 2, av. A. Einstein, 69626 Villeurbanne cedex, France. *david.farrusseng@ircelyon.univ-lyon1.fr*

The paper will deal with the assessment of Metal-Organic Framework adsorbents for CO_2/CH_4 separation. Polar zeolite are very selectivity but they show poor working capacity and regenerabilty. We will show that the substitution of unpolar groups by polar groups in MOF allow to mimic the effect of modifying the Si/Al ratio in zeolites. Although MOFs and zeolites posses very different pore size, similar isotherm-based performances can be obtained in terms of working capacity, selectivity and regenerability.

O 38
(548)

RkPSATM Gas Separation Technology by Xebec Adsorption Inc.

Soheil Alizadeh-Khiavi, Daryl Musselman
Xebec Adsorption Inc., 6961 Russell Ave., Burnaby, British Columbia, V5J 4R8, Canada, *skhiavi@xebecinc.com*

Conventional kinetic separation processes are limited to a short list of applications. Xebec has developed a rapid cycle kinetic pressure swing adsorption technology, RkPSA™, which overcomes the conventional limitations and enables the use of a wide range of kinetic adsorbent materials for variety of gas separation processes such as separation of CO_2 from Bio Gas. This novel process has been specifically developed to utilize the kinetic selectivity of gases in various adsorbents at very fast diffusion rates. The two key enabling pieces of technology in RkPSA™ are Xebec's proprietary Structured Adsorbent beds, and Xebec's proprietary Rotary Valves.

O 39
(86)

HyGenSys: a CO_2 ready process for large scale H_2 production

F. Giroudière[1], B. Fischer[1], J.L. Ambrosino[1]
[1]IFP Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France. *fabrice.giroudiere@ifp.fr*

HyGenSys (Hydrogen Generation System) is an enhanced steam methane reforming process (SMR) that combines a gas turbine and a reactor-exchanger for a production of typically 100,000 Nm3/h of pure hydrogen. The energy required by the reforming reaction is provided by the first part of the gas turbine. Downstream the reactor-exchanger the flue gas is then expanded to produce electrical power and hence avoid huge amount of steam that are generated in conventional SMR technologies. Several HyGenSys schemes, including CO_2 capture alternate, are possible. Operating conditions and equipments design take into account industrial perspectives.

Session II - Production of synthesis gas from natural gas, coal, biomass or waste; clean coal; syngas chemistry: purification, water gas shift (WGS), reverse WGS and synthetic natural gas (SNG)

O 1
(40)

Precious Metal Steam Reforming Catalysis: Effect of Sulphur.

Claire Gillan[1], Martin Fowles[2], Sam French[2] and **S David Jackson**[1]
[1]Centre for Catalysis Research, WestCHEM, Dept. of Chemistry, University of Glasgow, Glasgow, G12 8QQ Scotland.
sdj@chem.gla.ac.uk
[2]Johnson Matthey plc, Belasis Ave, Billingham TS23 1LB UK

The effect of ppm levels of hydrogen sulphide and methanethiol on ethane steam reforming was studied over a Pt/Al_2O_3 catalyst at 20 barg and 873 K. Methanethiol was found to be far more deleterious. Although some regeneration was possible, post-poisoned reaction gave an altered selectivity. The overall deactivation process can be rationalized on the basis of the different reactions that are occurring and their different susceptibility to poisoning. Ethane hydrogenolysis was the most affected and steam reforming the least affected.

O 2
(72)

Sulphur poisoning during the catalytic partial oxidation of methane on Rh catalysts partially substituted with Pt or Pd

S. Cimino, R. Torbati, L. Lisi, G. Russo
Istituto Ricerche sulla Combustione – CNR – P.le Tecchio 80 Napoli – Italy. *stefano.cimino@cnr.it*

The effect of partial substitution of $Rh/La\text{-}Al_2O_3$ monolith catalysts with either Pt or Pd during the CPO of methane in the presence of H_2S under self-sustained high temperature conditions was investigated. The catalysts were fully characterized by BET, SEM-EDS, SO_2-TPD and in situ DRIFTS of adsorbed CO at room temperature, which was used to investigate changes on the surface state of Rh before and after exposures to S species at high T and reducing conditions close to actual CPO. Both steady state and transient operation of the CPO reactor were investigated particularly with regards to poisoning/regeneration cycles and light-off phase.

O 3
(78)

Development of monolith catalyst for catalytic partial oxidation of natural gas

S. Kado, K. Imagawa, A. Kiryu, T. Minami, K. Kawazuishi, H. Kawai, K. Tomishige, A. Nakamura, Y. Suehiro
Research & Development Center, Chiyoda Corp., Yokohama, Kanagawa, 221-0022, Japan,
skado@ykh.chiyoda.co.jp

Chiyoda Corp., Tsukuba Univ., Inpex Corp. and JOGMEC (Japan Oil, Gas and Metals National Corporation) have jointly developed direct catalytic partial oxidation (D-CPOX) catalyst and process to produce synthesis gas. We have succeeded in demonstrating the D-CPOX reaction for 2,000 hours with high activity and stability at 0.9 MPaG and GHSV=1x10^{6} hr^{-1}. The results of steam addition test suggests that the D-CPOX reaction proceeds at first, then water gas shift reaction can follow the D-CPOX reaction on our proprietary catalyst. And we introduce the modularized D-CPOX-GTL process for small-scale gas field.

O 4
(287)

CO$_2$ reforming of CH$_4$ on doped Rh/Al$_2$O$_3$ catalysts

A. Sarusi, K. Fodor K. Baán A. Oszkó, **A. Erdőhelyi**
Institute of Physical Chemistry and Material Science, University of Szeged, Aradi vertanuk tere 1, Szeged, Hungary, H-6725,
erdohelyi@chem.u-szeged.hu

The reaction of CO$_2$ with methane was studied on V$_2$O$_5$ and TiO$_2$ promoted Rh/Al$_2$O$_3$ catalysts at 773 and 1073 K at high space velocity. It was found that the additives significantly increased the CO$_2$ and the CH$_4$ conversion at 773 K and the CO/H$_2$ ratio remained unchanged. At 1073 K the improvement was not so pronounced. DRIFT measurements revealed that during the reaction at 773 K CO and formate species were present on the surface of the catalysts. The amount of surface carbon formed during the reaction at 1073 K was the same in all cases but at 773 K on Rh/V$_2$O$_5$-Al$_2$O$_3$ about three times more carbon was accumulated than on Rh/TiO$_2$-Al$_2$O$_3$ or Rh/Al$_2$O$_3$.

O 13
(112)

Marked effect of mesopores for the prevention of Ni sintering and inactive carbon deposition in dry reforming of methane over ordered mesoporous Ni-Mg-Al$_2$O$_3$ nanocomposites

Shuichi Naito, Weihua Shen, Hideaki Momoi and AkihiroYoshida,
Department of Material and Life Chemistry, Kanagawa University, 3-27-1, Rokkakubashi, Kanagawa-ku, Yokohama,
221-8686, Japan, *naitos01@kanagawa-u.ac.jp*

The catalytic behaviour of ordered mesoporous Ni/MgAl$_2$O$_3$ for the reforming of CH$_4$ by CO$_2$ was investigated in depth and compared with non-porous Ni/MgAl$_2$O$_3$ catalysts. The dependences of the particle size of Ni as well as the added amount of Mg on the CH$_4$ conversion were studied to elucidate their roles in CH$_4$-CO$_2$ reaction. It was concluded that mesoporous structure can prevent the sintering of Ni metal particles (2-3 nm) inside the pore, and that added Mg can prevent the inactive carbon accumulation. *In-situ* FT-IR spectroscopy and *in-situ*-XPS were applied to elucidate the reaction mechanism and the active site structures.

O 14
(113)

Reforming of tar model compounds present during biomass steam gasification by iron /olivine catalysts

Mirella Virginie, **Claire Courson**, Yvan Zimmermann, Alain Kiennemann
Université de Strasbourg, LMSPC UMR CNRS 7515 25 rue Becquerel 67087 Strasbourg cedex 2
claire.courson@unistra.fr

Catalytic elimination of tar from the product gas is crucial to improve the process of biomass gasification in circulating fluidized bed gasifier, permitting gas cleanup. Natural olivine, often used as primary catalyst, was previously improved by Ni addition. Here we present preparation, characterizations before and after test (XRD, TPR, Mössbauer, MEB) of new Fe (10-20wt%)/olivine catalysts. Their catalytic efficiency has been evaluated in various conditions and compared to olivine and Ni/olivine for toluene and methylnaphthalene steam reforming. The new catalyst, cheap and non toxic, shows a similar activity and aging than 3.9wt%Ni/olivine.

O 15
(125)

Effect of Boron on the coking resistance of Ni/Al_2O_3 catalysts for the dry reforming of methane

A. Fouskas, M. Kollia, A. Kambolis, Ch. Papadopoulou, **H. Matralis**
University of Patras, Department of Chemistry, GR-26504 Patras, Greece. *matralis@chemistry.upatras.gr*

Boron modified Ni/Al_2O_3 catalysts (with B/(Ni+B) atomic ratio in the region of 0.0–0.7) were prepared by wet co-impregnation and their catalytic performance for the CO_2 reforming of CH_4 was investigated. The physicochemical properties of the fresh, reduced and used samples were studied by BET, XRD, DRS, SEM-EDS and TPR. Coke deposited on the used catalysts was determined by Temperature Programmed Hydrogenation. It was found that the modification of Ni/Al_2O_3 catalyst by B enhances the dispersion of the Ni particles and greatly reduces the amount of coke formation during dry reforming of CH_4 without significantly affecting activity and selectivity.

O 16
(140)

Catalytic and DRIFTS study of the WGS reaction mechanism on Pt-based catalysts

Ch. Vignatti, **C.R. Apesteguía**, T.F. Garetto
Catalysis Science and Engineering Research Group (GICIC), INCAPE (UNL-CONICET), Santiago del Estero 2654,
(3000) Santa Fe, Argentina. *capesteg@fiq.unl.edu.ar*

The WGS reaction mechanism was studied on Pt/SiO_2, Pt/CeO_2, and Pt/TiO_2 catalysts by in-situ DRIFTS technique. On Pt/SiO_2, the WGS reaction took place via a monofuncional redox mechanism on Pt. The CO conversion activity was clearly enhanced when Pt was supported on CeO_2 and TiO_2 because reducible supports provided an additional reaction pathway for activating water and forming formate species. But formate decomposition to generate CO_2 and H_2 was easier on Pt/TiO_2 than on Pt/CeO_2 which explained the higher WGS activity observed on Pt/TiO_2. Pt supported on high-surface area titania were the most active catalysts.

O 17
(154)

COx free hydrogen production by water gas shift reaction in a Multifunctional Hollow Fibre Catalytic Reactor.

F.R. Garcia-Garcia, M. A. Rahman, **K. Li**
Department of Chemical Engineering and Chemical Technology, Imperial College London, South Kensington Campus,
London SW7 2AZ, UK

A Multifunctional Pd hollow fibre catalytic reactor (MHFCR) has been designed in an attempt to improve the conversion in water gas shift (WGS) reaction. In the preparation of the MHFCR, first the Pd layer was deposited on the top of the hollow fibre by electroless plating and secondly the lumen of the system was impregnated with 22% CuO/CeO_2 catalyst by sol-gel coating. The catalytic activity tests were performed at 1atm between 200 and 400°C using different rate flows of sweep gas. The ratio between CO and H_2O in the feed was 1 to 2 with a space velocity of 160 L/g.h. An increase of 60% in the conversion in WGS reaction has been observed with MHFCR.

O 32 (491)

A comparison between copper and nickel-based catalysts obtained from hydrotalcite-like precursors for WGSR

E. Meza[1,2], L. A. Palacio[3], A. Faro[3], T.F. Silva[4], J. Mansur[4], M.C. Rangel[1]
[1]GECCAT/ UFBA. Campus Universitário de Ondina. 40190-280- Salvador, Bahia, Brazil, *e-mail: mcarmov@ufba.br*
[2]Facultad de Ciencias Exactas y Naturales, Campus de Zaragocilla, Universidade de Cartagena, Colombia
[3]Universidade Federal do Rio de Janeiro, Ilha do Fundão, 21941-909, Rio de Janeiro, RJ, Brazil
[4]Universidade Federal de São Carlos - Rd Washington Luiz, Km 233 13 565-905 São Carlos, SP, Brazil

Copper and nickel-based catalysts obtained from hydrotalcite-like precursors were compared in this work, in order to find alternative systems for the low temperature step of water gas shift reaction. Nickel-based catalysts were found to be more active than the copper-based solids, a fact that was related to differences in the specific surface area, the reduction properties and to the size of the metallic particles. These samples showed high activity, did not produce methane and was stable in the range of 200 to 350°C, being promising to be used in a single stage of WGSR at intermediate temperatures.

O 33 (516)

Methane conversion to syngas with lattice oxygen: mechanism leading to high selectivity

F. Mudu[1], B. Arstad[2], H. Fjellvåg[1], E. Bakken[2], **U. Olsbye**[1]
[1] Centre of Material Science and Nanotechnology, Institute of Chemistry, University of Oslo, P.O. Box 1126 Blindern, N-0318 Oslo.
unni.olsbye@kjemi.uio.no
[2] SINTEF Materials and Chemistry, Oslo, Norway

In this contribution we present two rhodium impregnated reducible oxides for the conversion of methane to syngas in the absence of gas phase oxygen. Conversion and selectivity above 80% are obtained at 873K. By a combination of catalytic tests and pO_2 variable thermogravimetric analysis we were able to propose a mechanism responsible for the selectivity in this type of transient reactions. Characterisation by means of in situ synchrotron XRD and semi in situ XPS were employed to investigate the bulk structure and the surface modifications during the reaction of the reducible oxides with methane.

O 34 (517)

Further insight into the mechanism of methanation of CO_2 over Rh /γ-Al_2O_3 catalyst

Antoine Beuls, Colas Swalus, Alejandro Karelovic, Marc Jacquemin and **Patricio Ruiz**
Unité de catalyse et chimie des matériaux divisés, Université catholique de Louvain, Louvain-la-Neuve, Belgium.
patricio.ruiz@uclouvain.be

Further insights into the mechanism of methanation are given. CO_2 and CO hydrogenations are compared. The influence of O_2 in the feed and of the temperature is studied in both cases.
It is confirmed that the methanation of CO_2 is performed with 100% of selectivity on Rh/γ-Al_2O_3 catalyst. The first step in the mechanism is the dissociation of CO_2. The amount of methane produced depends on the temperature, pressure and presence or absence of CO or O_2, in the feed. An important difference in the mechanism of methanation of CO_2 and CO is the dissociation step of CO_2. Dissociation of CO_2 seems to be responsible for the oxidation of the Rh catalysts. The oxidation state of the Rh plays an important role in the distribution of the adsorbed species on the catalysts. The gem-dicarbonyles species are the more reactive ones. The preferential formation of these species will be at the origin of the difference in the reactivity of CO_2 and CO. Oxygen, in low amount, has a positive effect in the methanation.

O 35
(532)

High temperature gas filter unit performance and particles characterisation during steam-oxygen blown gasification of biomass using magnesite as bed material

E. Simeone, M. Siedlecki, M. Nacken, S. Heidenreich, W. de Jong and A. H. M. Verkooijen
Process and Energy Department, Energy Technology Section, 3ME Faculty, Delft University of Technology,
Leeghwaterstraat 44, 2628 CA, Delft, The Netherlands, *e.simeone@tudelft.nl*

Filtration of gas from steam oxygen gasification of biomass performed at temperatures as high as 800ºC can have a combined effect on particles removal and changes in gas composition in terms of tar conversion and higher hydrogen yield. This study was performed at Delft University of Technology during an experimental campaign where magnesite was used as bed material. The filtration behaviour of ceramic filter candles was observed with continuous monitoring of the pressure drop during the build-up of the dust cake. Regeneration parameters were evaluated in order to achieve an optimal cleaning strategy. Analyses of ashes and of the candles were carried out.

O 55
(156)

Theoretical Insights into Catalytic C_1 Conversion Processes

Matthew Neurock[1], Corneliu Buda[1], Cathy (Ya-Huei) Chin[2], and Enrique Iglesia[2]
[1]Dept. of Chemical Engineering, University of Virginia, Charlottesville, VA 22904, (USA)
[2]Dept. of Chemical Engineering, University of California, Berkeley, CA 94720, (USA)
mn4n@virginia.edu

Ab initio density functional theory calculations and kinetic Monte Carlo simulations are use together with rigorous experiments to elucidate the mechanisms and the kinetics that govern methane reforming and oxidation over different transition metal surfaces. The resulting kinetics are set the metal as well as the process variables which control the surface coverages as well as the nature of the active sites that form.

O 56
(184)

Spatially resolved species and temperature profiles as novel tool to study mechanistic details in catalytic methane partial oxidation on platinum

O. Korup, **R. Horn**, M. Geske, R. Schlögl
Department of Inorganic Chemistry, Fritz Haber Institute of the Max Planck Society, Faradayweg 4-6, 14195 Berlin, Germany.
horn_r@fhi-berlin.mpg.de

A novel reactor concept with capillary species sampling and temperature probes was used to measure high resolution (~100 µm) species and temperature profiles in high temperature (T > 500 °C) and high pressure (1 < p < 50 bar) catalytic partial oxidation of methane on platinum. The metal nanoparticles were supported on reticulated α-alumina foam or sphere supports providing negligible pressure drop and enhanced radial mixing minimizing disturbances by the sampling process. The profiles can be measured from atmospheric pressure up to several atmospheres and provide information on reaction pathways, zoning effects in the catalyst bed, impact of mass and heat transport as well as gas phase chemistry.

O 57
(228)

Rh-$LaCoO_3$ based catalyst for tar conversion to syngas

P. Ammendola, R. Chirone, **L. Lisi** ,B. Piriou, G. Ruoppolo
Istituto di Ricerche sulla Combusione CNR Piazzale V. Tecchio, 80 125 Napoli Italia *lisi@irc.cnr.it*

A novel Al_2O_3 supported Rh/$LaCoO_3$ catalyst was investigated for the conversion of tar from biomass decomposition into a double fixed bed reactor rig by contacting the catalysts at 700°C with the mixture of gaseous and volatiles compounds emitted by the biomass in absence and in the presence of sulphurThe study was coupled with a DRITF in-situ analysis carried out under similar conditions in order to determine the active sites and the poisoning effect. Highly dispersed Rh centres are active in tar conversion. The perovskite contributes to tar conversion depressing coke deposition and prevents to some extent Rh poisoining by sulphur.

O 58
(237)

Improvement of the gaseous effluent of biomass air-gasification using CaO doped Ni/olivine as catalysts

D.C. Cárdenas-Espinosa, **J.C. Vargas Sáenz**
Departamento de Ingeniería Química y Ambiental, Universidad Nacional de Colombia, Ciudad Universitaria,
Avenida Carrera 30 No. 45-03, Bogotá-Colombia. *jcvargass@unal.edu.co*

Ni-CaO/olivine catalysts were prepared by wet impregnation technique varying the Ca content (0.0-3.7 wt.%Ca).The Ca-content effect was evaluated in methane dry reforming reaction with stoichiometric CO_2/CH_4 ratio, and the effect of H_2 and/or CO presence using a feeding-mixture according to the composition of gas produced by biomass air-gasification. The catalysts exhibited high activity in catalytic tests; therefore they are suitable for the conversion of non-interesting gaseous by-products of biomass gasification process. XRD, SEM, TEM and TPR techniques were used to characterise the catalysts before and after reactivity tests.

O 67
(57)

Millisecond Catalytic Partial Oxidation of Methane and Ethane on Rh and Pt: Measurement of Species and Temperature Profiles within the Catalyst

Brian Michael, David Nare, and **Lanny D. Schmidt**
Department of Chemical Engineering and Materials Science - University of Minnesota - Minneapolis MN 55455 - USA
schmidt@cems.umn.edu

Profiles of temperature and species have been measured in working monolith catalysts during the catalytic partial oxidation of methane and ethane over Rh and Pt, with and without addition of washcoat, Ce, and Sn. Rh catalysts go to nearly equilibrium products (H_2 and CO) within a few milliseconds of the catalyst, and O_2 has nearly reacted within the first millimeter. Ethane on Pt produces up to 80% ethylene, and O_2 conversion is lower. These results are explained in terms of the different activities and selectivities and the influence of additives on the reactions.

O 68
(252)

High efficiency SNG production from biomass

L.P.L.M. Rabou, C.M. van der Meijden
Energy research Centre of the Netherlands (ECN) - PO Box 1, 1755 ZG Petten, the Netherlands, *rabou@ecn.nl*

The Energy research Centre of the Netherlands (ECN) is developing technology for the production of Substitute Natural Gas (SNG) from biomass. The technology involves indirect gasification, tar removal, further gas cleaning, methanation and upgrading of the product to natural gas standards. The aim is to reach an energy efficiency of at least 70% from biomass to SNG. Results are presented of tests performed with various catalysts and biomass producer gas at lab-scale (about 1 Nm^3/hr).

O 69
(253)

Mutual promoting effect of Re and Pt in CH_4 partial oxidation

Shizhong (Jason) Zhao and Jae Hyung Kim
Süd-Chemie Inc. 1600 West Hill Street, Louisville, KY40210, USA. *Shizhong.zhao@sud-chemie.com*

Rhenium is added to modify the thermal stability of precious metals in CH_4 partial oxidation. It was a surprise that Re not only improves the stability of the catalysts but also boosts the activity of Pt. Recent XPS data show that majority of Re is kept in the metallic state by Pt in reaction. We attribute the performance enhancement to a mutual promoting effect between Pt and Re. Pt keeps Re from excessive oxidation that ensures the survival of the alloy particles and the continuation of the dynamic redox process on Re, while Re depletes CH_4 disassociation products on Pt and increases Pt's turn-over rate for C-H bond activation.

O 70
(273)

$LaNiO_3/\alpha\text{-}Al_2O_3$ catalyst prepared by a microwave-assisted combustion method: application to methane steam reforming reaction

B. S. Barros, D. M. A. Melo, A. Kiennemann
Departamento de Química - Universidade Federal do Rio Grande do Norte, Campus universitário av. Salgado Filho, 300,
bairro de Lagoa nova, Natal, Brazil. *brauliosb@yahoo.com.br*

$LaNiO_3/\alpha\text{-}Al_2O_3$ catalysts were prepared by a microwave-assisted combustion method and tested in the steam reforming of methane. High CH_4 conversion was observed for all samples. The catalysts prepared with fuel (glycine or urea) have a good aging and displayed mainly carbonaceous species oxidized at low temperatures. Preparation without fuel gives a worst aging probably due to the presence in great amount of carbonaceous species oxidized at high temperatures. The structure stability of La-Al-Ni perovskite oxide change with the preparation method and is related with the behavior observed in the samples prepared with fuel

O 71
(276)

Production of fuel gas from lignin in supercritical water over supported metal catalysts

A. Yamaguchi, N. Hiyoshi, O. Sato, M. Osada, **M. Shirai**
Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST),
4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan, *e-mail: m.shirai@aist.go.jp*

Lignin has attracted much attention as renewable energy source. Fuel gas production from lignin in supercritical water is a promising technique to reduce the lignin gasification temperature. We found that supported metal salt catalysts are active for the lignin gasification in supercritical water and the order of lignin gasification activity was the following: ruthenium > rhodium > platinum > palladium > nickel. The metal salts were reduced to metal particles during the lignin gasification, which were responsible for the lignin gasification activities in supercritical water.

O 86
(98)

Ni/SiO_2 fiber catalysts prepared by electrospinning technique for glycerol reforming to syngas

Prasert Reubroycharoen[1], Nattida Tangkanaporn[2], and Chaiyan Chaiya[3]
[1]Department of Chemical Technology, Faculty of Science, and Center for Petroleum,
Petrochemicals and Advanced Materials Chulalongkorn University, Bangkok 10330, Thailand
[2]Petrochemical and Polymer Program, Faculty of Science, Chulalongkorn University, Bangkok, Thailand
[3]Division of Chemical Engineering, Rajamangala University of Technology Krungthep, Bangkok, Thailand,
e-mail: prasert.r@chula.ac.th

The Ni/SiO_2 fiber catalysts were prepared by sol-gel and electrospinning technique and used as a reforming catalyst. Nickel acetate and TEOS (Tetraethyl-orthosilicate) were used as a source of nickel and silica at different Ni loading. The Ni/SiO_2 fiber catalysts were characterized by FT-IR, SEM-EDS, TEM, and TPR. SEM results showed that the average diameter of SiO_2 fiber was 1.28 μm-930 nm. The amount of Ni measured by EDS was close to that of Ni loading. The reaction test showed that the activity of fiber catalysts was higher than that of a Ni/SiO_2 porous catalyst. The fiber catalyst produced the syngas at H_2/CO ratio of 2.

This work was supported by the financial support from the Center for Petroleum, Petrochemicals and Advanced Materials.

O 87
(290)

Catalytic Partial Oxidation of CH_4 with Nickel-Lanthanum based catalysts

L.D. Vella[1], J.A. Villoria de la Mano[2], **S. Specchia**[1], V. Specchia[1], J.L.G. Fierro[2]
[1]Department of Materials Science and Chemical Engineering, Politecnico di Torino, Corso Duca degli Abruzzi24 10129 Torino, Italy - *stefania.specchia@polito.it*
[2]Instituto de Catàlisis y Petroleoquimica (CSIC), C/Marie Curie 2, 28049, Madrid, Spain

Starting from the perovskite $LaNiO_3$, various $LaNiO_3$–based catalysts were synthesized via Pechini method by substituting part of Ni with Co and part of Co with small atomic percentages of Pt. Their performance, in terms of CH_4 conversion and H_2 selectivity, was compared to that of a Rh/Al_2O_3 catalyst after testing in a CH_4 SCT-CPO fixed bed for syngas production. Notwithstanding the lower BET specific surface area of the $LaNiO_3$–based catalysts, they behave better than the Rh-based counterpart, in particular in terms of CH_4 conversion.

O 88
(490)

An operando study showing the irrelevance of IR-observable formates in the formation of ethane from syngas over a Co-MgO catalyst

J. Schweicher[1], A. Bundhoo[1], A. Frennet[1], N. Kruse[1], H. Daly[2], **Frederic C. Meunier**[3].
[1]Chemical Physics of Materials (Catalysis-Tribology), Université libre de Bruxelles, Brussels, Belgium
[2]CenTACat, Queen's University Belfast, Belfast BT9 5AG, United Kingdom
[3]Laboratoire Catalyse et Spectrochimie, CNRS, Caen, France. *frederic.meunier@ensicaen.fr*

The role of carbonyl and formate species observable by IR under syngas at ambient pressure over Co-MgO catalysts was investigated in relation to the formation of simple products resulting from C-C coupling, i.e. ethane in this case. These species were found to be spectators, while carbonyls could not be ruled out as potential reaction intermediates. This work reemphasises the importance of combining kinetic and IR studies.

O 89
(359)

CeO_2-ZrO_2-Al_2O_3 mixed oxide nanocomposites supported Rh: a promising catalyst for partial oxidation of methane to syngas

Sara Boullosa-Eiras, Tiejun Zhao, Estelle Vanhaecke, De Chen, Anders Holmen
Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), 7491, Trondheim, Norway.
boullosa@nt.ntnu.no

Methane partial oxidation (CPOM) is carried out on $Zr_xCe_{1-x}O_2$-Al_2O_3 nanocomposites supported Rh catalysts. The presence of high temperatures during the CPOM would lead to the solid particle sintering and the lost of activity. It is necessary to develop a high-temperature stable system which would help to stabilize the dispersed Rh particles. The formation of $Zr_xCe_{1-x}O_2$-Al_2O_3 is found to improve the thermal stability for both rare-earth metal oxide and alumina. After the ignition the catalysts containing Ce show the best performance, obtaining a product close to the thermodynamic equilibrium. CeO_2-containing catalysts could help for the methane conversion and the WGSR.

O 90
(460)

Advances in itm technology for syngas production

David W. Studer[1], Douglas L. Bennett[1], Michael F. Carolan[1], Edward P. Foster[1], Jack C. Chen, Matt Ferber
[1]Air Products and Chemicals, Inc., 7201 Hamilton Blvd., Allentown, PA, 18195 USA. *studerdw@airproducts.com*

The ITM Syngas process is a breakthrough technology that combines air separation and high-temperature syngas generation processes into a single ceramic membrane reactor, with significant capital cost and efficiency savings. Process and reactor design innovations have allowed continued ITM Syngas process advancement. Data will be presented that demonstrate the continued progress toward commercialization. Updates will include: methods for reliable operation under repeated startup and shutdown conditions, validation of commercial life projections through creep rupture tests, Process Development Unit operating tests and improvements in stable high fluxes.

O 91
(399)

Structured carbon nanofiber supported Cu-CeO_2 catalyst: Catalytic behavior in the preferential oxidation of CO in H_2-rich gases

Tiejun Zhao[1], Yingda Yu[2], De Chen[1], Magnus Ronning[1]
[1]Department of Chemical Engineering; [2]Department of Material Science and Technology; Norwegian University of Science and Technology (NTNU), 7491, Trondheim, Norway. *tiejun@chemeng.ntnu.no*

Special attention has been devoted to Cu-CeO_2 catalysts in preferential oxidation of CO (CO-PrO_x) for the low-temperature fuel cell-quality H_2 production. In this contribution, a novel and versatile strategy is demonstrated for the structured carbon nanofibers (sCNFs) supported Cu-CeO_2 catalyst prepared by impregantion of a room-temperature polymerizable solution on sCNF, followed by the low-temperature combustion. Thus produced catalyst exhibits higher conversion and higher selectivity to CO oxidation in the CO-PrOx than the corresponding powder samples probaly due to the smaller Cu-CeO_2 particles and high thermal conductivity of sCNF.

O 104
(423)

Methane Steam Reforming over Transition Metals and Alloys

Jens Sehested, Jon G. Jakobsen, Stig Helveg, Glenn Jones, Jens K. Nørskov, Shengguang Wang, **Thomas Bligaard**
Center for Atomic-scale Materials Design (CAMD), Department of Physics, Building 307, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark, *bligaard@fysik.dtu.dk*

We present DFT calculations and experimental studies of steam reforming over transition metals. Particle size distributions from transmission electron microscopy (TEM) and activity measurements were used to obtain turn over frequencies (TOF) and kinetics. TOF increased linearly with dispersion, indicating that the active sites are edge sites. Modeling shows TOF forms a 2D volcano plot with $\Delta E(C^*)$ and $\Delta E(O^*)$ as the variables. Both theory and experiment predict Ru and Rh to be the most active transition metals for methane steam reforming, while Ni, Ir, Pt, and Pd are significantly less active. We use the model to search for new alloys with high activity.

O 105
(424)

Single stage water gas shift catalyst: Role of Rhenium in Pt-Re/TiO_2

K. G. Azzam†, N. P. Lopez, I. V. Babich, B. L. Mojet, L. Lefferts, and K. Seshan
Catalytic Processes & Materials, Faculty of Science and Technology, University of Twente, PO Box 217, 7500 AE, Enschede,
The Netherlands. *k.seshan@utwente.nl*; †CAER, University of Kentucky, 2540 Research Park Drive, Lexington 40511, USA

The WGS activity and stability over Pt-Re/TiO_2 catalyst is significantly influenced by the catalyst preparation strategy. Impregnating Re precursor prior to Pt precursor without intermediate drying or calcinations, and using Pt/Re ratio of unity resulted in the optimum catalyst performance (stability and activity). Characterization studies on the optimum catalyst indicate existence of Pt and ReO_x phases. Under WGS conditions, however, interaction of Pt and Re (formed by reduction of ReO_x) is possible and improves catalytic properties.

O 106
(428)

Tail Gas Conversion for High Efficiency Coal-to-FT-Liquid Plants

K. Aasberg-Petersen, P. Seier Christensen, C. Stub Nielsen
Haldor Topsøe A/S, Nymøllevej 55, DK-2800 Lyngby, Denmark. *kap@topsoe.dk*

A new process for the catalytic treatment of the tail gas from a Fischer-Tropsch unit in a plant with coal feed has been developed and described. A key feature is pre-treatment of the tail gas to saturate olefins and to reduce the content of carbon monoxide. The pre-treated gas may be sent to a steam reforming unit to produce hydrogen and carbon monoxide. Process simulations have shown that the new scheme is superior to a scheme in which the tail gas is recycled directly to an FT reactor without catalytic conversion of hydrocarbons.

O 107
(445)

Development of Stable Supported Ni Catalysts for Low Temperature Dry Reforming of Methane

U. Rodemerck, A. Barkschat, D. Linke
Leibniz Institute for Catalysis at the University of Rostock., Albert-Einstein-Strasse 29a , D-18059 Rostock, Germany,
uwe.rodemerck@catalysis.de

Active and stable supported non-noble metal catalysts for low-temperature CO_2 reforming of methane have been developed using high-throughput preparation and testing methods. The screening included variation of support material and metal loading and resulted in supported Ni catalysts that are active at 400°C and show only slight deactivation over 100 hours. One of the best catalysts, namely Ni/ZrO_2-La_2O_3, was further improved by switching to a mesoporous support and optimising the calcination conditions. This results in a catalyst that gave stable yields of hydrogen and carbon monoxide for 200 hours without any deactivation by coke formation.

O 108
(386)

Pt-implanted intermetallides as the catalysts for CH_4-CO_2 reforming

L.A. Arkatova[1], O. V. Pakhnutov[1], A.N. Shmakov[2], Yu.S. Naiborodenko[3], N.G. Kasatsky[3]
[1]Tomsk State University, 36 Lenin Av., Tomsk 634050, Russia, *larisa-arkatova@yandex.ru*
[2]Boreskov Institute of catalysis, 5 lavrentieva Akademika Pr., 630090 Novosibirsk, Russia
[3]Dpt of structural Macrokinetics of TSC SB RAS, 10/3 Akademichesky Av., 634021 Tomsk, Russia

Methane reforming with carbon dioxide to synthesis gas was investigated over a series Ni_3Al catalysts promoted by Pt. These catalysts were characterized by XRD (*in situ, ex situ*), DTA-TG, SEM, TEM, EDS, XPS. A new nonordinary preparation method of self-propagating high temperature synthesis for Ni-Al systems has been developed. An effective approach based on the ion implantation has been developed for the modification of Ni_3Al intermetallide. Pt-implanted Ni_3Al superalloy was the highly active and durable metal catalyst for the reforming of methane with carbon dioxide to synthesis gas.

O 109
(130)

Fibrous Ni materials for methane decomposition to carbon nanofibers

Yong Li, Xiaowei Xie, **Wenjie Shen**
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China,
shen98@dicp.ac.cn

α-$Ni(OH)_2$ with hydrotalcite-like structure was prepared by liquid phase precipitation with the mediation of ethylene glycol. Thermal calcination of this precursor at 573-1073 K yielded nickel oxides having diameter of 3-8 nm with inter-layered structure. Hydrogen reduction of the NiO samples formed metallic nickel with fibrous-like morphology. These novel Ni materials were extremely active for methane decomposition carbon nanofibers, with the carbon yield of 503 g C/g Ni. The changes in particle size and morphology of Ni during the course of reduction have been extensively studied by XRD and TEM.

Session III - Synfuels: Fischer-Tropsch synthesis, gas to liquids, coal to liquids, biomass to liquids, methanol, higher alcohols and DME

O 5
(10)

Homogeneous Catalytic Approaches for Selective Conversion of Synthesis Gas to C_{2+} Products

J. E. Bercaw, P. R. Elowe, **J. A. Labinger**, A. J. M. Miller, N. M. West
Arnold and Mabel Beckman Laboratories of Chemical Synthesis, California Institute of Technology,
Pasadena, California 91125, USA; *jal@its.caltech.edu*

Multicomponent systems consisting of a cationic metal carbonyl complex for CO activation, a platinum complex that activates H_2 to form a nucleophilic metal hydride, and a Lewis or Brønsted acid to promote C-H and C-C bond formation, have been shown to effect all the key steps that would be needed for selective, homogeneously catalyzed transformation of syngas to valuable C_{2+} products under extremely mild conditions. Progress towards an actual catalytic system by tuning the various components will be discussed.

O 6
(15)

Oxidation and sintering of cobalt Fischer-Tropsch catalysts by water

G.L. Bezemer, I.A. Dugulan, T.J. Remans and S. van Bavel
Shell Global Solutions Int., Grasweg 31, 1031 HW Amsterdam, The Netherlands, *Leendert.Bezemer@Shell.com*

Deactivation of highly dispersed cobalt catalysts (4-10 nm) on carbon nanofibers was studied with Mössbauer spectroscopy at model conditions. Even for the catalysts with 5 nm sized cobalt particles, oxidation was absent up to the high H_2O/H_2 ratio of 2, proving earlier reports that oxidation is not responsible for deactivation at relevant FT conditions. If oxidation happened, this involved only the 5 nm sized super paramagnetic (SPM) particles and not the larger particles. Interestingly, at these conditions the oxidised SPM phase sintered away to metallic cobalt if the relative humidity was increased, pointing towards a new role of water in the deactivation of FT catalysts.

O 7
(19)

High-Throughput Experimentation in Syngas Based Research

Martin Lok, Marjolein Brasz
Avantium, Zekeringsstraat 29, 1014 BV, Amsterdam, The Netherlands, *martin.lok@avantium.com*

The potential of high-throughput technology platforms to study catalysts and processes in the field of syngas R&D will be demonstrated through a series of examples including Fischer-Tropsch. Various experimental line-ups for both low and high α-value will be described. Products up to C55 have been analyzed via a combination of on- and off-line measurements. Information regarding reactor-to-reactor reproducibility and mass balance closure in a 64-reactor system will be given and will reveal the potential of using high throughput workflows in the field of Fischer-Tropsch applications.

O 8
(42)

Catalytic conversion of alcohols into aliphatic hydrocarbons
New synthesis route to biofuel components

M.V. Tsodikov, **A.V. Chistyakov**, F.A. Yandieva, V. Ya. Kugel, F. Luck, Ya. V. Zubavichus, A.E. Gekhman, I.I. Moiseev
TIPS RAS, 119991,Leninskiy prospect,29, Moscow, Russia. *Chistyakov@ips.ac.ru*

A number of alcohols produced via the biomass fermentation can be catalytically converted into effective additives to fuels. In this work the results relates to alcohols treatment into alkane/alkene fraction in one step over original nanostructured catalysts are presented. Shown that glycerol addition to ethanol led to considerable increase of desirable olefins C_4-C_{12+} yield. Found a method of commercial Pt/Al_2O_3 catalyst pretreatment that radically change it's selectivity in alcohols' conversion and allows to obtain alkanes C_4-C_{12} fraction. Using XAFS, XPS, TPD and kinetic methods determined the relationships between the catalysts' structure and its' activity and selectivity.

O 18
(53)

Design and synthesis of maximum activity supported cobalt Fischer-Tropsch catalysts

T. Eggenhuisen, J.P. den Breejen, J.R.A. Sietsma, H. Friedrich, A.M. Frey, J.H. Bitter, **K.P. de Jong**
Inoranic Chemistry and Catalysis, Debeye Institute for NanoMaterials Science, Utrecht University,
3584 CA Utrecht, The Netherlands. *K.P.dejong@uu.nl*

Based on TEM histogram analyses and Fischer-Tropsch activities of carbon nanofiber supported cobalt catalysts a maximum activity was deduced (1 bar, 220ºC) at an optimum cobalt particle size of 4.7±0.2 nm. A comparison with the optimal Co/CNF catalyst found earlier stresses the need for a narrow Co particle size distribution. We applied this knowledge to synthesize an 18 wt% Co/SiO_2 catalyst prepared via impregnation and calcination in NO/He. This yielded a highly active catalyst, with a Co size close to the calculated optimum. The moderate C_{5+}-selectivity of this catalyst was enhanced by MnO addition.

O 19
(59)

Dynamic characterization of surfaces of Co/TiO_2 Fischer-Tropsch catalysts with infrared spectroscopy and DFT calculations

Jie Gao, Emiel de Smit, George Fitzgerald, Bert M. Weckhuysen, **Simon G. Podkolzin**
Department of Chemical Engineering and Materials Science, Stevens Institute of Technology, Hoboken, NJ 07030 USA
Simon.Podkolzin@Stevens.edu

Co/TiO_2 Fischer-Tropsch catalysts were characterized with microscopy, TPR, XPS and EXAFS measurements. In addition, *in-situ* IR spectra first with CO at room temperature and then with syngas at reaction temperatures were collected as a function of time. Analysis of the IR spectra with DFT calculations suggests that, contrary to traditional F-T reaction models, which assume a static catalytic surface, the surface changes dynamically between oxide CoO and metallic Co as a layer over an oxide CoO bulk. The results illustrate methodology for detection and description of dynamic changes in the composition and structure of catalytic surfaces under reaction conditions.

O 20
(174)

Deactivation cause in the direct DME synthesis from H_2 and CO

I. Sierra, J. Ereña, A.T. Aguayo, A.G. Gayubo, M. Olazar, J. Bilbao
Departamento de Ingeniería Química, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain; *irene.sierra@ehu.es*

In this paper the origin of deactivation of a $CuO\text{-}ZnO\text{-}Al_2O_3/\gamma\text{-}Al_2O_3$ bifunctional catalyst in the direct DME synthesis has been studied. Operating below 325ºC (limit temperature to avoid Cu sintering) and with an excess of acid function, the main cause of deactivation is the deposition of coke on the metallic function. Coke formation takes place in parallel to the methanol synthesis, by evolution to coke of methoxy groups formed in the interface between the metallic sites and Al_2O_3 support. The evolution of this coke progressively saturates the Al_2O_3 support of the metallic function and, subsequently, partially occupies the pores of the $\gamma\text{-}Al_2O_3$ acid function.

O 21
(101)

Literature review on the products of hydrothermal biomass liquefaction

Michael Kroeger, Andrea Kruse
German Biomass Research Centre, Torgauer Strasse 116, D-04347, *Michael.Kroeger@dbfz.de*

Several thermochemical processes for biomass liquefaction are investigated today. As one of them the hydrothermal liquefaction is a reasonable way to process wet biomass. Numerous tests were conducted in the past years with different input materials. For a better understanding of the process a literature review was done with a focus on the products of hydrothermal liquefaction and its relation to process parameters and input material. In a second step the products are compared to products from biomass pyrolysis processes. The review identifies several differences between the products.

O 22
(65)

Synthesis of ethanol from dimethyl ether and syngas with dual-catalyst bed reactor containing Cu-H-MOR and Cu/ZnO catalysts by one-step

X. Li, X. San, M. Meng, **N. Tsubaki**
School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, P.R. China. *xingang_li@tju.edu.cn*

Here, EtOH synthesis with a dual-catalyst bed reaction system is developed that dimethyl ether (DME) carbonylation occurred over the Cu partially ion-exchanged H-MOR catalyst with CO to produce methyl acetate (MA) in the first catalyst layer, and, consequently, the obtained MA can be hydrogenated to EtOH and methanol (MeOH) with H_2 over the Cu/ZnO catalyst in the second layer. This ethanol synthesis process is efficient and environmentally friendly without using any agriculture feed stocks and with the only by-product of water, as the formed MeOH can be further recycled to DME by dehydration.

O 28
(527)

Alumina Supported Nano-sized Cobalt Crystallites for the Fischer-Tropsch Synthesis

N. Fischer, E.van Steen, **M. Claeys**
Centre for Catalysis Research and change (DST-NRF Centre of Excellence in Catalysis)
Department of Chemical Engineering, University of Cape Town, Cape Town, 7701 South Africa, *michael.claeys@uct.ac.za*

In recent years the interest in nano-sized metal crystallites as catalysts increased enormously in the scientific community. In this study alumina supported nano-sized cobalt (hcp) crystallites have been prepared for testing in the Fischer-Tropsch synthesis (FTS). To gain further insight in the behaviour of cobalt crystallites during the FTS and the influence of their size on the activity and selectivity in-situ XRD measurements were done in conjunction with lab scale fixed bed tests. In addition emphasis was placed on temporal behaviour of the differently sized crystallites and large differences in their performance could be detected.

O 29
(134)

A Rate Equation for Dimethyl Ether synthesis from Syngas on an Alumina Supported Palladium Catalyst

M. Otarod[1], R. M. Suokowski[2], B.A. Langan[1]
[1]Katalyst Nanotehcnology and Alterntie Fuels, 10 Sterling Drive, Clarks Summit, PA 18411,
and Department of mathematics, University of Scanton, PA 17114, USA, *e-mail: KatalystNanotech@nni.com*
[2]Depatment of Chemistry and Physics, King's College Wilkes-Barre, PA 18711, USA

A rate expression for the production of dimethyl ether from carbon monoxide and hydrogen over alumina supported palladium catalyst is derived based on a mechanism consisting of eighteen elementary reaction steps. The derivation is based on a novel method of employing a combination of equilibrium and pseudo-steady-state hypotheses of the concentration of adsorbed intermediates. The rate equation shows that the rate of production of dimethyl ether is directly proportional to the partial pressures of carbon monoxide and the square root of hydrogen. Hydrogen adsorption appears to adversely impact the production of dimethyl ether.

O 30
(189)

Influence of sub-stoichiometric addition of organic agents on the structure and catalytic performance of alumina-supported cobalt Fischer-Tropsch catalysts

A. Jean-Marie, **A. Griboval-Constant**, A.Y. Khodakov, F. Diehl
Unité de Catalyse et de Chimie du Solide, USTL-ENSCL-EC Lille, Bât 59655 Villeneuve D'Ascq, France.
anne.griboval@univ-lille1.fr

This paper focuses on the influence of sub-stoichiometric addition of organic compounds on the catalyst structure and catalytic performance of alumina supported cobalt catalysts in FT synthesis. Addition of cheap and available organic agents (sorbitol and sucrose) during catalyst preparation resulted in much higher cobalt dispersion without detrimental effect on cobalt reducibility and enhances catalytic performance. This effect was less significant with amino-containing organic agents; these compounds can nevertheless be used however as promoters for cobalt reducibility.

O 31
(215)

Development of an Attrition Resistant Fischer-Tropsch Catalyst for Slurry Operation

Erling Rytter, Sigrid Eri, Dag Schanke, Hanne Wigum, Torild Hulsund Skagseth, Nonyameko Sincadu, Edvard Bergene
Statoil Research Centre Rotvoll, N-7005 Trondheim, Norway; *err@statoilhydro.com*

Careful control of catalyst particle size and shape, particle size distribution, particle density, cobalt distribution through the particles and attrition resistance are some of the requirements for a slurry Fischer-Tropsch catalyst. We have found that modifying an alumina support by 2-valent metals, including magnesium, nickel and zinc, followed by high temperature firing, results in superior mechanical and chemical attrition resistance of the catalyst. Further, a sufficiently high surface area is being stabilized. The catalyst's performance has been verified in a long term test in a semi-commercial plant, including very good wax separation and high wax purity.

O 40
(216)

MegaDME® – A Cost and Energy Efficient Technology

Bernd Ahlers, **Waldemar Liebner**, Martin Rothaemel, Eckhard Seidel
Lurgi GmbH, Lurgiallee 5, 60439 Frankfurt (Germany)

With Lurgi's MegaMethanol® technology methanol is available at a constant low price. The first derivative of methanol is DME which has a high potential as alternative to conventional diesel fuel and as LPG supplement. A process was developed integrating methanol synthesis and DME production which resulted in significant savings both in CAPEX and OPEX due to lower energy consumption, less equipment and the possible usage of stabilized methanol as feedstock. The first references are preparing for start-up and another full-size project is currently under implementation.

O 41
(230)

Highly Active and Stable Stearate-Based Cu Colloids for Methanol Synthesis

A. Rittermeier[1], S. Schimpf[1], Z. Liu[1], X. Zhang[2], D. Heeskens[1],R. A. Fischer[2], **M. Muhler**[1]
[1]Laboratory of Industrial Chemistry, Ruhr-University Bochum, Bochum, 44801 (Germany), *muhler@techem.rub.de*,
[2]Chair for Inorganic Chemistry II, Ruhr-University Bochum, Bochum, 44801 (Germany)

Copper colloids are a promising alternative catalyst for liquid phase methanol synthesis. Highly active and stable stearate-based colloids were synthesized by an efficient one-step process starting from inexpensive, air-stable salts and applied in the continuous liquid-phase synthesis of methanol. The structural changes during the reduction step and under catalytic conditions were investigated in detail. Especially in situ attenuated total reflection (ATR) infrared spectroscopy experiments proved to be highly useful to probe strong metal support interactions (SMSI) between Cu and ZnO in the colloidal system and in Cu-based powder catalysts used as reference.

O 42
(547)

Intrinsic Deactivation in Cobalt-Catalyzed Fischer-Tropsch Synthesis

Gabor Kiss, Stuart Soled, Chris Kliewer
ExxonMobil Res. and Eng. Co., Annandale, NJ, USA; *gabor.kiss@exxonmobil.com*

In this paper, we describe three intrinsic deactivation modes observed in experimental cobalt Fischer-Tropsch synthesis catalysts: cobalt oxidation reversible by mild hydrogen treatment, cobalt agglomeration, and cobalt-support mixed oxide formation. All three mechanisms involve redox transformation of the catalytically active cobalt metal.

O 43
(222)

Opportunities for CO_2 Capture in a GTL Plant

J. Sogge[1], E. Bek-Pedersen, T.P. Ursin, K. Gjerde, A.G. Folden Bakken, T. Sperle
[1]StatoilHydro Research Centre, Arkitekt Ebbels vei 10, Rotvoll, N-7005 Trondheim, Norway, *jso@statoilhydro.com*

StatoilHydro has recently performed an assessment of various measures for reducing the CO_2 emissions from a GTL plant. CO_2 avoidances from 40% to 80-90% have been investigated. CO_2 capture from various process streams within the syngas and F-T synthesis units, as well as from fired feed pre-heater flue gas, have been evaluated. This study showed that CO_2 avoidances up to around 60% can be favourably achieved by CO_2 capture from process streams. CO_2 capture from flue gas is not an attractive solution unless higher CO_2 avoidance around 80 – 90 % is demanded, where it is combined with process stream CO_2 capture.

O 44
(462)

Fischer-Tropsch synthesis over metallic honeycomb monoliths washcoated with a Co/Al_2O_3 state-of-the-art catalyst

C.G. Visconti, L. Lietti, E. Tronconi, G. Groppi, R. Zennaro, S. Rossini
Politecnico di Milano, Dipartimento di Energia, Piazza L. da Vinci 32, 20133 Milano (Italy) *carlo.visconti@polimi.it*

In principle, the application of monolithic catalysts to the Fischer-Tropsch synthesis (FTS) can solve many of the problems related to the classical FT reactors, in particular concerning the necessity to operate with short diffusion distances and low pressure drops, preferably according to the ideal plug-flow behavior, while still maintaining a reasonable inventory of catalytic material in the reactor volume. The preparation of prototype cobalt-based catalysts, washcoated onto metallic structured supports with different geometries, is described herein, together with the evaluation of the catalytic properties of such systems in the FTS at industrially relevant process conditions.

O 72
(265)

Fischer–Tropsch Synthesis over Rhodium-promoted Co/SiO_2 Catalysts

Zhen Yan, Dragomir B. Bukur and D. Wayne Goodman
Department of Chemistry, Texas A&M University, College Station, TX, USA, *goodman@mail.chem.tamu.edu*

The effects of the addition of Ag, Au or Rh to a 15 wt% Co/SiO_2 catalyst on the Fischer-Tropsch synthesis were studied. Both Au and Rh showed a promoting effect on the FT activity, whereas the addition of Ag decreased the activity. The addition of a small amount of Rh (0.1–0.5 wt%) increased the CO conversion by 50%, while the selectivity was not affected. The deactivated Rh-Co catalysts can be completely regenerated by reduction or by oxidation/reduction treatments. The promoting effect of Rh on Co/SiO_2 was studied by XRD, TEM-EDS and TPR/TPO.

O 73
(297)

New class of acid catalyst for methanol dehydration to DME

S. Ivanova, X. Nitsch, F. Romero-Sarria, B. Louis, M.A. Centeno, A.C. Roger, J.A. Odriozola
Instituto de Ciencia de Materiales de Sevilla, CSIC-US, Avda. Americo Vespucio 49, 41092 Sevilla, Spain, *svetlana@icmse.csic.es*

This study presents the preparation of a new class acid catalysts - organic-inorganic hybrids composed by different heteropoly acids and imidazolium based ionic liquids. The prepared systems presents excellent thermal stability and hydrophobicity. The physico-chemical properties and activity of the systems strongly depends on the initial heteropoly acid and on the type of the ionic liquid. The hybrids shows high catalytic activity and selectivity to dimethyl ether and excellent stability in time on stream. In addition the synthesized hybrids reveals their potential as a oxidation catalysts at high temperatures.

O 74
(332)

Syngas conversion to alcohols over MoP catalysts

Sharif F. Zaman and **Kevin J. Smith**
Department of Chemical & Biological Engineering, University of British Columbia
2360 East Mall, Vancouver, V6T 1Z3, BC, Canada. *kjs@interchange.ubc.ca*

The conversion of synthesis gas to liquid oxygenates over a series of 5, 10, and 15 wt % MoP on SiO_2, promoted with 1 and 5 wt % K is reported at 548 K, 8.27 MPa and $H_2/CO=1$. The highest C_{2+} oxygenate selectivity (76.6 C atom %) and lowest CH_4 selectivity (9.7 C atom %) occurred on the 5%K-10%MoP-SiO_2 catalyst. The major oxygenates were acetaldehyde, acetone and ethanol. Low selectivity to methanol (<5 C atom%) was characteristic of the MoP catalysts. Addition of 1 wt% Rh stabilized the catalyst and similar kinetic parameters suggested a common reaction intermediate for ethanol and acetaldehyde formation over the Rh-K-MoP/SiO_2.

O 75
(349)

Effect of ppm level sodium on CoRe/Al_2O_3 catalyst for the Fischer-Tropsch reaction studied by SSITKA

Jia Yang; A. Helland Lillebø; De Chen; A. Holmen
Department of Chemical Engineering, Norwegian University of Science & Technology, NO-7491 Trondheim Norway.
holmen@chemeng.ntnu.no

Alkali promotion for Fischer-Tropsch catalyst has been studied extensively. To understand the effect of sodium on Co based FT catalyst, CoRe/Al_2O_3 catalysts with 50 – 500 ppm Na were prepared and studied with Steady-State Isotopic Transient Kinetic Analysis. It was found out that the presence of Na enhances the binding strength of CO with Co. The activities of Co catalysts depend on the amount of Na added. Addition of Na changed the intrinsic activity ($k=1/\mathbf{t}_{12CH(x)}$) of active sites rather than changing the total number of surface active sites ($N_{CH(x)}$).

O 76
(334)

Carbon nanotube and zeolite beta-supported Ru nanoparticles as selective Fischer-Tropsch catalysts for direct synthesis of diesel fuel and gasoline

Ye Wang, Jincan Kang, Qinghong Zhang, Lei Zhang, Weiping Deng
State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China.
wangye@xmu.edu.cn

We have found that the Ru/H-beta and Ru/CNT catalysts with the supports appropriately pretreated are highly selective Fischer-Tropsch catalysts for C_5-C_9 and C_{10}-C_{20} productions. The unique adsorbed hydrogen species and acid sites on catalyst surfaces are two crucial factors in determining the product selectivities. By systematically regulating the acidities of the supports, we can control the product distributions. The size of Ru particles affects not only the TOF for CO conversion but also the product selectivities.

O 82
(356)

Deactivation of a cobalt based Fischer-Tropsch synthesis catalyst- Nature of the carbon species present on the spent catalyst

Ph. Bichon, **L. Pinard**, J. L. Lemberton, C. Canaff, J.D. Comparot, F. Maugé, Ph. Bazin, A. Popov,
E. Falabella S. Aguiar and P. Magnoux.
Laboratoire de Catalyse en Chimie Organique, UMR 6503, Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers (France). *ludovic.pinard@univ-poitiers.fr*

During the Fischer Tropsch reaction, cobalt catalysts deactivate with the time on stream. This deactivation is usually explained by a modification of the metallic function, and/or by carbon deposition. Carbon deposits may block the catalyst pores which creates diffusional limitations, poison the metal surface by binding irreversibly or even encapsulale metal particles. In this study, we show the carbon species present on the spent catalyst were mainly carboxylic acids and n- alcohols. Their evolution with time on stream will be presented and will allow to understand their role on the catalyst deactivation.

O 83
(400)

Studies of Cobalt based catalysts using Modified Alumina support for Fischer-Tropsch Synthesis

Moon Ju Park[1,2], Jung Shik Kang[1,2] and **Dong Ju Moon**[1]
[1]Clean Energy Center, Korea Institute of Science and Technology(KIST), Seoul, Korea, *djmoon@kist.re.kr*
[2]Department of Chemical & Biological Engineering, Korea University, Seoul, 130-701, Korea

The cobalt-based catalysts supported on Al_2O_3 and modified Al_2O_3 were prepared by impregnation method and characterized by N_2-adsorption, XRD, SEM, TEM, and TPR techniques. The broadening of XRD peak and TEM data revealed nanosized Co_3O_4 crystallites less than 6nm. The performance of these catalysts for FTS were tested in a fixed bed reactor under the conditions 240°C, 2.0 MPa, H_2/CO feed molar ratio of 2.0. The dependence of crysrallite size and reducibility of Co_3O_4 influenced by support were investigated with FTS activity. $Co/Al_2O_3+TiO_2$_A catalyst showed good selectivity at diesel range liquid fuel product.

O 84
(157)

Versatility of alumina-supported cobalt catalysts during Fischer-Tropsch synthesis

H. Karaca, **O. V. Safonova**, S. Chambrey, P. Fongarland, P. Roussel, A. Griboval-Constant, M. Lacroix and **A.Y. Khodakov**
Swiss-Norwegian Beamlines, ESRF, BP 220, 38043 Grenoble Cedex (France) *olga.safonova@esrf.fr*;
UCCS, USTL-ENSCL-EC Lille, 59655 VIlleneuve d'Ascq (France) *andrei.khodakov@univ-lille1.fr*

The present work addresses structural modifications of supported cobalt catalysts studied at different conditions of FT synthesis using *in-situ* XRD/XAS combined with on-line evaluation of catalyst performance. Original direct in-situ characterization has clearly shown considerable versatility of alumina-supported cobalt catalysts. Cobalt sintering and carbidization occurred at the first hours of FT reaction and resulted in a decrease in catalytic activity. Cobalt carbidization followed by hydrogenation selectively led to cobalt hcp phase, which seems to be more active than cobalt fcc phase. Cobalt oxidation by water was not observed at the realistic conditions of FT synthesis.

O 85
(436)

Conceptual study and simulation of a clean coal to methanol plant

P. Herrenschmidt, N. Girault, L. Courthial, M. Lelievre, C. Cruciani
TOTAL S.A. - GEN/ITR/TEC/PROC, 2 place Jean Millier, La Défense 6 F-92078, Paris La Défense, France,
lucile.courthial@total.com

To be able to determine the stakes and technical aspects of Coal To Hydrocarbons plants, Total Gas & Power has undertaken a study of a plant that processes 4 million metric tons per year of coal to produce methanol. The inside battery limit of the plant begins from the raw coal conveyor, and involves all the process sections with the utilities and off-sites. For a better understanding of the plant and a potential extension of the results to different feedstocks, designs and operating conditions, a simulation work was carried out. The simulator represents a fast means to test different plant configurations and analyse the consequences on the methanol production and utility consumptions.

O 98
(223)

Mechanism of the reduction of Cu-Zn mixed oxide model methanol synthesis catalyst

A.A. Khassin, H. Jobic, E.V. Dokuchits, G.A. Filonenko, A.V. Khasin, L.P. Davydova, N.V. Shtertser, L.M. Plyasova, T.M. Yurieva
Boreskov Institute of Catalysis, 5, pr. Lavrentieva, Novosibirsk 630090 Russia. *aakhassin@catalysis.ru*

Inelastic neutron scattering, *in-situ* FTIR/MS, and TG-DSC/MS data give prove that (Cu, Zn)O mixed oxide when treated in H_2 at 200°C accumulates 6H/Cu as hydroxyl groups and formates. The reduction of copper in (Cu, Zn)O mixed oxide (model methanol synthesis catalyst) occurs via reversible redox interaction with H_2 and absorption of protons as OH^--groups with $\nu = 3250$ cm^{-1} and $\delta = 1430$ cm^{-1}. The weight loss during the reduction is due to decomposition of carbonate groups admixtures to CO_2. Formates are plausible intermediates of this process, which is catalysed by molecular hydrogen.

O 99
(251)

The Roles of Carbon in Fe-based Fischer-Tropsch Catalysts under Realistic Conditions: a Combined Experimental-Theoretical Characterization Study

E. de Smit, F. Cinquini, A. M. Beale, P. Sautet, B. M. Weckhuysen
Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands. *e.desmit@uu.nl*

In this work, the different roles of carbon in the phase chemistry of Fe-based Fischer-Tropsch Synthesis catalysts were studied in situ, under realistic, high pressure reaction conditions using a combination of spectroscopic/diffraction characterization techniques, supplemented with Density Functional Theory (DFT) calculations. This approach enabled us to systematically study the stability of the different carbide and oxide phases formed during FTS as a function of the carbon and oxygen chemical potential and provided new insights into the complex structure of the Fe-based FTS catalyst system.

O 100
(439)

The History of Fischer-Tropsch Reactor Development in South Africa

A.P. Steynberg
Fischer-Tropsch & Reforming Technology Manager, Sasol Technology, P.O. Box 1, Sasolburg, South Africa,1947
andre.steynberg@sasol.com

Fischer-Tropsch technology was imported into South Africa in the 1950's. The Synthol reactors were scaled-up, in the 1970's, by a factor of about 3 for application at the world's largest industrial site that was ever constructed at a single time and thenadapted, in the 1980's, for use with the pioneering Gas-to-Liquids (GTL) plant in Mossel Bay. Also in the 1980's, a design was prepared for a demonstration scale Sasol Advanced Synthol (SAS) reactor. The demonstration facility used for the SAS reactor development was subsequently modified to provide the data to design slurry phase Fischer-Tropsch reactors for use with both iron and cobalt catalysts.

O 101
(407)

High Throughput Experimentation Techniques for the Development of new Gas-to-Liquid (GTL) Catalysts and Processes

Martin Kuba, A. Haas, P. Kolb, A. Sundermann
hte Aktiengesellschaft, Heidelberg, *Germany.Martin.Kuba@hte-company.de*

The challenges of addressing GTL reactions (MTG, FTS, HAS) with “high-throughput experimentation” will be discussed, along with the solutions and test protocols pioneered by hte AG. We illustrate a case study describing the parallel testing of Co-alumina based FTS-catalysts. Fully mass balanced hydrocarbon product distributions and ASF-plots in the carbon number range between C1-C50 can be calculated. The control of these conditions in experiments for 1-3 months time-on-stream allows for simultaneous measurement of the kinetics of 16 FTS-catalysts under industry-relevant conditions (high conversion, productivity) with high accuracy and precision.

O 102
(498)

Fischer-Tropsch synthesis in fixed bed milli-reactor: comparison with conventional laboratory fixed bed and slurry reactors

S. Chambrey, **P. Fongarland**, H. Karaka, S. Piché, A. Constant-Griboval, D. Schweich, F. Luck, S. Savin and A. Y. Khodakov
UCCS, Ecole Centrale de Lille, Cite scientifique, Bât C3, 59655 Villeneuve d’Ascq, France. *pascal.fongarland@ec-lille.fr*

Milli- and microreactors represent an attractive opportunity for intensification of the FT process increasing heat and mass transfer especially when a powdered catalyst is used. The present paper addresses particularities of FT synthesis in a milli-fixed bed reactor over a $CoPt/Al_2O_3$ catalyst. An attempt has been made to get insight in the so-called “better” performances of the fixed bed milli-reactor as compared with conventional laboratory fixed bed and slurry phase reactors for the catalytic activity and deactivation behavior.

O 103
(408)

Preparation of Co/MCM-41 with bimodal pore and its effect on Fischer-Tropsch synthesis

Jungang Wang[1,2], Debao Li[1], Bo Hou[1], Litao Jia[1],Jiangang Chen[1], **Yuhan Sun**[1], *
[1]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry,
The Chinese Academy of Sciences, Taiyuan 030001, Shanxi, China;
[2]Graduate University of Chinese Academy of Sciences, Beijing 100049, China
*Corresponding author, *Email:yhsun@sxicc.ac.cn; dbli@ sxicc.ac.cn*

The mono- and bi-modal catalysts with pore size distribution 2.5-0 nm, 2.5-17 nm and 2.5-65 nm were prepared by IWI, denoted as Co/SM-MCM-41, Co/DM-MCM-41 and Co/MM-MCM-41, respectively. The cobalt crystallite size of Co/DM-MCM-41 was smallest and the interaction of cobalt and support was weakest, which were proved by XRD, Raman spectroscopy and TPR. The FTs results showed that bimodal catalysts exhibited better activity than monomodal one, especially the double mesoporous catalyst presented the higher selectivity to C_5-C_{18} hydrocarbons and lower methane selectivity, due to the appropriate mesoporous confinement to the increase of Co particles.

NGCS
LYON
2010

Session IV - Direct-indirect conversion of methane to oxygenates, olefins, aromatics; C_1-C_3 intermediates to chemicals

O 9
(121)

Dehydro-aromatization of methane with continuous regeneration in a new model of fluidized bed reactor

M. P. Gimeno[1], J. Soler[2], J. Herguido[1], M. Menéndez[1]
[1]Aragón Institute for Engineering Research (I3A), c/María de Luna 3, University of Zaragoza, 50018 Zaragoza. Spain.
qtmiguel@unizar.es
[2]Nanoscience Institute of Aragon, c/Pedro Cerbuna 12, University of Zaragoza, 50009 Zaragoza, Spain

The direct catalytic conversion of methane into aromatics and hydrogen is a quite new route for natural gas conversion to liquids, but suffers the problem of a fast catalyst deactivation. Therefore, new contact modes must be explored to avoid the deactivation process by coke formation. The aim of this research is to develop new designs of Two Zone Fluidized Bed Reactors (TZFBR) allowing a continuous coke removal and thus keeping high catalyst activity and BTX selectivity. Moreover, a Mo/HZSM-5/Bentonite catalyst has been developed with suitable particle size and mechanical resistance for being used in Fluidized Bed Reactors (FBR).

O 10
(62)

C-H Bond Activation of Methane on M- and MO-ZSM-5 (M=Ag, Au, Cu, Rh and Ru) Clusters: A Density Functional Theory Study

Mehmet Ferdi Fellah[1,2],Isik Onal[1]
[1]Department of Chemical Engineering, Middle East Technical University, Ankara, 06531, Turkey
[2]Department of Chemical Engineering, Yuzuncu Yil University, Van, 65080, Turkey

DFT calculations are employed to study C-H bond activation of methane on $[(SiH_3)_4AlO_4(M, MO)]$ (where M= Ag, Au, Cu, Rh and Ru) cluster models representing ZSM-5 surfaces. The following activity order of clusters in terms of their activation barriers based on transition state could be classified as: Au >> Rh > Cu ~ Ru >Ag for M-ZSM-5 clusters and AgO > CuO > AuO >> RhO > RuO for MO-ZSM-5 clusters. AgO- , CuO- and AuO-ZSM-5 clusters are much more active than all the other clusters for C-H bond activation of methane (3.85 kcal/mol, 5.18 kcal/mol and 8.59 kcal/mol, respectively).

O 11
(66)

Continuous stirred tank reactor for ethylene oligomerization catalyzed by NiMCM-41

M. Lallemand, A. Finiels, F. Fajula, **V. Hulea**
Institut Charles Gerhardt, UMR 5253, CNRS-UM2-ENSCM-UM1, Matériaux Avancés pour la Catalyse et la Santé,
8 rue de l'Ecole Normale, 34 296 Montpellier Cedex 5, France. *vasile.hulea@enscm.fr*

The performances of Ni-exchanged MCM-41 as catalyst for the ethylene oligomerization were evaluated in a continuously operated slurry reactor (CSTR) operated at 30°C and 3.5 MPa over a period of 170 h time on stream. During the catalytic test the ethylene conversion was higher than 95%, indicating that the catalyst deactivation was insignificant. The reaction was highly selective, resulting mainly in C_4, C_6, C_8, C_{10} and C_{12} olefins. The CSTR unit developed in our laboratory proved to be an effective and useful tool for performing complex catalytic studies, involving three-phase systems.

O 12
(26)

Combined technologies for the oxidative coupling of methane to ethylene over W-Mn catalyst system

Jian Yang, Jun Zhao, Huanling Song, **Lingjun Chou**, Shuben Li
State Key laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China, *e-mail : ljchou@lzb.ac.cn*

Several combined processes in relation to the OCM were explored based on W-Mn/SiO_2 catalyst system. In order to pursue the more target products of ethylene, the series process with two OCM reactors was developed and 26% yield of ethylene was obtained. The combined route which steam reforming of methane was followed the OCM reaction has been applied in order to acquire higher methane utilization. For utilizing exothermic reaction of OCM x reaction coupling of OCM with steam reforming of methane was designed, ethylene and syngas were acquired simultaneously.

O 45
(551)

Kinetic Consequences of the Coverage and Reactivity of Chemisorbed Oxygen in Methane Reactions on Supported Pt, Rh, and Pd Clusters

Ya-Huei (Cathy) Chin[1], Corneliu Buda[2], Matthew Neurock[2], and **Enrique Iglesia**[1]
[1]Department of Chemical Engineering, University of California, Berkeley, CA 94720, (USA)
[2]Department of Chemical Engineering, University of Virginia, Charlottesville, VA 22904, (USA)
iglesia@berkeley.edu

Partial oxidation does not occur at the molecular scale on Pt, Rh, and Pd clusters. CH_4–O_2 mixtures form synthesis gas solely via combustion-reforming pathways. Combustion turnover rates, measured under conditions of strict kinetic control, exhibited four distinct kinetic regimes, corresponding to changes in kinetically-relevant steps and oxygen coverage as O_2/CH_4 ratios decreased. These regimes correspond to C-H bond activation on O*-O*, O*-*, and *-* and O_2 dissociation on *-* pairs as the relevant steps. Rate equations, isotope effects, and theoretical treatments, as well as measured effects cluster size on turnover rates, confirmed these mechanistic conclusions.

O 46
(147)

Effect of Zeolite Structure and Composition on Vapor-Phase Carbonylation of Dimethoxymethane

Fuat E. Celik, Tae-Jin Kim, **Alexis T. Bell**
Department of Chemical Engineering, University of California, Berkeley, CA 94720-1462, *bell@cchem.berkeley.edu*

We have recently shown that the carbonylation of dimethoxymethane (DMM) over acid zeolites provides a highly selective, low-pressure route to methyl methoxyacetate (MMAc), a precursor to ethylene glycol, avoiding ethene, the current and expensive feedstock in MEG production. At a carbon monoxide pressure of three atmospheres, a MMAc selectivity of 79% at a DMM conversion of 13% was obtained using H-FAU with a Si/Al ratio of 30. FAU showed the highest selectivity of common zeolites because its large supercages disfavored the formation of byproducts. High Al content zeolites showed lower rates due to repulsive interactions between surface species.

O 47
(124)

Selective oxidation of light alkanes with nitrous oxide

B.Z Dlugogorski, C. Evans, R.W.Joyner, E.M. Kennedy, O Sonntag1, A Stafford and M. Stockenhuber
PRC*f*E, Chemical Engineering, University of Newcastle, Callaghan Campus, NSW 2308, Australia,
michael.stockenhuber@newcastle.edu.au

In this communication we report the interdependence of catalyst properties and the performance of microporous catalysts in selective paraffin oxidation. It was found that methane and ethane conversion and oxygenate yield was dependent on a synergistic effect between acid sites and the transition metal redox function. This synergistic effect was concluded from comparison of microreactor results with temperature programmed desorption and in situ infrared spectroscopy. We can show that for Cu exchanged zeolites α iron formation is crucial for selective oxidation of methane to methanol.

O 48
(446)

Investigation of Methane Aromatization over Mo/ZSM-5 Catalysts with Operando Spectroscopy and DFT Calculations

Yong-Ming Dai, Jih-Mirn Jehng, Simon G. Podkolzin, **Israel E. Wachs**
Department of Chemical Engineering, Lehigh University, Bethlehem, PA 18015, USA *iew0@Lehigh.edu*

This investigation represents the first operando molecular spectroscopic study of methane conversion to benzene over supported Mo/ZSM-5 catalysts. The study determines the molecular structures of supported Mo species under different environments and the nature of surface carbon reaction intermediates. Additional molecular structural and reaction mechanistic insights are provided from complementary DFT calculations. The supported Mo phase is present as hydrated Mo_8O_{24} species under ambient conditions, isolated dioxo surface MoO_4 species upon dehydration and reduced amorphous MoC_x or MoO_xC_y species during methane activation to benzene.

O 49
(337)

Methanol Conversion over HZSM-22: the reaction mechanism and the effect of olefins/aromatics addition

Jinzhe Li, Yingxu Wei, Yue Qi, BingLi, Fuxiang Chang, Yanli He, **Zhongmin Liu**
National Engineering Laboratory of Methanol to Olefin, Dalian Institute of Chemical Physics, Chinese Academy of Sciences,
116023 Dalian, P. R. China, *e-mail: liuzm@dicp.ac.cn*

Methanol to olefin (MTO) conversion was studied on a home-made pulse reaction system. Under proper reaction conditions, complete conversion of methanol into olefins can be achieved over HZSM-22, which was previously reported to fail in the conversion of methanol to olefins. ^{13}C labelling experiments and the addition of olefins and aromatics all indicate that the methanol conversion followed hydrocarbon pool mechanism is prohibited over HZSM-22 and the olefins methylation and cracking mechanism predominantly occurs.

O 59
(350)

Methane to Propylene - Development of A New Combined Process

Kaoru Fujimoto[1], Xingdong Yuan[1], Hiroshi Kaneko[2]
[1]Department of Chemical and Environmental Engineering, Faculty of Environmental Engineering, The University of Kitakyushu,
1-1 Hibikino, Wakamatsu-ku, Kitakyushu, Fukuoka 808-0135, Japan, *fujimoto@env.kitakyu-u.ac.jp*
[2] Japan Gas Synthesis CO.,LTD, Nishi-shinbashi Home Bldg, 12-10, Nishi-shinbashi 1-Chome, Minato-Ku, Tokyo
105-0003, Japan

A novel industrial technologies which pass through the DME production has been developed. Especially, novel catalysts and processes which makes propylene with high efficiency has been proposed and demonstrated. The specially designed catalyst system and the recycle of by-product olefin makes possible it to produce propylene with the yield as high as 75%. The catalyst can be used at least 1 year.

O 60
(351)

Conversion of methane to methanol over Cu-ZSM-5 zeolites: A quantitative structure – performance relationship

Nadzeya V. Beznis , Bert M. Weckhuysen, Johannes H. Bitter
Inorganic chemistry and Catalysis Group, Department of Chemistry, Faculty of Sciences, Utrecht University, Sorbonnelaan 16,
3584 CA Utrecht, the Netherlands, fax: +31-30-251 -1027, *e-mail: j.h.bitter@uu.nl*

Cu-ZSM-5 materials are able to convert methane to methanol in one step using oxygen as the oxidant at low temperature. TEM results and FT-IR measurements with the co-adsorption of pivalonitrile and NO confirmed the presence of at least two copper species in Cu-ZSM-5 zeolite. i.e. copper oxide clusters on the outer surface and highly dispersed copper inside the zeolite channels. The intensities of the IR band of adsorbed NO on copper inside the channels relates linearly to the amount of produced methanol, thus indicating that copper inside the channels is relevant for the catalytic activity. This is, however, a minor species in all Cu-ZSM-5 samples under study.

O 61
(378)

Formation and interaction of Li-induced defects on MgO (001) surface: A theoretical study of Li/MgO catalyst for oxidative coupling of methane.

S. Levchenko, M. Scheffler
Fritz Haber Institute of Max Planck Society, Faradayweg 4-6, Berlin 14195, Germany, *sergey@fhi-berlin.mpg.de*

We use theoretical calculations to evaluate electronic structure and formation energies of the substitutional Li defects in the(001) surface, subsurface, and bulk MgO. Using the ab initio atomistic thermodynamics analysis, we determine the distribution of various Li-induced defects as a function of temperature and oxygen partial pressure. The analysis suggests that islands containing 50% molar concentration of the Li substitutional defects are present at the top surface at relevant temperatures. Within the islands, the oxygen vacancy formation energy is greatly decreased, possibly accounting for the high catalytic activity of Li-doped MgO.

O 62
(433)

Selective hydrocarbon conversion on ceramic oxygen membranes

J.M. Serra, S. Escolástico
Instituto de Tecnología Química (UPV-CSIC), Av. Los Naranjos s/n, 46022 Valencia, Spain, *jsalfaro@itq.upv.es*

Ceramic oxygen membranes operating at high temperatures will play an important role in future in several industrial fields. In this work it is shown the application of perovskite-based oxygen conducting membranes to oxygen separation and to the catalytic conversion of hydrocarbons into added-value chemicals as olefins. The hydrocarbons studied were methane and ethane whereas the main reaction products were ethylene and syngas. The operating conditions of the catalytic membrane reactor (temperature, gas flows and feed composition) were studied on thick disk-shaped membranes in order to maximize the catalytic selectivity and productivity.

O 110
(552)

Mechanistic Insights into the Selective Homologation of Dimethyl Ether to Branched Alkanes on Acidic Zeolites

John Ahn, Dante Simonetti, Burcin Temel and **Enrique Iglesia**
Department of Chemical Engineering, University of California at Berkeley, Berkeley, USA, *iglesia@berkeley.edu*

The selective conversion of dimethyl ether (DME) to triptane and isobutane (~80% combined selectivity) was achieved on acidic zeolites at modest temperatures (400-500 K) and DME pressures (60-250 kPa). This remarkable selectivity reflects preferential methylation to form chains with a linear C_4 backbone that terminate selectively at triptane; these chains do not readily crack or isomerize as they grow, but do so readily upon growth beyond triptane to form isobutane as the preferred β-scission product. Adamantane co-catalysts allow co-homologation of alkanes and C_1 species to give isobutane-triptane mixtures without significant unsaturated by-products.

O 111
(553)

Bio-inspired approach for mild oxidation of methane

Authors L. X. Alvarez, E. V. Kudrik, P. Afanasiev, J. M. M. Millet, D. Bouchu, **A. B. Sorokin**
Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS - Université de Lyon,
2, av. A. Einstein, 69626 Villeurbanne cedex, France. *alexander.sorokin@ircelyon.univ-lyon1fr*

N-Bridged iron phthalocyanines show remarkable catalytic properties in the oxidation of CH_4 in water at near-ambient temperatures via oxo-transfer chemistry as evidenced by low temperature UV-vis, EPR, ESI-MS, Mössbauer, XANES and EXAFS data. High turnover numbers (TON>220) were attained. The system keeps the same catalytic activity upon successive additions of H_2O_2 indicating a high stability of catalyst and even a possibility of recycling. Readily accessible solid catalyst, H_2O_2 as the clean oxidant, water as the clean reaction medium are important practical and green features of this novel approach for transformation of hydrocarbons.

O 112
(512)

Methanol conversion to light olefins on mesopore-modified SAPO-34

T. Álvaro-Muñoz, E. Sastre, C. Márquez-Álvarez
Instituto de Catálisis y Petroleoquímica, CSIC, c/. Marie Curie 2, 28049 Madrid, Spain. *c.marquez@icp.csic.es*

Microporous silicoaluminophosphate SAPO-34 with intracrystalline mesoporosity was synthesized by carbon black and chitosan templating. Mesopore-modified SAPO-34 showed improved initial conversion of methanol to light olefins. Catalyst deactivation would be promoted due to poor mesopore interconnection. Creation of oxygen functionalities on the surface of carbon black particles did not modified the effectiveness of carbon incorporation into the crystals, but improved catalyst stability.

O 113
(494)

Heteropolyacid encapsulated in $Cu_3(BTC)_2$ nanocrystals: an effective esterification catalyst

L. H. Wee[1], N. Janssens[1], S. R. Bajpe[1], I. Herman[2], C. E. A. Kirschhock[1], **J. A. Martens**[1]
[1]Centre for Surface Chemistry and Catalysis,Catholic University of Leuven, Kasteelpark Arenberg, B-3001, Leuven, Belgium.
johan.martens@biw.kuleuven.be
[2] Inst. for Chemical & Bio-Engineering, ETH Zürich, Switserland

An original synthesis approach to prepare $Cu_3(BTC)_2$ incorporated Keggin-type heteropolyacids (HPAs) involving mixing of reagents at room temperature, quenching in liquid nitrogen and freeze drying has resulted in the formation of nanocrystals having an average particle size of 50 and 65 nm in diameter, depending on the concentration of the starting solution. The X-ray diffraction (XRD) patterns revealed that the as-synthesized materials were highly crystalline possessing the framework of HKUST-1 and accommodating Keggin anions in the smaller cavities. The catalytic properties of the as-synthesized nanocrystalline materials were assessed using the model reaction of esterification of acetic acid with 1-propanol. Much higher catalytic activity compared to ultrastable Y zeolite (CVB 720) and hydrothermally synthesized $Cu_3(BTC)_2$ incorporated HPAs was obtained. No HPAs leaching nor framework deformation was observed according to both XRD and thermogravimetry analysis (TGA) confirming the stability of the as-synthesized nanomaterials. A spectroscopic characterization of the Brønsted acid sites and interaction with reagents and solvents will be presented.

O 114
(280)

The Challenges of Scale up of Methane Oxidative Coupling using the Fluidized Bed Reactor

S. Zarrinpashne, Z. Fakhroeian, E. Zhale-Rajabi,
Research Institute of Petroleum Industry (RIPI), West Side of Azadi Sport Complex, Tehran, Iran. *zarrinpashnes@ripi.ir*

When a high performance OCM catalyst is utilized in a larger scale fluidized bed reactor, the performance declines. Here, the measures to resolve the low YC_{2+} (C_{2+} yield) in a mini-Pilot fluidized bed reactor are discussed. By utilizing a new generation catalyst with nano-Perovskite structure, it has become possible to increase YC_{2+} from below 12% for the previous generation $Mn/Na_2WO_4/SiO_{2+}MgO$ catalyst, to above 15%, both at 4 bar operating pressure. By further tuning of the operating conditions, it may possible to increase the yield further. According to RIPI and JOGMEC study in 2007, a minimum YC_2+ of 18% is required for an economically feasible OCM process.

O 115
(329)

Catalytic selective oxidation of propane to acrylic acid in a fixed-bed reactor with an O_2-distributor

Wen Fang, **Qingjie Ge**, Jiafeng Yu and **Hengyong Xu**
Laboratory of Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
xuhy@dicp.ac.cn; *geqj@dicp.ac.cn*

Propane selective oxidation to acrylic acid was carried out by sequential oxidative dehydrogenation (ODH) of propane and selective oxidation to acrylic acid (SOA) of propylene steps, using a two-catalyst bed. A novel approach to improving the selectivity of target products has been presented. Based on the use of an O_2-distributor, the reaction system of propane to acrylic acid could provide a ~80% of acrylic acid selectivity and a ~19% of propane conversion at 340°C, C_3H_8 / O_2 / N_2 (mol%) = 11.0/ 20.9/ 68.1 of feed gases.

NGCS
LYON
2010
9

Session V - Energy (IGCC, catalytic combustion, hydrogen production from C_1-C_4 gases) **and novel concepts for feedstock activation** (plasma, dense membrane, etc)

O 23
(82)

H_2 production from methane reactions using $LaNiO_3$ perovskite-type precursors: Influence of the substitution of Rh and Pt

M.E. Rivas[1], C.E. Hori[2], M.R. Goldwasser[3] and **J.L.G. Fierro**[1]
[1]ICP-CSIC, Marie Curie nº 2, Cantoblanco, 28049 Madrid, Spain. *jlgfierro@icp.csic.es*
[2]FEQ – UFU Av. João Naves de Ávila 2121 Campus Santa Mônica -Bloco 1K, 38400-902 Uberlândia – MG, Brazil,
[3] Centro de Catálisis Petróleo y Petroquímica, Escuela de Química, Facultad de Ciencias, Universidad Central de Venezuela, 47102, Los Chaguaramos,

The dry reforming and the catalytic decomposition of methane are an attractive alternative for the production of hydrogen. In this study, the effect of Rh and Pt addition on the catalytic performance of $LaNiO_3$ oxide precursor during DRM and CDM reaction was investigated. The mixed oxides were prepared by sol-gel. Catalytic activity data obtained during both reactions of methane showed differences in the catalytic behavior depending on the noble metal used and the composition. The addition of Rh generates more active catalysts, incorporation of Pt composition led to a marked drop in catalytic activity.

O 24
(91)

PtM/Mg(Al)O (M = Sn,Ge) catalysts for Hydrogen Production via Ethane and Propane Dehydrogenation: Effects of M/Pt ratio

G. Siddiqi, P. Sun, **A.T. Bell**
Department. of Chemical Engineering, University of California, Berkeley, CA 94720-1462, USA *bell@cchem.berkeley.edu*

Highly active and selective dehydrogenation catalysts for the production of co-production of hydrogen and alkenes from ethane and propane are synthesized and characterized. The activity and selectivity of PtSn/Mg(Al)O and PtGe/Mg(Al)O catalysts for C_2 and C_3 dehydrogenation was found to depend strongly on the M/Pt ratio. This dependence is attributed to electronic and geometric effects of the modifiers on the supported Pt clusters. Catalyst performance was also found to depend on H_2/alkane feed ratios, with the preference of a hydrogen assisted dissociation creating a peak in activity for low H_2/alkane ratios.

O 25
(186)

Hydrogen production by glycerol steam reforming on noble metal (Rh, Ru)-doped CeZrCo mixed oxides catalysts

M. Araque, L.M. Martinez, J.C. Vargas, **A.C. Roger**
Laboratoire de Matériaux, Surfaces et Procédés pour la Catalyse (LMSPC), UMR 7515 CNRS - Université de Strasbourg,
25 rue Becquerel, 67087 Strasbourg Cedex 2, France, *annececile.roger@unistra.fr*

Selective H_2 production by glycerol steam reforming was performed on (Rh, Ru)-doped CeZrCo mixed oxides. The mixed oxides were synthesised by the pseudo sol-gel like method and characterised before and after catalytic test using XRD, TEM-EDXS, TPR, TPD and TPO. The effect of the noble metal introduction and the Ce/Zr ratio, for the CeZrCoRh mixed oxides, was evaluated. The results show that the presence of Rh and Ru modifies the CeZrCo reduction profile, improving the catalyst stability. The H_2 yield is also favoured by increasing Ce/Zr ratio in the mixed oxide.

O 26
(187)

Hydrogen production by chemical looping reforming of methane using $NiO/NiAl_2O_3$ as oxygen carrier

F-X. Chiron[1], G. Patience[1], S. Rifflart[2]
[1]Department of Chemical Engineering,. École Polytechnique de Montréal, C.P. 6079 Succ. C.V. Montréal, H3C 3A7, Québec, Canada. *francois-xavier.chiron@polymtl.ca*
[2]TOTAL S.A., Gaz & Énergies nouvelles, place Jean Millier, Paris La Défense, 92078 Cedex, France

H_2 production via chemical looping reforming of methane was investigated in a micro-fixed bed reactor loaded with 200 mg of $NiO/NiAl_2O_5$. The NiO is subsequently contacted with a synthetic air stream to reconstitute the surface and combust carbon deposited on the surface. Methane conversion nears completion but to maximize hydrogen production, the oxidation state of the carrier was maintained below 30%. Co-feeding water together with methane resulted in stable hydrogen production. Although, the carbon deposition increased with time during the reduction cycle, the production rate of hydrogen remained virtually constant.

O 27
(241)

Redox Performance of Modified Iron Oxides for Hydrogen Production

D. Yamaguchi[1], L.G. Tang[1], N. Burke[1], D. Trimm[1], **K. Chiang**[1], K. Nguyen[2]
[1]Division of Petroleum Resources, The commonwealth Schientific and Industrial Research Organisation (CSIRO), Clayton, VIC3168, AUSTRALIA, *ken.chiang@csiro.au*
[2]Chevron Energy Technology Company, Houston, TX77042, USA

This study reports the improved performance of iron oxide (Fe_2O_3) based oxygen carriers in a chemical looping scheme for hydrogen production. Various iron-based metal oxides modified with CeO_2 and/or ZrO_2 were prepared via urea co-precipitation. Two-step isothermal experiments consisted of reduction with CH_4 and re-oxidation with H_2O were carried out in a fixed bed quartz reactor. Fe_2O_3 modified with CeO_2 and ZrO_2 showed improved redox properties and thermal stability. This led to significant increases of H_2 yield and the purity of hydrogen produced.

O 63
(254)

Activation of methane and carbon dioxide in a dielectric-barrier discharge-plasma reactor to produce hydrocarbons

V. Goujard, M. H. Pham, J.M. Tatibouët, **C. Batiot-Dupeyrat**
LACCO, ESIP, UMR-CNRS 6503 - 40, avenue du recteur Pineau 86022 Poitiers cedex, France.
catherine.batiot.dupeyrat@univ-poitiers.fr

We report here our results in the transformation of methane in the presence of carbon dioxide to produce hydrocarbons. The influence of the dilution by helium, the molar ratio CH_4/CO_2 and the reaction temperature was studied. We showed that CH_4 and CO_2 conversions increases the dilution by helium due to a “penning ionization” phenomenon. The the molar ratio CH_4/CO_2 has a strong effect on reactants transformation, the selectivities of hydrocarbons (C_2 to C_4) reaches about 50% when CH_4 is used in excess. An increase in the reaction temperature (until 600°C) leads to an increase of the methane conversion and selectivty of hydrocarbons.

O 64
(116)

CH_4 Decomposition on Ni and Co Thin Layer Catalysts to Produce H_2 for Fuel Cell

F. Frusteri[1], G. Italiano[2], C. Espro[2], F. Arena[1]
[1]Institute CNR-ITAE, Via S. Lúcia 5, 98126, Messina, Italy
[2]Messina University, Dept of Industrial Chemistry, Salita Sperone 31 – 98166 S. Ágata, Messina - Italy

Paper is addressed to evaluate the behaviour of Ni and Co thin layer catalysts in the methane decomposition reaction to produce pure hydrogen for fuel cell (FC) system. Further to investigate the potentiality of a multi-layer reactor to produce H_2 in a dual-step process, the attention was focused to investigate the coke formation mechanism. Results clearly demonstrate that on Co catalysts characterized by strong metal-support interaction the carbon growing mechanism is mainly of "base-growth" type, whereas on Ni catalysts the low metal support interaction favours the formation of filamentous carbon with Ni at the tip.

O 65
(348)

Circulating fluidized bed reactor for Sorption-Enhanced Methane Steam Reforming

B. Arstad[1], C. Sprung[2], U. Olsbye[2], R. Blom[1]
1SINTEF, P.O.Box 124 Blindern, N-0314 Oslo, Norway. *bjornar.arstad@sintef.no*
2Department of Chemistry, Center for Materials Science and Nanotechnology, University of Oslo, P.O. Box 1033 Blindern, NO-0315 Oslo, Norway.

Sorption-enhanced methane steam reforming (SE-SMR) is acknowledged as a potential economically viable route for hydrogen production from natural gas with simultaneous CO_2 capture/separation. In this work we present catalyst development/studies and work applying a circulating fluidized bed reactor for continuous hydrogen production by SE-SMR. Together with fix bed reactor studies this unique reactor system has been used to study different aspects of process conditions, catalyst- and sorbent properties in SE-SMR.

O 66
(294)

Influence of the solvent used during preparation on the behaviour of Pd/α-Si_3N_4 catalysts in two distinct reactions : total oxidation of methane and 1,3-butadiene hydrogenation

F.J. Cadete Santos Aires, G. Garcia-Cervantes, I. Kurzina, J.C. Bertolini
IRCELYON, Institut de Recherches sur la Catalyse et l'Environnement de Lyon. UMR 5256
CNRS/Université Lyon I. 2 Av. A. Einstein. 69626 – Villeurbanne cedex. France. *francisco.aires@ircelyon.univ-lyon1.fr*

Pd/α-Si_3N_4 catalysts prepared by Pd acetate impregnation either in water or in toluene show different catalytic behaviour. While the catalyst prepared in toluene shows very good activity and stability in the total oxidation of methane, the one prepared inwater deactivates during reaction. The same catalysts used for the hydrogenation of 1,3-butadiene show roughly the same activity after stabilisation at 20°C; however, the catalyst prepared in water shows a much better selectivity to butenes. The results are discussed in terms of the possible migration of Si atoms from the silicon nitride support to the surface of the palladium particles, when the catalyst is prepared in water.

O 92
(375)

Experimental Investigation of Hysteresis in Methane Catalytic Combustion over Platinum

D. Dalle Nogare, S. Salemi, P. Canu
University of Padova, Department of Chemical Engineering Principles and Practice via Marzolo, 9, 35131, PD (Italy);
daniela.dallenogare@unipd.it.

A honeycomb monolith with a Pt/ γ-Al_2O_3 catalyst has been tested in order to explain the hysteresis of CPOM. At first, a CH_4/O_2=1 ratio was chosen. With different T policies it has been shown that hysteresis occurs only after ignition of the catalyst. Its dependence on the feed composition was also discussed. The hysteresis, not present for lean mixtures, has its maximum for rich and almost stoichiometric mixtures and then decreases for the richest compositions. The ignition temperature lowers with rising the CH_4/O_2 ratio. The final experiment proofs that it is possible to decrease the ignition temperature, with the only limit given by the thermal insulation capabilities.

O 93
(451)

Catalytic steam reforming of methane under conditions of applicability with Pd membranes over supported Ru catalysts

M. A. Soria[1], C. Mateos-Pedrero[1], I. Rodríguez-Ramos[1], A. Guerrero-Ruiz[2]
[1]Instituto de Catálisis y Petrol., CSIC, Madrid Spain.
[2]Dpto. Química Inorgánica y Técnica, Facultad de Ciencias UNED, Paseo Senda del Rey nº 9, 28040 Madrid Spain,
e-mail: *aguerrero@ccia.uned.es*

Three Ru catalysts supported on SiO_2, ZrO_2-SiO_2 and ZrO_2-La_2O_3 have been prepared, characterized and tested in the methane steam reforming reaction. Conditions of catalytic studies have been selected for the subsequent application in a hydrogen extraction Pd membrane reactor. That is, reaction temperatures in the range of 673-823 K and with different masses of catalyst in order to work close to the equilibrium conversion conditions. All the supported Ru samples exhibit high catalytic activity and similar CO and H_2 yields. Concerning the CO_2 produced by WGSR, yields are lower than 5%. Finally these catalysts are fully stable under reaction conditions at 813 K.

O 94
(306)

Synergetic effect of plasma/catalysis hybrid system for CH_4 removal

Alexandre Baylet
Laboratoire de Catalyse en Chimie Organique (LACCO), UMR CNRS 6503 – Université de Poitiers - 40, Avenue du Recteur Pineau 86022 Poitiers Cedex (France), *alexandre.baylet@univ-poitiers.fr*

Elimination of CH_4 in a gas mixture was performed by a plasma-catalyst reactor. For plasma experiments carried out without catalyst, the CH_4 conversion reaches 33% for 1.0 vol.% CH_4 and 49% for 0.3 vol.% CH_4 in a $N_2/O_2/CO_2/H_2O$ gas mixture ($T=200°C$, $E \sim 2000\ J.L^{-1}$). The CO is the only product. The CO yield reaches 29% and 49% for 1.0 and 0.30 vol.% CH_4, respectively. Experiments performed with a plasma-catalytic hybrid system (Pd/Al_2O_3/cordierite) show two different behaviours depending on the catalyst position. In IN-plasma position, the catalyst inhibits CH_4 conversion by decreasing the plasma volume between electrodes and eliminates CO. In POST-plasma position, the catalyst does not modify CH_4 conversion and oxidizes CO into CO_2.

O 95
(484)

Synergistic effect of Pt, Pd and perovskite oxide for water gas shift reaction

R. Watanabe[1], **Y. Sekine**[1,2], M.Matsukata[1], E.Kikuchi[1]
[1]Department of Applied Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku, Tokyo, Japan.
[2]JST CREST, 3-4-1 Okubo, Shinjuku, Tokyo, Japan. *ysekine@waseda.jp*

Water gas shift (WGS) reaction is one of the effective reactions for CO reducing process. We tried to develop a new catalyst for WGS reaction based on Pt and/or Pd catalysts supported on perovskite. Pt/$LaCoO_3$ showed high initial activity, then deactivated immediately. While, Pd/$LaCoO_3$ showed lower activity than Pt/$LaCoO_3$ but had high stability of activity. Therefore we added Pd onto Pt/$LaCoO_3$ for stabilizing the activity. 0.5 wt%-Pd/1 wt %-Pt/$LaCoO_3$ catalyst showed higher activity and stability than a commercialized catalyst. Then, we found out RedOx mechanism mainly proceeded on 0.5 wt%-Pd/1 wt-%Pt/$LaCoO_3$ catalyst by a transient test.

O 96
(537)

$LaNiO_3$ perovskite catalyst for co-production of CNTs and pure H_2 from rapid decomposition of CH_4

T. Maneerung, K. Hidajat, **S. Kawi**
Department of Chemical & Biomolecular Engineering, National university of Singapore, Singapore 117576, *chekawis@nus.edu.sg*

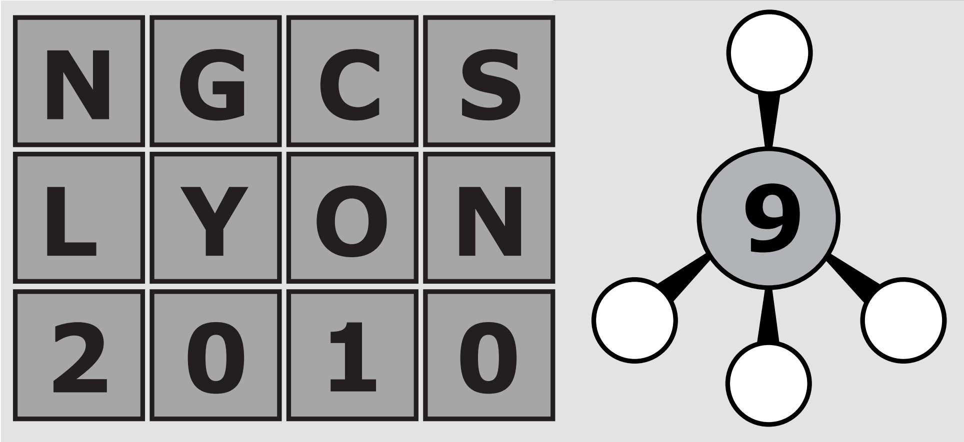
$LaNiO_3$ perovskite has been used as crystalline catalyst precursors for the decomposition of methane. Their advantages, when compared with Ni-supported catalyst, are found in this study as follows: (1) their ability to perform at higher temperature to achieve high CH_4 conversion, (> 75% at 750°C vs. 55% at 650°C for NiO/La_2O_3), (2) no deactivation of $LaNiO_3$ catalyst; and (3) their ability to maintain high activity for a long reaction time (> 20 h) due to the formation of CNTs. CNTs obtained from $LaNiO_3$ have a uniform diameter of ~25 nm, while NiO/La_2O_3 mostly formed encapsulating carbon which caused rapid deactivation of catalyst at high temperature.

O 97
(355)

Hydrogen production from dimethyl ether by steam reforming over copper alumina catalysts prepared using the sol-gel method

Kaoru Takeishi
Department of Materials Science and Chemical Engineering, Shizuoka University.
3-5-1, Jouhoku, Naka-ku, Hamamatsu-shi, Shizuoka-ken, 432-8561, Japan. *tcktake@ipc.shizuoka.ac.jp*

Dimethyl ether (DME) is expected as a clean fuel for the 21st century, from the reasons that DME burns without PM and SOx, etc. DME will be a carrier and storage of hydrogen. We have developed excellent catalysts for hydrogen production from DME steam reforming. The copper catalysts prepared using the sol-gel method have excellent hydrogen production ability compared with the usual DME steam reforming catalysts, mixture of DME hydrolysis catalysts and methanol steam reforming catalysts. It is the reason that the sites for DME hydrolysis and methanol steam reforming are co-existed and dispersed well on the catalyst surface.



Session VI - Technical-economical studies, technology demonstration, industrial processes and plant operation

O 50
(104)

Bio-SNG compared to other biofuel options from lignocellulosic feedstocks

R. Schmersahl, S. Rönsch, M. Zeymer, A. Ortwein, S. Majer, M. Klemm
Deutsches Biomasseforschungszentrum gGmbH (DBFZ), Torgauer Straße 116, 04347 Leipzig, Deutschland. *ralf.schmersahl@dbfz.de*

Sustainably produced lignocellulosic biomass is a renewable energy source that allows for the thermochemical conversion into liquid and gaseous biofuels. Three reference processes for the production of Bio-SNG, FT-Diesel and Bio-DME from lignocellulosic biomass are analysed regarding technical, economic and environmental parameters. Compared to BtL-fuels, Bio-SNG offers a promising performance in terms of fuel conversion efficiency, greenhouse gas emissions and fuel production costs. Due to the combination of a comparatively high fuel yield with low electrical power consumption, the net conversion efficiency (LHV) can reach roughly 60%.

O 51
(138)

Advantages of the Casale Plate-Cooled Converter Design

G. Germani, E. Filippi
Ammonia Casale SA, Via Pocobelli 6, 6900 Lugano, Switzerland, *g.germani@casale.ch*

Because of environmental and economical concerns, chemical plants must continuously enhance their process efficiency. This can be achieved by improving the key unit operations, which are very often reactors. The Casale Group has been involved in the design and development of advanced reactors for almost one century. The proprietary plate-cooled converter design can meet the stringent demands of process intensification because of the several advantages that it offers. Namely: high performance with low catalyst volumes, flexibility during operation, high single-train productivity, mechanical reliability and easy access to the converter internals.

O 52
(526)

Fischer-Tropsch technology demonstration - What is the right scale-up strategy from pilot plant to industrial size reactors ?

L. Fischer[1], J.-C. Viguié[1], A. Forret[1], J.-P. Héraud[1], F. Hugues[1], C. Della Torre[2], E. Mignone[2], S. Rossini[2], R. Zennaro[3]
[1]IFP Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France. *lars.fischer@ifp.fr*
[2]Eni S.p.A.Refining 1 Marketing Division, Via Maritano 26, 20097 San Donato Milanese (Mi) Italy
[3]Eni S.p.A.Exploration & Production Division, via Emilia 1 20097 S. Donato Milanese (MI) Italy

Eni and IFP have shown the pertinence of combining a 20 barrels per day (BPD) unit in Eni's Sannazzaro refinery, with non reactive slurry bubble columns equivalent to 20 and 1000 BPD and a special "Large-Validation-Tool" which reproduces the combined effect of chemical reaction conditions stress and mechanical stress equivalent to a 15000 BPD industrial unit. In view of catalyst fines formation and catalytic performances, the approach to check, improve and validate catalysts with the combination of those units has been found possible and even necessary.

O 53
(88)

Economy and Efficiency of SNG

R. Cenni, Michael Andersen, Troels Stummann, Christian Wix
Haldor Topsøe A/S, Nymøllevej 55, 2800 Kgs. Lyngby, Denmark. *roc@topsoe.dk*

The manufacture of Substitute Natural Gas, SNG, allows upgrading low quality carbonaceous feedstock to a sulphur-free gas containing over 95% methane. The process affords comparatively low emissions of CO_2 with respect to other synfuels. The design of a solid-feedstock to SNG plant depends upon a number of parameters, like choice and availability of feedstock, cost of feedstock and utilities, options for sales and disposal of sulphur-based products, fiscal policies on import and CO_2 and technical options for CO_2 sequestration. This article discusses the implications that these parameters have on the plant design and thus on the economy and efficiency of SNG.

O 54

Controlling selectivity of catalytic oxidation of C_1-C_4 alkanes

E.A. Mamedov
Sabic Technology Center, 1600 Industrial Boulevard, Houston, Texas 77478, USA. *emamedov@americas.sabic.com*

Several approaches to controlling selective oxidation of light alkanes are presented and discussed by means of representative examples. The emphasis is laid on (a) tuning catalyst properties by adding promoters to the catalyst as well as to the reaction feed, (b) controlling oxidant reactivity and/or concentration in contact with catalyst, and (c) conducting reaction in a non-conventional way. Efficiency of these approaches depends on both reaction and catalyst that makes none of them universal. The combination of catalyst design and reaction engineering is believed to deliver results economically attractive for industry.

Session VII - FP7 EU projects

O 77
(543)

Syngas production from biomass on Ni and Rh/Ni: the pilot tests in CHRISGAS Project

F. Basile[a], S. Albertazzi[a], D. Barbera[a], P. Benito[a], J. Brandin[b], W De Jong[c], G. Fornasari[a], M. Siedlick[c], E. Simeone, F. Trifirò[a].
A. Vaccari[a]
[a]Dept. Chim. Ind. e dei Mat., Univ. of Bologna, V.le Risorgimento 4, 40136 Bologna, Italy, *f.basile@unibo.it*
[b]School of technology and design, Division of Chemistry, University of Växjö, Sweden
[c]Dpt of Proc. and En., Deft Univ. of technology, Leeghwaterstraat 44, NL 2628 CA Deft, the Netherlands

The combination of hot gas filtration and reforming are the bases of the high efficiency goal in syngas production from biomass gasification. It has been studied in pilot plants using a Ni commercial like and a Rh/Ni novel catalyst comparing results with real gas from gasifier. The reforming reaction with >100 ppm H_2S leads to a [CO+H_2]>60% in the outstream (CH_4 conv 75%) using a Ni catalyst at an outlet T of around 980°C. Similar conversion has been obtained using an outlet T = 945°C with a Rh/Ni catalyst. The possibility to have catalyst with higher tolerance of sulphur (i.e. Rh/Ni) could lower the operative temperature and increase the catalyst stability.

O 78
(192)

Scientific Challenges and Recent Developments in Gas Conversion Catalysis and Processes

JL Casci
Johnson Matthey Technology Centre, Belasis Avenue, Billingham, UK. *John.casci@matthey.com*

This presentation will provide an overview of key technologies across the flowsheet: catalysts and process and the requirement to integrate. Specific technology areas that will be exemplified will include purification, synthesis gas generation and methanol and Fischer-Tropsch synthesis. In addition, using examples from our own laboratories, the key role of advanced characterisation and diagnostic tools in the elucidation of structure across the length scales will be highlighted.

O 79
(521)

Catalytic synthesis of methanol from CO_2 over layered double hydroxide-derived Cu-Zn-Al-Zr-O and Cu-Zn-Al-Ga-O mixed oxide catalysts

J J. Plona, M. Śliwa, D. Mucha, M. Zimowska, R. Dula, R. Grabowski, E. M. Serwicka
Institute of Catalysis and Surface Chemistry PAS, Niezapominajek 8, Krakow, 30-239 Poland, *ncplona@cyf-kr.edu.pl*

Two series of Cu-Zn-Al-Zr-O and Cu-Zn-Al-Ga-O catalysts (with different amount of Zr or Ga) and their Cu-Zn-Al-O analogues were synthesised at pH 7 and 9. All samples were characterised by XRD, TG/DSC, EGA-MS, ICP-OES, *in situ* high temperature XRD, BET and TPR techniques. Selected materials were tested in synthesis of methanol from CO_2/H_2 mixture at temperature range 180-240°C and pressure of 80 bars. Catalysts containing Zr and Ga obtained at pH=9 gave higher yield of methanol than both CuZnAl analogues and commercial catalyst. CuZnAlZr sample with Al:Zr ratio 2:1 obtained at pH=9 exhibited the highest catalytic activity.

O 80
(169)

Methane Aromatisation Kinetics Based Upon Elementary Steps

K. S. Wong, **J. W. Thybaut**, G. B. Marin
Laboratory for Chemical Technology, Ghent University, Krijgslaan 281-S5, B-9000 Ghent, Belgium,
e-mail: *Joris.Thybaut@UGent.be*

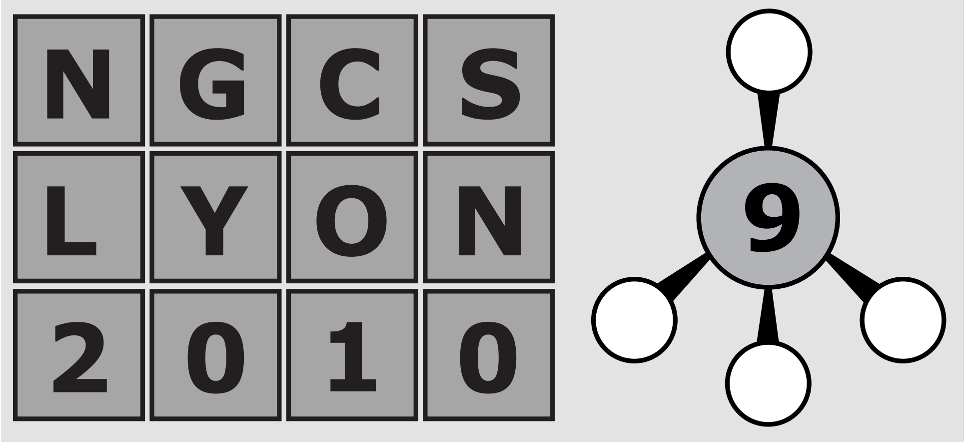
A microkinetic model is being developed for methane aromatisation and applied to a literature reported experimental data set that was obtained on a Mo/H-ZSM-5 catalyst at atmospheric pressure in a temperature range from 640 to 700°C. The model parameters can be divided in kinetic and catalyst descriptors. In the first instance adequate values are determined by (microkinetic) model regression to experimental data sets. Secondly, the catalyst descriptors can be varied in order to determine the ideal catalytic behaviour in terms of catalyst activity, selectivity and/or stability. The actual synthesis of the ideal catalyst closes the model based catalyst design loop.

O 81
(293)

Dry reforming of methane over Pt/LnCeZrO catalysts: Factors controlling performance and stability to coking

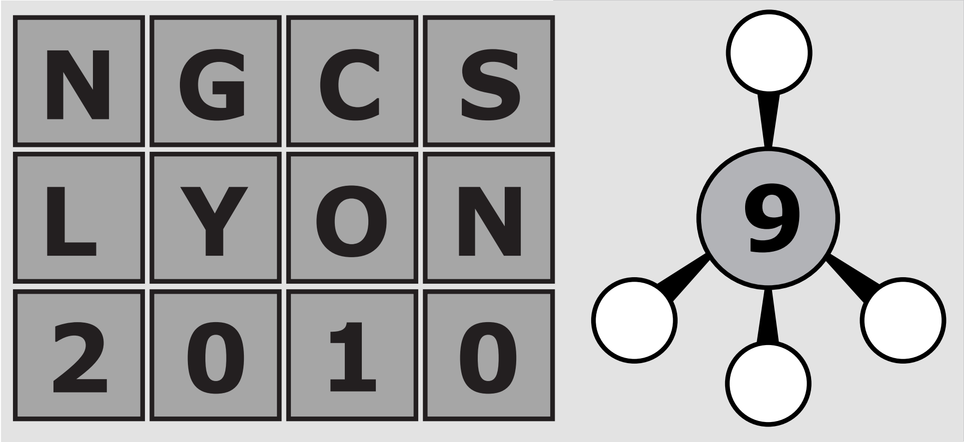
E. Gubanova, N. Sazonova, V. Sadykov, A. Bobin, G. Alikina, A. Lukashevich, S. Pokrovskaya, N. Chumakova, N. Mezentseva, C. Mirodatos
Boreskov Institute of Catalysis SB RAS, 630090, pr. Lavrentieva 5, Novosibirsk, Russia, e-mail: *gubanova@catalysis.ru*

Kinetic and transients studies of dry reforming (DR) of methane to synthesis gas over $Pt/Ln_{0.3}Ce_{0.35}Zr_{0.35}O_x$ (Ln = Pr, Gd, La) catalysts supported on walls of corundum monolith channel as well as situated within it as powders were carried out. Effect of process parameters, composition of complex oxide and Pt loading on catalytic performance was investigated. The lattice oxygen mobility and Pt-support interaction were shown to be main factors controlling catalytic activity and stability. Constants of basic steps of reaction sequence were estimated by numerical analysis of kinetic transients.



Novel Gas Conversion Symposium
C1-C4 chemistry: from fossil to bio resources

POSTER PRESENTATIONS



Session I - Natural gas and biogas purification

(filtration, CH_4/CO_2 separation, sulfur and nitrogen removal, etc)

P121
(18)

Regenerability of Zeolites for CO_2 Removal from Natural Gas

M. Tagliabue, C. Rizzo, N.B. Onorati, E.F. Gambarotta, A. Carati
Eni S.p.A., Divisione Refining & Marketing, via F. Maritano 26, 20097, San Donato Milanese, Italy
marco.tagliabue@eni.it

Zeolite adsorbents are widely used for the removal of contaminants from Natural Gas (NG).
Typically, raw NG is passed through packed columns, obtaining a CH_4-rich stream suitable for pipeline transmission or further processing. After defined service time, bed regeneration is requested.
Adsorbent chemical composition and porous texture are key parameters influencing both specific capacity and regenerability. A case-study, concerning Na-FAU zeolites, applied for CO_2 bulk removal from NG, is discussed.

---

p122
(20)

The Role of Cobalt Oxide on Deleterious Chlorine Ion over PdO/SiO_2 for CO Oxidation

Fang Wang, **Gongxuan Lu**
State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, P. R. China E-mail: *gxlu@lzb.ac.cn*

The regulating role of CoOx on deleterious Cl- over PdO/SiO_2 for CO oxidation has been thoroughly studied. By comparing the catalyst prepared from $Pd(NO_3)_2$ and $PdCl_2$, the deleterious effect of Cl^- has been confirmed. The addition of CoOx leads to the significant temperature-dependent variation of catalysts performance. The presence of CoOx is able to inhibit the agglomeration of PdO at high temperature, leads catalyst showing higher activity. The addition of CoOx can stabilize PdO species, which provide more active centers for the adsorption of reactants.

P123
(84)

Challenges in the use of anaerobic digestion gases in solid oxide fuel cells for the production of heat and power

E. Agante[1], D. J. L. Brett and N. P. Brandon
[1]Department of Earth Science and Engineering, Imperial College London, London SW7 2AZ / United Kingdom
E-mail: *e.agante06@imperial.ac.uk*

The use of anaerobic digesters combined with fuel cells is thought to result in higher generating efficiencies than traditional combustions engines. However, the efficiency modelling of the overall system, from an initial stage of decomposition in anaerobic digesters to the energy production, is also not completely understood. Moreover, the effect of the presence of hydrogen sulphide on the fuel cells degradation is well known, even at very low concentrations; and biogas cleanliness therefore needs to be ensured. To respond to this, system integration issues and operational issues, besides an analysis of sulphur removal technology systems are considered in our work.

P124
(129)

Title Development of tar removal catalyst for sewage sludge gasification

T.Haneda, T.Matsui, T. Amano,
Technology Research Institute, Tokyo Gas Co, Ltd, 7-7, Suehiro-cho 1 chome, Tsurumi-ku, Yokohama,
Kanagawa 230-0045, Japan, Japan. *haneda@tokyo-gas.co.jp*

The gasification system has been developed in order to realize incineration and energy production from sewage sludge simultaneously. Meanwhile, one of the biggest problems for the gasification system is the tar removal technology. One of the best methods for the tar removal is using catalyst, but there have been no practical tar removal catalyst for the gasification system with high sulphur concentration. Therefore we have been developing a tar removal catalyst with high sulfur tolerance. In this study, we found that $BaTiO_3$ has good performance as a tar removal agent of the gasification gas with high concentration of H_2S in the range of more than 500ppm.

P125
(201)

Characterization of Silver Species in AgNa-Y Interacting with Tetrahydrothiophene (THT)

Eun Duck Park[1], Sun Hee Choi[2], Doohwan Lee[3], Hyun Chul Lee[3]
[1]Division of Energy Systems Research, Ajou University, Republic of Korea
[2]Pohang Accelerator Laboratory, Pohang University of Science and Technology (POSTECH), Republic of Korea
[3]Samsung Advanced Institute of Technology, Republic of Korea.
edpark@ajou.ac.kr

The interaction between silver species in AgNa-Y and tetrahydrothiophene (THT), which is one of sulfur odorants in a pipeline natural gas. The formation of Ag-S bond with concomitant decreasing the interaction between Ag^+ and oxygen in the lattice as well as the interaction of Ag-Ag in the metallic Ag can be observed during the adsorption of THT at ambient temperature. This Ag-S bond was transformed into the Ag-Ag bond during the heat treatment in an inert gas above 673 K. However, the fresh chemical and electronic state of Ag can be recovered after the heat treatment in air above 673 K.

P126
(286)

Process design analysis of CO_2 capture from natural gas by fixed site carrier membrane

Arshad Hussain, **May-Britt Hägg**
Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway
E-mail: *may-britt.hagg@chemeng.ntnu.no*

In this work, a multi-stage membrane process for the separation of CO_2/CH_4 is proposed based on a novel fixed site carrier membrane which has the potential to meet the CO_2/CH_4 separation and durability requirement. A simulation analysis has been conducted to investigate the effect of process parameters on the natural gas processing cost. This analysis shows that permeate pressure has significant effect on the required membrane area, energy and ultimately on the gas processing cost. Moreover, it is possible to achieve 90% CO_2 recovery and 90% purity at relatively lower gas processing cost by employing fixed site carrier membranes.

P127
(300)

Rh-$LaCoO_3$ based catalyst for tar conversion to syngas

P. Ammendola, R. Chirone, **L. Lisi**,B. Piriou, G. Ruoppolo
Istituto di Ricerche sulla Combusione CNR Piazzale V. Tecchio, 80 125 Napoli Italia *lisi@irc.cnr.it*

A novel Al_2O_3 supported Rh/$LaCoO_3$ catalyst was investigated for the conversion of tar from biomass decomposition into a double fixed bed reactor rig by contacting the catalysts at 700°C with the mixture of gaseous and volatiles compounds emitted by the biomass in absence and in the presence of sulphurThe study was coupled with a DRITF in-situ analysis carried out under similar conditions in order to determine the active sites and the poisoning effect. Highly dispersed Rh centres are active in tar conversion. The perovskite contributes to tar conversion depressing coke deposition and prevents to some extent Rh poisoining by sulphur.

P128
(318)

Preferential CO oxidation in hydrogen-rich stream over an electrochemically promoted Pt catalyst

A. de Lucas-Consuegra, A. Princivalle, A. Caravaca, F. Dorado, C. Guizard, J.L. Valverde, P. Vernoux
Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de Castilla-La Mancha.
Avenida Camilo José Cela 12, 13005 Ciudad Real, Spain; *Antonio.lconsuegra@uclm.es*

Preferential CO oxidation in hydrogen-rich steam (PROX) was performed by coupling catalysis and electrochemistry i.e., by using an electrochemical catalyst (Pt/K-βAl_2O_3). It was shown that the PROX activity and selectivity of a Pt catalyst can be strongly enhanced by the phenomenon of electrochemical promotion or NEMCA effect. The catalytic experiments were supported by different in-situ characterization techniques (open circuit potential measurements and cyclic voltammetry), which provided useful information on the competitive chemisorption of the reactants species under different reaction conditions.

P129
(396)

Adsorptive separation of CO_2 and CH_4 on Barium and Lithium exchanged Mordenite : Simulation and Experimental Studies

Kartik S. Iyer, Sachin N. Milmile, Viorica Parvulescu, **Rajesh B. Biniwale**
National Environmental Engineering Research Institute,Council of Scientific and Industrial Research, Nagpur -440020, India,
E-mail: *rb_biniwale@neeri.res.in*

Adsorption of CO_2 and CH_4 has been studied in lithium and barium exchanged mordenite by Grand Canonical Monte Carlo simulations. The mordenite has definite unit cell composition $Na_5Al_5Si_{43}O_{96}$. Exchange of cations is made at different levels in the unit cell and adsorption of CO_2 and CH_4 is studied by generating isotherms. Polar nature of CO_2 resulted in its substantial uptake on Li – exchanged mordenite ($Na_4LiAl_5Si_{43}O_{96}$) in comparison with CH_4 where the separation selectivity is about 20 at 120°C and 100kPa. Iso-steric heat profile for both CO_2 and CH_4 indicate the presence of heterogeneous surface for adsorption of CO_2 and CH_4, where intermolecular interactions are predominant for CH_4 sorption.

P130
(418)

Polymeric Blend Membrane in Natural Gas Sweetening – Durability Study

M. W. Uddin, T.-J. Kim, C. Hesstvedt, **M.-B. Hägg**
Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), NO-7491 Trondheim, Norway,
E-mail: *may-britt.hagg@chemeng.ntnu.no*

A patented in-house blended composite membrane consisting of a fixed-site-carrier CO_2-selective polyvinylamine (PVAm) blended with a mechanically strong polyvinylalcohol (PVA) shows high performance to separate CO_2 from natural gas stream. The membrane is found durable and stable as the performances almost unaffected while exposed to typical synthetic natural gas having impurities (H_2S, higher hydrocarbons). The durability of the polymeric membrane is documented with respect to changes in process parameters such as pressure, exposure time as well as the degree of cross linking. The membrane is very promising for natural gas sweetening.

P131
(495)

Characterization of commercial solid materials for extreme hydrogen sulphide removal

Giulia Monteleone, Massimo De Francesco, Stefano Galli, Valentina Naticchioni*
ENEA R.C. Casaccia, Via Anguillarese 301, 00123 S.Maria di Galeria (RM)- *giulia.monteleone@enea.it*
* Univ. Rome "La Sapienza", Dept. of Chem. Engineering, Material and Environment

Biogas production and utilization is constantly increasing, since it represents a renewable energy available from anaerobic digestion of different organic sources. Nevertheless, due to the presence of the harmful and toxic hydrogen sulphide (H_2S) as contaminant (300÷1000 ppm), the biogas have to be purified to allow its good and safe exploitation. Fuel cells technology shows low tolerances H2S, than its fraction has to be dramatically reduced to the lower tolerance limit (<0.5 ppm). Desulphurization processes and economical, regenerable, with high selectivity, adsorbents and catalysts are investigating.

P132
(509)

Comparison of Two types Nanoporous Molecular Sieves for Efficient Adsorption of CO_2 from Natural Gas

M .Salmasi, M. Doroudian, F. Jadidi, **Sh. Fatemi**
Department of chemical engineering, university of Tehran, e-mail: *shfatemi@ut.ac.ir*

Zeolite T and SAPO-34 zeotype molecular sieves were synthesized for separation CO_2 from CH_4. The manufactured samples were used in CO_2/CH_4 separation process. The adsorption experiments of CO_2 and CH_4 were carried out in temperature of 298 K and various pressures on the surface of synthesized adsorbents and CO_2/CH_4 selectivity was determined. The results revealed that these two types of molecular sieves can be good candidates for purification of CH_4 from CO_2. Zeolite T with selectivity of about 6 had better selectivity in compare with SAPO-34.

Session II - Production of synthesis gas from natural gas, coal, biomass or waste; clean coal; syngas chemistry: purification, water gas shift (WGS), reverse WGS and synthetic natural gas (SNG)

P1
(11)

New methane conversion catalysts on the base of porous nickel for efficient synthesis gas production

V. Kirillov, Z. . Sabirova, Danilova, N. Kuzin, Yu. I. Amosov, V.V. Kireenkov
Boreskov Institute of Catalysis SB RAS, Novosibirsk, 630090 Russia, e-mail: *vak@catalysis.ru*

The present work considers the effect of preparation conditions on the phase composition and texture of the supports based on MgO/porous nickel, and performance of the synthesized nickel catalysts for the reaction of methane steam reforming. For characterization of the supports and catalysts, the methods of X-ray diffraction analysis, low-temperature nitrogen adsorption, electron microcopy and local X-ray spectrum analysis were used. The synthesized catalysts demonstrated stable activity during 50 h; no coke formation was observed. Comparative analysis showed that activity of the synthesized nickel catalyst supported on MgO/porous nickel exceeded that of the commercial catalyst.

P2
(23)

Effective Ni-based Catalysts supported on La_2O_3 for Methanation of Carbon Dioxide

Huanling Song, Jian Yang, Jun Zhao, **Lingjun Chou**
State Key laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China, e-mail : *ljchou@lzb.ac.cn*

An efficient Ni/La_2O_3 catalyst for methanation of CO_2 was developed and different preparation methods were investigated. More than 1000g kg^{-1} h^{-1} of space-time yield to methane with selectivity of 100% was obtained over these catalysts at 380°C and 1.5MPa pressure. Characterization results of in-situ XRD, XPS and H_2-TPR indicated the stabilities of catalysts were affected by preparation methods. The interaction between Ni and La_2O_3 and formation of lanthanum oxycarbonate ($La_2O_2CO_3$) could play the important role in excellent catalytic performance of Ni/La_2O_3 catalysts.

P3
(27)

Dry reforming of methane over mesoporous Pt/ La_2O_3-Al_2O_3 catalysts: Effect of the lanthana content on the catalytic activity.

J. C. S. Araujo[1], A. N. Pinheiro[1], A.Valentini[1], J. M.C. Bueno[2], J. L. G. Fierro[3], A. C. Oliveira[1]
[1]University Federal of Ceará, bloco 940, 60.000-000, Fortaleza, Ceará, Brazil. *alcineia@ufc.br*
[2]University Federal of São Carlos, C.P. :676, 13565-905,São Carlos,São Paulo, Brazil.
[3]Institute of Catalysis y pertoleoquimica, C.P.CSIC, Cantoblanco, 28049, Madird, Spain.

The effect of the lanthana content on the textural and structural properties of Pt/ La_2O_3-Al_2O_3 was studied. All catalysts were prepared by the sol-gel method using appropriate Al and La precursors. A 1wt% of platinum was incorporated to the solids. The catalysts were characterized by XRD, chemical analysis, ^{27}Al MAS NMR, N_2 adsorption isotherms, TPR as well as DRIFTS. The increased activity observed during the dry reforming of methane was due to the ability of [LaPtOx]Pt^0-like entity to eliminate the coke. The accessibility of the Pt species to methane and carbon dioxide promoted the reaction by increasing the La_2O_3 content.

P4
(28)

Detailed study of the nickel aluminates properties during the dry reforming of methane

A. N. Pinheiro, A.Valentini, A. C. Oliveira[1]
[1]University Federal of Ceará, bloco 940, 60.000-000, Fortaleza, Ceará, Brazil. alcineia@ufc.br

A series of Ni-containing catalysts were synthesized and calcined under N_2 or air atmosphere. Analyses by DSC, TG, DRX, and TPR evidenced that Ni^o entities with low accessibility to CH_4 and CO_2, were responsible for the low catalytic performance of the N_2 calcined samples. However, samples calcined under air atmosphere produced $Ni^o/NiAl_2O_4$ highly active for CH_4 conversion. For sake of comparison, we increase the Ni content from 3 to 13wt% as well as the temperature of calcinations (ca. 700-900°C) and the best result obtained for 13wt% of Ni at 700°C indicated the $Ni^o/NiAl_2O_4$ activity and stability towards methane conversion.

P5
(36)

CO_2 reforming of methane to synthesis gas over Rh-Ni/Ce-Al_2O_3 catalysts

Marco A. Ocsachoque[1,2], Claudia E. Quincoces[1,3], F. Pompeo[1,3], M.G.González[1,2]
[1]Centro de Investigación y Desarrollo en Procesos Catalíticos Dr J.J.Ronco, CONICET, UNLP, 47 Nro 257, 1900 La Plata, Argentina, *mgg@quimica.unlp.edu.ar*
[2]Facultad de Ciencias Exactas, [3]Facultad de Ingenieria 47 y 115, 1900 La Plata, Argentina

A serie of Ni/Ce-Al_2O_3 catalysts modified by Rh, were tested in order to observe the effect on activity, stability and deactivation during CO_2 reforming of methane. The catalysts were characterized by DRX, TPR, BET, TGA, TEM and catalytic test. The results show that the addition of 0.5% of Rh improve to Ni based catalyst exerted an important effect on the activity and the stability on Ni/CeAl(650), which showed the best performance for the CO_2 reforming of CH_4. The modification of support with CeO_2 improve the metallic dispersion and decrease the carbon formation.

P6
(41)

Design of stable Pt and Ni based catalysts for biomass gasification

B. Matas Guell, I.V. Babich, L. Lefferts, K. Seshan
Catalytic Processes & Materials, Faculty of Science and Technology, University of Twente, PO Box 217, 7500 AE, Enschede, The Netherlands, *k.seshan@utwente.nl*

Catalyst stability, affected negatively by deposition of carbonaceous species (coke), is strongly influenced by the nature of the catalyst support and can be improved by presence of oxygen in gas phase. A comparison between Pt/ZrO_2 and Pt/CeO_2 in the absence and presence of oxygen clearly indicates that ceria improves catalyst stability significantly as both oxygen and water can be used as oxidants. Ni-based catalysts (Ni/ZrO_2) promoted with potassium and/or lanthanum show improved stability due to enhanced gasification of carbonaceous species by facilitating the formation of reactive OH groups or by forming an lanthanum oxy-carbonate phase during reaction.

P7
(47)

Conversion of biomass products into syngas and hydrogen using porous membrane catalytic systems

M. Tsodikov, V. Teplyakov, A. Fedotov, V. Zhmakin, D. Roizard, A. Kiennemann, C. Courson, I. Moiseev
A.V. Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences (TIPS RAS),
Leninsky pr.29, 119991, Moscow, Russia. *tsodikov@ips.ac.ru*

This study presents the original membrane systems with catalytic activity in processes of methane and other biomass products conversions into syngas and hydrogen at moderate temperatures (600-650°C). It was shown that the most active catalysts from the list of studied samples in dry methane reforming are La-Ce and Pd-Mn on Ni-Al membrane. In steam reforming of ethanol, acetic acid and glycerin the membrane catalytic systems, modified by Pd, Pd-Zn and Pd-Co catalysts, showed complete conversions of substrates with high hydrogen selectivity.

P8
(50)

High-Temperature Oxidation of Natural Methane with Hydrogen Peroxide

Z.Y.Ramazanova[1], L.M.Gasanova[1], **T.M.Nagiev**[1,2]
[1]Nagiev Institute of Chemical Problems, National Academy of Sciences of Azerbaijan.
29 H.Javid Av., 370143 Baku, Azerbaijan Republic;
[2] Baku State University, 370143 Baku, Azerbaijan Republic,
e-mail: *tnagiev@azeurotel.com, tnagiev@azeriland.com*

As observed in the experiment, a variation of H_2O_2 concentration in the aqueous solution and other basic parameters of the process may induce the synthesis of gas with given H_2/CO ratio for its further application in methanol or ammonia synthesis. In the latter process, low CO concentration is required. Compared with the common high-temperature conversion of natural gas and further carbon oxide conversion on a catalyst, the current process promotes process simplification: the reaction is implemented at relatively low temperature (860-900°C instead of 1400-1600°C for existing non-catalytic processes of methane conversion) and an additional unit for catalytic conversion of carbon oxide is excluded (in NH_3 production).

P9
(58)

Methane dry reforming over nickel-based bimodal pore catalyst

Kai Tao, Yi Zhang, Soichiro Terao, Yoshiharu Yoneyama, **Noritatsu Tsubaki**
Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku 3190, Toyama 930-8555, Japan,
e-mail: *tsubaki@eng.u-toyama.ac.jp*

In this study, Ni/Al_2O_3-SiO_2, Ni/ZrO_2-SiO_2 bimodal pore catalyst and Ni/SiO_2 were investigated for methane dry reforming at 973K. The XRD and chemisorption results confirmed that bimodal catalysts showed smaller Ni particle size and higher Ni metal dispersion, when compared with unimodal catalyst (Ni/SiO_2). Ni/Al_2O_3-SiO_2 bimodal catalyst showed the best catalytic performance. The addition of CeO_2 increased the stability of Ni/Al_2O_3-SiO_2 catalyst and there was no deactivation observed over $Ni/CeO_2/Al_2O_3$-SiO_2 catalyst during 20h reaction under the reaction condition of the present study. (T=973K, P=0.1MPa, W/F=0.25 g-cat.h/mol, CH_4/CO_2/Ar=5/5/1).

P10
(61)

Water gas shift reaction over CuB_2O_4 catalyst

S. Boumaza[1], A. Boudjemaa[1], A. Auroux[2], S. Bennici[2], M. Trari[1], A. Bouguelia[1] and **R. Bouarab**[3]
[1]Laboratoires C. G. N. et L. S. V. E. R., Faculté de Chimie, USTHB, BP32, El-Alia, Bab-Ezzouar, Algiers, Algeria.
[2]Institut de Recherches sur la Catalyse et l'Environnement de Lyon, UMR 5256, CNRS-UCB Lyon1, 2 Avenue Albert Einstein, 69626, Villeurbanne Cedex, France.
[3]Laboratoire des Biotechnologies Environnementales et de Génie des Procédés, E. N. S. Polytechnique, 10 ave H. Badi, Algiers, Algeria.
rabah.bouarab@enp.edu.dz

The WGS Reaction is catalysed industrially over two types of catalysts, namely Fe-Cr (HTS) and Cu-Zn (LTS).
In this study, we develop a series of CuB_2O_4 spinel catalysts *(with B = Al, Zn, Mn, Co, Cr and Fe)*. The catalysts have been prepared by the co-precipitation method, characterized by XRD, TG, BET and H_2- TPR and tested in the CO + H_2O reaction at atmospheric pressure. In the temperature range 150-250°C, it was found that the conversion of CO to CO_2 is dependent on the Cu particle size. The tested systems can be ranked as follows: Cu-Al > Cu-Zn-Al > Cu-Mn > Cu-Cr > Cu-Fe >> Cu-Co at 250°C.

P11
(67)

Methanation of CO_2 over Ni-$Ce_{0.72}Zr_{0.28}O_2$ catalysts: influence of metal loading on catalyst structural properties and on catalytic performance

Fabien Ocampo, Benoit Louis, Anne-Cécile Roger
Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse, LMSCP, UMR CNRS 7515, ECPM – Université de Strasbourg, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France. *fabien.ocampo@ulp.u-strasbg.fr*

Ni-$Ce_{0.72}Zr_{0.28}O_2$ catalysts containing different amounts of Nickel were prepared, characterized and subsequently tested in the CO_2 methanation reaction. The effects of the pre-treatment and of reaction temperature were investigated as well as the impact of Rh addition to the catalytic system.
Ni^{2+} partial insertion into the fluorite structure was found to be a major parameter, increasing the activity and stability of the catalysts. Extremely high CO_2 conversions were achieved at 350°C, together with full selectivity towards methane (>98%). The catalysts also exhibited high stability during 150 h on stream.

P12
(94)

Syngas production using Ni-Ce catalysts supported on delaminated clay. Effect of Ni content.

C. E. Daza[1], A. Kiennemann[2], S. Moreno[1], **R. Molina**[1]
[1]Estado Sólido y Catálisis Ambiental. Departamento de Química, Facultad de Ciencias, Universidad Nacional de Colombia, AK 30 No. 45-03, Bogotá, Colombia; Fax: (571)-316-5220. *ramolinag@unal.edu.co*
[2]Laboratoire des Matériaux, Surfaces et Procédés pour la Catalyse LMSPC, UMR CNRS 7515, ECPM - Université Louis Pasteur, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France.

Ni catalysts with 3%Ce supported on Al-PVA delaminated clay were obtained. The effect on the Ni loads between 5 and 20%wt was studied. The catalysts synthesized showed high catalytic conversion and selectivity to produce syngas with H_2/CO ratios between 0.8 and 1.0 by means of CO_2 reforming of methane. The Ni load has a significant effect on conversions and especially on the formation of coke. Loads of 15 and 20% caused a significant increase in coke formation which was associated with increasing particle size and the formation of large quantity of low interaction NiO species.

P13
(95)

Steam reforming of glycerol on Ni-Mg-Al catalyst. Product distribution

M.L. Dieuzeide[1],Adriana Romero[1], **N. Amadeo**[1]
[1]Laboratorio de Procesos Catalíticos. Departamento de Ing. Química. Facultad de Ingeniería. Unversidad de Buenos Aires. Pabellón de Industrias. Ciudad Universitaria. 1428 C.A .B.A. Argentina. *norma@di.fcen.uba.ar*

The aim of this work is to study the product distribution of glycerol steam reforming using a catalyst based on NiMgAl hydrotalcite as precursor, in order to propose the reaction scheme. Experiments have been carried out at atmospheric pressure and space velocities of 0.01-0.118 h^{-1} and temperature between 500-700°C. Under these operating conditions it has been found that the reactions that seem to take place are: glycerol decomposition, water gas shift and methane steam reforming reactions. At low space velocity and 600°C the hydrogen yield obtained is 94.7% of the stoichiometric one.

P14
(96)

Ni-Pr Catalysts supported on clays modified for the reaction of the reforming of methane with CO_2

O. Gamba, J.Carriazo, S. Moreno, **R. Molina**
Facultad de Ciencias, Universidad Nacional de Colomiba, AK 30 No. 45-03, Bogotá. Colombia. *ramolinag@unal.edu.co*

Methane can be transformed into syngas through the CO_2 reforming reaction. This catalytic process has great advantages due to the consumption of two gases related to the greenhouse effect and production of liquid fuels. Nevertheless, its industrial application must overcome different disadvantages, where the deactivation of the catalysts by the coke formation is the main aspect of it. The present work describes the synthesis of catalytic systems based on modified clay minerals with nickel and praseodymium, which shows a benefic effect due to Pr on the catalytic activity and the reduction of coke.

P15
(110)

Removal of CO in reformate gas by high temperature WGSR on Cr-free metal oxide catalysts

Joon Yeob Lee, Dae-Won Lee, Seongmin Kim, **Kwan-Young Lee**
Department of Chemical and Biological Engineering, Korea University, Seoul, 136-701, South Korea, *kylee@korea.ac.kr*

Cr-free metal oxide catalysts were prepared by coprecipitation method and the catalytic activity of these to high temperature water gas shift reaction were performed under reformate gas condition at ambient pressure. Cr-free Fe-based catalysts with containing appropriate amounts of nickel showed higher catalytic activity than that of the commercial catalyst (Fe-Cr) for high temperature WGSR of fuel processor using LNG. Fe-Ni metal oxide catalysts were characterized by XRD, BET, etc.

P16
(111)

Analysis of a Rh-based C_3H_8-CPO autothermal reformer: reaction kinetics, reactor modelling and pilot-scale testing

A. Donazzi, D. Livio, M. Maestri,A. Beretta, **G. Groppi**, E. Tronconi, P. Forzatti
LCCP-Laboratory of Catalysis and Catalytic processes, Dipartimento di Energia, POlitecnico di Milano,
piazza Leonardo da Vinci 32, 20133 Milano, Italy. *gianpiero.groppi@polimi.it*

The dynamic and steady state performances of a C_3H_8-CPO reformer were tested at the pilot scale and analyzed based on a detailed reactor model which incorporates surface kinetics, independently derived. The thermal behaviour represents a critical issue for the reactor stable operation. Much higher temperatures are reached than in the case of CH_4-CPO. In both processes, O_2 consumption is mass transfer limited. Though, C_3H_8 steam reforming tends to be slower than CH_4 steam reforming since gas-solid diffusion resistances are more important. The balance between exo- and endo-thermic reactions is thus less efficient. Catalyst ageing causes further T-increase.

P17
(119)

Effect of Sodium Addition on Co/ZnO Catalyst for Ethanol Steam reforming

Kyoung Suk Kim, So Yun Lee, Jin, **Yong-Kul Lee**
Department of Chemical Engineering, Dankook University, 126 Jukjeondong, Yongin, 448-801, Korea
yolee@dankook.ac.kr

Effect of sodium addition on Co/ZnO catalysts were investigated by varying the amount of sodium content on the catalyst samples and were applied for ethanol steam reforming. A wide range of techniques was employed to characterize the catalysts : XRD, TPR, TPO, EXAFS. Activity test performed at 773K and GHSV of 60,000h^{-1} showed that sodium promoted catalysts had better activity (75% H_2) than unpromoted one (69.6% H_2). EXAFS analysis confirmed that cobalt phase remained after reaction for sodium-promoted sample, indicating that sodium addition is likely to improve the stability of cobalt phase.

P18
(126)

Nanostructured Ni alumina supported catalysts for CO_2 reforming of methane

[1]M. García-Diéguez, [1]I.S. Pieta, [1]M.C. Herrera, [1]M.A. Larrubia, [2]R. Pereñíguez, [2]J.P. Holgado, [2]A. Caballero, [1]**L.J. Alemany**
[1]Dpto. de Ingeniería Química, Facultad de Ciencias, Campus de Teatinos, UMA. E-29071, Málaga Spain, *luijo@uma.es*
[2]Instituto de Ciencia de Materiales de Sevilla and Dep. Química Inorgánica (USE-CSIC)
Avda. Américo Vespucio 49, 41092, Sevilla, Spain

Monometallic Ni catalysts supported on a nanofibrous alumina and prepared by two different methods, reverse microemulsion (ME) and incipient wetness impregnation (IM), were studied for the dry reforming of methane. Support and catalysts were characterized (XRD, TEM, XPS, Raman and Elemental Analysis) and tested under reaction conditions. Characterization results showed that preparing the catalyst by ME avoids the formation of $NiAl_2O_4$, promotes the reducibility of Ni and its dispersion. Moreover, the catalyst prepared by ME and supported on the nanostructured alumina was more stable for the CO_2 reforming and its net carbon formation was minimal.

P19
(127)

High stable and carbon free NiMg/Al_2O_3 catalyst for CO_2 reforming of Natural Gas components

M. García-Diéguez, I.S. Pieta, M.C. Herrera, M.A. Larrubia, **L.J. Alemany**
[1]Departamento de Ingeniería Química, Facultad de Ciencias, Campus de Teatinos,Universidad de Málaga, E-29071, Spain,
luijo@uma.es

A NiMg catalyst supported on a nanofibrous alumina and prepared by the reverse microemulsion method was studied for the dry reforming of Natural Gas components (methane and propane). The catalyst was characterized by conventional methods and tested under reactions conditions. Characterization results after reaction revealed a nanostructured system with MgO segregated over the nanofibrous alumina and the presence of Ni0 well dispersed and reduced, without metal sintering. The catalyst was highly selective to H_2 and CO in the CO_2 reforming of methane and propane, registering a minimal net formation of carbon.

P20
(128)

Effect of the synthesis methods in the reactivity of $LaNiO_3$ for the dry reforming of methane

[1]R. Pereñíguez, [1]V.M. González-delaCruz, [2]M. García-Diéguez, [2]M.A. Larrubia, [2]**L.J. Alemany**, [1]J.P.Holgado, [1]A. Caballero
[1]Instituto de Ciencia de Materiales and Dpto. Química Inorgánica, (CSIC –Univ. de Sevilla) Av. Américo Vespucio, 49.
41092 Sevilla, Spain, *caballero@us.es*
[2]Departamento de Ingeniería Química, Facultad de Ciencias, Campus de Teatinos, Universidad de Málaga E-29071, Málaga Spain

Dry reforming can be used to obtain synthesis gas (syngas) with a low H_2/CO ratio, suitable for the preparation of valuable chemicals. The Ni-based catalysts present the best balance between economical cost and catalytic performance, but are very sensible to deactivation due to coke deposition. Perovskite $LaNiO_3$ was prepared by four diverse methods and characterized to study the effect of the synthesis in the final properties of the catalyst and their activity as a precursor for carbon dioxide reforming of methane. In this word we have studied niquelites prepared by four methods resulting in $LaNiO_3$ rombohedral phase and the presence of an amorphous NiO phase in different proportions which could be responsible of the decrease of conversion.

P21
(133)

Au/ZrO_2 catalysts for low-temperature water gas shift reaction: Influence of particle sizes

Wenjie Shen, Juan Li, Na Ta, Wei Song, Ensheng Zhan, Yong Li
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
shen98@dicp.ac.cn

The activity of Au/ZrO_2 catalysts for low-temperature WGS reaction could be greatly improved by reducing the sizes of zirconia particles, which affected significantly the Au-ZrO_2 contact boundaries where the reaction takes place. For the Au/ZrO_2-T catalysts with similar Au particle size, the increase in the size of ZrO_2 particle decreased the concentrations of surface OH groups as well as the Au-ZrO_2 periphery, leading to a remarkably reduced reaction rate. The dominant reaction pathway for the WGS reaction on the current Au/ZrO_2 catalyst is the associative formate route with surface regeneration of the zirconia support.

P22
(145)

Coupling CO_2 Capture in catalytic reactions for the Conversion of Biomass to H_2

L. He, **D. Chen**
Department of Chemical Engineering, Norwegian university of Science and Technology, Sem Sælands vei 4,
Trondheim, NO-7491, Norway. *de.chen@chemeng.ntnu.no*

With regard to hydrogen production, thermodynamic analysis is performed on coupling CO_2 capture to the reaction process for reforming methane, ethanol, glycerol, sorbitol and glucose, representative of fossil fuel and biomass-derived chemicals. Coupling CO_2 capture with reforming reactions is expected to improve hydrogen yield and purity to a large extent by improving the equilibrium conversion. In addition, glycerol, sorbitol and glucose, are proved to be competitve candidates as feedstocks in the CO_2 capture integrated process by yeilding high hydrogen purity.

P23
(163)

Oxygen feeding alternatives for the ATR of methane

M. L. Rodríguez[1], D. E. Ardissone[2], M. N. Pedernera[1], D. O. Borio[1]
[1]PLAPIQUI (UNS-CONICET), Camino La Carrindanga Km. 7 , 8000 Bahía Blanca, Argentina.
[2]FICES (UNSL), Av de Mayo 384, 5730 Villa Mercedes (San Luis), Argentina. *mlrodriguez@plapiqui.edu.ar*

A simulation study of the ATR of CH_4 in three different reactor designs is presented. Each design represents a different O_2 feed distribution. The axial temperature profiles of the reactors and their performance are analyzed by means of a 1-D , pseudo-homogeneous model considering a *Varying Degree of Reduction* (VDR) of the Ni catalyst.

The results suggest that the hot spots are closely related to the degree of reduction of the Ni catalyst. At high O_2 concentrations, the degree of reduction is not enough to enable the evolution of the steam reforming reactions in parallel with the methane oxidation. The axial distribution of the O_2 feed strongly affects the reactor performance.

P24
(165)

Effect of synthesis method on structural proprieties and dry methane reforming activity of Ni-Co catalysts supported over MgO nanoparticles

Edder García, **Lynda Belandría**, Jairo Rondón, Freddy Imbert
Laboratorio de Cinética y Catálisis, Departamento de Química, ULA, Hechicera, Mérida, Venezuela, *lyndabelandria@ula.ve*

Ni and Co and bimetallic Ni-Co particles were supported over MgO nanoparticles by: a conventional impregnation method (CIM), an impregnation with surfactant method (ISM) and a urea combustion method (UCM). Ni-Co catalysts have a higher activity (TOF) that those Ni or Co monometallic, also the synthesis method affect the catalytic performance. All catalysts were characterized by XRD, EDX-SEM, N_2 adsorption, H_2 chemisorption and temperature-programmed reduction (TPR). It was revealed that, the preparation method affect the metallic particle side and the interaction with the support.

P25
(180)

Pyrolysis of individual and mixed biomass, plastics and used tires

M. Bajus, M.Batík, E. Hájeková
Faculty of Chemical and Food Technology, STU Radlinského 9, 812 37 Bratislava
martin.bajus@stuba.sk

The pyrolysis processes was carried out in batch reactor, keeping the range of temperature from 450 to 570°C. We have investicated qualitative and quantitative composition of gases, liquids and solid residue (coke). The main constituents of pyrolysis gases were carbon dioxide, carbon oxid as non-hydrocarbons and hydrocarbons. At higher temperatures pyrolysis (500°C) of mixed biomass and plastics, the amount of carbon oxides was decreasing and the amount of hydrocarbons from C_1 to C_3 were increasing.

P26
(185)

Development of Ni/MgO-ZrO_2 catalysts for dry reforming of methane

B.M. Nagaraja[1], D.A. Bulushev[1], S. Beloshapkin[2], J.R.H. Ross[1]
Charles Parsons Initiative, Department of Chemical & Environmental Science[1] and MSSI[2], University of Limerick, Limerick, Ireland.
bhari.mallanna.nagaraja@ul.ie

Novel Ni/MgO-ZrO_2 catalysts have been developed for dry reforming of methane to synthesis gas. The importance of the MgO/ZrO_2 ratio, the catalyst preparation method, the pre-treatment and the Ni loading have all been shown.
A 10 wt.% Ni/MgO-ZrO_2 catalyst had a high activity and stability similar to that of a 10 wt.% Ni/MgO catalyst and a much higher activity than that of a 10 wt.% Ni/ZrO_2 catalyst. Almost no carbon deposition took place on these catalysts under reaction conditions at 1023 K. The catalysts were characterised by XRD, XPS, BET surface area measurements and HRTEM/EDS.

P27
(188)

Methane Conversion to Syngas over Supported Low-loaded Ni Catalysts: The Powerful Enhancement of Performance at Low Temperatures by Traces of Rh

Claudia Berger-Karin,Uwe Rodemerck, **Evgenii V. Kondratenko**
Leibniz-Institute for Catalysis, Albert-Einstein-Str. 29A, 18059 Rostock, Germany. *evgenii.kondratenko@catalysis.de*

It has been demonstrated that alumina-supported bimetallic catalysts with low loadings of Ni (3 wt.%) and Rh (0.005 - 0.03wt.%) are active and selective for syngas production via partial oxidation of methane. The presence of tiny amounts of Rh is an essential requirement for producing syngas at temperatures as low as 600°C. The catalytic performance of bimetallic materials was close to that of one catalyst containing 0.15 wt% Rh. It should be especially noted that the order of impregnation of alumina with Rh and Ni solutions influenced the catalytic activity of the bimetallic system; it appears that Ni should be deposited prior to Rh.

P28
(194)

Comparison of Oxygen Permeability and Stability of Perovskite Type BSCFMO (M =Al, Co, Mn, Fe) Membranes in order to apply into a POM membrane reactor

Ensieh Ganji Babakhani, Jafar Towfighi, Akbar Zamanian
Gas Department, Research Institute of Petroleum Industry (RIPI), P.O. Box 18745/4163,Tehran , Iran, *ganjie@ripi.ir*

Perovskite-type $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.1}M_{0.1}O_{3-\delta}$ (M = Al, Co, Mn, Fe) oxide membranes were synthesized and oxygen permeation through these membranes was studied by the GC method using a high-temperature permeation cell. High permeation fluxes were observed. The permeation flux of BSCFAlO membrane reached about 3.0 cm^3min^{-1} cm^{-2} under air/He gradients at 950°C. In order to successfully apply these materials into the fabrication of membrane reactors for the partial oxidation of methane (POM) to syngas, the structure stability of these materials under a reducing atmosphere of syngas was investigated by H_2-TPR technique.

P29
(196)

Effect of synthesis method on structural proprieties and dry methane reforming activity of Ni-Co catalysts supported over MgO nanoparticles

Edder García, **Lynda Belandría**, Jairo Rondón, Freddy Imbert
Laboratorio de Cinética y Catálisis, Departamento de Química, ULA, Hechicera, Mérida, Venezuela, *lyndabelandria@ula.ve*

Ni and Co and bimetallic Ni-Co particles were supported over MgO nanoparticles by: a conventional impregnation method (CIM), an impregnation with surfactant method (ISM) and a urea combustion method (UCM). Ni-Co catalysts have a higher activity (TOF) that those Ni or Co monometallic, also the synthesis method affect the catalytic performance. All catalysts were characterized by XRD, EDX-SEM, N_2 adsorption, H_2 chemisorption and temperature-programmed reduction (TPR). It was revealed that, the preparation method affect the metallic particle side and the interaction with the support.

P30
(197)

Characterization of coked and regenerated USHY zeolites by temperature programmed oxidation.

A. Benamar, A. Miloudi
Laboratoire d'Etude Physicochimique des Matériaux et Application à l'Environnement, Faculté de Chimie, BP 32 Elalia, Bab ezzouar, USTHB, Alger, Algérie, e-mail: *aichabenamar2000@yahoo.fr*

Regenerated and coked USHY samples during mx transformation are characterized by temperature programmed oxidation under O_2/He flow from 100 to 900°C with a heating rate of 5°C/min. Unconsumed O_2 and CO_2 formed are the only products detected by TCD analysis. The water evolved was trapped at the outlet of the reactor. Whatever the coke content before regeneration, TPO profiles show that H_2, contrary to air, can not remove completely the coke from the zeolite and that the remaining coke is harder after H_2 stripping.

P31 (200)

The Effect of Support on Water-Gas Shift Reaction over Supported Pt and Pt-CeO_x Catalysts

Y.T. Kim, **E.D. Park**
Division of Energy Systems Research and Division of Chemical Engineering and Materials Engineering, Ajou University, Wonchun-Dong Yeongtong-Gu Suwon , 443-749, Republic of Korea. *edpark@ajou.ac.kr*

We prepared Pt and Pt-CeO_x catalysts supported on various supports such as CeO_2, ZrO_2 and TiO_2 and applied them to water-gas shift reaction. The effect of support with different specific surface area on water-gas shift reaction was intensively investigated. Several characterization techniques such as ICP, N_2-physisorption, H_2-TPR, and CO chemisorptions were conducted. Among tested catalysts, Pt-CeO_x/TiO_2 with a moderate surface area showed the largest amount of surface active sites and the highest initial catalytic activity.

P32 (205)

Kinetic study of methane steam reforming over core-shell structured bimetal Ni based catalyst

Hongmin Wang[2], Anh H. Dam[2], D. Wayne Blaylock[1], Teppei Ogura[1],Yian Zhu[2], Anders Holmen[2],
William H. Green[1]*, and **De Chen**[2]**
[1]Massachusetts Institute of Technology, Cambridge, MA 02139 (USA)
[2]Norwegian University of Science and Technology, Trondheim, NO-7491 (Norway)
**whgreen@mit.edu* ***de.chen@chemeng.ntnu.no*

Nickel is the preferred methane steam reforming (MSR) catalyst because of its cost and availability; however, it is susceptible to deactivation due to carbon formation. Thus, the design of new MSR catalysts that are inexpensive but resistant to deactivation is of particular interest. To aid in this search for improved catalysts, we seek an improved understanding of the processes occurring on the catalyst surface. DFT calculations indicate that the addition of transition metals on the Ni surface can destabilize intermediates leading to surface carbon formation, and thus improve the catalyst stability. In the present work, a series of hydrotalcite-based Ni catalysts modified by different loadings of the transition metals Ag, Rh, Pt, and Pd were prepared by surface redox reaction. The catalysts were characterized by many different techniques such as TPR, XRD, TEM and XPS. The effect of surface alloying of Ni catalysts with different metals on the kinetic activity and carbon formation was studied by using methane steam reforming as a probe reaction. The activity test indicate that methane steam reforming reaction rates over the catalysts modified by different metals show the trend of Rh>Ni>Pt>Pd>Ag. The results of this study are helpful for the design of a high performance catalyst for methane steam reforming.

P33 (207)

Synthesis gas by ethanol reforming over Ni-Pd incorporated MCM-41-like catalysts

C. Sener, G. Dogu, **T. Dogu**, K. Arishtirova, S. Damyanova
Middle East Technical University, Chemical Engineering Department, Ankara, Turkey, e-mail: *tdogu@metu.edu.tr*

Catalytic activities of the Ni and Ni-Pd impregnated MCM-41 like mesoporous catalysts with ordered pore structures were tested in steam reforming of ethanol. Ni and Pd nanoballs having diameters less than 20 nm were shown to be uniformly distributed within these catalysts having surface area values higher than 600 m^2/g. Incorporation of Pd over Ni-MCM-41 enhanced the activity and hydrogen selectivity of the catalysts in ethanol reforming. Complete conversion of ethanol with very high hydrogen yield values, approaching to five (per mole of ethanol fed to the reactor), was achieved at about 375°C, at a space time of 0.12 $s.g.cm^{-3}$.

P34
(212)

Synthesis gas (syngas) production over Ni/Al_2O_3-ZnO catalyst

L. S. Neiva[1], H. M. C. Andrade[2], A. C. F. M. Costa[1], **L. Gama**[1]
[1]Federal University of Campina Grande, Academic Unit of Engineering Materials, Avenue Aprígio Veloso – 882, Bodocongó, 58109 – 970, Campina Grande – PB, Brazil, e-mail: *lucianna@dema.ufcg.edu.br*
[2]Chemistry Institute – Federal University of Bahia, Ondina, Salvador – BA, Brazil.

In this work the steam reformig of the methane reaction at 700°C over Ni/Al_2O_3-ZnO catalyst was investigated. The Al_2O_3-ZnO catalytic support was synthetized by reaction combustion method by means of two distinct procedures. The catalytic active species (1.5%Ni) was incorporated to support by means humid impregnation method. The catalytic support was submitted the several structural and physical characterizations. The catalytic test in row of seats scale showed that the developed catalyst in this work presented satisfactory catalytic performance in methane in syngas conversion at 700°C.

P35
(227)

Production of synthesis gas from ethanol. Study of catalyst deactivation and reaction mechanism

S.M. de Lima, A.M. da Silva, L.O.O. da Costa, U.M. Graham, G.Jacobs, B.H. Davis, L.V. Mattos, **F.B. Noronha**
Instituto Nacional de Tecnologia -, Av. Venezuela 82, CEP 20081-312, Rio de Janeiro - Brazil, Tel. (55-21) 2123 1177,
e-mail: *fabio.bellot@int.gov.br*

The aim of this work is to provide further insight into the mechanistic pathways of ethanol conversion reactions and to shed light on the deactivation mechanism of ethanol steam reforming. The nature of the support and metal directly influence the product distribution and catalyst stability during ethanol conversion reactions. A reaction mechanism was proposed based on DRIFTS analyses carried out under reaction conditions. This reaction mechanism is valid for all the metals studied. However, some of the reaction pathways are favored on specific metals.

P36
(232)

The effect of crystal size of perovskites on methane partial oxidation

Oana Mihai, De Chen, Anders Holmen
Department of Chemical Engineering, Norwegian University of Science & Engineering (NTNU), NO-7491 Trondheim, Norway
oana.mihai@chemeng.ntnu.no

Kinetic study of methane partial oxidation by the lattice oxygen of perovskites type oxides catalysts was studied. The perovskites were prepared by combustion and spray drying methods and were characterized by different techniques. The experiments were performed in a fixed-bed quartz reactor at high temperatures. The catalyst was oxidized by O_2/Ar flow and reduced by CH_4/Ar flow. The reduction step of the perovskite obtained by citrate method for ten cycles was studied. The crystal sizes of perovskites depend strongly on the preparation method and might have a significant effect on both activity and selectivity.

P37
(233)

First Principles Insights into the Water-Gas-Shift Reaction on Rhodium

Matteo Maestri[1,2] and Karsten Reuter[1]
[1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany; [2]Politecnico di Milano, Milano, Italy
maestri@fhi-berlin.mpg.de

Guided by a previous UBI-QEP based microkinetic analysis we perform a density-functional theory study of the water-gas shift reaction on Rh surfaces. We explore the energetics of the elementary steps at different surface coverages and compare with the predictions from the semi-empirical UBI-QEP method. On the one hand, this enables a rational refinement of the microkinetic model. On the other hand, it is the knowledge from the latter that identifies the critical points and helps to focus the first-principles calculations.

P38
(234)

Thermal optimisation alternatives for a WGS-membrane reactor

M. Adrover[1], D.Borio[1], **M. Pedernera**[1]
[1]Planta Piloto de Ingeniería Química (PLAPIQUI), UNS-CONICET, Camino La Carrindaga Km 7, 8000 Bahía Blanca, Argentina.
mpedernera@plapiqui.edu.ar

The steady-state operation of a non-isothermal multitubular membrane reactor (MR) is simulated by means of a 1-D pseudo-homogeneous mathematical model. The catalyst is packed in the shell while the H_2 is collected inside the membrane tubes. The effect of the sweep gas on the performance of the MR is studied for three different flow configurations: i) saturated steam as sweep gas, ii) no sweep gas, and iii) pure H_2 as sweep gas. Each studied configuration presents advantages and drawbacks. Further optimization studies are required in order to obtain maximum H_2 production rate with minimum temperature and pressure increments.

P39
(236)

Partial Oxidation of Methane to Syngas over Mesoporous Co-Al2O3 Catalyst Prepared by One-Pot Synthesis

C.J. Huang, R.Y. Liu, N.W. Zhang, C.C. Wang, W.Z. Weng, **H.L. Wan**
State Key Laboratory for Physical Chemistry of Solid Surfaces, Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. *huangcj@xmu.edu.cn; hlwan@xmu.edu.cn*

A highly ordered mesoporous cobalt-alumina catalyst with high thermal stability was prepared in a single step via self-assembly of metal precursor and aluminum isopropoxide in the presence of P123. The synthesized catalyst showed much higher activity and stability for partial oxidation of methane to syngas, as compared to commercial alumina- and mesoporous alumina-supported cobalt catalysts prepared by impregnation. A series of techniques including N_2-adsorption, XRD, TEM, TPR, Raman, XPS and diffuse reflectance UV-vis spectra were used to characterize catalyst structure, and the relationship between structure and catalytic performance was studied.

P40
(244)

Dry reforming of methane over La(Sr)$Fe_{1-x}Ni_xO_{3-\delta}$ perovskites and their composites with Gd-doped ceria

S. Pavlova, G. Alikina, V. Zarubina, R. Bunina, V. Sadykov, T. Krieger, A. Ishchenko, V. Rogov
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia; *pavlova@catalysis.ru*

The performance of La(Sr)$Fe_{1-x}Ni_xO_{3-\delta}$ perovskites and their nanocomposites with $Ce_{0.9}Gd_{0.1}O_{2-\delta}$ in methane dry reforming along with the structural and redox properties has been studied. The activity of perovskites and nanocomposites depends on the Ni content and Sr presence and correlates with the redox properties of the systems. Nanocomposites possess the highest catalytic activity at short contact times ~0.01-0.005 s due to a high mobility and reactivity of their surface and bulk oxygen. The long-term testing of the most active catalysts has shown their high stability to coking.

P133
(248)

Dry reforming of methane over Ru and Mg incorporated Ni-MCM-41 mesoporous catalysts

S. Ozkocer, S. Yasyerli, N. Yasyerli, **G. Dogu**
Department of Chemical Engineering, Gazi University Ankara, Turkey, *gdogu@gazi.edu.tr*

Nickel incorporated MCM-41-like mesoporous materials, which were synthesized following a one-pot hydrothermal route, were promoted by Ru and Mg, for better catalytic performance in reforming of methane with CO_2. Ru incorporation was shown to decrease the contribution of reverse water gas shift reaction, giving high H_2 yields and a synthesis gas with a $CO/H_2 \approx 1.0$. Catalytic test results (at 600°C) with different feed compositions showed that the catalyst containing 1% Ru and a Ni/Si wt ratio of about 0.48 gave the best catalytic performance. Mg incorporation over this catalyst caused further improvements in hydrogen selectivity and in coke formation.

P134
(249)

Biogas reforming for syngas production over Ni/CeO_2-ZrO_2 catalysts.

T. A. Maia[1], A. F. Lucrédio[1], J. M. Assaf[2], **E. M. Assaf**[1]
[1]Universidade de São Paulo, Instituto de Química de São Carlos,Av. Trabalhador São-carlense 400 – São Carlos, SP -13560-970, Brasil. *eassaf@iqsc.usp.br*
[2]Universidade Federal de São Carlos, Departamento de Engenharia Química, Rodovia Washington Luís, km 235, São Carlos, SP – 13565-905, Brazil.

The biogas reforming over Ni/CeO_2-ZrO_2 catalysts was investigated for syngas production. The catalysts were prepared by polymeric precursor method and characterized by XRD, TPR, N_2-physisorption and Raman spectroscopy. The catalytic tests showed that the higher the temperature of reaction the better the CH_4 and CO_2 conversions. The NiC50Z catalyst presented lower C deposition than 5NiC and 5NiZ catalysts. The addition of O_2 increased the CO production indicating the occurrence of the partial oxidation reaction and decreased the C deposition. Thus, the O_2 addition, along with the support C50Z favored the gasification of carbon species.

P135
(250)

Biogas reforming on Ni catalysts Supported on CeO_2 modified with MgO

J.D.A. Bellido, A.F.Lucredio, **E.M. Assaf**
Universidade de São Paulo, Instituto de Química de São Carlos, Av. Trabalhador São-Carlense 400 - São Carlos,
SP 13560-970, Brazil. *eassaf@iqsc.usp.br*

Biogas has a typical composition of 55–70 vol% CH_4 and 27–44 vol% CO_2. This composition allows the use of biogas to produce syngas throughout its own reforming. Nickel catalysts supported on MgO modified CeO_2 were synthesized with 4, 8 and 12 mol% MgO. The catalytic reactions were made with mixed feeds of CH_4/CO_2 =1.5/1 with 48 mL.min^{-1} of CH_4 and $CH_4/CO_2/O_2$ = 1.5/1.0/0.25 with 45 mL.min^{-1} of CH_4. Addition of MgO into the CeO_2 lattice used as Ni catalyst support improved the CH_4 conversion and the resistance to coke formation. It was found that the 8% mol MgO as the optimal composition for a better CH_4 conversion.

P136
(256)

Water Gas Shift catalytic studies in co-gasification processes

M. Maroño[1], M.M. Barreiro[1], E. Ruiz[1], J.M. Sánchez[1]
[1]CIEMAT, Combustion and Gasification Division, 22, av. Complutense, 28040 Madrid, Spain. *Marta.marono@ciemat.es*

This paper reports on the results of the experimental work carried out by CIEMAT to study the WGS reaction under conditions typical of different gasification technologies. Oxygen-pressurized gasification process at ELCOGÁS IGCC plant and oxy-fuel gasification concept that is being proved under the FLEXGAS project have been considered in this work. The influence of main operating parameters on the performance of a high temperature shift catalyst has been evaluated with special emphasis on feed gas composition. Best operating conditions and suitability of the catalyst for the processes studied are discussed.

P137
(257)

Autothermal reforming of methane to produce fuels of low-potential pollutant

A.E.A.M. Souza[1], L.J.L. Maciel[1], V.O. Cavalcanti-Filho[1], N.M. Lima Filho[1], C.A.M. Abreu[1]
[1]DEQ, CTG, UFPE, Av. Prof. Artur de Sá, s/nº - Cidade Universitária, Recife-PE - 50740-521, Brazil. *aleksandros.souza@gmail.com*

Autothermal reforming of methane (ATR) was performed to produce syngas and hydrogen, aim to obtain low-potential pollutant fuels, employing a $Ni/\gamma\text{-}Al_2O_3$ catalyst. Stoichiometric and thermodynamic studies lead to favourable conditions to hydrogen production, and a kinetic-operational mechanism were suggested. Simulations were compared with the experimental results. It was reached high molar ratios H_2/CO, validating the proposed model.

P138 (258)

Evaluation of the tri-reforming process of methane for syngas production

L.J.L. Maciel[1], A.E.A.M. Souza[1], A. Knoechelmann[1], C.A.M. Abreu[1]
DEQ, Univesidade Federal de Pernambuco, Recife PE, 50740-520, Brazil, e-mail: *leonardolins@hotmail.com*

The conversion of natural gas was carried out via tri-reforming of methane in a fixed bed reactor employing a $Ni/\gamma\text{-}Al_2O_3$ catalyst. The operational evaluations were performed in a temperature range of 923-1123K under atmospheric pressure. At temperatures above 1000 K, methane and carbon dioxide conversions of 96.44% and 45.41% respectively produced hydrogen with yields of 37.35%. The effects due to the water and the oxygen addition to the feed of the process were examined in terms of the yields of hydrogen and carbon monoxide.

P139 (264)

Microchannel reactor for methane steam reforming

S.A Cruz, **O. Sanz**, R. Poyato, D. Hufschmidt, L.C. Almeida, F. Romero-Sarria, M.A. Centeno, G. Arzamendi, L.M. Gandia, E.F. Souza-Aguiar, M. Montes, J.A. Odriozola
Inst. of Mat. Scien. of Seville, CSIC-U. of Seville, Avda. Américo Vespucio 49, 4109 Seville, Spain. *odrio@us.es*

Microreactor technology has become an attractive means to intensify methane-to-syngas production processes for portable power applications as well as off-shore methane steam reforming. The final goal is to couple in the same device the endothermic steam reforming of methane with the exothermic combustion of methane in air for heating purposes. The effect of the different operating variables for welding and washcoating of the catalyst in microchannel reactors has been analysed and the best conditions selected. The $Ni\text{-}La/\gamma\text{-}Al_2O_3$ and $Pd\text{-}La/\gamma\text{-}Al_2O_3$ are stable and active for methane steam reforming and combustion respectively.

P140 (268)

A comparative study on CH_4 and CO_2 dry reforming performed on $Ni/MgAl_2O_4$ and $Ni/Ce_2Zr_2O_8$ catalysts

Alain Kiennemann[1], László Guczi[2], Anita Horváth[2], Györgyi Stefler[2], Agnieszka Pietraszek[1]
[1]University of Strasbourg 1 ECPM-LMSPC, Ecole Chimie Polymeres et Materiaux 25 rue Becquerel FR-67087 Strasbourg Cedex 2 France, e-mail: *kiennemann@unistra.fr* and [2]Institute of Isotopes of the HAS, P. O. Box 77, H-1525 Budapest, Hungary

$Ni/MgAl_2O_4$ and $Ni/Ce_2Zr_2O_8$ catalysts in methane dry reforming with CO_2 by means of temperature reaction (TPR) and transmission electron microscopy (TEM) have been investigated. The main difference in the carbon structure on the catalyst surface is the carbon structure. While on $Ni/MgAl_2O_4$ the small nickel particles are enveloped in multi-wall nanotubes (CMWNT), the carbon formed on the $Ni/Ce_2Zr_2O_8$ are rather filamentous type one. The results are discussed.

P141
(271)

Membrane Module Preparation with Carbon Hollow Fiber for Catalytic Reactors

A.J.Pacheco[1], J. S. do Nascimento, M. Anacleto[1], C.P.Borges[2], **V.M.M. Salim**[1]
[1]NUCAT/PEQ/COPPE – Federal University of Rio de Janeiro, Rio de Janeiro, P.O. Box 68502, Brazil. *vera@peq.coppe.ufrj.br*
[2]PAM/PEQ/COPPE – Federal University of Rio de Janeiro, Rio de Janeiro, P.O. Box 68502, Brazil

New membrane applications have been emerging, especially those combining reaction and separation for H_2. Therefore, a natural choice is the carbon membranes. The main objective of this work is the preparation of carbon hollow fiber membranes (CF) by pyrolysis of polyetherimide (PEI)/ polyvinylpyrrolidone (PVP) hollow fibers and the membrane module characterization. The results confirm the great potencial of carbon fibers for coupling with catalyst reactors as well as highly selective to hydrogen ($H_2/CO_2 = 54$).

P142
(272)

Reforming of Biogas: effect of support and Ce addition on Ni catalysts

A.F.Lucrédio, J.D.A. Bellido, J.M. Assaf, **E.M. Assaf**[1]
[1]Universidade de São Paulo, Instituto de Química de São Carlos, Av. Trabalhador São-Carlense 400 -
São Carlos, SP 13560-970 Brazil. *eassaf@iqsc.usp.br*

In the present paper, Ni catalysts supported on γ-Al_2O_3 (NiAl) and Mg-Al (NiMgAl) and promoted with Ce (NiCe and NiCeMg) were prepared. The samples were analyzed by EDS, BET, TPR, in situ-XANES and the catalysts were tested in the reforming of biogas with O_2 addition. The catalysts were active for the reaction and did not favor the decomposition of the excess of CH_4 present in the biogas composition. The Ce addition decreased the C formation for the catalyst supported on γ-Al_2O_3. The O_2 addition increased the CH_4 conversion and eliminated the C formation, for all catalysts, with no deactivation.

P143
(274)

Fuel gas production from paper wastes over supported metal catalysts in high-temperature liquid water

A. Yamaguchi, N. Hiyoshi, O. Sato, M. Shirai
Research Center for Compact Chemical Process, National Institute of Advanced Industrial Science and Technology (AIST),
4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan, e-mail: *a.yamaguchi@aist.go.jp*

Production of gaseous fuel from the paper wastes, which cannot be recycled, is a promising technique from the view point of establishing a sustainable society. We carried out gasification of paper wastes in water at low temperature (523 K) to produce methane and hydrogen. The order of the catalytic activities for the gasification was: ruthenium > rhodium > platinum > palladium. The charcoal supported ruthenium catalyst (Ru/C) was most effective for the gasification of paper and cellulose in water. Printed paper was also gasified at 523 K in water, demonstrating that fuel can be produced from paper wastes using this technique.

P144
(278)

Pt-supported ceria-based nanocrystalline catalysts of CH_4 dry reforming: effect of support composition/defect structure and Ni/Pd additives

T. Kuznetsova, G. Alikina, E. Paukshtis, S. Korenev, and V. Sadykov
Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia, e-mail : *tgkuzn@catalysis.ru*

For dry reforming of CH_4, the effects of defect structure of the surface/subsurface layers of Ce-Zr-La(Ca)-O and Ce-Sm-O nanodispersed fluorites after supporting Pt, Pt+Pd and Pt+Ni+La and their diffusion parameters are considered. For these materials, besides the activation of CH_4 on small (1-2 nm) uncovered Pt^0 clusters, additional route of both reagents activation is proposed. Complex cluster defect containing $Pt^{\delta+/2+}$ species and interstitial oxygen-isolated anion vacancy pairs facilitates conjugation of CH_4 activation and oxygen insertion for CO production. Oxygen diffusion parameters affect the efficiency of this process.

P145
(281)

The Influence of Preparation Conditions on ZrO_2 Nanoparticles as Ni Support with Different PEG-PPG-PEG surfactants

Hamide Eltejaei, H.Reza Bozorgzadeh, Jafar Towfighi and M.Reza Omidkhah
Department of Chemical Engineering, Faculty of Engineering, Tarbiat Modaress University, P.O.Box 14115-143, Tehran, Iran

Zirconia powder with high surface area was prepared by using PEG-PPG-PEG new block copolymer. The surfactant molecular weight, zirconium to surfactant molar ratio, PH of precipitation,aging time and zirconium molarity were optimized by the Taguchi method of experimental design and Minitab Software.The samples were calcined at 700°C for 8h. The ZrO_2 powders were characterized by means of XRD and BET .The BET surface area of powders was 114-175 m^2/gr and the particles size was 5-9 nm.The sample prepared under optimized conditions will be used as Ni support in CO_2/Steam reforming reaction.

P146
(288)

Influence of the preparation method on the performance of Rh catalysts on CeO_2 for WGS reaction

P. Djinović, **C. Galletti**, S. Specchia, J. Batista, J. Levec, A. Pintar, V. Specchia
Department of Materials Science and Chemical Engineering, Politecnico di Torino, Corso Duca degli Abruzzi 24, 10129 Torino, Italy.
camilla.galletti@polito.it

The Water Gas Shift (WGS) reaction is one of the most intensively studied catalytic reactions related to the development of fuel processors for fuel-cell power systems. The about 10% CO concentration of H_2–rich gas from reformer is dramatically reduced by the WGS reaction. The present work deals with the development and screening of catalysts for CO abatement via WGS from a synthetic reformate. Rh-based catalysts on CeO_2, prepared by both Solution Combustion Synthesis and Hard Template methods, were characterized and tested to evaluate the influence of the preparation method on the performance of the WGS reaction.

P147
(296)

Substituted hexaaluminates $ANiAl_{11}O_{19-\delta}$ (A = La, Ca, Ba et Sr) Catalysts in carbon dioxide reforming of methane

K. Ikkour[1], D. Sellam[1], A. Kiennemann[2], S. Tezkratt[1], O. Cherifi[3]
[1]Laboratoire de Recherche de Chimie Appliquée et Génie Chimique - Université M. Mammeri Tizi-Ouzou
[2]Laboratoire Matériaux, Surfaces, Procédés pour la Catalyse (LMSPC)- Université de Strasbourg 25 rue Becquerel
67087 Strasbourg Cedex 2 France
[3]Laboratoire du gaz naturel USTHB Bab Ezzouar,
e-mail : *saidtezkratt@yahoo.fr*

A series of nickel substituted hexaaliminate materials, $ANiAl_{11}O_{19-\delta}$ (A = La, Ca, Ba et Sr) and $LaNiAl_{11}O_{19-\delta}$ using different solvent were prepared. Pure hexaaluminates phases was formed for La $NiAl_{11}O_{19-\delta}$ catalysts. The catalyst prepared by citric acid method present high perfomance compared to the other methods. Both $CaNiAl_{11}O_{19-\delta}$ and $BaNiAl_{11}O_{19-\delta}$ catalysts exhibited high catalytic activity for carbon dioxide reforming of methane to synthesis gas, the CO_2 and CH_4 conversion was kept over 90%.

P148
(298)

The effect of the $CeZrO_2$ content on the performance of $Pt/CeZrO_2/Al_2O_3$ catalysts on the partial oxidation of methane.

F.A. Silva[1], K.R. Souza[2], L.V. Mattos[3], E.F. Souza-Aguiar[4], M. Montes[5], C.E. Hori[1], **F.B. Noronha**[2]
Instituto Nacional de Tecnologia, Av. Venezuela 82, Rio de Janeiro - Brazil, *fabio.bellot@int.gov.br*

The aim of this work is to study the effect of the $CeZrO_2$ content on the performance of $Pt/CeZrO_2/Al_2O_3$ catalysts on partial oxidation of methane. $Pt/CeZrO_2/Al_2O_3$ catalysts with 10 and 20 wt.% of $CeZrO_2$ were quite stable whereas the catalysts with higher mixed oxide loading exhibited significant deactivation. XRD and TPR results revealed that the increase of mixed oxide loading led to the formation of a heterogeneous solid solution with segregation of ZrO_2 phase. Therefore, the oxygen storage capacity of the catalysts with high mixed oxide content is not enough to keep the balance between methane decomposition and oxygen transfer and then they deactivate.

P149
(301)

Reforming of CH_4 with CO_2 on Pt- supported catalysts Effect of the reaction temperature

S. Bakri[1], S. Tezkratt[1], S. Menad[1], O. Cherif [2].
[1]Laboratory of Chemistry and Chemical engineering - University M. Mammeri. Tizi-Ouzou. Algeria. Fax: 020.60.08.22,
e-mail: *sabiha_bakri@yahoo.fr*
[2]Laboratory of natural gas, Faculty of Chemistry, USTHB BP32 El Alia Bab-Ezzouar, Algiers.

In this work, we study the effect of the reaction temperature on catalytic activity of Pt – based catalyst supported on γ- Al_2O_3, prepared by impregnation and calcined at 750°C. Our catalyst was characterized by different methods of analyses (XRD, FTIR, and BET). The results of the catalytic tests, showed that the catalytic activity increases with increasing the temperature of reaction (450°C – 550°C) and decreases with increasing temperature (550°C – 700°C). Pt /γ- Al_2O_3, present the best catalytic activity, with a good stability at 550°C.

P150
(307)

Evaluation of the tri-reforming process of methane for syngas production

L.J.L. Maciel[1], A.E.A.M. Souza[1], A. Knoechelmann[1], C.A.M. Abreu[1]
DEQ, Univesidade Federal de Pernambuco, Recife PE, 50740-520, Brazil, e-mail: *leonardolins@hotmail.com*

The conversion of natural gas was carried out via tri-reforming of methane in a fixed bed reactor employing a Ni/γ-Al_2O_3 catalyst. The operational evaluations were performed in a temperature range of 923-1123K under atmospheric pressure. At temperatures above 1000 K, methane and carbon dioxide conversions of 96.44% and 45.41% respectively produced hydrogen with yields of 37.35%. The effects due to the water and the oxygen addition to the feed of the process were examined in terms of the yields of hydrogen and carbon monoxide.

P151
(308)

Characterization of commercial solid materials for extreme hydrogen sulphide removal

Giulia Monteleone, Massimo De Francesco, Stefano Galli, Valentina Naticchioni*
ENEA R.C. Casaccia, Via Anguillarese 301, 00123 S.Maria di Galeria (RM)- *giulia.monteleone@enea.it*
* Univ. Rome “La Sapienza”, Dept. of Chem. Engineering, Material and Environment

Biogas production and utilization is constantly increasing, since it represents a renewable energy available from anaerobic digestion of different organic sources. Nevertheless, due to the presence of the harmful and toxic hydrogen sulphide (H_2S) as contaminant (300÷1000 ppm), the biogas have to be purified to allow its good and safe exploitation. Fuel cells technology shows low tolerances H_2S, than its fraction has to be dramatically reduced to the lower tolerance limit (<0.5 ppm). Desulphurization processes and economical, regenerable, with high selectivity, adsorbents and catalysts are investigating.

P152
(312)

Catalytic Co-Gasification of Black Liquor and Wastewater Sludge for Fuel Gas Production

V. Sricharoenchaikul, C. Sirinawin, W. Kripittayakorn, **D. Atong**
National Metal and Materials Technology Center, Thailand Science Park, Pathumthani 12120 Thailand. *duangdua@mtec.or.th*

Sludge from pulp and paper wastewater plant was gasified with black liquor in order to investigate the optimal operating condition and product gas distribution from this process. Specially synthesized tri-metallic sequential- impregnated 5wt%La - 5wt%Mg - 10wt%Ni catalysts on alumina support was also added to improve conversion and selectivity of the process. High temperature of 900°C with ER of 0.4 result in acceptable conversion and formation of gas with high energy content. Higher sludge content helps reduce the corrosive property of black liquor but reduce quality of product gas. Less tar and more char were found in runs with higher sludge content.

P153
(316)

Water Gas Shift Reaction in Microstructured Reactors - Catalyst Preparation and Lab-Scale Reaction Test

P. Piermartini, P. Pfeifer, G. Schaub
Institute for Micro Process Engineering (IMVT), Karlsruhe Institute of Technology (KIT),
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany, *paolo.piermartini@ kit.edu*

For the production of liquid synfuels from biomass and low-hydrogen fossil materials, application of pressure and temperature in water gas shift reaction may be advantageous with respect to minimum energy loss. Due to the short diffusion length of the reactants to the catalyst and excellent heat transfer properties, the microchannel reactor may be operated with a decreasing temperature profile, thus enabling better performance for this equilibrium reaction. Catalyst preparation, reaction kinetics, catalyst stability against poisoning and potential byproduct formation at high pressure conditions were investigated with Platinum and Ruthenium catalyst systems.

P154
(317)

Influence of Ba incorporation on the catalytic performances of noble metals in the dry reforming of methane

Madani Ghelamallah[1], Pascal Granger[2]
[1]Département de Physique et de Chimie, Faculté des Sciences et Technologies,
Université de Mascara, B.P. 305 Route de Mamounia, Mascara 29000, Algerie, *gh-madani@hotmail.com*
[2]Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Université de Lille 1, Bâtiment C3, 59655 Villeneuve d'Ascq, France

This paper reports the influence of La and Ba-modification of α-alumina on mono- and bimetallic Pt and Rh based catalysts in the dry reforming of methane. It has been shown that interaction with noble metals induces changes in the selectivity behaviour reflected by the molar H_2/CO ratio. A detrimental effect of barium in the production of H_2 is clearly evidenced which has been related to an extensive reduction of the support material. In parallel, It was found that Rh addition of Pt has a positive effect in favour of H_2 formation.

P155
(319)

Syngas production via dry reforming in a fluidized bed reactor

J. A. Pacífico[1], N. M. Lima Filho, A. C. Cabral, L. C. Maranhão, A. Knoechelmann, C. A. M. Abreu
[1]Laboratory of Catalytic Processes (LCP) – Federal University of Pernambuco, Av. Prof. Moraes do Rego, 1235,
Cidade Universitária, CEP - 50670-901, Recife-PE Brasil. *adairpacifico@hotmail.com*

The methane reform with carbon dioxide for syngas production was performed in a fluidized bed reactor in the presence of a Ni/Al_2O_3 catalyst, with a conversion of 51.54% in relation to CH_4 and 45.51% in relation to CO_2 and the yields of H_2, CO, and syngas were 47.72%, 49.95, and 97.67% respectively. The selectivities of the products at the exit of the reactor due to the model and experimental measurements reached an order of magnitude of 48.05% and 98.35% for hydrogen and syngas, respectively.

P156
(320)

Ni/Al Molar Ratio Effect of Hydrotalcites Derived Catalysts for Methane Dry Reforming Reaction

F. Touahra[1], Z. Abdessadek[1], K. Bachari[2], A. Saadi[1], O. Cherifi[1], **D. Halliche**[1]*
[1]Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, USTHB, BP32, El-Alia, Alger, Algeria.
[2]Centre de recherches scientifiques (CRAPC), BP 248, Alger, 16004, Algeria. *dhalliche@yahoo.fr*

The NiAl-R hydrotalcite derived catalysts were prepared by coprecipitation method at constant pH of 11.0 with various molar ratios ((Ni^{2+})/(Al^{3+}) = R= 2,3,5,8,10) The samples were calcined for 8h at 800°C. The lower surface areas of samples decreased when R decreases from 10 to 2. We have studied theCH_4/CO_2 reaction at various temperatures using a 1:1 CO_2 / CH_4 feed ratio. The studied catalysts exhibit catalytic performances at 650°C, which vary in the following sequence: NiAl-R2 > NiAl-R3 > NiAl-R5 > NiAl-R8 > NiAl-R10.

P157
(327)

Catalytic Reaction of Methane or Propane with Carbon Dioxide

Toshiaki Sodesawa, Junshi Matsui
Graduate School of Engineering ,Chiba University,1-33, Yayoi, Inage, Chiba 263-8522, Japan,
e-mail: *sodesawa@faculty.chiba-u.jp*

The present energy situation has renewed interest in the effective use of $C_1 - C_4$ hydrocarbons as a natural gas. The steam reforming of methane have been investigated by many researchers. However, the reaction of methane or propane with carbon dioxide has not yet been studied in detail. This is considered to produce CO and H_2 favourably, provided that reaction temperature is relatively high because it is strongly endothermic. The equilibrium constant for this reaction becomes greater than 1.0 when the temperature is above 636°C. Ni catalysts supported on silica showed high activities and selectivity for CO_2 reforming of methane or propane.

P158
(589)

Modelling of Fixed Bed Catalytic Reactor for Bio-Methane Production from Biomass Gasification

P.R. Naren, S. Chambrey, A. Khodakov, N. Fatah and **P. Fongarland**
Unité de Catalyse et de Chimie du Solide (UCCS), UMR CNRS 8181, Ecole Centrale de Lille, Cite Scientifique,
BP 42, 59651, Villeneuve d'Ascq Cedex, France. *pascal.fongarland@ec-lille.fr*

Methanation is a key process in the production of synthetic natural gas (SNG) from synthesis gas. The present work deals with the development an industrial fixed bed reactor (FBR) model for the methanation process. In the first stage of this work, various reported literature and experimental kinetics for the CO conversion to methane were compared. Effectiveness factor was computed for various particle sizes and also sensitivity analysis of constituent model parameters was also done. The intra and interparticle and interphase transport effects were also computed. The work would help in further selection of catalyst particle size for the performance of laboratory kinetic experiments.

P159
(331)

Phase Composition of Carbon Dioxide Methane Conversion Catalyst based on the Product of Nickel Aluminide Self-Propagating Thermosynthesis

A.N.Shmakov[1], L.A.Arkatova[2]
[1]BoreskovInstitute of Catalysis, Siberian Division of Russian Academy of Science, Acad.Lavrentiev Ave., 5, Novosibirsk, 630090, Russian Federation. *A.N.Shmakov@inp.nsk.su*
[2]Tomsk State University, Department of Chemistry, Lenin Ave., 36, Tomsk, 634050, Russian Federation

The phase composition of the Ni-Al systems, prepared by self-propagating high-temperature synthesis, and phase composition alteration has been investigated by *in situ* XRD during carbon dioxide reforming of methane. It was shown that initially the carbon dioxide methane reforming catalyst consists of Ni_3A_l, non-stoichiometric solid solution $Ni_{3-y}Al_y$, metallic Ni and disordered NiAl. At the beginning of the reaction the phase composition does not change. At long time under reaction mixture the dissolution of carbon within the catalyst appears and graphite forms on the surface that leads to catalyst deactivation.

P160
(339)

High Temperature WGSR Catalyst Based on the Nanodispersed Metastable Fe oxyhydroxide, 2-Line Ferrihydrite

A.A. Khassin, T.P. Minyukova, N.A.Baronskaya, G.A. Filonenko, T.M. Yurieva
Boreskov Institute of Catalysis, 5, pr. Lavrentieva, Novosibirsk 630090 Russia. *aakhassin@catalysis.ru*

Cr, Cu -doped 2-line ferrihydrite (2-LFH) demonstrates high catalytic activity, especially at low temperature (300-350°C) that allows reducing the starting temperature in adiabatic HT WGS reactor. Kinetic analysis data show that promotion of 2LFH by Me^{3+} cations can dramatically change the activation energy and the rate of crystallization to hematite. Metastability of Cr-promoted 2LFH and its transformation to hematite doesn't restrict application of 2LFH in catalytic reactions at moderate temperatures.

P161
(352)

Rhodium hydrotalcite as catalyst precursor for ethanol steam reforming

F. Basile[1], **I. Bersani**[1,2], P. Del Gallo[3], G. Fornasari[1], D. Gary[3] and A. Vaccari[1]
[1]Dip. Chim. Ind. Materiali, Alma Mater Studiorum-Univ. di Bologna, Bologna, Italy
[2]Consorzio INSTM, Firenze, Italy, [3]Air Liquide, Centre de Recherche Claude Delorme, Jouy-en-Josas Cedex, France

Ethanol steam reforming was studied on three catalysts based on Rh/Mg/Al with same amount of rhodium. The effects of anion interlayer and ratio Mg/Al were investigated at very low contact time. Best results are obtained with the catalyst with carbonate and ratio Mg/Al equal to 68/32. Catalysts with silicate and Mg/Al ratio equal to 80/20 show similar product selectivity trend: high intermediates selectivity and low amount of CO and CO_2. An effect of rhodium particle size on the selectivities is observed: too small rhodium particle size caused higher amount of intermediates because the break of C-C bond can be more difficult.

P162
(358)

Plasma Modified Nickel Catalysts for Biomass Conversion

D. T. Lundie[1], S. Fiddy[1], J.A. Rees[1], S. Hodgson[2], M. Olea[2] and W. Wang[2]
[1]Hiden Analytical Ltd, 420 Europa Boulevard, Warrington, WA5 7UN, UK. *dlundie@hiden.co.uk*
[2]School of Science and Technology, University of Teesside, Middlesbrough TS1 3BA, UK.

Organic waste through biomass conversion can be used for energy production and the synthesis of a variety of chemicals. One of the synthesis routes is via biogas to syngas catalytic conversion, by CO_2 reforming of CH_4. Ni shows good catalytic activity for this reaction, especially when well dispersed on the support. Plasma modification of Ni catalysts shows some potential for modifying their catalytic properties. Comparison of Ni catalysts with plasma modified Ni catalysts will be presented.

P163
(362)

Reforming of CO_2 containing gases

E. Turpeinen & R.L. Keiski
University of Oulu, Department of Process and Environmental Engineering, P.O.Box 4300, FIN-90014 University of Oulu, Finland,
esa.turpeinen@oulu.fi

Synthesis gas (CO and H_2) is an important intermediate in chemical industry. It can be produced by reforming from almost any carbon-hydrogen containing source. Various sources such as by-products of industrial processes may be potential alternatives for synthesis gas production. The objective of the present work was to study the possibility to use refinery gas and coke oven gas as feedstocks for synthesis gas production by the reforming process. Besides industrial gases, CO_2-containing landfill gas was taken into account as a feedstock. Steam reforming, partial oxidation and dry reforming of those gases were cases under investigation.

P164
(364)

Hydrogen production from aqueous-phase reforming of glycerin over metal-supported alumina catalysts

Seung-hwan Lee[1], Changkyou Jung[1], Eun Huh[1], Min-ji Kim[1], Hyun Mee Park[2], Sang Deuk Lee[1] and **Dong Ju Moon**[1]
[1]Clecn energy research center, Korea Institute of Science and Technology, Seoul, Korea
[2]Chemical Analysis Center, Korea Institute of Science and Technology, Seoul, Korea
djmoon@kist.re.kr

Aqueous-phase reforming(APR) of glycerin over metal-supported alumina catalyst was carried out at 498 K 25 bar for hydrogen production. The catalysts were prepared by wetness impregnation methods and Ni, Pd and Pt was selected as active metal. The glycerin gas conversion was 10~12 % over Pt and Ni-supported catalysts at 8h on-stream. H_2 and CO_2 were the mostly composition of the product gas. Pt-supported catalyst showed the highest H_2 volumetric fraction in this work. Prepared catalysts were characterized by XRD and N_2 physisorption.

P165
(369)

Improving performances and stability of Rh/SiO_2 catalyst in partial oxidation of methane by Zr and Ti promotion

A. Karelovic, C. Fernández, R. Wojcieszak, P. Ruiz, X. García, A. L. Gordon.
Laboratorio de Carbones y Catálisis, Universidad de Concepción, Chile, *akarelov@gmail.com*

We studied the addition of Zr and Ti as promoters to Rh/SiO_2 catalyst for partial oxidation of methane. The incorporation of Ti increases the activity and stability of Rh/SiO_2 catalyst. Zr promotes the reduction of Rh, while Ti promotes the oxidation of Rh and avoids sinterization of Rh particles. It is concluded that higher catalytic performances could be obtained when the size of Rh particle is small and the oxidation state is high.

P166
(370)

Partial oxidation of methane over Ru/MoO_3-ZrO_2, Ru/WO_3-ZrO_2 and Ru/CeO_2-ZrO_2 catalysts.

Valerio Choque, Narcís Homs, **Pilar Ramírez de la Piscina**,
C/Martí i Franquès 1-11, 08028 Barcelona, Spain. *pilar.piscina@qi.ub.es*

Ru catalysts supported on MoO_3-ZrO_2, WO_3-ZrO_2 and CeO_2-ZrO_2 were studied in the partial oxidation of methane (CPOM). Supports were prepared by sol-gel methods and $RuCl_3$ was used as ruthenium precursor. The addition of Mo, W and Ce to the ZrO_2 support determines the behaviour of the catalysts. Materials were characterised by different techniques. RuO_2, present on calcined catalysts, was reduced under reaction conditions to Ru^{o}. Catalysts supported on CeO_2-ZrO_2 showed the best performance in the CPOM. The Ru/6CeZr catalyst was more active and selective to syngas (H_2/CO ratio ca. 2) than the other systems studied and led to low CO_2 selectivity.

P167
(371)

Sour water gas shift reaction over Pt/CeO_2 catalysts

Bing Liu, **Hengyong Xu***, Qingjie Ge and **Andreas Goldbach****
[1]Laboratory of Applied Catalysis , Dalian Institute of Chemical Physics, CAS, 116023 Dalian, P.R. China,
e-mail: **xuhy@dicp.ac.cn*, ***goldbach@dicp.ac.cn*

The WGS reaction was investigated over Pt/CeO_2 catalysts between 573 and 723 K in natural gas-derived reformate containing H_2S. WGS conversion remained practically unchanged at 90% over a catalyst with 2 wt% Pt during a 100 h test at 673 K and atmospheric pressure after introduction of 20 ppm H_2S while CH_4 selectivity dropped to zero within 10 h. H_2S reappeared almost quantitatively at the reactor exit. No sulfur could be detected by XPS on the catalyst but IR spectroscopy revealed traces of sulfate species. Studies are under way to further elucidate the sulfur tolerance of Pt/CeO_2 catalyst under WGS conditions.

P168
(372)

Nano iron oxide catalysts for pyrolysis of biomass

Ravikrishna V.Chatti,N.K.Labhsetwar,Vivek Polshettiwar,Trevor C. Drage, **Sadhana S.Rayalu**
National Environmental Engineering Research Institute(NEERI),Nagpur, India, e-mail: *s_rayalu@neeri.res.in*

A nano iron oxide catalyst has been synthesized by using microwave hydrothermal technique. It was observed that the hydrogen yield of the nano iron oxide catalyst was to the tune of 6855 μmoles/g of cellulose as compared to 5405 μmoles/g for the commercial catalyst and was much higher than that for synthetic cellulose which was 4295 μmoles/g. This excellent catalytic behaviour may be due to the nano-structure of the catalyst. However, the catalyst activity decreased upon silylation, indicating blockage of active sites. Thus, the unsilylated catalyst plays an important role of oxidation of the CO produced, thus enriching the product gas stream with hydrogen.

P169
(373)

Catalytic Pyrolysis of Biomass on Iron Oxides Prepared by Template Methods

Nitin Labhsetwar, R.V. Chatti, D. Valechha, S. Lokhande, J. Sadafule and S. Rayalu
National Environmental Engineering Research Institute (NEERI-CSIR), Nagpur-440020, India
nk_labhsetwar@neeri.res.in

Templated iron oxide based catalysts with different structures show excellent catalytic activity for low temperature pyrolysis of representative biomass namely cellulose to hydrogen. It is was possible to generate hydrogen from cellulose at as low as 130°C temperature, while the overall yield of hydrogen was also substantially higher in case of catalyzed pyrolysis. It is interesting to observe different catalytic activity for different Fe_2O_3 catalysts, which confirm the role of intrinsic properties of present low cost and environmentally safe Fe_2O_3 based catalysts for future energy requirements through biomass. Surface area and ordered structure of Fe_2O_3 catalysts also appear to influence catalytic properties.

P170
(383)

Hydrogen production via steam reforming of ethanol over Ni/Mg-Zn-Al mixed oxide catalysts

Guangming Zeng, Lihong Zhang, **Yongdan Li**
Tianjin Key Laboratory of Applied Catalysis Science and Technology and State Key Laboratory of Chemical Engineering (Tianjin University), School of Chemical Engineering, Tianjin University, Tianjin 300072, China, e-mail: *ydli@tju.edu.cn*

A series of 15 wt% Ni-loaded Mg-Zn-Al mixed oxide catalysts, was prepared from hydrotalcite-like material by co-precipitation, and was evaluated via ethanol steam reforming by temperature-programmed reaction in the temperature range 400-800°C at a feed molar ratio $H_2O:C_2H_5OH = 3:1$. The catalyst was characterized using ICP-AES, XRD, TPR, TPO, TG-DTA, TEM, and N_2 physisorption. The results demonstrate that Ni supported on hydrotalcite derived materials incorporating Mg and Zn at a appropriate atomic ratio (Mg :Zn = 4 :1) give superior activity, high H_2 (5.51 mol/(mol ethanol)) and CO_x product selectivity, and stability.

P171 (387)

CO_2 Reforming of Methane Over Hydrotalcite Derived Catalysts

B.Djebarri[a],V. G.z-Delacruz[c], K. Bacharri[b], A.Saadi[a], O. Cherifi[a], J.P.Holgado[c], A.Caballeroc, **D.Halliche**[a],
[a]Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, USTHB, BP32, El-Alia, Alger, Algérie, *dhalliche@yahoo.fr*
[b]Centre de recherches scientifiques (CRAPC), BP 248, Alger, 16004 Algérie, [c]Instituto de Ciencia de Materiales de Sevilla, Departemento de Quimica Inorganica, Avda Americo Vespucia, 49, 41092 Seville, Spain.

Considerable attention has been paid to the CH_4/CO_2 to synthesis gas in recent years. In this paper, we intend to compare Ni/Mg/Al/Si hydrotalcites derived catalysts. These samples were prepared by coprecipitation at basic pH and calcined at 800°C. The catalysts are characterized by atomic absorption spectroscopy, XRD, FTIR, BET, TEM and TPR method. The data obtained from chemical analysis of the calcined catalysts confirmed that the $(M^{2+})/(M^{3+})$ ratio is close to 2. These catalysts are tested for CH_4/CO_2 reaction at 750°C. It was found that performances of catalysts depend of the Mg and Si introduction in the HDL structure.

P241 (388)

A new improvement in the H_2 production technology. Application of the NEMCA effect in the methane steam reforming

A. de Lucas-Consuegra, **A. Caravaca**, P.J. Martínez, F. Dorado, J.L. Valverde
Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de
Castilla-La Mancha. Avenida Camilo José Cela 12, 13005 Ciudad Real, Spain; *angel.caravaca@uclm.es*

The methane steam reforming reaction was novelty studied by coupling catalysis and electrochemistry, i.e., by using an electrochemical catalyst (Pt porous catalyst film supported on K-βAl_2O_3 solid electrolyte). The resultant electrochemical catalyst showed a good catalytic activity at low temperature (below 500°C) in the methane steam reforming reaction. In addition it was observed that both: the catalytic activity and the poisoning resistance to Carbon deposition could be modified by electrical polarizations in the system through the NEMCA effect.

P242 (389)

Effect of preparation method of supports La_2O_3-Al_2O_3 on catalytic properties of Pd catalysts in steam and autothermal reforming of CH_4

W.H. Cassinelli[1], F.S. Soares[1], D.O. Oliveira[3], D. Zanchet[3],C.M.P. Marques[1], **J.M.C. Bueno**[2]
[1,2]Department of Chemistry and Chemical Engineering, Federal University of São Carlos, P.O. Box 676, São Carlos, Brazil.
[3]Brazilian Synchrotron Light Laboratory – LNLS, P.O. Box 6192, Campinas, Brazil.
jmcb@ufscar.br

The Pd catalysts with 1% wt. were prepared by wetness impregnation of the supports using aqueous solution of $Pd(NO_3)_2$. The supports were obtained by two methods: i) impregnation of La on γ-Al_2O_3; and ii) solgel method. The catalysts were tested in steam reforming (SRM) and autothermal reforming (ATR) of CH_4. The addiction of La on γ-Al_2O_3 promoted the formation of $Pd^o{*}Pd^{\delta+}$O-La species responsible for the high activity on SRM. The La-containing catalyst obtained by solgel method showed higher stability on ATR of CH_4 than PdAl catalysts. These facts may be reflecting the high thermally stability of support due the interaction of La-O-Al into matrix.

P243 (393)

Experiments and Simulations for the Steam Reforming of Methane over Ni/MgAl Catalyst

Yun Ju Lee[1,2], Byung Gwon Lee[1], Suk In Hong[2] and **Dong Ju Moon**[1]
[1]Clean Energy Center, Korea Institute of Science and Technology, Seoul, Korea. *djmoon@kist.re.kr*
[2]Department of Chemical & Biological Engineering, Korea University, Seoul, Korea

Steam reforming (SR of LNG) is a major route for the industrial production of H_2. In this work, steam reforming of methane over Ni-based catalyst was carried out for applications in fuel processor, hydrogen station and compact-GTL process applications. The Ni-based catalyst was prepared by co-precipitation and characterized by N_2 physisorption, CO-chemisorption, XRD, SEM, TEM and TPR. The equilibrium conversion and product compositions for SR were calculated thermodynamically as a function of temperature based on the principle of Gibb's free energy minimization.

P244 (402)

Tri-reforming of methane over structured Ni/La_2O_3/Al_2O_3/cordierite catalysts

S.A.Soloviev, Ie.V.Gubareni, Ya.P.Kurilets,
Department of catalytic redox processes, L.V.Pisarzhevsky Institute of Physical Chemistry, National Academy of Sciences of Ukraine.
Prosp. Nauki, 31, Kyiv 03028, Ukraine, e-mail: *soloviev@inphyschem-nas.kiev.ua*

Conditions of the running process of methane tri-reforming – synergetic combination of CO_2-, H_2O-reforming and partial oxidation of methane over Ni/Al_2O_3 catalyst, synthesized on ceramic matrix, have been studied. It is shown that modification of Ni/Al_2O_3 catalyst by La_2O_3 increases its stability in oxygen medium and decreases formation of coke on catalyst surface. Results of experimental researches and numerical analysis show that the realization of idea of tri-reforming makes possible not only to obtain syn-gas with necessary ratio of H_2/CO, but also to decrease high endothermicity of process which is a serious obstacle in CO_2-reforming.

P245 (403)

Mechanistic study of methane partial oxidation to syngas over supported Ru, Rh and Pt catalysts

M. L. Wang, J. M. Li, **W. Z. Weng**, H. Z. Zheng, X. D. Yi, W. S. Xia, C. J. Huang, H. L. Wan
State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters and Department of Chemistry, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, China. *wzweng@xmu.edu.cn*

The catalytic partial oxidation of methane (POM) to syngas over Ru/SiO_2, Rh/SiO_2 and Pt/Al_2O_3 catalysts was investigated by in situ microprobe Raman spectroscopy. Raman bands of carbon species originated from methane decomposition were clearly observed on the catalyst located at the entrance of catalyst bed under the POM condition. For the reaction at 700°C, significant amount of CO was detected at the front end of 3wt% Pt/Al_2O_3 catalyst bed where large amount of O_2 was still available in the reaction feed. These results indicate that pyrolysis-oxidation (direct) mechanism is responsible for syngas formation on the catalyst located in the oxidation zone.

P246 (405)

The Effect of Soot Deposition on Catalytic Activities in the Steam Reforming of a Simulated Producer Gas

E. S. Wangen, A. Malik, J. Pagels, M. Lindskog, M. Sanati, **E. A. Blekkan**
Department of Chemical Engineering, Norwegian University of Science and Technology, NO-7491 Trondheim, Norway.
edd.blekkan@chemeng.ntnu.no

The effect of soot deposition on the catalytic activities in the steam reforming was investigated. A quenched diffusion flame burner was employed for the size-selective generation of soot particles, whereupon the soot was deposited onto 4 commercial nickel based steam reforming catalysts. The amount of combustible materials deposited was 0.5 – 1.0 wt-%, as determined by TPO. The catalytic activity was tested in a microactivity setup, with steam reforming of a simulated producer gas from biomass gasification as the test reaction. The soot deposition was found to reduce the reforming activity with up to 50 % due to blocking of the catalyst surface.

P247 (411)

Dry reforming of methane to syngas on Rh catalysts modified by grafting zirconium on alumina support. Evidence of a synergistic effect between Rh/γ-Al_2O_3 and Rh/ZrO_2

C. Fernández, A. Karelovic, R. Jiménez, X.García, R. Wojcieszak, P. Ruiz, A.Gordon
Departamento de Ingeniería Química, Universidad de Concepción, Concepción, Chile. *camfernandez@udec.cl*

Rh/γ-Al_2O_3 catalysts were modified by grafting Zirconium(IV) n-propoxide on the support. Crystallites of tetragonal zirconia were detected on the surface and the contact between the coexisting phases was simulated by mechanically mixing Rh/γ-Al_2O_3 with Rh/ZrO_2. As a result of the zirconia incorporation, the catalytic activity during dry reforming of methane increases and carbon species formation is inhibited. It is suggested a catalytic cooperation effect where oxygen species formed by the dissociation of CO_2 on Rh/γ-Al_2O_3 migrate on Rh/ZrO_2 catalysts promoting the oxidation of Rh in it. Such effect would be magnified in grafted catalysts.

P248 (419)

LSCF 6428 hollow-fibre membrane for the production of syngas through the partial oxidation of methane

Luiz Carlos L. Santos[1], C. Moraes[2], R. Hughes[3], Ian S. Metcalfe[4]
[1]Federal University of Bahia, Escola Politécnica, DCTM, Rua Professor Aristides Novis 02, 3º Andar, Federação, CEP 40210-630, Salvador/BA, Brazil. *lclsantos@ufba.b*r, [2]Federal University of Rio de Janeiro, DEQ Av Horácio Macedo 2030, Rio de Janeiro/RJ, Brazil, [3]University of Statford, Greater Manchester, M5 4WT, UK, [4]School of Chemical Engineering and Advanced Materials, Newcastle Univ. NE1 7RU, UK

A ceramic membrane reactor operating at high temperatures (> 650°C) was used to study the syngas production of the LSCF 6428 hollow-fibre membranes. The experiments were done by using air and a mixture of 5% methane diluted in helium as inlet gases in a co-current flow. The results showed that by using 5% methane diluted in helium the main reaction is the total oxidation. This was probably due to the high oxygen content, supplied by the membrane, related to methane. It was also observed that although the LSCF 6428 presents some catalytic activity, a catalyst might improve the partial oxidation reaction.

P249
(435)

Catalytic Activity of Co-Pb Mixed Metal Oxide on the Lignite Gasification

A. Kanca[1,2], **D. Uner**[1]
[1]Department of Chemical Engineering, Middle East Technical University, Ankara, 06531 Turkey, *uner@metu.edu.tr*
[2]On leave Department of Chemical Engineering, Ataturk University, Erzurum, 25240 Turkey

Oxidation and gasification characteristics of lignite samples were investigated by using thermal gravimetric analysis and semi-batch reactor experiments with on-line gas chromatography, in the presence and in the absence of catalysts. The gasification process temperature could be lowered to 330 °C, producing H_2, CO and CH_4. It was observed that increase in the catalyst amount lead to the total oxidation of lignite to CO_2. The effect of oxide crystal structure on the activity and selectivity will be presented.

P250
(437)

Structural polymorphism of zirconia and its effect on the performance of supported Pt catalyst on water-gas shift reaction

A.M. Duarte de Farias, E.M. Albuquerque, C.A. Franchini, M.T. Rodrigues, M.A. Fraga
Instituto Nacional de Tecnologia/MCT, Laboratório de Catálise, Av. Venezuela, 82/518, 20081-312
Rio de Janeiro, Brazil. *marco.fraga@int.gov.br*

In this work the influence of zirconia polymorphism on water gas shift reaction and the deactivation process were investigated. It was found that the structure of zirconia indeed plays a decisive role in determining the catalyst activity, most likely due to the presence of bridged hydroxyl surface groups. The monoclinic supported sample showed to be markedly more active, reaching a conversion level 75% higher than that accomplished with tetragonal phase. The formation of carbonate species on the surface of used catalysts was observed; however, it was suggested that their occurrence is not the main factor on catalyst deactivation process.

P251
(442)

Catalytic conversion of methane over actinide bimetallic oxides with O_2 or N_2O

A.Ferreira, A. Janeco, N. Pinhão, A.P. Gonçalves and J. B. Branco
Instituto Tecnológico e Nuclear, Estrada Nacional 10, 2686-953 Sacavém, Portugal, e-mail: *acferreira@itn.pt*

Methane, which is a by-product formed in several industrial processes and a major hydrocarbon air pollutant has a much larger detrimental greenhouse effect than carbon dioxide and contributing to stratospheric ozone layer depletion. The oxidation of methane with O_2 constitutes a proper way to produce syngas ($CO+H_2$) and provides a suitable H_2/CO ratio for the methanol and Fischer-Tropsch synthesis. On the other hand, N_2O has been shown to be an excellent oxidant for performing oxidation processes. In this work, we studied the performance of binary intermetallic compounds of the type $AnNi_2$ (An=Th, U) and $ThCu_2$ as bimetallic Ni or Cu-actinide oxide catalysts.

P252
(449)

Preparation of Ni/Ce-ZrO_2-Al_2O_3 catalysts for steam reforming of methane

A. J. Abreu[1] and E. M. Assaf[1]
[1]Institute of Chemistry of São Carlos – University of São Paulo (Brazil),
Av. Trab. São-carlense, 400 CP 780 São Carlos, SP CEP 13560-970. *eassaf@iqsc.usp.br*

In this study, $Ni/_{(50-x)\%}Ce\text{-}_{(x)\%}ZrO_{2\text{-}50\%}Al_2O_3$ catalysts were studied for steam reforming of methane. The $_{(50-x)}Ce_{-(x)}ZrO_{2\text{-}50}Al_2O_3$ supports were prepared by co-precipitation and the Ni was added on the supports by impregnation. The catalysts were characterized by DRX, TRP, UV-vis and Raman spectroscopy. The reactions were carried out at 700°C using a feed molar ratio methane:water of 2:1. All catalyst showed activity for methane steam reforming. The increase in the cerium content improved the methane conversion and the products formation.

P253
(457)

$La_{1-x}Sr_xNiO_3$ catalysts in the Partial Oxidation of Methane

Paulo V. S. Ferreira[1], Otanéa B. Oliveira[1], Soraia T. Brandão[2], Pascal Bargiella[2], Maria G. C. Rocha[2], Kátia R. Souza[3], Fabio B. Noronha[3]
[1]Universidade Federal da Bahia, Escola Politécnica, Engenharia Química/PPEQ, Salvador, Bahia – Brazil
[2]Universidade Federal da Bahia, Instituto de Química, Campus de Ondina, Salvador, Bahia – Brazil.
[3]Instituto Nacional de Tecnologia, LACAT, Av. Venezuela, Rio de Janeiro – Brazil

The $La_{1-x}Sr_xNiO_3$ catalysts were studied in the partial oxidation of methane (POM). Results of textural analysis and SEM indicated that Sr promotes an increase of the porosity of the catalysts. TPSR experiments showed that the activation of the catalytic sites is more favoured in the presence of Sr which is in agreement with TPR and XPS results. The catalytic tests showed that these perovskites are promising in the POM, reaching high CH_4 conversion and H_2 and CO selectivities. Another important result is the decreasing of carbon deposition in the catalysts after test, indicating that Sr minimizes coke formation by the increase of the mobility of oxygen species.

P254
(463)

Effect of the metallic additions on catalysts Ni-M / SiO_2 and Ni-M / ZnO (M = Cu, Cr and Mn) in methane steam reforming.

Akila Belhadi, Ouiza Cherifi
Laboratoire de chimie du Gaz Naturel, Faculté de Chimie, U S T H B, BP32, El-Alia, Bab-Ezzouar, Alger, Algérie.
sarakila@yahoo.fr

Catalysts containing(4%wt) Ni supported on SiO_2 or on ZnO and promoted by a metal M (2% wt) (M=Cu, Cr and Mn) were applied for steam reforming of methane to obtain singas, at atmospheric pressure between 475-600°C. These catalysts have been characterized by: atomic absorption, BET technique, X-ray and TPR.The catalysts Ni/SiO_2 is more active than the Ni/ZnO. For The catalysts promoted by metallic addition, it has been a change of activity according to the reduction of the nickel more or less facilitated by the presence of the metal.

P255
(469)

Catalytic partial oxidation of methane using rhodium and nickel substituted hexaaluminate

N.B.Touahri, R.chebout, P.Ruiz, **A.Benadda** and A.Barama
LMCCCO, Faculté de chimie USTHB BP 32, ElAlia, Bab Ezzouar Alger Algérie, e-mail : *benaddaamel@yahoo.fr*

Citrate route was used to prepare hexaaluminate based catalysts containing nickel or rhodium as active phase ; the solids were calcined at 1000, 1300 and 1400°C. Their catalytic behavior was studied in the partial oxidation of methane. The hexaluminate structure was formed successfully after calcination at 1400°C. The activity of rhodium based catalysts didn't depend on the temperature calcination or the loading whereas the activity of nickel catalysts increased when the calcination temperature and the loading increased.

P256
(477)

The effect of temperature on the activity of zirconia-supported cobalt for WGSR

I. Barros[1], P.Querino[1], A.Souza[2] and M.C.Rangel[1]
[1]Grupo de Estudos em Cinética e Catálise, Instituto de Química-Universidade Federal da Bahia. Campus Universitário de Ondina. Federação. 40190-280- Salvador, Bahia, Brazil. e-mail: *mcarmov@ufba.br*

Zirconia-supported cobalt catalysts were studied in this work in order to find alternative systems for the water gas shift reaction (WGSR) at high temperatures. Solids with different amounts of cobalt were prepared and evaluated at several temperatures in this reaction. The most active catalyst was that with 20% Co, which was active and stable to WGSR in the range of 330 to 410°C, due to its highest amount of active sites. This solid is stable under this temperature range and is more active than a commercial catalyst, evaluated at 370°C, being thus promising to commercial applications.

P257
(481)

Ultra-low temperature steam reforming of methane with novel catalytic system in an electric field

Y. Sekine, M. Haraguchi, M. Tomioka, M. Matsukata, E. Kikuchi
Department of Applied Chemistry, School of Science and Engineering, Waseda University, Okubo, Shinjuku, Tokyo, Japan.
ysekine@waseda.jp

Steam reforming of methane is a highly-endothermic reaction, so it requires high temperature. Recently we found that some catalysts in an electric field showed high activities for steam reforming of methane at ultra-low temperature like as 423 K. The catalytic reaction in an electric field (electreforming) is not a faradic electrochemical reaction, not plasma and not by the electric heat. This non-faradic reaction showed higher water-gas shift activity simultaneously which is an exothermic reaction. The energy efficiency of the electreforming was very high and has rapid on-off response.

P258
(483)

Hydrogen production by steam reforming of ethanol over supported Fe/Co catalyst

Y. Izutsu, **Y. Sekine**, A. Kazama, M. Matsukata, E. Kikuchi
Department of Applied chemistry, Faculty of Advanced Science and Technology, Waseda University
ysekine@waseda.jp

Steam reforming of ethanol for hydrogen production over Co/α-Al_2O_3 and Fe/Co/α-Al_2O_3 catalysts was studied. The reaction on supported Co catalyst is following sequential reactions: dehydrogenation of ethanol to acetaldehyde, decomposition of acetaldehyde to CH_4 or steam reforming to CO, and water-gas shift of CO to CO_2. To obtain higher hydrogen yield, acetaldehyde should be reformed without decomposition. Fe/Co/α-Al_2O_3 catalyst showed higher activity for steam reforming of acetaldehyde. Carbon formation proceeded by adsorbed acetaldehyde on the catalyst surface and the carbon precursor is oxidized by the active species on the catalyst.

P259
(493)

The effects of La promotion on the activity of alumina supported Pt catalysts in Steam Methane Reforming and in situ temperature-resolved XAFS for Partial Oxidation of Methane.

K. O. Rocha, D. Zanchet, C.M.P. Marques, **J. M. C. Bueno**
Chemical Engineer Department, Federal University of Sao Carlos, Rod Washington Luiz, Km 235, Sao Carlos, SP, Brazil.
jmcb@ufscar.br

Pt supported in La_2O_3-Al_2O_3 was prepared by subsequent impregnation of Al_2O_3 sol-gel. In situ XANES of partial oxidation of methane (POM) coupled to Mass Spectrometer shows that POM occurs preferentially by direct pyrolytic mechanism, where CH_4 decompose to elementary C* and H_2 on metal and the CO of formed thorough the reaction of C* and surface O* species. The results of activity in Steam Methane Reforming shows that the formation of adduct Pt^{o}*$Pt^{\delta+}$O-La improves the removal of elementary carbon, been the 1%wt Pt/La_2O_3-Al_2O_3 an optimum balance between the density of Pt sites expose and Pt site coverage by adduct.

P260
(497)

Sulphur adsorption studies on ZrO_2-based biomass gasification gas clean-up catalysts

Inkeri Kauppi[1], Hanne Rönkkönen[1], Juha Linnekoski[1], Pekka Simell[2], Matti Reinikainen[2], Marita Veringa Niemelä1 and Outi Krause[1]
[1]Helsinki University of Technology, Department of Biotechnology and Chemical Technology, P.O. Box 6100, FI-02015 TKK, Finland.
Fax: +358 9 451 2622, e-mail: *inkeri.kauppi@tkk.fi*
[2]Technical Research Centre of Finland (VTT), P.O.Box 1000, FI-02044 VTT, Finland. Fax: +358 20 722 7048.

Zirconia based catalysts are active catalysts for gasification gas clean-up when O_2 is added to the gas. The effect of 500 ppm of H_2S was studied on Y_2O_3-ZrO_2, SiO_2-ZrO_2 and ZrO_2 in gasification gas clean-up. The interaction between H2S and these catalysts was studied via temperature-programmed desorption of H_2S. H_2S adsorption on ZrO_2 and Y_2O_3-ZrO_2 occurred on one kind of sites which was related to a high naphthalene conversion. H_2S adsorption with SiO_2-ZrO_2 takes place at least on two distinct sites.

P261 (503)

SiC supported rhodium and nickel catalysts for Catalytic Reforming of Methane with Carbon Dioxide

Rujing Shang[ab], Uwe Rodemerck[c], Claudia Berger-Karin[c], Yingyong Wang[a], Guoqiang Jin[a], Axel Schulz[c],
Hendrik Kosslick[c*], **Xiang-Yun Guo**[a**]
[a]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Taiyuan 030001, PR China
[b]Graduate University of the Chinese Academy of Sciences, Beijing 100039, PR China
[c]Leibniz Institute for Catalysis at the University of Rostock, Rostock 18059, Germany
[**](X. Y. Guo) - Tel: +86-351 4065282, e-mail: *xyguo@sxicc.ac.cn*
[*](H. Kosslick) - Tel: +49-381 498 6383, e-mail: *Hendrik.Kosslick@catalysis.de*

A study on SiC supported rhodium catalysts for carbon dioxide reforming of methane was investigated and compared with that of a Ni/SiC catalyst tested under same reaction conditions. The experimental results indicate that the initial activity for CO_2 reforming increases with growing rhodium loading (0.5-1.5 wt.-%) and reaction temperature. At high temperature (700°C), the activity for CH_4 reforming with CO_2 is similar high for all Rh/SiC and Ni/SiC catalysts and approaches the thermodynamic equilibrium. The 5 wt.-% loaded Ni/SiC catalyst shows a better catalytic performance than 0.5 wt.-% loaded Rh/SiC. However, the Rh catalysts (Rh $\geq$ 1 wt.-%) show high activity and long-time stability at low temperature (600°C, 650°C).

P262 (507)

Gasification of Agricultural Waste

P.Pramanik
Department of chemistry, Indian Institute of Technology, Kharagpur 721302, India

The conversion of agriculture waste is an emerging challenge to globe. Every millions of tons of agricultural waste is generated as rice straw, rice husk, wheat straw ,wood chips etc. Most of them are burned as raw fuel or buried in the ground. One of the efficient use of he agricultural is the gasification to semi-water gas and its conversion to organic–liquid. We have studied the reaction of these carbonaceous mass to semi-water gas using controlled amount air and steam at different temperature. The temperature is controlled by controlling the air flow. It is noted that metal catalyst incorporated in organic mass has tremendous effect on the kinetics of gasification. We have attempted with Fe, Cr, Mn, Zn. The best result was obtained with Fe salt. The Fe salt used is Fe-nitrate. The concentration required is very low. It is in the order of 0. 01% with respect organic mass. Because the conversion is facilitated at lower temperature, so oxygen intake visa-vice loss of carbon as CO_2 is minimum. The evolved gas is free from any tarry mass (less than 1ppm).

P263 (510)

Electrosynthesis of hydrotalcites on FeCrAlloy foams, precursors of methane conversion catalysts

F. Basile[1], P. **Benito**[1], G. Fornasari[1], M. Monti[2], E. Scavetta[2], D. Tonelli[2], A. Vaccari[1]
[1]Dip. Chimica Industriale e dei Materiali, ALMA MATER STUDIORUM-Università di Bologna, V.le Risorgimento 4,
40136 Bologna, Italy, *pbenito@ms.fci.unibo.it*
[2]Dip. Chimica Fisica e Inorganica, ALMA MATER STUDIORUM- Università di Bologna, V.le Risorgimento 4, 40136 Bologna, Italy

Rh-containing hydrotalcite-type (HT) compounds have been electrosynthesized on the surface of FeCrAlloy foams in order to prepare Rh-based catalysts active in syngas conversion processes such as steam reforming and catalytic partial oxidation. The effects of the synthesis conditions (potential applied and time) on the mophological and chemical properties of the catalytic film as well as on the catalytic performances are studied. The amount of active phase and the homogeneity of the film, which can be modified with the synthesis conditions, play a key role in the development of structured catalysts.

P264
(511)

Bimetallic Pd-Ni catalyst supported on Y_2O_3: Active and Stable Catalyst for Oxy-CO_2 Reforming of Methane

O.Usman, K. Hidajat, **S. Kawi**
Department of Chemical and Biomolecular Engineering
National University of Singapore, 4 Engineering Drive 4, Singapore 117576
chekawis@nus.edu.sg

A series of Pd-Ni catalysts were synthesized by impregnation method over Y_2O_3 in order to study the effect of Pd addition to Ni catalyst in oxy-CO_2 reforming of methane. TPR, XPS, and XRD results show that there is stronger interaction between Pd and the support compared to pure Ni catalyst interaction with its support. The stability tests show that Ni deactivates very fast due to high formation of carbon nanotubes, while Pd shows a stable performance with a lower activity. However, PdNi catalyst at the ratio 1:1 shows the highest activity with a stable performance. This can be attributed to formation of bimetallic Pd-Ni particles and strong interaction between Pd and support.

P265
(514)

Effect of various ratios of La doping on Al support over Ni catalyst in oxy-CO_2 reforming of methane

K.Yasotha, K.Sutthiumporn, **S. Kawi**
Dept. of Chemical and Biomolecular Eng., National University of Singapore, *Singapore.chekawis@nus.edu.sg*

Nickel based catalysts are widely investigated for catalyzing the reaction of carbon dioxide reforming of methane for syngas production. Despite having high activity and being obtainable at low cost, nickel is prone to carbon deposition and thus deactivates easily. Therefore the challenge is to increase the resistance of Ni-containing catalysts and enhance its application for commercial usage. In this work, we have explored the effect of various atomic ratios of La doping on Al supports for Ni based catalysts (with 10 wt% loading) in order to determine the most stable catalyst composition with miminal coke formation in the O_2 enhanced CO_2 reforming of methane.

P266
(515)

Sr- or Ga-doped $LaNiO_3$ perovskite catalysts: Role of oxygen mobility on CO_2 reforming with methane to hydrogen

K.Sutthiumporn and **S. Kawi**
Dept. of Chemical and Biomolecular Eng., National University of Singapore, *Singapore.chekawis@nus.edu.sg*

It has been reported that the addition of Sr or Ga on the perovskite structure enhances oxygen deficiency, which may lead to higher oxygen adsorption. Therefore, our study is to investigate the effects of Sr or Ga doped in $LaNiO_3$ perovskites on their catalytic performance for dry CO_2 reforming of methane (DRM) to hydrogen. Our results show that Sr doping in the perovskite structure can create mobile oxygen species which can promote the activity of C-H bond, hence increasing methane conversion and hydrogen production. Due to these mobile oxygen species, Sr-doped $LaNiO_3$ perovskite catalyst has very high catalytic performance and stability in DRM.

P267
(519)

The effect of cerium content on the properties of zirconia-supported gold catalysts for WGSR in the presence of hydrogen

H. S. Ferreira[1], A. Albarnoz[2], M. C. Rangel[1]
[1]GECCAT/ UFBA. Campus Universitário de Ondina. 40190-280- Salvador, Bahia, Brazil, e-mail: *mcarmov@ufba.br*

The effect of cerium on zirconia-supported gold catalysts was studied in this work, in order to find alternative supports for catalysts to WGSR, which can be able to operate in the presence of hydrogen, in the range of 190-300°C. The best catalytic performance of mixed oxides, as compared to zirconia-based one is related to more active sites on the surface, due to gold and to the presence of cationic and/or metallic gold species. The amount of cerium affects the activity and the most promising catalyst was the $Au/Ce_{0.58}Zr_{0.42}O_2$ sample, which was the most active and stable in all temperature range.

P268
(528)

Reaction mechanism of partial oxidation of methane over Ru based catalysts

Roberto Lanza[1], Paolo Canu[2], Sven Järås[1]
[1]KTH - Royal Institute of Technology, Department of Chemical Engineering and Technology SE-100 44 Stockholm (Sweden),
lanza@kth.se
[2]Universitä degli Studi di Padova, Department of Principles and Practice, Padova 35013 (Italy)

In this work the results of an investigation on the mechanism followed by the partial oxidation of methane are presented. Running specific tests of steam, dry reforming and water gas shift reaction allowed to determine that the catalysts tested (Ru-Pt on alumina and also Ru on TiO_2, on SiO_2 and on CeO_2) catalyze the reaction according to the indirect combustion and reforming mechanism. After a first step of complete combustion of the methane fed, the CO_2 and the H_2O produced react with the residual CH_4 to give the final products (H_2 and CO in a ratio equal to 2). Experimental results have been compared to thermodynamic equilibrium calculation.

P269
(529)

Metal dusting in synthesis gas applications

Thoa Nguyen, Martin Skjøth-Rasmussen
Haldor Topsæe A/S. Nymøllevej 55, DK-2800 Kgs. Lyngby. Denmark. *ttmn@topsoe.dk*

Metal dusting is a type of corrosive disintegration of metals and alloys into powders. It is often encountered in synthesis gas applications, where carbon monoxide dissociates on the surfaces of metallic equipment, forming metastable carbides, which subsequently decompose into metal dusts and graphite. Extensive research on metal dusting has been conducted at Haldor Topsøe A/S in the past few decades, predominantly on alloys and coatings, on both laboratory and industrial scales. In addition, fundamental research has been carried out to gain better understanding of the phenomenon and find ways to suppress metal dusting.

**P270
(530)**

Thermodynamic assessment of reaction pathways to convert ethanol into hydrogen, ethyl acetate, acetic acid and ethylene

C.N. Ávila-Neto, C.E. Hori, A.J. Assis*.
*Federal University of Uberlândia, School of Chemical Engineering , Av. João Naves de Ávila, 2121, Bl. 1K, Campus Santa Mônica, CEP: 38408-100, Uberlândia-MG, Brazil, e-mail: *adilsonjassis@gmail.com*

The goals of this study are to conduct a thermodynamic analysis for specific ethanol-based chemical reactions and to assess the influence of key operational variables on chemical equilibrium using an in-house code. Such reactions comprise the steam, dry, oxidative and autothermal reforming of ethanol; production of ethyl-acetate via an ethanol dehydrogenation process and also using an oxidative route; acetic acid formation from the ethanol oxidation reaction; and the dehydration of ethanol into ethylene. The systems of non-linear algebraic equations are calculated by means of the Lagrange multipliers method using the function "fsolve" of the software Scilab.

**P271
(531)**

Investigation of preparation method and influence of Ce on stability of Pt/Al_2O_3 catalysts to partial oxidation of methane by in situ XAS analysis

A. P. Ferreira[1], **J. M. C. Bueno**[1]
1Chemical Engineering Department (DEQ), PO Box 676 - Universidade Federal de São Carlos, Rod. Washington Luís, Km 235, SP-310, 13565-905, São Carlos, SP, Brazil. *jmcb@ufscar.br*

Method preparation was investigated to influence the structural and electronic properties of Ce-containing Pt catalysts. XANES analysis provided evidences of Pt-O-CeAl interaction by electronic transference that helps Pt to be reduced easily promoting lower ignition temperature, Pt redispersion at partial oxidation of methane (POM) conditions, stronger anchoring Pt that avoids sintering by PtO_2 sublimation and carbon removing from metal surface that improves the catalysts activity. The preparation method provided particular metal-support interactions that affected the catalysts dispersion and performance. POM mechanism was figured out as combustion-reforming.

**P272
(540)**

Syngas production by steam reforming of methane and biofuels over Ni -based composite catalysts: from design of active component to pilot-scale level

N. Mezentseva, V. Sadykov, G. Alikina, R. Bunina, V. Pelipenko, S. Tikhov, V. Usoltsev, J.R.H. Ross
Boreskov Institute of Catalysis SB RAS, 630090, pr. Lavrentieva, 5, Novosibirsk, Russia, e-mail: *mnv@catalysis.ru*

The nanocomposite catalysts comprised of Ni particles, complex fluorite or perovskite oxides and precious metals were prepared using polymerized polyester precursor (Pechini) route and successive impregnation procedures including those using a Hamilton Microlab robotic workstation. Procedures for supporting thin layers of nanocomposite active components on different substrates were developed. This work presents results of research aimed at design of such catalysts and characterization of their performance parameters in steam reforming of methane and biofuels at lab-scale and pilot-scale levels.

P273
(542)

Oxidation partial of Methane by storage of oxygen On Pd/CeO_2, Pd/ZrO_2 and Pd/CeO_2-ZrO_2

Said Alim[1], Farida Sadi[1], Daniel Duprez[2]
[1]Laboratory of Physicochemical Study of Materials and Application to the Environment Faculty of Chemistry, U.S.H.T.B.
[2]LACCO University of Poitiers de Chimie 40 Which occurred of Doctor Pinneau,
e-mail: *mustapha_alim2007@yahoo.fr*

The oxidation of the gas methane presents both economical and ecological interests. This reaction has been studied, in this work by a new method which is oxidation by oxygen stored on catalysts containing palladium (1% in weight) supported on cerine (CeO_2), zirconia (ZrO_2) and on mixed oxide (CeO_2-ZrO_2). The catalysts used are prepared by the method of impregnation. They are characterized by various physicochemical methods such as: the hydrogen H_2 chemisorption, titration O_2-H_2, TPR, TPD of H_2, DRX and MEB. The catalysts are tested in oxidation of methane at various temperatures from 250 to 500°C under He orAr flow. Oxygen storage capacity of the catalysts is classified as follows: Pd/CeO_2- ZrO_2 >> Pd/CeO_2> Pd/ZrO_2. The catalytic activity in oxidation of methane depends on the temperature of reaction and catalyst used. The conversion of methane follows the same classification as that of the storage capacity of oxygen

---

P274
(558)

Aluminium modified Algerian clay and grafted silicates layers by Rh, Ni, Pd and Ce. New catalysts (3,10)%Me/Al-PILC containing hexagonal phases very active in the dry reforming of CH_4.

S. Barama[1], E. Bordes-Richard[2], **O.Mohhammedi-Bakhti**[3]
[1]Laboratoire des Matériaux Catalytique et Catalyse en Chimie Organique, Bp32 El Alia Bab Ezzouar 16079 USTHB d'Alger, Algérie
[2]Unité de Catalyse et de Chimie du Solide, UMR 8181, Université des Sciences et Technologies, 59655 Villeneuve d'Ascq, France.
[3]Laboratoire de Chimie-Physique Moléculaire et Macromoléculaire, Faculté des Sciences, Université de S. Dahleb de Blida, Algérie.

The (3,10)%Me/Al-PILC catalysts (Me=Rh, Ni, Pd, Ce) were prepared by the grafting process of metals on the calcined precursor Al-PILC following the adsorption mechanism of metallic ions in aqueous solution.The design, synthesis and characterization of (3,10)%Me/Al-PILC have been the subject of large and intersting work. The porous structures of Me/Al-PILC and N_2 adsorption isotherms have considerable informations about catalysts geometric topology and surface properties. Catalytic results of CO_2-reforming of CH_4 over Me/Al-PILC show elevated conversions.The high conversion%=88 and the H_2/CO ratio=1.11 are exhibited by Rh catalyst.

P275
(559)

UBI-QEP evaluation of Ni(100) and Ni(111) sites for syngas formation

Bjørn Christian Enger, Rune Lødeng, Anders Holmen
Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway
bjornce@chemeng.ntnu.no

Methane activation is typically the rate determining step towards syngas formation. Using the UBI-QEP formalism for calculating chemical heats of adsorption and activation energy barriers on Ni(100) and Ni(111) surfaces, we here illustrate how sites with different coordination numbers may play different roles on the catalytic surface during methane activation for syngas formation. We also illustrate that surface species which are rarely observed experimentally, such as CH_xO, may provide pathways with substantially lower barriers for methane activation as compared to dissociation of CH_x, $x \leq 4$.

P276
(561)

Pyrolysis of individual and mixed biomass, plastics and used tyres

M. Bajus, M. Bartík, E. Hájeková
Faculty of Chemical and Food Technology, STU, Radlinského 9, 812 37 Bratislava
martin.bajus@stuba.sk

The pyrolysis processes was carried out in batch reactor, keeping the range of temperature from 450 to 570°C. We have investigated qualitative and quantitative composition of gases, liquids and solid residue (coke). The main constituents of pyrolysis gases were carbon dioxide, carbon oxide as non-hydrocarbons and hydrocarbons. At higher temperatures pyrolysis (500°C) of mixed biomass and plastics, the amount of carbon oxides was decreasing and the amount of hydrocarbons from C1 to C3 were increasing.

P277
(564)

CO_2 reforming of methane to syngas over non reduced spinel catalysts.

N. Salhi[1], C. Petit[2] , A. A. Kiennemann[2], and C.Rabia[1].
[1]Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, USTHB 109 El-Alia Bab Ezzouar, Alger-Algérie.
[2]Ecole de Chimie, Polymères et Matériaux – Laboratoire Matériaux, Surface, Procédés pour la Catalyse (LMSPC) UMR CNRS 7515 - 25, rue Becquerel 67087 Strasbourg Cedex France. *NAS.SALHI@yahoo.fr*

A series of mixed oxides: $NiAl_2O_4$, $5\%NiO/NiAl_2O_4$, $Ni_{(1-5\%)}Al_2O_4$ were prepared by sol-gel method. If Ni/Al is higher than 0.5, free NiO is present on spinel and favours the reduction of nickel at low temperature. The formed NiO is in strong interaction with spinel form. If the Ni/Al ratio is lower than 0.5, a solid solution of Al_2O_3-$NiAl_2O_4$ was formed. Catalytic testing was performed for CO_2 reforming of methane. The presence of nickel both inside and outside the structure for the $5\%NiO/NiAl_2O_4$ catalyst confers a high stability and strong dispersion for the metallic particles and limits the growing of the Ni particles.

P278
(570)

Conversion of Natural Gas to syngas by Pulsed Compression Reactor

T. Roestenberg, M. Glushenkov, A. Kronberg, A.A. Verbeek, Th.H. vd. Meer
University of Twente, PO box 217, 7500 AE Enschede, The Netherlands, *t.roestenberg@utwente.nl*

The Pulsed Compression Reactor promises to be a compact, economical and energy efficient alternative to conventional chemical reactors. In this article, the production of synthesis gas using the Pulsed Compression Reactor is investigated. This is done experimentally as well as with simulations. The experiments are done by means of a single shot reactor. Simulations are done with a relatively simple method, which uses different models for the chemistry and thermodynamic properties of the species in the reactor. Simulation results show very good agreement with the experimental data, and give great insight into the reaction processes that occur within the cycle.

P279
(573)

High Temperature vs. Low Temperature Dry Reforming: a surprising effect of tin doping on Ni, Rh and Pt nanoparticles supported on SiO_2.

David Baudouin, Chloé Thieuleux, Jean-Pierre Candy, Uwe Rodemerck, Christophe Copéret
Université de Lyon, Institut de Chimie de Lyon, C2P2, UMR 5265 (CNRS-CPE-Universite Lyon 1), CPE Lyon F308,
43 Boulevard du 11 Novembre 1918, F-69616 Villeurbanne Cedex, France – *david.baudouin@lcoms.cpe.fr*

Silica supported nickel, platinum and rhodium nanoparticles have been selectively doped with tin, via a reaction between tetrabutyltin and surface metal hydrides. The MSn_x/SiO_2 ($0 < x < 0,5$) catalysts were tested at high temperature dry reforming and as expected, the tin doped catalysts exhibit better stability than pure metal nanoparticles. In low temperature dry reforming, the same catalysts exhibited very different behaviours: 1) pure nickel catalysts present similar activities than rhodium and platinum ones, 2) tin doping just lead to a decrease of activity, without any significant effect on stability or selectivity.

P280
(577)

Factorial design applied to the CO_2 reforming of CH_4 for syngas production over Ni/SiO_2 catalyst.

T.P. Braga[1], F.A.G.M. Junior[1], A.Valentini[1], R.C.R. Santos[1],C.L.Lima[2], J.M. Filho[2], B.C. Viana[3], A.C. Oliveira[1]
[1]University Federal of Ceará, bloco 940, 60.000-000, Fortaleza, Ceará, Brazil. *alcineia@ufc.br*
[2]University Federal of Ceará, Physics department, 60.000-000, Fortaleza, Ceará, Brazil.
[3]University Federal of Piaui, Physics department CCN, Teresina, Piaui, Brazil.

Factorial design was applied to the CO_2 reforming of CH_4 for syngas production over Ni/SiO_2 catalyst.

From the results, it is shown that the best H_2/CO ratio is achieved at high CH_4/CO_2 ratios and temperatures higher than 700°C. The analysis of carbon deposits point to MWNTs formation. However, lower temperature and lower feed ratios (CH_4/CO_2) gives I_G/I_D of 0.46, which indicates a large amount of amorphous carbon on these conditions.

P362
(590)

Effect of doping and synthesis conditions on the physico-chemical properties of $Cu/ZnO/Al_2O_3$ catalysts obtained from hydrotalcite-like precursors

J. Plona, D. Mucha, B. Napruszewska, M. Zimowska, R. Dula, E. M. Serwicka
Institute of Catalysis and Surface Chemistry PAS, Niezapominajek 8, Krakow, 30-239 Poland. *ncplona@cyf-kr.edu.pl*

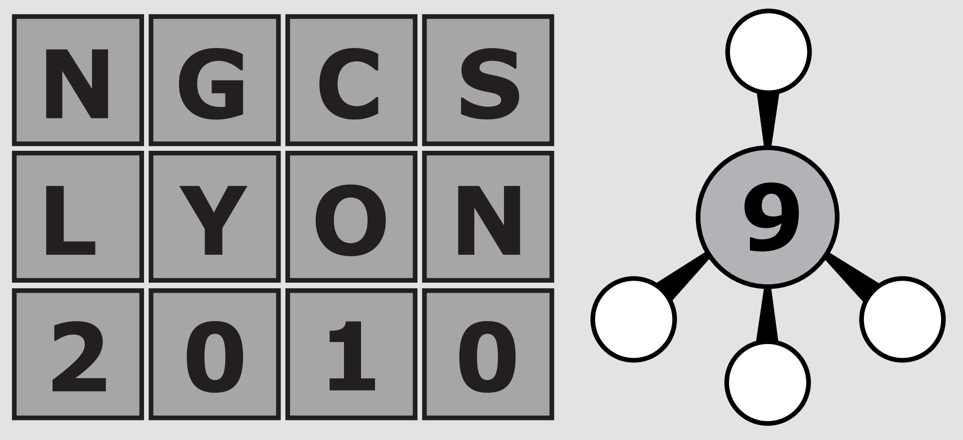
Three series of Cu-Zn-Al-Zr-O, Cu-Zn-Al-Ga-O and Cu-Zn-Al-Mn catalysts (with different amount of Zr, Ga or Mn) and their Cu-Zn-Al-O analogues were obtained from HTlc precursors synthesised at pH 7 and 9. All samples were characterised by XRD, TG/DSC, EGA-MS, ICP-OES, BET and TPR techniques. The only crystalline phase in precursors obtained at both pH values is HTlc, higher crystallinity being observed for pH=9. Addition of Ga has a positive effect on the HTlc structure while Zr and Mn have the opposite effect. Calcined materials exhibit significant differences in the course of reduction depending on the additive used.

P363 (179)

Methane conversion to synthesis gas by CO_2 reforming over bimetallic Ni- Pt and Ni-Pd catalysts

F. Menegazzo[1], M. Signoretto[1], F. Pinna[1], N. Pernicone[2]
[1]Dip. Chimica, Univ. Ca' Foscari and Consorzio INSTM UdR Venezia, DD2137, Ve (Italy) *fmenegaz@unive.it*

The major problem preventing commercialization of CH_4/CO_2 reforming is the quick deactivation of the catalyst due to carbon deposition. In order to improve the stability of Ni-based samples, we have studied the promotion of Ni by a small amount of noble metal. Samples were tested in CO_2 reforming temperature-programmed reaction, in coking reaction either via CH_4 ($CH_4 \rightarrow C+2H_2$) or CO ($2CO \rightarrow C+CO_2$) temperature-programmed decompositions. Results clearly show that the addition of a noble metal (Pt or Pd) to monometallic Ni-based samples hinders the accumulation of coke on the catalyst surface, improving the stability of the catalytic system.



Session III - Synfuels: Fischer-Tropsch synthesis, gas to liquids, coal to liquids, biomass to liquids, methanol, higher alcohols and DME

P41
(21)

The solvent effects during prepararion of fischer-tropsch synthesis catalysts

Yi Zhang[a], Yusuke Endo[b], Noritatsu Tsubaki[b], Jianfeng Chen[a]
[a]Research Center of the Ministry of Education for High Gravity Engineering and Technology, Beijing
[b]University of Chemical Technology, Beijing, 100029, China, e-mail: *yizhang@mail.buct.edu.cn*

The acetic acid solvents were applied, during preparation of Fischer-Tropsch synthesis (FTS) catalysts, to modify the surface properties of silica supports. The different acetic acid should modify the properties of silica surface, such as nature of hydroxyl groups or oxyl groups, resulting in forming different catalytic property of relative catalyst. The modification of silica supports by acetic acid improves the reduction degree and dispersion of supported cobalt simultaneously, realizing higher catalytic activity. The obtained catalysts were characterized by XRD, TPR, in situ DRIFT and H_2 chemisorption.

P42
(43)

Catalytic conversion of methanol to light olefins in a fluidized bed reactor: Preparation of catalyst and presentation of a kinetic model

Niloufar Fatourehchi, **Morteza Sohrabi**, S. Javid Royaee, S. Mahdi Mirarefin
Department of chemical Engineering, Amirkabir university of Technology, Tehran 15914, Iran, e-mail: *sohrabi@aut.ac.ir*

In the present study, conversion of methanol to light olefins in presence of acidic SAPO-34 molecular sieve as the reaction catalyst has been investigated. SAPO-34 was synthesized by hydrothermal method, applying morpholine as the template. The molecular sieve was then changed into protonated form by ion exchange process with ammonium chloride. A kinetic study was carried out within the temperature range of 375-425°C and 4bar pressure using a differential fixed-bed reactor. An appropriate kinetic model was presented and the kinetic parameters were evaluated as functions of temperature. In addition, formation of light olefins was implemented in a fluidized bed.

P43
(46)

Commercial Methanol Synthesis Catalysis: Effect of Acetic Acid Addition

Stuart D. Blain and **S. David Jackson**
Centre for Catalysis Research, WestCHEM, Department of Chemistry, University of Glasgow, Glasgow G12 8QQ , Scotland
sdj@chem.gla.ac.uk

The effect of acetic acid on methanol synthesis was investigated over a $Cu/ZnO/Al_2O_3$ catalyst at 50 bar and 523 K using $CO/CO_2/H_2$ and CO/H_2 feeds. The introduction of the acid decreases methanol production and gives rise to ethanol and methyl acetate with a $CO/CO_2/H_2$ feed whereas with a CO/H_2 feed the yield of methanol increases. Under the $CO/CO_2/H_2$ feed no carbon laydown was observed whereas under the CO/H_2 feed significant deposition was detected. Using isotopically labeled acid it was possible to specify each of the reactions occurring and to obtain a detailed analysis on the fate of both the methyl and carbonyl carbons.

P44
(63)

Identity and evolution of Fe active phase during Fischer-Tropsch Synthesis catalysis

M. Ojeda, F.J. Pérez- Alonso, T. Herranz, S. Rojas, J.L.G. Fierro
Institute of Catalysis and Petrochemistry (CSIC). C/ Marie Curie 2, 28049 Madrid, Spain, e-mail: *mojeda@icp.csic.es*

We provide here a detailed characterization study of unpromoted and Ce- or Mn-promoted Fe-based catalysts subjected at different pretreatments (H_2, CO, CO/Ar and H_2/CO) with the aim of determining the identity of the bulk and surface species that are formed. Moreover, the evolution of these species during the reaction and the relationship with the observed catalytic performance is investigated.

P45
(64)

Effect of supercritical fluid of CO_2 drying during Cu/ZnO catalyst preparation on methanol synthesis from syngas at low temperature

X. Li, F. Meng, M. Meng, Y. Ishizaka, **N. Tsubaki**
School of Chemical Engineering and Technology, Tianjin University, Tianjin, 300072, P.R. China. *xingang_li@tju.edu.cn*

For methanol synthesis from syngas using alcohol as solvent at low temperature, the Cu/ZnO catalyst prepared through supercritical fluid of CO_2 (SCF-CO_2) drying showed excellent catalytic performances than that of the Cu/ZnO catalyst prepared by the conventional method. This is due to the SCF-CO_2 drying preventing the sintering of the CuO, ZnO and Cu_2O in the Cu/ZnO catalyst. The obtained Cu/ZnO catalyst achieved a large surface area and Cu specific surface area, which improved the dispersion of metallic Cu and increased the number of active Cu sites, resulting in a high methanol yield.

P46
(68)

Nanoscale Chemical Imaging of the Reduction Behavior of an Iron-based Fischer-Tropsch Synthesis Catalyst Particle

E. de Smit, I. Swart, J. F. Creemer, H. W. Zandbergen, F. M. F. de Groot and B. M. Weckhuysen
Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Sorbonnelaan 16, 3584 CA Utrecht, The Netherlands. *e.desmit@uu.nl*

An in situ Scanning Transmission X-ray Microscopy (STXM) methodology was developed to image the distribution and chemical identity of Fe species during temperature programmed reduction of a $Fe_2O_3/CuO/K_2O/SiO_2$ catalyst. STXM uses a soft X-ray (200-2000 eV) probe to image (~15 nm resolution) and characterize (by X-ray Absorption Spectroscopy) samples. It was illustrated that in situ STXM is a versatile tool for the characterization of catalytic solids. Different Fe phases were found to be present in a heterogeneous spatial distribution; strongly influenced by the local (nanoscale) catalyst formulation and morphology.

P47
(74)

Inhibiting effect of decan-1-ol on the transformation of N-hexadecane over a Pt/siO_2-Al_2O_3 catalyst

A. S. Guedes[1], C. Fontaine[1],C. Bouchy[2], **S. Brunet**[1]
[1]Laboratoire de Catalyse en Chimie Organique (Poitiers), UMR 6503 CNRS - Université de Poitiers, Faculté des Sciences Fondamentales et Appliquées, 40 av. du Recteur Pineau, 86022 Poitiers Cedex, France. *sylvette.brunet@univ-poitiers.fr*
[3]IFP-Lyon, Direction Catalyse et Séparation, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France

An important and negative impact of the alcohol on the transformation of N-C_{16} (a model molecule representative of those obtained by Low Temperature Fischer Tropsch process in order to produce diesel) was observed. This effect increased with the amount of alcohol introduced. This impact leads to irreversible modifications of the catalyst (sintering of platinum and decrease of Brønsted acidity) corresponding to a strong decrease in conversion and an irreversible modification of selectivity towards isomerisation and cracking, promoting isomerisation.

P48
(76)

A rusty technology?: Iron catalysed Fischer Tropsch

S. Gaemers[1], D.C. Griffiths[1], P. Cong[2], Y. Wang[2], G. Bian[2], H. Mao[2], H. Han[2]
[1]BP - Conversion Technology Centre, Refining & Marketing Research & Technology, DL10, Saltend, Hull, HU12 8DS, United Kingdom. *Sander.Gaemers@bp.com*
[2]Accelergy Shanghai R&D centre, Building #5, 3000 Longdong Avenue, Zhangjiang High-Tech Park, Pudong, Shanghai 201203, China.

As the world experiences ever increasing crude oil prices, concerns about security of energy supplies and tighter regulations on environmental standards the development of high quality synthetic transportation fuels continues to present a tantalising opportunity. BP and Accelergy have collaborated in a focussed research programme regarding the use of novel preparation methods and material compositions of Iron based Fischer Tropsch catalysts. The use of state of the art high throughput experimentation technologies have allowed the rapid optimisation of catalyst composition, catalyst preparation methods and screening of Fe-Mn FT catalysts containing K and Cu promoters under industrially relevant conditions. The application of technologies which allow the rapid preparation and screening of large libraries of materials have resulted in the discovery of some unique materials with unexpected catalytic properties in particular a reduced CO_2 selectivity.

P49
(77)

Higher Alcohols from Synthesis Gas: Nanostructured Ruthenium and Molybdenum Supported Catalysts

Manuel Franco, Mónica Bartolini, Lindora D'Ornelas, M. Josefina Pérez-Zurita, **Mireya Goldwasser**
Centro de Catálisis, Petróleo y Petroquímica, Escuela de Química, Fac. Ciencias, UCV, Caracas, Venezuela,
e-mail: *mireya.goldwasser@ciens.ucv.ve*

Mo promoted Ru nanostructured catalysts supported on γ-Al_2O_3 were synthesized by incipient wetness of $RuCl_3$ and $(Ru(acac)_3$ and by soft decomposition of (Ru(COD)(COT) complex for production of higher alcohols via FTS. Formation of nanostructured solids was evidence by TEM and XRD analyses, the last one showing formation of RuO_2 phase with a rutile type structure. Ru(COD)(COT and $Ru(acac)_3$, showed production mostly of C_2-C_5 hydrocarbons. Incorporation of Mo to RuCODCOT catalyst, increased selectivity towards alcohols, with methanol and ethanol as the main alcohols obtained, attributed to formation of Ru-Mo mixed species.

P50
(80)

Influence of metallic component modification of bifunctional catalysts on its activity in direct synthesis of dimethyl ether from syngas.

M. Śliwa, R. Grabowski, M. Ruggiero-Mikołajczyk, M. Zimowska
Institute of Catalysis and Surface Chemistry PAS, Cracow, Poland, *ncsliwa@cyf-kr.edu.pl*

The series of metalic components of bifunctional catalyst, based on Cu/Zn/Al and Cu/Zn/Zr oxides modified with Mn and Ga, have been synthesised. The commercial montomorllonite (K10) was used as acidic component. The bifunctional catalysts for the STD process (syngas to dimethyl ether) were obtained by physical mixture of metalic functions and montmorllonite. The influence of the composition and additives on the metalic function on its physical – chemical properties has been studied. The activity of bifunctional catalysts composed of different metalic components was investigated in the STD process in the temperature range 553 – 633K and 40 bar.

P51
(83)

Thermodynamic analysis and kinetic modeling of single-step DME synthesis

I. Sierra, D. Mier, J. Ereña, A.T. Aguayo, J.M. Arandes, J. Bilbao
Departamento de Ingeniería Química, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain; *irene.sierra@ehu.es*

A thermodynamic analysis has been carried for the single-step synthesis of dimethyl ether from (H_2+CO) and (H_2+CO_2) feeds. This process shifts the thermodynamic equilibrium (because methanol is transformed in situ), and, consequently, the yield of oxygenates is significantly higher than that corresponding to the synthesis of methanol. Moreover, an original kinetic model that considers the inhibiting effect of water in the kinetic steps and the formation of hydrocarbons is proposed. This model is essential for the design of the reactor and forestablishing an optimum reaction-regeneration strategy that will condition the viabilityof the process at industrial scale.

P52
(87)

Hydrothermally stable HZSM-5 zeolite based catalysts for transformation of crude bio-oil into hydrocarbons

B. Valle, A.G. Gayubo, A.T. Aguayo, M. Olazar, J. Bilbao
Chemical Engineering Dept., University of the Basque Country, P.O. Box 644, 48080 Bilbao, Spain. *beatriz.valle@ehu.es*

The catalysts prepared with HZSM-5 zeolite with high SiO_2/Al_2O_3 ratio (80) or with HZSM-5 zeolite (SiO_2/Al_2O_3 =30) modified by incorporation of 1 wt% of Ni are highly active for bio-oil valorisation by catalytic transformation into hydrocarbons carried out in a two-step process (thermal-catalytic) and co-feeding methanol, which are strategies that attenuate the pyrolytic lignin deposition and catalyst deactivation (by coke deposition). Both catalysts achieve high initial conversion (above 90 wt %) and have a high hydrothermal stability, maintaining its kinetic behaviour in ten reaction-regeneration cycles carried out under severe reaction conditions.

P53 (93)

Effect of the pressure on the CO_2/H_2 conversion and on the mechanisms of the CO_2/H_2 reaction on a co-precipitated $CuO/ZnO/Al_2O_3$ catalyst

Rachid Sahki[1], Said Tazkratt[1], Ouiza Chérifi[2] and Smain Hocine[1]
[1]Laboratoire de Chimie Appliquée et de Génie Chimique Université M. Mammeri de Tizi-Ouzou
BP .17 R.P 1500 Tizi-Ouzou Algeria
[2]Laboratoire de Chimie du Gaz Naturel, Institut de Chimie , BP32, El-Alia, 16111Bab-Ezzouar, Alger, Algeria

Our results show the great influence of the operating pressure on the kinetics of the CO_2/H_2 reaction on $CuO/Zno/Al_2O_3$ catalysts. Methanol is produced directly from CO_2 whatever the pressure whereas carbon monoxide stems either from decomposition of methanol at low pressure or from CO_2 directly at high pressure. The method of preparation has no influence on the reaction mechanisms, nor does the copper content of the studied solids.

P54 (99)

Effects of solvent impregnation on the activity of Co/SiO_2 catalysts prepared from cobalt acetate

Prasert Reubroycharoen[1], Noritatsu Tsubaki[2]
[1]Department of Chemical Technology, Faculty of Science, and Center for Petroleum, Petrochemicals and Advanced Materials
Chulalongkorn University, Bangkok 10330, Thailand
[2]Department of Applied Chemistry, School of Engineering, University of Toyama, Gofuku, Toyama 9308555, Japan,
e-mail: *prasert.r@chula.ac.th*

Cobalt/silica catalysts were prepared from cobalt acetate using different impregnating solvent such as water, alcohol, nitric acid, ammonium nitrate solution. The catalyst prepared from water, a common solvent, was difficult to be reduced leading to low reduction degree and activity. Using the solvents besides water for preparing catalysts improved the reducibility resulting in high activity of the catalysts. Among experiment, 2M NH_4NO_3 was the best one for preparing the highly active Fischer-Tropsch catalyst. This work was supported by the financial support from the Center for Petroleum, Petrochemicals and Advanced Materials.

P55 (584)

Fischer-Tropsch synthesis: optimization of the activation treatment with H_2 in a Fe/SBA-15 catalyst

S.J.A. Figueroa, S.J. Stewart, L.A. Cano, J.F. Bengoa, M.V. Cagnoli and S.G. Marchetti
ESRF. 6 Rue Jules Horowitz, BP 220, 38043 Grenoble, France, e-mail:Santiago.figueroa@esrf.fr

Bimetallic Co-Fe catalysts supported on γ-Al_2O_3 and promoted with Potassium and Ruthenium were prepared using co-impregnation method. It was found that bimetallic catalysts exhibit good catalytic performance for the conversion of biomass-derived syngas with a H_2/CO molar ratio ca. 1. Almost 90% of H_2 was consumed when a reactant mixture with similar composition to the biomass-derived syngas ($H_2:CO:CO_2$= 1:1:1) was employed. As compared to Co/Al_2O_3 catalyst, bimetallic catalysts can achieve the same level of methane selectivity and C_{5+} hydrocarbon selectivity operating a slightly higher temperature, but with a significantly higher conversion level.

P56
(109)

Support influence on Fischer-Tropsch synthesis with Ru-based catalysts

J. M. González-Carballo, R. Ladera, F. J. Pérez-Alonso, M. Ojeda, **S. Rojas**, J. L. G. Fierro
Instituto de Catálisis y Petroleoquímica (CSIC), C/Marie Curie 2, 28049 Madrid, Spain, *srojas@icp.csic.es*

Hydrocarbon production on a series of supported Ru-based catalysts has been studied. Ru-based catalysts (3 %wt.) were prepared by incipient wetness impregnation on two types of TiO_2 (with different rutile/anatase ratios) and $SiO_2 \cdot Al_2O_3$ from $RuCl_3 \cdot nH_2O$ and $Ru(NO)(NO_3)_3$. A correlation between characterization data (XPS, DRIFT, TPR, STEM) and the catalytic performance in a fixed bed type reactor reveals that CO conversion and hydrocarbon production is directly related to the dispersion of the Ru onto the supports. The best catalyst, in terms of CO conversion, was obtained when a TiO_2 containing both the rutile and anatase phases was used as support.

P57
(115)

The synthesis of DME at low temperature

Chaiyan Chaiya[1] and Prasert Reubroycharoen[2,3]
[1]Division of Chemical Engineering, Faculty of Engineering, Rajamangala University of Technology Krungthep,
Bangkok 10120, Thailand.
[2]Department of Chemical Technology, Faculty of Science, Chulalongkorn University, Bangkok 10330, Thailand
[3]Center for Petroleum, Petrochemicals and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand,
e-mail: *chaiyan.c@rmutk.ac.th*

Dimethyl ether was synthesized at low temperature by using alcohol as a catalytic solvent to change the reaction pathway. The results showed the selectivity of DME was high, indicating that the acidity of HZSM-5 was strong enough to efficiently convert methanol to DME at 443 K. In STD process, the reaction route of methanol synthesis was the same as a conventional process in which hydrogenation could not proceed at low temperature. However, an activity of STD process was slightly observed, described by the synergistic effect which one of the products from each reaction is a reactant for the next reaction, leading to some activity of STD process. It can be concluded that methanol synthesis is the key to DME synthesis at low temperature.

P58
(122)

New approach to the template synthesis of fischer-tropsch catalysts

Anton S. Ivanov, Nikolay B. Cherkasov, Nataliya N. Martynova, Evgeniya V.Suslova, Sergey V. Savilov, Valery V. Lunin
Chemistry Department of Lomonosov Moscow State University, Moscow, Russia
Suslova_genya@mail.ru and *savilov@chem.msu.ru*

The new approach to the synthesis of Fischer-Tropshc (FT) catalysts was discussed. One step template synthesis of FT catalysts is suggested when carbon nanotubes were prepared *in situ* with high content of metallic iron particles. In this way the morphology and particle size can be control.

P59
(142)

Selective Adsorption of Manganese onto Cobalt for Optimized Mn/Co/TiO$_2$ Fischer-Tropsch Catalysts

T. E. Feltes[1], L. Espinosa-Alonso[2], E. de Smit[2], Y. Zhao[3], L. D'Souza[1], R. F. Klie[3],
R. J. Meyer[1], B. M. Weckhuysen[2], **J. R. Regalbuto**[1]
[1]Department of Chemical Engineering, University of Illinois at Chicago, Chicago, IL 60607, USA. *jrr@uic.edu*
[2]Inorganic Chemistry and Catalysis, Utrecht University, 3508-TB Utrecht, The Netherlands
[3]Department of Physics, University of Illinois at Chicago, Chicago, IL 60607, USA

The rational design of a Mn promoted Co/TiO$_2$ catalyst for Fischer-Tropsch (FT) synthesis was investigated using the Strong Electrostatic Adsorption (SEA) method for the deposition of [MnO$_4$]- selectively onto supported Co$_3$O$_4$. Characterization results of the prepared catalysts displayed preferential association of the Mn species with Co$_3$O$_4$ and not the TiO$_2$ support. The SEA method proved to minimize the migration of Mn away from the Co surface to the TiO$_2$ support during the reduction procedure, ensuring a more intimate interaction between the Mn and Co species during FT reactivity measurements, leading to increased C$_{5+}$ selectivity and chain growth probability.

P60
(585)

Fischer-Tropsch synthesis for BTL process over precipitated iron-support complex catalysts

K. Asami, S. Ishii, A. Ketcong, A. Iwasa, N. Igarashi, K. Yamamoto, and K. Fujimoto
Faculty of Environmental Engineering, The University of Kitakyushu
Hibikino 1-1, Wakamatsu-ku, Kitakyushu 808-0135, Japan. *asami@env.kitakyu-u.ac.jp*

Several complex catalysts composed of co-precipitated Fe-Cu and support materials were prepared and their catalytic performance for FTS was investigated. Complex catalyst composed of co-precipitated Fe-Cu and SiO$_2$ or MgO gave very low activity, whereas complex catalysts containing carbon such as graphite and carbon fiber showed high activities for FT synthesis. CO conversion increased with an increase in the specific surface area of carbon. CH$_4$ selctivity was quite low (< 5%) in every case. Potassium addition promoted the activity of all the catalysts ; CO conversion increased to 70-80% at 260°C and 2.0 MPa.

P61
(158)

Comprehensive study of cobalt catalyst selectivity under Fischer-Tropsch conditions

MC. Marion, R. Chenevier, F. Diehl, L. Fischer, F. Hugues
IFP Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France. *m-claire.marion@ifp.fr*

Cobalt catalyst selectivity was investigated under various Fischer-Tropsch (FT) conditions. Impact of pressure, H$_2$/CO ratio, H$_2$O/H$_2$ conditions etc on FT and water gas shift reactions was carefully followed. The catalyst selectivity appears directly connected with the reactants and products concentration (adsorbed species) at the surface of the cobalt active sites. A high CO partial pressure is favourable to polymerisation process (long chain hydrocarbons formation) whereas a low CO partial pressure can increase H$_2$ and H$_2$O accessibility to active sites and favour termination process, methanation and/or water gas shift reaction.

P62
(159)

Kinetics studies of nano-structured iron catalyst in Fischer - Tropsch synthesis

Ali Nakhaei Pour[a,b], Mohammad Reza Housaindokht[a], Sayyed Faramarz Tayyari[a]
[a]Department of Chemistry, Ferdowsi university of Mashhad, P.O.Box: 91775-1436, Mashhad, Iran
[b]Gas Research Division, Research Institute of Petroleum Industry , P.O.Box: 18745- 4163, Tehran, Iran, *nakhaeipoura@ripi.ir*

A nano-structured iron catalyst for syngas conversion to hydrocarbons in Fischer-Tropsch synthesis (FTS) prepared by micro-emulsion method. Kinetic parameters of nano-structured iron catalyst in Fischer-Tropsch synthesis catalysts is studied in a wide range of synthesis gas conversions and compared with conventional catalyst ones. The results indicated that in Fischer–Tropsch rate expression, the rate constant (k) increased and the adsorption parameter (b) decreased when the catalyst particle size decreased from conventional to nano-structured.

P63
(160)

Selective dehydration of methanol to dimethyl ether catalysed by Brønsted acidic ionic liquids

Martin P. Atkins, Kenneth R. Seddon, **Małgorzata Swadźba-Kwaśny** and Laurent Vanoye
QUILL, The Queen's University of Belfast, Belfast, BT9 5AG, United Kingdom, e-mail: *quill@qub.ac.uk*

Dehydration of methanol to dimethyl ether (DME) was carried out using Brønsted acidic ionic liquids as catalysts. The reaction was carried out at 180 to 220°C, lower than extant industrial processes (250 to 500°C), with very high selectivities and conversions. Homogenous catalysis in the liquid state represents a novel, and improved, approach to DME synthesis.

P64
(161)

Support effects on the catalytic activity and products selectivity of cobalt Fischer–Tropsch catalysts

Behnam Hatami, **Ali Nakhaei Pou**r and Sanaz Anahid
Gas Research Division, Research Institute of Petroleum Industry , P.O.Box: 18745- 4163, Tehran, Iran, *nakhaeipoura@ripi.ir*

Co supported on γ-Al_2O_3, SiO_2, CNT and MCM-40 were prepared by incipient wetness impregnation. The influence of the different supports on the size of cobalt particles and dispersion, catalyst reducibility and water–gas shift (WGS) activity and FTS activity and products selectivity was studied by different techniques, including X-ray diffraction, H_2 chemisorption, N_2 adsorption measurements, temperature-programmed reduction, and O_2 titration.

P65 (173)

Production of Ultra-Clean Fuels (Diesel, Gasoline) from Methanol over Gold-Based Catalysts

A. Mpela[1], M. Bhamjee[1], H. Chiba[1], **M. S. Scurrell**[2]
[1]School of Chemical & Metallurgical Engineering, University of the Witwatersrand,Johannesburg, South Africa
[2]Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa
Michael.scurrell@wits.ac.za

It has been found that the catalytic behaviour of zeolites of the H-ZSM-5 type in the conversion of methanol to liquid hydrocarbons can be significantly altered in the presence of gold-zinc oxide. Higher selectivity to diesel range product and higher activity are associated with the presence of gold.

P66 (177)

Development of Kinetics Model for Fischer-Tropsch Synthesis Reaction over Ru/Co/Zr-P/SiO_2 Catalyst

Seung-Ho Kwack[1], **Myung-June Park**[1], Jong Wook Bae[2], Kyoung-Su Ha[2], Seung-Moon Kim[2], Ki-Won Jun[2]
[1]Department of Chemical Engineering, Ajou University, Suwon 443-749, Korea. *mjpark@ajou.ac.kr*
[2]Korea Research Institute of Chemical Technology (KRICT), Daejeon 305-600, Korea

Kinetic mechanism for FTS reaction over cobalt-based catalyst (Ru/Co/Zr-P/SiO_2) has been newly suggested under the assumption of polymerization mechanism for hydrocarbon products. Simulation results with the estimated kinetic parameters are in good agreement with the experimental data under a variety of reaction conditions. The developed kinetic model also predicts the effect of operating conditions such as temperature, pressure, SV and H_2/CO molar ratio on CO conversion and the entire product distribution with a reasonable precision.

P67 (178)

Optimization of a Fixed-bed Reactor for Fe-based Fischer-Tropsch Synthesis

Du-Yeong Hwnag[1], Yun Ha Kim[2], Eun Duck Park[2], Ho-Jung Chae[3], Sang-Bong Lee[3], **Myung-June Park**[1]
[1]Department of Chemical Engineering, Ajou University, Suwon 443-749, Korea. *mjpark@ajou.ac.kr*
[2]Division of Energy Systems Research, Ajou University, Suwon 443-749, Korea
[3]Korea Research Institute of Chemical Technology (KRICT), Daejeon 305-600, Korea

A mathematic model was developed to predict the dynamic behaviour of a bench-scale fixed-bed reactor for Fe-based Fischer-Tropsch synthesis. Simulation results are in good agreement with experimental data, and the model was applied for the determination of optimal operating strategy for both high yield and safe operation, with both inert fraction and wall temperature specified as manipulated variables. The result clearly shows that the maximum production rate is achieved with the peak temperature in the reactor maintained within the safe operating range.

P68
(190)

Reduction properties of Re promoted Co/Al_2O_3 catalysts for Fischer-Tropsch synthesis

Pan, Z., Farhat, K., Boskovic, G., **Bukur, D. B.**
Department of Chemical Engineering, Texas A&M at Qatar, Doha, *dragomir.bukur@qatar.tamu.edu*

The reducibility of Co/Al_2O_3 F-T catalyst was studied as a function of Re promoter loading and the type of solvent used during catalyst preparation. TPR/DTG data revealed that nitrate precursor decomposes easier with Re addition, due to its better distribution, associated with Re acting as textural promoter. Hydrogen spillover assisted reduction in the presence of Re is limited to the Co^{2+}-oxide. Differences in reducibility between catalysts prepared by aqueous IWI and acetone IWI become smaller upon Re addition. The observed ratio Co/O << 1 points out to the presence of a non-stoichiometric solid solution formed during calcination (Co^{2+} diffusion through Al_2O_3 support).

P69
(191)

Iron Fischer-Tropsch Catalysts – Recent Advances in Structure and Properties

J L Casci & G J Kelly
Johnson Matthey Technology Centre, Belasis Avenue, Billingham, UK. *Gordon.kelly@matthey.com*

Iron-based FT catalysts are complex assemblies and this presentation will describe the structure of a typical commercial catalyst across the length scales from the macroscopic catalyst particle to the location of promoters and additives. To provide this information a range of techniques are employed including x-ray microtomography to electron microscopy.

P70
(220)

In situ and *operando* structural characterization of Fischer-Tropsch supported cobalt catalysts

A. Rochet[1,2], V. Briois[2], V. Moizan[1], F. Villain[2], C. La Fontaine[2], C. Pichon1, F. Diehl[1]
[1]IFP Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France, *amelie.rochet@ifp.fr*
[2]Synchrotron SOLEIL, L'Orme des Merisiers, Saint-Aubin, BP 48, 91192 Gif-sur-Yvette Cedex, France

In order to improve cycle length and catalytic properties of cobalt-based catalysts a better comprehension of the behaviour of supported nano-sized metallic cobalt in Fischer-Tropsch synthesis is meaningful. Thanks *in situ* XRD studies and new equipments implemented on SAMBA beamline at SOLEIL (Quick-EXAFS monochromator, *in situ* cell…), we are able to solve local structure of FT catalysts under working conditions. Taking advantage of the good time resolution available with QEXAFS, one can fully characterize structural changes during the entire reaction (activation, deactivation…) and improve our knowledge of catalytic property-structure relationship.

P172
(243)

Influence of pretreatment methods on Co/SiO_2 catalyst for Fischer-Tropsch synthesis

Shifang Mu[a,b], Debao Li[a], Bo Hou[a], Litao Jia[a] , Jiangang Chen[a], **Yuhan Sun**[a]
[a]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, The Chinese Academy of Sciences Taiyuan 030001, PR China
[b]Graduate University of Chinese Academy of Sciences, Beijing 100039, PR China,
e-mail: *yhsun@sxicc.ac.cn* (Y.H. Sun)

The effects of three pretreatment methods on the microstructure of Co/SiO_2 catalysts and the activity for Fischer-Tropsch synthesis (FTS) were investigated. The pretreated catalysts were characterized by TEM, HRTEM, XRD, XPS, H_2-TPD, TG and TPR. The results showed that, after the pretreatments, the specific morphological of the Co species changed to form new Co active surface species, Co particles redispersed and Co species were facile to be re-reduced. The Co/SiO_2 catalysts pretreated by different method showed different catalytic performance. The catalyst treated by the reduction-passivation had higher activity and C_5^+ selectivity for FTS.

P173
(246)

The effect of Ru and Re modification of Co/Al_2O_3 catalyst on its reducibility and performance in Fischer-Tropsch synthesis

V. Rubáš, K. Jíša, P. Šimáček, J.Chudoba, **D. Kubička**
Institute of Inorganic Chemistry, Department of Refining and Petrochemical Research, Záluží 1, 43670 Litvínov, Czech Republic.
david.kubicka@vuanch.cz

The effect of Ru and Re modification of Co/Al_2O_3 has been investigated. The modification resulted in both cases to decrease of the reduction temperature of Co oxides supported on alumina to metallic Co species.The effect of Ru was more pronounced than that of Re. Consequently, the distribution of Fischer-Tropsch-synthesis (FTS) products was affected as well. Ru-modified catalyst yielded FTS waxes with higher molecular weight than Re-modified catalyst, which can be attributed to higher chain-growth probability over the Ru-modified Co/Al_2O_3 catalyst.

P174
(247)

Synthesis of Dimethyl Ether from Syngas in a Fixed Bed Reactor - Simulation and Experimental Study

Fatemeh Hayer[1], Hamidreza Bakhtiary D.[1], Rune Myrstad[2], Peter Pfeifer[3], Anders Holmen[1], **Hilde J. Venvik**[1].
[1]Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim, Norway. *hilde.venvik@chemeng.ntnu.no*
[2]SINTEF Materials and Chemistry, N-7465 Trondheim, Norway
[3]Karlsruhe Institute of Technology, Institute for Micro Process Engineering, D-76344 Eggenstein-Leopoldshafen, Germany

The synthesis of dimethyl ether (DME) from syngas in a laboratory fixed bed reactor has been studied using two different catalyst mixtures, CuO-ZnO- Al_2O_3/γ-Al_2O_3 and CuO-ZnO- Al_2O_3/HZSM-5. The effect of parameters such as H_2/CO feed gas ratio, Gas Hourly Space Velocity (GHSV), reaction temperature and pressure are investigated. A 2D pseudo-homogeneous dispersion model is found to represent the reactor performance reasonably well compared to experimental data. The HZSM-5 based catalyst performs better as the catalytic capacity of γ-Al_2O_3 appears to be limited by adsorption of H_2O on the lewis acid sites.

P175
(260)

The catalytic performance of Fe-ZSM5 catalyst in Fischer-Tropsch synthesis : study of reaction conditions

Yahya Zamani, S.H Yousefian ,A.Nakhaeipour, B.Moshtari, S.A.Taheri, E.Ganji Babakhani
Research Institute of Petroleum Industry(RIPI), National Iranian Oil Company; West Blvd., Near Azadi Sports Complex P.O.BOX 14665-137,Tehran,Iran. *zamaniy@ripi.ir*

Converting of a mixture of hydrogen and carbon monoxide from natural gas or coal into hydrocarbons has been known as Fischer–Tropsch synthesis. Iron catalyst prepared by co-precipitation method then physically mixed with HZSM5 zeolite. We investigated effect of operation conditions on catalyst activity and product selectivity. Experimental design was performed for three different parameters: temperature (T), pressure(P) and H_2 to CO ratio. The catalyst performance was tested in a fixed bed reactor. Increasing T, P and H_2 to CO ratio resulted in increasing feed conversion, catalyst activity and rate of catalyst deactivation. The effect of T is more than two other parameters.

P176
(267)

Preparation of nano iron catalyst for Fischer-Tropsch synthesis

Y.Zamani[1], M.Rahimizadeh[2], A.Mohajeri1,H.Eshghi[2]
[1]Research Institute of Petroleum Industry(RIPI), National Iranian Oil Company; West Blvd., Near Azadi Sports Complex P.O.BOX 14665-137,Tehran,Iran. *zamaniy@ripi.ir*
[2]Department of Chemistry Ferdowsi University of Mashhad, Azadi Square, Mashhad, 91735-48974, Iran

Nano-structured Fe_2O_3, CuO and La_2O_3 components were prepared by micro-emulsion method and then Fe/Cu/La nano-structure catalyst prepared by mixing . Structural characterization of nano-structured Fe_2O_3, CuO and La_2O_3 components was performed by X-ray diffraction. Using Transmission Electron Microscopy (TEM) images determined particles size of components. Catalytic activity and product selectivity were determined in a fixed-bed stainless steel reactor. Using results of gas chromatograph were calculated feed conversion, CO_2 ,CH_4,C_2-C_4, C_5^+ , H_2O and oxygenate compounds selectivities.

P177
(277)

Alumina supported Co-Ru nanoparticles for Fischer-Tropsch synthesis : Ru effect on the reducibility of Co

Yun-Jo Lee, Jo-Yong Park, Pawan K. Khanna, **Ki-Won Jun**, and Jong Wook Bae
Petroleum Displacement Technology Research Center, Korea Research Institute of Chemical Technology (KRICT), P.O. BOX 107, Yuseong, Daejeon, 305-600, Korea, e-mail: *kwjun@krict.re.kr* (K.-W. Jun)

Co-Ru oxide nanoparticles with different Ru contents in similar sizes were synthesized by solvothermal method and supported on γ-Al_2O_3 to prepare Co-Ru_x alloyed Fischer-Tropsch catalysts. The catalysts were characterized by XRD, TEM, H_2-TPR, H_2- and O_2- chemisorption. The particle size of reduced Co-Ru_x metal decreased after reduction treatment and the reducibility of the oxide increased with the increase of Ru content. CO conversion in Fisher-Tropsch reaction showed volcanic curve with Ru content. and maximized at low amount of Ru such as Co/Ru=100, showing very effective promotion of Co by Ru and intimate contact of between Co and Ru.

P178
(279)

Efficient scale-up methodologies using multi-channel fixed-bed reactor for Fischer-Tropsch catalyst

Jong Wook Bae, **Kyoung-Su Ha**, Seung-Moon Kim, Sun-Ju Park, Yun-Jo Lee and Ki-Won Jun
Petroleum Displacement Technology Center, Korea Research Institute of Chemical Technology (KRICT), P.O. BOX 107, Yuseong, Daejeon, 305-600, Korea, *filoseus@krict.re.kr*

The efficient scale-up method of the exothermic Fischer-Tropsch Synthesis (FTS) catalyst using multi-channel fixed-bed reactor (MCFBR; 5 rectangular channels with 5 mm in width) is one of the promising methodologies to control the heat generated in catalyst-bed during FTS reaction. The catalytic performance in tubular fixed-bed reactor (TFBR) and MCFBR is not much altered due to the efficient removal of hot-spot in catalyst-bed with the aid of micro-channel heat-exchanger. The further studies to fine out appropriate catalytic system and mathematical simulation of temperature profiles in MCFBR are underway.

P179
(283)

Effect of preparation conditions on catalytic properties of Alumina supported Co catalysts utilized in Fischer-Tropsch Synthesis

M. R. Hemmati M[1,2], M. Kazemeini[2], J. Zarkesh[1], F. Khorashe[2]
[1]Research Institute of Petroleum Industry (RIPI), NIOC, Tehran, Iran, *hemmatimmr@ripi.ir*
[2]Sharif University of Technology, Department of Chemical and Petroleum Engineering, Tehran, Iran

Deposited Cobalt particles on different supports led to catalysts utilized to convert the Syngas into hydrocarbons which is known as the Fischer-Tropsch synthesis. A major difference between such catalysts will be due to their different preparation conditions. Gamma-Alumina, in particular, is one of the most popular supports utilized for this purpose. In the present research, effects of different preparation conditions including ; the number of calcinations after each or final impregnation and concentration of Lanthanum in alumina on the main catalytic properties of interest namely, the pore volume, specific surface area, Co cluster size and TPR behavior are investigated.

P180
(284)

Effect of reduction conditions on the activity of supported iron-based Fischer-Tropsch catalysts

Hak-Joo Kim, Jong-Gun Kim, Young-Gul Hur, Soon-Taek Hyun, Dong-Hyun Chun, Jung-Hoon Yang, Jung-Il Yang, Ho-Tae Lee, Heon Jung
Korea Institute of Energy Research, 71-2 Jang-dong Yuseong-gu, Daejeon, Republic of Korea, *hakjukim@kier.re.kr*

Fischer-Tropsch synthesis (FTS) was carried out using supported iron-based catalysts prepared by incipient wetness method activated at different conditions. The reaction was performed in a continuously stirred tank reactor (CSTR) with volume of 500ml equipped with internal filtering system for proper separation of the catalyst and the waxy products. Temperature programmed reduction (TPR) analysis showed that supported iron-based catalysts needed to be activated at much more severe conditions than the conventional co-precipitated catalysts. Catalytic activity of various supported iron-based catalysts were reported relevant to different pre-treatment conditions.

P181 (292)

Rationalizing the impact of thermal activation protocols on the nature and intrinsic activity of Co^0 in Co/SiO_2 Fischer-Tropsch catalysts.

G.Prieto, **A. Martínez**, P. Concepción, R. Murciano
Instituto de Tecnología Química, Avd. Los Naranjos s/n, 46022, Valencia, Spain. *amart@itq.upv.es*

The thermal activation protocol during preparation of Co/SiO_2 FT catalysts, i.e. temperature of calcination (Tc) and calcination followed by reduction versus direct reduction, has an impact on the degree of bulk cation disorder (LRS) and surface composition (XPS) of Co_3O_4 NPs, as well as on the reduction behaviour (H_2-TPR and H_2-XRD) and final metal dispersion, but hardly affects the Co^0 crystalline microstructure (XRD) after homogeneous H_2-reduction. The thermal history produces marked changes in the surface Co^0 site topology (CO-FTIR) as well, leading to variations of up to 300% inTOF and up to 460% in Co-time yield during FTS under real conditions.

P182 (299)

Simulation of c-number distribution in the Fischer-Tropsch synthesis based on the dynamic kinetics

Y. Suehiro, M. Murayama, J. To, K. Fujimoto
Oil & Gas Technology Research & Development, Japan
Oil, Gas and Metals National Corp.,1-2-2 Hamada,Mihama-ku, Chiba, 261-0025, Japan. *suehiro-yoshifumi@jogmec.go.jp*

It is well known that the FTS products contains fairly large amount of olefins (mainly 1-olefin), its contents decreases with increasing carbon number(c-number) of the products and usually the C_{20}+ products contains little olefins. On the basis of experimental results, a new reaction network including the reactive 1-olefin was presented. In this paper, we show a reaction model and analyze it by a simulation method to elucidate the rate parameters which control the carbon number distributions, and also the effect of added olefins.

P183 (305)

Role of promoters and carriers on the catalytic functionality of Cu-based catalysts in the CO_2-to-methanol hydrogenation reaction

G. Bonura, F. Arena, C. Cannilla, O. Di Blasi, G. Mezzatesta, L. Spadaro, F. Frusteri
CNR-ITAE “Nicola Giordano”, Salita S. Lucia 5, I-98126 (Messina), Italy. *giuseppe.bonura@itae.cnr.it*

The aim of this paper is to disclose the nature of active sites and working mechanism of Cu catalysts in the CO_2-to-CH_3OH hydrogenation reaction, through a systematic study of the effects of promoters and carriers (i.e., Zn, Ga, Mo, Ce, Zr) and activation treatment (“pure” or “diluted” H_2 stream) on the physico-chemical and catalytic properties of the active phase. Irrespective of composition and metal dispersion, a dual-site reaction path allows explaining the superior functionality of ZnCuCeZr systems in terms of optimum density of H_2 and CO_2 activation sites at the metal/oxide(s) surface.

P184
(328)

Effect of hydrothermal treatment of SBA-15 with different reagents on properties of Co/SBA-15 catalysts for Fischer-Tropsch synthesis

Hongmin Duan, Qingjie Ge, **Hengyong Xu**
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, 457 Zhongshan Road, Dalian, 116023, Liaoning, China.
hyxu@dicp.ac.cn

SBA-15 supports were hydrothermally treated with different reagents such as distilled water, acetic acid, ammonia and ammonium acetate. Co/SBA-15 catalysts were characterized by N_2-physisorption, XRD, H_2-TPR and H_2-TPD. The treatment of SBA-15 with ammonium acetate significantly improves Fischer-Tropsch activity of the Co/SBA-15 catalyst. The reason is most probably that large amount of spillover hydrogen resulted from hydroxyl groups on SBA-15 create the active sites where olefins can be re-adsorbed and further hydrogenate to produce corresponding paraffins.

P185
(336)

Effect of Formulation on Preparation of Fe-based Extrudate as F-T catalysts for BTL Process

Ho-Jeong Chae, Jeong-Hwan Seo, Tae-Wan Kim, Kwang-Eun Jeong, Chul-Ung Kim and **Soon-Yong Jeong**
Green Chemistry Research Division, Korean Research Institute of Chemical Technology (KRICT), Daejeon 305-600, Korea,
syjeong@krict.re.kr

BTL (Biomass to Liquids) synthetic fuel has attracted a great deal of interest as a next generation clean fuel. The backbone technology of BTL process is F-T (Fischer-Tropsch) catalytic reaction. F-T catalyst should be formed by extrusion to be applied to a tubular packed-bed reactor. Therefore, in this study, the extrusions of Fe-based F-T catalysts were carried out by using a variety of binders, plasticizers and additives. The physicochemical properties and catalytic performance of the catalysts were also examined. F-T catalyst is very sensitive to the type and amount of binder, especially inorganic binder, due to the bulk structure of F-T catalyst.

P186
(338)

Effect of Cu-Zr mixed oxide structure on kinetics of copper reduction and catalytic properties in carbon oxides hydrogenation reactions

A.A. Khassin, G. Bonura, T.P. Minyukova, N.V. Shtertser, G.A. Filonenko, F. Frusteri
Boreskov Institute of Catalysis, 5, pr. Lavrentieva, Novosibirsk 630090 Russia. *aakhassin@catalysis.ru*

Cu-Zr-containing mixed oxides of different structure can be prepared depending on cationic composition and method of preparation. The Cu-Zr mixed oxide structure affects a lot the kinetics of copper cations reduction and structural parameters of the reduced Cu/oxide state. The structure of Cu-Zr-containing catalysts also has a crucial influence on the catalytic activity in reactions of CO and CO_2 hydrogenation to methane and to methanol as well as WGSR. The role of surface sites on the occurrence of these processes is disclosed.

P187 (340)

Fischer-Tropsch synthesis on Ru/Co/ZrO_2-Al_2O_3: effect of Zr content

Jong Wook Bae, Seung-Moon Kim, Yun-Jo Lee, Kyoung-Su Ha and **Ki-Won Jun**
Petroleum Displacement Technology Center, Korea Research Institute of Chemical Technology (KRICT), P.O. BOX 107, Yuseong, Daejeon, 305-600, Korea. *kwjun@krict.re.kr*

The effect of ZrO_2 content on ZrO_2-Al_2O_3 mixed oxides on the structure of Fischer-Tropsch catalyst was discussed with its relation to the dispersion of cobalt particles and reducibility to activity and product distribution. The optimum concentration of ZrO_2 in ZrO_2-Al_2O_3 is found to be around 5wt.% to obtain a small particle size and appropriate degree of reduction. The observed high C_5+ selectivity on CoZA(ZrO_2/Al_2O_3=0.05) catalyst could be attributed to the well-developed crystalline phase of cobalt species with small particle size with the help of an appropriate incorporation of ZrO_2 on Al_2O_3 support.

P188 (346)

A facile solvothermal route to synthesize monodispersible Co_3O_4/MCM-41 nanocomposites using polyvinylpyrrolidone as capping reagent and the performances in Fischer-Tropsch synthesis

Rongyong Xie[1, 2], Bo Hou[1], Debao Li[1], Jiangang Chen[1], **Yuhan Sun**[1]
[1]State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, P.O. Box 165, Taiyuan, Shanxi 030001, PR China. *yhsun@sxicc.ac.cn.dbli@sxicc.ac.cn*
[2]Graduate University of Chinese Academy of Sciences, Beijing 100039, China

Monodispersible Co_3O_4/MCM-41 nanocomposites was synthesized via hydrothermal route using polyvinylpyrrolidone (PVP) as capping reagent. Nanocomposites characterization showed that Co_3O_4 nanoparticles were completely coated by mesoporous silica. The performances of Co/MCM-41 catalyst in Fischer-Tropsch synthesis showed that selectivity towards C_{5-18} fraction was high, and selectivity towards CH_4 and C_{19}^+ fraction were both lower compared with the performances of Co/MCM-41 catalyst. The Co/MCM-41 catalyst which was prepared by incipient wetness impregnation method was less selective towards C_{5-18} fraction, while selectivity towards CH_4 and C_{19}^+ fraction were both high. This results indicated that narrow pore structure of mesoporous silica shell could produce a chain growth hindrance benefiting from the confined reaction conditions and tailor the product distribution towards the C_{5-18} fraction.

P189 (587)

A simple and realistic model for investigating FTS catalyst activity at lab-scale and extrapolating to industrial conditions

A.Sharma, R. Philippe, B. Tymowski, C. Pham-Huu, F. Luck and D. Schweich
Laboratoire de Génie des Procèdes Catalytiques (LGPC)UMR 2214 CNRS/CPE Lyon, France, e.mail: *ash@lobivia.cpe.fr*

This work proposes a ready-to-use tool in form of a comprehensive fixed-bed reactor model (2-D pseudo-homogeneous gas-solid steady state) to extrapolate a restricted set of laboratory experiments obtained with different catalysts to realistic industrial conditions. The model gives the possibility to qualitatively determine the performance of a FT reactor and also to compare the trends obtained by using different morphology of the catalyst. Thus a feedback to catalyst formulation can be obtained for industrial reactor conditions.

P190
(365)

Deactivation of a cobalt based Fischer-Tropsch synthesis catalyst- Nature of the carbon species present on the spent catalyst.

Ph. Bichon, **L. Pinard**, J. L. Lemberton, C. Canaff, J.D. Comparot, F. Maugé, Ph. Bazin,
A. Popov, E. Falabella S. Aguiar and P. Magnoux.
Laboratoire de Catalyse en Chimie Organique, UMR 6503, Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers (France). *ludovic.pinard@univ-poitiers.fr*

During the Fischer Tropsch reaction, cobalt catalysts deactivate with the time on stream.This deactivation is usually explained by a modification of the metallic function, and/or by carbon deposition. Carbon deposits may block the catalyst pores which creates diffusional limitations, poison the metal surface by binding irreversibly or even encapsulale metal particles. In this study, we show the carbon species present on the spent catalyst were mainly carboxylic acids and n- alcohols (1). Their evolution with time on stream will be presented and will allow to understand their role on the catalyst deactivation.

P191
(367)

Photoreduction of carbon dioxide using TiO_2 photocatalyst in basic solution

B. Michalkiewicz, I. Łukasiewicz, A. W. Morawski
Institute of Chemical and Environment Engineering, West Pomeranian University of Technology, ul. Pulaskiego 10,
70-322 Szczecin, Poland. *beata.michalkiewicz@zut.edu.pl*

TiO_2 was used as a photocatalyst for carbon dioxide reaction with water. NaOH or NH_4OH were used to increase carbon dioxide dissolving in water. The only carbon product detected was methanol. The formation of methanol was found much more effective when the ammonium solution was used. Although NaOH is generally used for the basic solution generation when TiO_2 or Cu/TiO_2 are used as photocatalyst it is not favorable. Na^+ ions bind the electrons photogenerated in TiO_2 under UV irradiation. The use of the ammonia solution is advantageous. NH_4^+ ions do not bind the electrons.

P192
(376)

High performance of Fischer-Tropsch synthesis over modified Cobalt-based catalyst

Chun Chen,Hisashi Yuuda, **Xiaohong Li**
Department of Chemical Processed and Environments, Faculty of Environmental Engineering,
The University of Kitakyushu, Kitakyushu, Fukuoka 808-0135, Japan

Sol-gel eggshell structured Co/SiO_2 catalysts for FT synthesis were prepared by a spray method using silica gel as the support and Co-based sol-gel as the precursors. EPMA result demonstrated that Co particles just dispersed on the surface of SiO_2 support. The catalytic test result of FT synthesis in the slurry reactor show that sol-gel eggshell Co/SiO_2 catalysts exhibit evidently higher CO conversion, lower methane selectivity and higher hydrocarbon generating velocity than conventional impregnation and eggshell Co/SiO_2 catalysts.

P193
(384)

The catalytic performance of Cu-Fe based catalysts for higher alcohols synthesis via syngas

Hongfeng Ran[1, 2], Kegong Fang[1], Minggui Lin[1], Dong Jiang[1], Ning Wang1[, 2], **Yuhan Sun**[1],
State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, shanxi 030001, P. R. China Tel.: +86 351 4121877, e-mail: *yhsun@sxicc.ac.cn*

A series of Cu-Fe based catalysts for higher alcohols synthesis were prepared by coprecipitated and sequential precipitation methods. The texture and structure properties were characterized by BET, XRD, SEM, XPS and H_2-TPR. XPS investigation revealed that copper was presented as Cu^{2+} state. H_2-TPR showed that iron promoted CuO dispersion and thus decreased CuO reduction temperature. As HAS catalysts, co-precipitated catalysts show high alcohol activity for mixed alcohols synthesis, which displayed alcohol space-time-yield of 0.21g/g-cat.h and the $C_{2+}OH$ selectivity towards total alcohol of 64.42%.

P281
(401)

Structural Effects of Support in Fischer-Tropsch Synthesis over Cobalt Based Catalysts

Jung Shik Kang[1,2], Moon Ju Park[1],Sojung Kim[1], **Hyun-Mee Park**[1], Suk-In Hong[2] and **Dong Ju Moon**[1]
[1]Clean Energy Research Center, Korea Institute of Science and Technology, Seoul, Korea.
djmoon@kist.re.kr and *phm4556@kist.re.kr*
[2]Department of Chemical & Biological Engineering, Korea University, Seoul, Korea

The mesoporous materials have been used as a supports for many catalytic reaction. Because of the wide and unique shapes of pores, the mesoporous materials have an advantage to mass transfer of the products and to selective growth of carbon chain in Fischer-Tropsch synthesis (FTS). In this study, mesoporous materials such as SBA-15 and silica hollow sphere (SHS) were prepared and active metals were added by incipient wetness method. The prepared catalysts were characterized using XRD, HR-TEM, SEM, N_2-physisorption and TPR techniques.

P282
(417)

One step synthesis of di-methyl ether with microreactors

S. Tauro, P. Pfeifer, A. Wenka, R. Dittmeyer
Karlsruhe Institute of Technology, Institute for Micro Process Engineering (IMVT), 76344 Karlsruhe, Germany
silvia.tauro@imvt.fzk.de

Dimethylether (DME) is an important chemical material and a clean alternative fuel. Higher CO reaction rates can be achieved over hybrid catalysts in the one-step process for DME synthesis, even operating at lower pressures and higher temperatures than a two step conventional method.

Within our contribution we will report on the application of a novel laboratory microreactor for catalytic wall coating and micro fixed bed approaches, the synthesis of hybrid catalysts as coatings and first catalyst screenings. The activity results of our home made catalysts will be compared with reactor simulation.

P283
(425)

Selectivity control through fundamental mechanistic insight in the conversion of methanol to hydrocarbons over zeolites

S. Svelle, S. Teketel, M. Bjørgen, P. Beato, C. Hviid Christensen, K.P. Lillerud, Unni Olsbye
SMN Center for Materials Science and Nanotechnology/inGAP Center for Research Based Innovation, Department of Chemistry,
University of Oslo, P.O.Box 1033 Blindern, N-0315 Oslo, Norway, *stian.svelle@kjemi.uio.no*

In this report we have demonstrated the possibility controlling of the product selectivity based on intimate knowledge about the reaction mechanism for the conversion of methanol to hydrocarbons. By carefully choosing a catalyst topology likely to favor product formation via alkene cracking and methylation, we have discovered a system that yields a non aromatic product consisting primarily of branched C_{5+} alkenes, offering additional product flexibility in this process.

P284
(429)

Metal dusting in synthesis gas applications

Thoa Nguyen, Martin Skjøth-Rasmussen
Haldor Topsæe A/S. Nymøllevej 55, DK-2800 Kgs. Lyngby. Denmark. *ttmn@topsoe.dk*

Metal dusting is a type of corrosive disintegration of metals and alloys into powders. It is often encountered in synthesis gas applications, where carbon monoxide dissociates on the surfaces of metallic equipment, forming metastable carbides, which subsequently decompose into metal dusts and graphite. Extensive research on metal dusting has been conducted at Haldor Topsøe A/S in the past few decades, predominantly on alloys and coatings, on both laboratory and industrial scales. In addition, fundamental research has been carried out to gain better understanding of the phenomenon and find ways to suppress metal dusting.

P285
(430)

Highly Active Cobalt on Silica Fischer-Tropsch Catalysts: Melt Infiltration *versus* Solution Impregnation

T. M. Eggenhuisen, J. P. den Breejen, D. J. Verdoes, P. E. de Jongh and K. P. de Jong
Inorganic Chemistry and Catalysis, Utrecht University, 3584 CA Utrecht The Netherlands, *t.m.eggenhuisen@uu.nl*

Melt infiltration (MI) was used as a simple alternative precursor loading step for solution impregnation (SI) in the synthesis of cobalt on mesoporous silica catalysts for the FT reaction. With DSC, the pore volume loading of the support with cobalt nitrate salt after melt infiltration was determined. Differences in Co_3O_4 dispersion and distribution after MI and SI induced by different calcination conditions were studied in detail. A surprisingly high FT activity was observed for the MI catalyst after calcination under high N_2 flow. It showed 60% higher activity than the solution impregnated catalyst at similar selectivity, while more severe Co_3O_4 agglomeration was observed.

P286
(431)

Transformation of n-heptane in presence of phenol or guaiacol over H-ZSM-5 zeolite at 350 and 450°C

I. Graca[1,2], M. Badawi[1], **S. Laforge**[1], P. Magnoux[1], M.F. Ribeiro[2], J.M. Lopes[2], F. Ramôa Ribeiro[2]
[1]Laboratoire de Catalyse en Chimie Organique, UMR 6503 CNRS - Université de Poitiers, 40 avenue du Recteur Pineau, 86022 Poitiers Cedex, France. *sebastien.laforge@univ-poitiers.fr*
[2]IBB, Institute for Biotechnology and Bioengineering, Centre for Biological and Chemical Engineering, Instituto Superior Técnico, Universidade Técnica de Lisboa, Av. Rovisco Pais, 1049-001 Lisboa, Portugal

The transformation of n-heptane has been performed over H-ZSM-5 zeolite in presence of phenol or guaiacol at 350 or 450°C. This model reaction should provide information concerning the possibility to replace (almost partly) the classical feedstock of Fluid Catalytic Cracking (FCC) units by the bio-oils obtained from biomass liquefaction or pyrolysis. Whatever the reaction temperature, the addition of the oxygenated compound leads to a very fast and strong deactivation of the zeolite, due to their strong adsorption on the zeolite acid sites.These results suggest that the phenolic compounds might be removed from the bio-oils before their use in FCC units.

P287
(443)

The isomerization of n-butanol of the $Li_3 Fe_2(PO_4)_3$ catalyst

Vasile Georgescu
Institute of Physical Chemistry "Ilie Murgulescu", Romanian Academy, Spl. Independentei 202, Bucharest, Romania,
e-mail: *vgeorgescu@icf.ro*

Alcohol-based fuels have been important energy sources. Butanol is a chemical that has excellent fuel characteristics and the value of octane boosting is dependent of its isomers content $Li_3Fe_2(PO_4)_3$ catalyst possessed high catalytic activity and stability in the dehydration and isomerization of butanol. The catalyst was prepared by solid state synthesis.
The activity of $Li_3Fe_2(PO_4)_3$ in butanol transformations was studied for four surface states: initial sample and after plasma chemical treatment in oxygen, hydrogen and argon.

P288
(447)

Performance of a microstructured packed bed reactor in the synthesis of methanol

Hamidreza Bakhtiary D.[1], Fatemeh Hayer[1], Xuyen Kim Phan[1], Rune Myrstad[2], Peter Pfeifer[3], **Hilde J. Venvik**[1], Anders Holmen[1]
Norwegian University of Science and Technology (NTNU), NO-7491, Trondheim, Norway, *hilde.venvik@chemeng.ntnu.no*

The performance of a multi channel Integrated Micro Packed Bed Reactor-Heat Exchanger (IMPBRHE) in the methanol synthesis was studied. It was shown experimentally that methanol could be produced over an active undiluted $Cu/ZnO/Al_2O_3$ catalyst packed inside the IMPBRHE to a comparable conversion and selectivity as lab. scale dilued and undiluted fixed bed reactors. The comparison strategy for the two reactor types was discussed. The IMPBRHE can be operated isothermally with negligible mass transfer limitations. A 2D pseudo-homogenous model developed for IMPBRHE is capable of predicting the productivity as well as thermal behaviour.

P289 (452)

The effect of TiO_2 and Al_2O_3 addition on the catalytic performance of Co/SBA-15 catalysts for Fischer-Tropsch synthesis

G. Di Carlo, M. Lualdi, L.F. Liotta. S. Järås, A.M. Venezia, M. Boutonnet
ISMN-CNR, Via Ugo la Malfa 153, 90146, Palermo, Italy, e-mail: *dicarlo@pa.ismn.cnr.it*

The deposition of cobalt nanoparticles over ordered mesoporous supports is receiving increasing attention in order to get high metal dispersion and improved catalytic performance. The role of titania and alumina addition on the catalytic performance of Co/SBA-15 catalysts has been investigated in Fischer-Tropsch synthesis for the production of liquid fuels using syngas obtained from biomass, coal or natural gas. The insertion of Ti or Al into the SBA-15 framework affects the reducibility and the dispersion of supported cobalt nanoparticles. The effect of titania and alumina addition on syngas conversion and selectivity to hydrocarbons will be presented.

P290 (455)

Average structural analysis of tar obtained from pyrolysis of pine

Diana López, Nancy Acelas, Fanor Mondragón
Institute of Chemistry, University of Antioquia, A.A. 1226, Medellín, Colombia
diana_lopez@yahoo.com

Conventional analytical methods such as ^{1}H-NMR, VPO and elemental analysis were used to characterize the tar obtained from pyrolysis of pine.

The major fraction of tar obtained during pyrolysis at different temperatures was the insoluble fraction in n-heptane which corresponds to asphaltenes; this fraction was characterized and analyzed using average structural parameters. The structural unit of the tar is composed of one aromatic ring substituted by aliphatic chains, olefinic groups and the presence of oxygenated groups.

P291 (461)

Preparation and performance of Cu-based monoliths for methanol synthesis

Xuyen Kim Phan[1], Hamidreza Bakhtiary D.[1], Rune Myrstad[2], **Hilde J. Venvik**[1], Janina Thormann[3], Peter Pfeifer[3], Anders Holmen[1]
[1]Norwegian University of Science and Technology (NTNU), N-7491, Trondheim, Norway. *Hilde.Venvik@chemeng.ntnu.no*

Methanol synthesis from syngas was carried out in steel monoliths coated with Cu-based catalysts. The Cu-based coatings were prepared using different techniques: slurry, sol-gel, colloid + impregnation and colloid + deposition-precipitation. The coatings were characterized and the productivity of the monoliths was compared to a laboratory scale FBR. Monoliths with high Cu dispersion and good activity in the methanol synthesis reaction could be prepared by coating with slurry prepared from a $CuO/ZnO/Al_2O_3$ powder. Superior activity of such monoliths relative to the FBR was obtained due to the thermal properties of the steel monolith.

P292
(467)

On the catalytic behavior of promoted nanostructured Co/SBA-15 for the Fischer-Tropsch Synthesis

F. E. Oropeza, V. Sazo, M.R. Goldwasser, E. Lira, J. Alvarez, M. Bartolini, A. de Figueiredo Costa[1],
E. Falabella Sousa-Aguiar[1] and M. J. Pérez Zurita. *maria.perez@ciens.ucv.ve*
Universidad Central de Venezuela, Facultad de Ciencias, Escuela de Química, Centro de Catálisis, Petróleo y Petroquímica, Apartado Postal 40646, Los Chaguaramos, Caracas-Venezuela
[1]Petrobras, Cenpes, Ilha do Fundão – Q7 – Cidade Universitária CEP 21941-915 Rio de Janeiro RJ-Brazil

The influence of promoters (Pt, Ru, Zr) on the chemical-physics and catalytic properties of Co nanoparticles supported on SBA-15 for the FTS, were studied. The catalysts were prepared using an ethylene diamine cobalt complex which enabled the formation of small cobalt particles in the nano scale order . Due to the strong interaction of the small cobalt particles with the support, unpromoted Co/SBA-15 catalyst showed low activity and high methane selectivity. The excellent cobalt dispersion obtained coupled with the promoting effect of Zr, Ru and/or Pt, produced a dramatic increase in the catalyst activity without changing significantly the C5+ selectivity.

P293
(468)

Biofuel for catalytic cracking of biomass derived

Carlos Alfonso Álvarez Vásquez and Luis Javier hoyos Marín
Instituto Colombiano del Petróleo, Km 7 via a Piedecuesta, Santander- Colombia,
carlos.alvarez@ecopetrol.com.co and/or *caav1234@yahoo.com*

Biorefineries process renewable feedstock to produce biofuels. Catalytic cracking is a typical process of hydrocarbon refinery directed for production of gasoline. This process can also be used to process biomass and thus produce biofuel. The catalytic cracking of tree representative of biomass derived of such as castor oil, palm oil and glycerol were converted to a products as GLP, gasoline, and diesel when passed over FCC equilibrium catalyst and ZSM-5. The catalytic runs were carried out in a MAT and pilot transport riser reactor at atmospheric pressure, temperature of 300-530°C, catalyst-to-oil ratio (CTO) of 5–14, is reported in this investigation.

P294
(470)

Evolution of phases in Cu-Fe based catalyst during CO hydrogenation for higher alcohols synthesis

M.G. Lin, K.G. Fang, D.B. Li, **Y.H. Sun**
State Key Laboratory of Coal Conversion, Institute of Coal Chemistry,Chinese Academy of Sciences, Taiyuan, 030001, P. R. China,
e-mail: *yhsun@sxicc.ac.cn*

XRD and MES showed the carburization of Fe over both activated and working Cu-Fe based catalysts and the amount of X-Fe_5C_2 went through a maximum at 220°C during CO hydrogenation. Graphitization began to occur at 220°C, and is dependent on reaction temperature slightly. But, the change of carbonaceous species was not the rise in carbon content other than its graphitization during CO hydrogenation. Combined with the evaluation results, it is proposed that the progressive graphitization of carbon over Cu-Fe catalyst with increasing temperature destroyed the synergism between Cu and Fe, which weakened the ability of chain growth for higher alcohols synthesis.

P295
(472)

Fischer-Tropsch Synthesis on re-usable silicon carbide containing cobalt catalyst

Maxime Lacroix, Lamia Dreibine, Behrang Madani, Benoit de Tymowski, David Edouard, Marc Jacques ledoux,
Izabela Janowska, Patrick Nguyen, Charlotte Pham, Sabine Savin-Poncet, Jacques Bousquet, Francis Luck, Daniel Schweich,
Régis Philippe, **Cuong Pham-Huu**
Laboratoire des Matériaux, Surfaces et procédés pour la Catalyse (LMSPC), UMR 7515 CNRS-ECPM, Université de Strasbourg,
25, rue Becquerel, 67087 Strasbourg Cedex 02, France,
e-mail: *cuong.lcmc@ecpm.u-strasbg.fr*

Fischer-Tropsch synthesis (FTS) reaction has received an overincreasing industrial interest since the last decades. It is thought that for this exothermic reaction upport with high thermal conductivity could allowed to get a better temperature control during the reaction and thus, the selectivity of the reaction. Here we report the use of a thermal conductivity medium surface area SiC as catalyst support for the FTS reaction which significantly improve the C_{5+} selectivity, i.e. > 80%, compared to that obtained on the insulator alumina support, i.e. 60%.

P296
(473)

$(CuO/ZnO/Al_2O_3)$/ Protonated Clinoptilolite as a potential dual catalyst for the one-step syn-gas to dimethylether transformation reaction

Sara Aslan, **Cavus Falamaki** and Morteza Sohrabi
Chem. Eng. Dept., Amirkabir University of Technology, P. O. Box 15875-4413, Tehran , Iran, *c.falamaki@aut.ac.ir*

The catalytic behavior of a dual catalyst, C79-7GL / modified clinoptilolite, for the one-step synthesis of dimethylether (DME) from syn-gas has been studied. The kinetic behavior of the dual catalyst was investigated using an integral reactor loaded with 2 g catalyst, under a working pressure of 20 atm in the temperature range of 250-270°C. The effect of inlet H_2/CO molar ratio, reaction temperature and weight percent zeolite in the dual catalyst on the reactor outlet composition was investigated and the kinetics was modeled. The composite catalyst shows a relatively high yield for DME. There exists an optimum zeolite concentration in the composite catalyst.

P297
(474)

Ethanol synthesis from syngas over metal modified order mesoporous carbon-supported Rh-based catalysts

Xiangen Song, Yunjie Ding, Weimiao Chen, Yanpeng Pei, Juan Zang, Wenda Dong and Yuan Lu
Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical physics,
Chinese Academy of Sciences, 116023 Dalian China, e-mail: *dyj@dicp.ac.cn*

In this paper, metal modified ordered mesoporous carbons (MMOMCs) prepared by organic-organic self-assembly were first used as the support for ethanol synthesis from synthesis gas. Just by changing the molar ratio of between resorcinol and metal salt, MMOMCs have been prepared under acidic conditions associated with a direct carbonization process.The catalytic reaction was investigated using a fixed-bed reactor. The selectivity of ethanol was as high as 34.7%. The catalysts were characterized using nitrogen sorption, XRD, XPS, CO chemisorptions, TPD and TEM techniques.

P298
(475)

Evidence for CO insertion mechanism of Fischer-Tropsch synthesis on Ru (0001) surface: A periodic DFT study

H. P. Li, G. Fu, **X. Xu**, **H. L. Wan**
State Key Laboratory for Physical Chemistry of Solid Surfaces; College of Chemistry & Chemical Engineering, Department of Chemistry, Center for Theoretical Chemistry, Xiamen University, Xiamen, 361005, China

Density Functional Theory (DFT) studies reveals that C-C coupling mechanism of FT synthesis on Ru (0001) surface is not the CH_x+CH_x (x=0~3) mechanism but an alternative CO insertion mechanism involved CH+CO.

P299
(478)

Role of cobalt carbide in high alcohols (C_1-C_{18}) synthesis from syngas over activated carbon supported cobalt catalysts

Yanpeng Pei, **Yunjie Ding**, Hejun Zhu, Xiangen Song, Juan Zang, Wenda Dong and Yuan Lu
Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical physics, Chinese Academy of Sciences, 116023 Dalian China, e-mail: *dyj@dicp.ac.cn*

The role of cobalt carbide in high alcohols synthesis from synthesis gas o ver Co/AC catalysts was discussed in this paper. Pure Co_2C samples were prepared from Co_3O_4 precursor according to literature, activated carbon supported cobalt catalysts with different loadings of Co_2C were also prepared, evaluated under the reaction conditions of 230°C, 3.0Mpa H_2/CO=2 and GHSV=1000h^{-1}, and characterized using nitrogen sorption, X-ray diffraction, TG-DTA, and TEM techniques. The CO adsorption on Co_2C samples was detected by FT-IR spectroscopy and CO uptake measurements. The results obtained showed that there was an optimal content of Co_2C for achieving the high selectivity of high alcohols (C_1-C_{18}).

P300
(480)

Rh-catalyzed syngas conversion to ethanol: Studies on the promoting effect of FeO_x

Jingjuan Wang, Qinghong Zhang, **Ye Wang**
State Key Laboratory of Physical Chemistry of Solid Surfaces, National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen 361005, China. *wangye@xmu.edu.cn*

FeO_x is an efficient promoter in the Rh-catalyzed selective conversion of syngas to ethanol. The impregnation of the FeO_x-SiO_2 binary oxide prepared by a sol-gel method with $Rh(NO_3)_3$ followed by calcination and reduction affords a better catalyst for ethanol formation than the co-impregnation or co-sol-gel method. An ethanol selectivity of 42% can be obtained at a CO conversion of 12% over a 5 wt% Rh/5 wt%FeO_x-SiO_2 catalyst. The strong interaction between Rh species and FeO_x is crucial for obtaining high ethanol selectivity. We propose that the co-existence of Rh^0 and Rh^{3+} plays a key role in ethanol formation.

P301
(492)

Effect of the cobalt content on the selectivity of aluminosilicate-based catalysts for Fischer-Tropsch synthesis

A. L. C. Pereira[1], J. M. González-Carballo[2], F. J. Pérez-Alonso[2], S. Rojas[2], J. L. G. Fierro[2], M. C. Rangel[1]
[1]Grupo de Estudos em Cinética e Catálise, Instituto de Química-Universidade Federal da Bahia. Campus Universitário de Ondina.
Federação. 40190-280- Salvador, Bahia, Brazil, e-mail: *mcarmov@ufba.br*

The effect of the cobalt content (5, 10 and 20 %) on the selectivity of amorphous aluminosilicate-based catalysts was studied in this work, in order to develop bifunctional catalysts for Fischer-Tropsch synthesis, an important route to produce fuels and chemicals. It was found that cobalt amount affects both activity and selectivity. The most promising catalyst to produce olefins and light hydrocarbons was that with 10 % Co while the catalyst more suitable to obtain heavy hydrocarbon is the sample with 20 % Co. These catalysts showed similar activities while the solid with 5 % Co was the least active.

P302
(501)

Modeling thermodynamic non-ideal behavior of vapor–liquid phase equilibrium, mass and energy transfer in a binary system using CFD methods

Mohammad Irani[1,2], Mahmoud Reza Pishvaie[2], Ramin Bozorgmehry Boozarjomehry[2], Ahmad Tavassoli[1]
[1]Research Institute of Petroleum Industry, Tehran, Iran, P.O.Box 18745-4163
[2]Department of Chemical and petroleum Engineering, Sharif University of Technology, P.O.Box 11365-9465, Azadi Av., Tehran, Iran

A numerical framework has been derived to model dynamically varying vapor–liquid phase equilibrium for thermodynamic non-ideal behavior binary systems by computational fluid dynamics (CFD). Mass transfer during condensation and vaporization is modeled; the rate of mass transfer was obtained using U-P flash calculation in two-phase cells. Condensation and evaporation are simulated within a multiphase Eulerian framework in such a manner that the components undergoing phase change map the non-ideal phase equilibrium diagram locally at steady state. Equilibrium is assumed at the phase boundary during transient mass transfer prior to reaching global steady conditions. The proposed framework can simulate the hydrodynamic behavior of multi-component multi-phase systems with thermodynamic non-ideality.

P303
(502)

Synthesis of some baria modified γ-Al_2O_3 catalysts for methanol deshydratation to dimethyl ether

Hoda Safaee, **Morteza Sohrabi** and Cavus Falamaki
Chem. Eng. Dept., Amirkabir University of Technology, P.O. Box 15875-4413, Tehran, Iran, *sohrabi@aut.ac.ir*

In the present study the catalyst preparation for methanol dehydration to dimethyl ether, using some baria modified γ-Al_2O_3 as the reaction catalyst, have been presented. Three catalysts samples were prepared consisted of γ-Al_2O_3 impregnated by Ba^{2+}, using barium nitrate solution. It was noted that the Ba^{2+} content of the catalysts had a high impact on the activity of the letters. The operating temperature range was 260-290°C and the pressure was 1 atm. The experimental runs were performed applying a constant molar rate of feed. Catalysts activity and kinetic measurements were carried out using a catalytic fixed bed microreactor.

P304
(538)

Innovating *operando* characterization of cobalt supported catalysts by coupled XRD-DRIFT measurements

L. Braconnier[1], I. Clémençon[1], F. Diehl[1], C. Legens[1], B. Rebours[1], Y. Schuurman[2]
[1]IFP Lyon, Rond-point de l'échangeur de Solaize, BP 3, 69360 Solaize, France, *laure.braconnier@ifp.fr*
[2]Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS - Université de Lyon,
2, av. A. Einstein, 69626 Villeurbanne cedex, France.

An innovating characterization method has been developed including in *operando* XRD and DRIFT analysis. In the XRD reaction cell, observation using infra-red in diffuse reflectance (DRIFT) will also be possible. Both techniques have been associated to optimize Fischer-Tropsch catalysts characterization under optimistic FT synthesis conditions : interior cell pressure can reach 30 bars and temperatures can climb up to 550°C. Gaseous reactants will travel through the cell via a fixed bed reactor.

P305
(554)

Evaluation of the Co/MCM-41 catalysts in the Fischer-Tropsch Synthesis

Bianca Viana de Sousa[1], Meiry Gláucia Freire Rodrigues[1], Leonardo Andrés Cano[2], María Virginia Cagnoli[2],
José Fernando Bengoa[2], Sérgio Gustavo Marchetti[2], Gina Pecchi[3]
[1]UFCG/CCT/UAEQ/LABNOV. Av. Aprígio Veloso, 882, Bodocongó, CEP 58.429-970, Campina Grande – Paraíba, Brazil,
e-mails: *biancaviana_cg@yahoo.com.br, meiry@deq.ufcg.edu.br*
[2]CINDECA/UNLP/FCE – Calle 47 n. 257, 1900 – La Plata – Argentina
[3]Facultad de Ciencias Químicas, Universidad Concepcion, Concepcion, Chile

In this work, molecular sieve MCM-41 was prepared as well as the Co/MCM-41 catalysts and these catalysts have been evaluated at the Fischer-Tropsch reaction. The attainment of the mesoporous molecular sieve was confirmed by the XRD analyses. This analysis shows the cobalt well dispersed in the form of Co_3O_2 in the catalysts being in concordance with TEM. The TPR profiles of the Co/MCM-41 catalysts showed the presence of distinct peaks. The results obtained from the synthesis of Fischer-Tropsch for catalysts with 5 wt% and 15 wt% Co/MCM-41 presented high selectivity for commercially important hydrocarbons (C_2-C_4). These catalysts presented diffusion limitations, which gave high selectivity for methane gas, whereas for hydrocarbons in the C_5+ range the selectivity was low.

P306
(555)

Identification of surface cobalt oxide as a tool for optimizing Fischer-Tropsch catalysts on alumina-based carriers

I.G. Solomonik ,V.B. Rybakov, V.Z. Mordkovich
Technological Institute for Superhard and Novel Carbon Materials, 7a,Centralnaya St., Troitsk, Moscow region, 142190,
Russian Federation, *solomonik@ntcstm.troitsk.ru*

Characterization of cobalt catalysts on alumina-based carriers is strongly complicated by the difficulty in distinguishing cobalt oxides from cobalt aluminates by X-ray diffraction. Investigation of catalysts and model systems with XRD and thermal analysis allowed finding correlations for measuring concentration of excess surface cobalt oxide. It is shown that formation of an optimized catalyst 20% $Co/CoAl_xO_y$ requires gibbsite as a preferable precursor.

P307
(560)

Direct Dimethyl ether synthesis from CO-rich syngas over composite catalysts

M. Stiefel, **M. Döring**
Institute for Technical Chemistry (ITC-CPV), Karlsruher Institute of Technology,
Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany. *Manfred.Doering@kit.edu*

Dimethyl ether (DME) synthesis from CO-rich syngas, which could be delivered for example from biomass, was studied concerning the influence of various methanol catalysts in the catalyst system. Systems like Cu/Zn/Cr and Cu/Zn/Al/Zr were developed and used in combination with α-Al_2O_3 for DME synthesis. The prepared systems delivered less CO conversion than a commercial one, but where enhanced towards temperature stability. Further, the Cu/Zn/Cr-system showed good long term stability and was less deactivated by HCl.

P308
(565)

Synthesis of H-ZSM-5/SAPO-11 and MTO activity

Tian-Sheng Zhao, Bin Li, Lijuan Gao and Qingxiang Ma
Key Laboratory of Energy Resources & Chemical Engineering, Ningxia University, Yinchuan, 750021, *zhaots@nxu.edu.cn*

Composite zeolite catalysts of H-ZSM-5 and SAPO-11 were prepared by post-chemical synthesis, and showed adjusted pore distribution and acidity compared with H-ZSM-5. When the as-synthesized H-ZSM-5/SAPO-11 zeolites used in the reaction of methanol conversion to olefins (MTO), higher one-pass propylene selectivity and total olefin selectivity were achieved compared with H-ZSM-5 or SAPO-11 under typical test conditions. Although single SAPO-11 showed poor activity towards the conversion of methanol to olefins, its introduction into H-ZSM-5 with different compositing ratios enhanced the selective conversion of methanol. The mechanical mixing of H-ZSM-5 with SAPO-11 also exhibited similar catalytic activity for the MTO reaction.

P309
(566)

Gas to Liquid Processes in the Australian Context

V. Sage[1], N. Burke[2], D. Trimm[2]
[1]CSIRO Earth Science and Resource Engineering, Australian Resources Research Centre, 26 Dick Perry Avenue,
Kensington, WA 6151, Australia
[2]CSIRO Earth Science and Resource Engineering, Ian Wark Laboratory, Bayview Ave, Clayton, Victoria, 3168, Australia

Although Australia has large reserves of coal and gas, it cannot supply all of its requirements for transport fuels from indigenous oil reserves. A Gas to Liquids (GTL) fuel industry would go some way towards delivering security of supply in vital transport fuels and would provide a new export industry and expertise in the area.

CSIRO is conducting research in GTL technologies, through investigations in catalyst and reactor design, as well as process optimisation, for the development of stranded, off-shore, and associated gas reserves, the minimisation of the size of production facilities and the minimisation of GHG emissions.

P310
(567)

Rentech process: overview

Belma Demirel and Harold Wrights
Rentech, Inc., Rentech Energy Technology Center, 4150 East, 60th Avenue, Commerce City, CO 80022, USA, *bdemirel@rentk.com*

Rentech built first renewable facility in 1992 to produce alternative fuels from landfill gas. Rentech's Product Demonstration Unit (PDU) located in Commerce City, Colorado is the only operating synthetic transportation fuels facility in the USA, and thousands of gallons of ultra-clean synthetic fuels including military jet fuel, commercial Jet A and Jet A-1 and ultra low sulfur diesel have been produced and shipped to potential customers, including the United States Air Force for testing. The Rentech-SilvaGas biomass gasifier is one of a few biomass gasifiers that have operated on a commercial scale. Rentech is curretly working on waste-to-energy projects, including a facility in Rialto, California that would produce about 640 bbd of renewable synthetic fuels and 35 megawatts of renewable power. Rentech is also working on commercial-scale fossil projects, including a facility to produce 30,000 bbd of synthetic fuels and chemicals in Adams County, Mississippi.

P311
(568)

A novel magnetometer for characterisation of Fischer-Tropsch catalysts at working conditions

Michael Claeys[1], Eric van Steen[1], Jakobus Visagie[2], Jan van de Loosdrecht[2]
[1]Centre for Catalysis Research, Department of Chemical Engineering, University of Cape Town,
Private Bag X3, Rondebosch, 7701, South Africa
[2]Sasol R&D, Sasolburg, 1947, South Africa. *michael.claeys@uct.ac.za*

This paper describes the development of an in-situ magnetometer which allows following effects of catalyst oxidation/reduction as well as sintering under fully realistic reaction conditions of temperature and pressure. Although originally developed for use in Fischer-Tropsch synthesis this novel instrument can be applied to investigate any ferro-magnetic matter in a controlled environment.

P312
(575)

Parametric Study Of The Fischer-Tropsch Synthesis In Catalytic Microchannels

Gamze Gumuslu, Mustafa Karakaya and **Ahmet K. Avci**
Department of Chemical Engineering, Bogazici University, Bebek 34342, Istanbul, Turkey, *avciahme@boun.edu.tr*

This work aims at exploring the Fischer-Tropsch (FT) synthesis in catalytic microchannels through a parametric analysis employing computer-based techniques. The FT process is exothermic and demands precise temperature control since the product spectrum is susceptible to temperature excursions. This requirement can be fulfilled by a microchannel approach involving the FT reaction and coolant flows running in parallel, micrometer-size channels. Parametric search of a number of operating and geometric parameters indicate that the heat transfer into the coolant flow in adjacent channels can be adjusted to provide a nearly isothermal environment for the FT synthesis.

P313 (581)

Energy Research Faster & Better by Automated High-Output Solutions – Biomass Conversion

Olaf Köhler
Chemspeed Technologies, Rheinstr. 32, CH-4302 Augst, Switzerland, *olaf.koehler@chemspeed.com*

The Biopolymer Hydrolysis and the Organosolv process are two commonly used methods to generate fermentable sugars from so called 2nd generation renewables. A third, the Ammonia Fiber Expansion (AFEX), is a mild yet highly efficient method to fraction the lignocellulose into readily fermentable sugars. It has proven substantially increases in rate and extent of enzymatic digestion of glucan and xylan. The executed reactions screen the effect of different moisture amounts, temperature effects and reaction times under pressure control. This poster will give an overview of the three methods with emphasis on the AFEX treatment.

P314 (582)

Energy Research Faster & Better by Automated High-Output Solutions – Catalyst Precipitation

Olaf Köhler
Chemspeed Technologies, Rheinstr. 32, CH-4302 Augst, Switzerland, *olaf.koehler@chemspeed.com*

Most chemicals have their origin in fossil energy resources and require catalysis based refining. One of the main compounds of heterogeneous catalysts is the solid support. Its preparation requires well-defined conditions, i.e. pH control in the precipitation process. In this poster we will describe the automated high-output precipitation of aluminiumoxid-hydroxid yielding daily up to 60 fresh Bauxit batches.

P361 (588)

Enhanced Production of Chemicals via co-Feeding of Ammonia during Fischer-Tropsch Synthesis

M. Claeys[1], E. van Steen[1], T. Sango1, C. de Vries[1], R. Henke[1,2], A.K. Rausch[2], F. Roessner[2]
[1]Centre for Catalysis Research and c*change (DST-NRF Centre of Excellence in Catalysis)
Department of Chemical Engineering, University of Cape Town, Cape Town, 7701, South Africa
[2]Industrial Chemistry 2, University of Oldenburg, Oldenburg, 26111, Germany
michael.claeys@uct.ac.za

Addition of ammonia during the Fischer-Tropsch synthesis can lead to significant changes of the product composition. Importantly larger selectivity of valuable chemicals can be obtained, with higher olefin concentrations and additional valuable linear products containing nitrogen. This optimization could result in fundamental and economically favorable modifications to Fischer-Tropsch synthesis.

Session IV - Direct-indirect conversion of methane to oxygenates, olefins, aromatics; C_1-C_3 intermediates to chemicals

P71
(22)

Dry reforming of methane to syngas over $NiAl_2O_4$ catalyst: effect of temperature of calcination on the carbon formation.

N. Salhi[1], C. Petit[2], A. A. Kiennemann[2] and C.Rabia[1]
[1]Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, USTHB 109 El-Alia Bab Ezzouar, Alger-Algérie.
[2]Ecole de Chimie, Polymères et Matériaux – Laboratoire Matériaux, Surface, Procédés pour la Catalyse (LMSPC) UMR CNRS 7515 - 25, rue Becquerel 67087 Strasbourg Cedex France. *NAS.SALHI@yahoo.fr*

Catalysts spinel $NiAl_2O_4$ were prepared by sol-gel method and calcinated at 725°C, 800°C and 900°C noted respectively S_{725}, S_{800} and S_{900}. The solids were characterized by XRD, SEM, TEM, BET and TPR. Catalytic testing was performed for CO_2 reforming of methane. The crystallisation goes on during increasing of temperature of calcination. High purity and homogeneity were observed by MEB and TEM for the S_{900} spinel catalyst. The surface areas decreased strongly between 725°C and 900°C. The catalytic results showed that more the calcinations' temperature increased more the crystallization of the spinel formed was higher and more the formation of carbon was limited.

P72
(24)

Oxidative Dehydrogenation of Propane to Propylene over W-Mn Catalysts

Huanling Song, Jian Yang, Jun Zhao, **Lingjun Chou**
State Key laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China, e-mail : *ljchou@lzb.ac.cn*

The oxidative dehydrogenation (ODH) of propane was studied over $2.5\%Ce\text{-}5\%Na_2WO_4\text{-}2\%Mn/SiO_2$, $10\%Na_2WO_4\text{-}2\%Mn/MgO$ and $10\%Na_2WO_4\text{-}2\%Mn/ZrO_2$ catalysts. The conversion of propane of 77%, 83% and 80%, respectively, was obtained over these catalysts at 700°C with GHSV of $20000h^{-1}$ and propane/oxygen of 1.1. The highest yield to propylene was achieved to $2g.g^{-1}h^{-1}$ on the latter two catalysts; however, the yield of propylene was only $0.5g.g^{-1}\ h^{-1}$ for the former at the similar reaction conditions. XRD and XPS characterizations show the bulk and surface of every catalyst for W and Mn was different.

P73
(25)

Characterization of Ce-W-Mn Catalysts for oxidative coupling of methane

Jian Yang, Jun Zhao, Huanling Song, **Lingjun Chou**, Shuben Li
State Key laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, PR China, e-mail : *ljchou@lzb.ac.cn*

The CeO_2 promoted $W\text{-}Mn/SiO_2$ catalysts had excellent performance for the OCM under atmosphere pressure were detected. The relation between structure characterization and catalytic performance was discussed. The oxygen storage capability in $W\text{-}Mn/SiO_2$ catalyst was enhanced with adding CeO_2. A synergistic interreaction occurs positively among Ce, Mn, W over the CeO_2 doped $W\text{-}Mn/SiO_2$ catalyst. Shake-up peak of Ce^{3+} and Mn^{2+} in Ce_{3d} and Mn_{2p} was detected. Suggesting that the OCM reaction over Ce-W-Mn catalyst also followed the Redeal-Redox mechanism.

P74
(33)

Direct Conversion of Methane to Methanol: Modeling and Experimental Study

Morteza Sohrabi[1] & Leila Vafajoo†
[1]Amirkabir University of Technology, Department of Chemical Engineering, Tehran 15914, Iran

In the present study, the single step (direct) conversion of methane to methanol has been investigated in a tubular reactor packed with V_2O_5/SiO_2 particles as the reaction catalyst. A dynamic model for such a reaction has been presented. The effects of certain pertinent parameters of the system such as temperature, pressure, concentration of oxygen in the feed, and gas hourly space velocity (GHSV) on the conversion of methane and selectivity of the products have been investigated. The data predicted from the model have been correlated with the experimental results. The degree of agreement was between 80-90%.

P75
(44)

Structured Zeolite Catalysts with Hierarchical Channel Structure and Applied in Methane Aromatization Reaction

Lijun Gu, **Ding Ma**, Xinhe Bao
Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China, *dma@dicp.ac.cn*

Composite of mesoporous ZSM-5 matrixed over silicon carbide was successfully prepared through *in situ* procedure. The obtained structured-zeolitic-catalyst with multimodal porosity showed evidently improved catalytic performance in the methane aromatization reaction. This method also provided a means (ZSM-5/CNTs/SiC) to immobilize catalytically active CNTs onto shape-tunable inorganic substrates. The immobilized CNTs by themselves, or after loading with catalytically active metal or metal oxide, can have potential applications in scaled-up catalytic reaction processes.

P76
(45)

Direct conversion of methane in formaldehyde at very short residence time (20-40 ms)

J. Zhang, **V. Burklé-Vitzthum**, P-M. Marquaire, G. Wild, J-M.Commenge
Département de Chimie Physique des Réactions (DCPR), UMR 7630 CNRS - INPL, 1 rue Grandville, 54001 Nancy cedex, France.
Valerie.vitzthum@ensic.inpl-nancy.fr

We are investigating the partial oxidation of methane in gas phase in order to identify the conditions which maximize the yield and the selectivity in formaldehyde. Preliminary investigations showed that some formaldehyde is formed at high temperature (1300K) and short residence time (20-40 ms). Microreactors might be particularly adapted for this synthesis because they permit to achieve the low residence times required. First we are presenting the design of the chosen microreactor and then some experimental results of yields and selectivities, as a function of temperature, residence time and composition of the reactants (x_{O2}/x_{CH4}).

P77
(51)

Conjugated Oxidation of Methane to Formaldehyde with Hydrogen Peroxide

L.M.Gasanova[1], **T.M.Nagiev**[1.2]
[1]Nagiev Institute of Chemical Problems, National Academy of Sciences of Azerbaijan.
29 H.Javid Av., 370143 Baku, Azerbaijan Republic;
[2]Baku State University, 370143 Baku, Azerbaijan Republic,
e-mail: *tnagiev@azeurotel.com; tnagiev@azeriland.com*

Under optimal conditions formaldehyde is synthesized directly from methane without intermediate methanol formation. At higher temperature (above 520°C) and long-term contact, formaldehyde is synthesized according to parallel scheme with further transformation to severe degradation products, CO and CO_2. For example, the target product is mostly after-oxidized to CO and its contribution to the CO_2 formation rate is low, whereas for methanol the opposite situation is observed. Based on the above results, it may be concluded that selective oxidation of methane to formaldehyde with hydrogen peroxide is implemented by a mechanism different from that in which methanol is formed as the intermediate oxidation product.

P78
(52)

Oxidative coupling of methane: influence of phase composition of silica based catalysts

A.G. Dedov, G.D. Nipan, A.S. Loktev, V.A. Ketsko, T.N. Koltsova, A.A. Tyunyaev, I.I. Moiseev
Department of General and Inorganic Chemistry - Gubkin Russian State University of Oil and Gas, 65 Leninsky pr. 119991 GSP-1 Moscow, Russia. *genchem@gubkin.ru*

In this work results of OCM reaction catalyzed by silica-based composites Mn/W/Na (Li, K, Rb, and Cs)/SiO_2 synthesized by an enhanced method are report. Dependence of catalytic properties of these materials from phase composition was demonstrated. The reached C_{2+} yield values (25-29%) are close to the limiting values calculated from kinetic data.

P79
(54)

Direct Methane Oxidation to Methanol with Hydrogen Peroxide Under Pressure

T.M.Nagiev[1,2], U.V.Nasirova[1], I.T.Nagieva[2]
[1]Nagiev Institute of Chemical Problems, National Academy of Sciences of Azerbaijan.
29 H.Javid Av., 370143 Baku, Azerbaijan Republic;
[2]Baku State University, 370143 Baku, Azerbaijan Republic,
e-mail: *tnagiev@azeurotel.com; tnagiev@azeriland.com*

Based on a direct single-step oxidation of methane to methanol with hydrogen peroxide under pressure in a pilot plant, a radically new high-selectivity method providing a significant degree of conversion was developed. The method makes it possible to reduce the pressure and temperature of the process and to simplify the technology. It was found experimentally that the oxidation of methane proceeds by a mechanism of chemical conjugation, in which free hydroxyl radicals play the role of a leading induction intermediate. Kinetic modeling was used to establish the most probable free-radical mechanism.

P80
(55)

Influence of porous structure of mesoporous amorphous rare earth silicates on proceeding of methane oxidative coupling

A.G. Dedov[1], A.S. Loktev[1], N.O. Tel'pukhovskaya[1], **K.V. Parkhomenko**[2], M.V. Geraschenko[1],
V.K. Chernysheva[1], I.E. Muhin[1], I.I. Moiseev[1]
[1]Gubkin Russian State University of Oil and Gas, 65 Leninskii pr-t, 119991, Moscow, Russia, *genchem@gubkin.ru*
[2]Université de Strasbourg, 67000, 4 Rue Blaise Pascal, Strasbourg, France, *kparkhomenko@chimie.u-strasbg.fr*

In this work we report on the catalytic activity of mesoporous amorphous rare earth materials based on SiO_2 in the methane oxidative coupling reaction. Lanthanum and cerium ions or their mixture were introduced into the structure of the materials during synthesis. A synergistic catalytic effect of lanthanum and cerium introduced together into mesoporous silicate matrix in the methane oxidative coupling reaction has been revealed. Possible influence of porous structure on catalytic action is discussed.

P81
(60)

Reaction mechanism of reforming of DME with carbon dioxide over Cu-Zn + γ-Al_2O_3 mixed catalyst

K. Asami and K. Seto
Faculty of Environmental Engineering, The University of Kitakyushu
Hibikino 1-1, Wakamatsu-ku, Kitakyushu 808-0135, Japan. *asami@env.kitakyu-u.ac.jp*

Reaction mechanism of CO_2 reforming of DME was investigated over Cu-Zn + γ-Al_2O_3 mixed catalyst. It was found that the title reaction proceeds through the reverse reactions of the DME direct synthesis from syngas, that is, reverse water gas shift reaction, DME hydration to methanol, and methanol decomposition to CO and hydrogen. Hydrogen as an initiator of the reaction can be formed by DME decomposition and the oxidation of DME with surface Cu oxide species. Redox cycle between metallic Cu and Cu oxide as another mechanism for the DME reforming would also be possible.

P82
(71)

Catalytic oxidative conversion of methane to ethylene and acetylene over modified zeolite

A.M.Aliyev, A.O.Azizov, T.N.Shakhtakhtinsky, R.Yu.Agayeva
Institute of Chemical Problems of NA S of Azerbaijan, AZ1 143, Baku, H.Javid ave., 29, Azerbaijan, e-mail: *itpcht@itpcht.ab.az*

It has been synthesized by ion exchange method a range of catalysts for the reaction of oxidative conversion of methane to ethylene and acetylene on the basis of natural zeolites with different silicate modulus and different quantities of calcium and lithium ions. It has been shown that dealuminated natural clinoptilolite with silicate modulus $SiO_2/Al_2O_3=10.8$ containing 7.0 wt% Ca^{2+} and 8.0 wt% Li^+ is efficiency catalyst for this reaction. The test of the activity of the prepared catalysts were carried out in the flow quarts tube reactor with to beds of the same catalyst ($V^{I}_{cat}=V^{II}_{cat}$) by means of sectional feed oxygen.

P83
(75)

V containing SBA-15 catalysts prepared by in situ coating route for oxidative dehydrogenation of propane

Xiaodong Yi, Xiaodan Sun, Jianping Guo, Chuanjing Huang, Weizheng Weng, **Huilin Wan**
State Key Laboratory for Physical Chemistry of the Solid Surfaces. National Engineering Laboratory for Green Chemical Productions of Alcohols, Ethers and Esters. Chemistry Department, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, P. R. China,
e-mail: *xdyi@xmu.edu.cn* (Xiaodong Yi); *hlwan@xmu.edu.cn* (Huilin Wan)

Well organized VO_x-SBA-15 catalysts synthesized by in situ coating route in a one-pot process showed good catalytic performance for oxidative dehydrogenation of propane to propene. The catalysts were characterized by BET, XRD, in-situ Raman, H_2-TPR, XPS, NH_3-TPD and Py-IR. The results showed that the higher performance of VO_x-SBA-15 catalysts was related to the better reducibility and dispersion of the pseudotetrahedral monovanadate VO_4 species on the surface.

P84
(85)

Synthesis of acetic acid from water-ethanol mixture over $Cu/ZnO-ZrO_2-Al_2O_3$ catalyst

V. Brei, M. Sharanda, S. Prudius, Yu. Datsyuk
Institute for Sorption and Endoecology Problems of the National Academy of Sciences of Ukraine,
General Naumov Str., 13, Kyiv, 03164, Ukraine, e-mail: *brei@ukr.net*

It was found that water-ethanol solution can be transformed to acetic acid over the bifunctional $Cu/ZnO-ZrO_2-Al_2O_3$ catalyst. Such parameters as ethanol concentration, reaction temperature, and feeding rate for obtaining of high yield of acetic acid (8 mmol/g_{cat}/h) at 70% conversion of ethanol have been determined. Main by-product of studied process is hydrogen.

P85
(92)

Oxidation of methane to C_1 oxygenates over $H_4PM_{o10}WVO_{40}$ catalyst

S. Mansouri[1], O. Benlounes[1], C. Rabia[2], R. Thouvenot[3] and S. Hocine[1]
[1]Laboratoire de Chimie Appliquée et de Génie Chimique Université M. Mammeri de Tizi-Ouzou BP .17 R.P 1500 Tizi-Ouzou Algeria
[2]Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, USTH, B.P 32 El- Alia Bab-Ezzouar 16111 Alger Algeria
[3]Institut Parisien de Chimie Moléculaire, UMR 7201, Université Pierre et Marie Curie Equipe Polyoxométallates Case Courier 42, 4 Place Jussieu, 75252 Paris cedex 05, France.

The partial oxidation of methane into C1 oxygenates over $H_4PMo_{10}WVO_{40}$ catalyst was investigated and the effect of temperature reaction on the catalytic activity was examined. The products obtained were methanol, formol and carbon oxides. The results obtained have shown that both IR, UV, NMR spectroscopy and X-ray diffraction indicate for $H_4PMo_{10}WVO_{40}$, the presence of a single crystalline phase and IR spectra typical of the Keggin anion. After reaction $H_4PMo_{10}WVO_{40}$ were decomposed into P_2O_5, V_2O_5, MoO_3 and WO_3.

P86
(100)

Dynamic behaviour of catalytic reactor for methane non oxidative dehydro-aromatization

Bohumil Bernauer, Vlastimil Fíla and Zdeněk Sobalík
Institute of Chemical Technology, Prague, Technická 5, 166 28 Prague 6, Czech Republic, e-mail: *Bohumil.Bernauer@vscht.cz*

This study addresses the catalytic transformation of methane on the Mo catalysts supported on microporous molecular sieves (H-ZSM-5 and MCM-22). The catalytic activity of these materials was studied in continuous flow catalytic microreactor with the catalyst particles dispersed in a mineral support. The reactivation of the deactivated catalysts by the pulses of CO_2 has been investigated and optimal conditions for reactivation procedure were found. A mathematical model of catalyst behaviour dynamics has been developed and used for kinetic parameters estimation and process

---

P87
(102)

Non-oxidative conversion of methane over nanostructured catalysts prepared by metal-vapor method

Vagif M. Akhmedov[1], Abdulaziz A. Bagabas[2]
[1]Department of Chemistry, Baku Branch of Moscow State University, F.Agayev St. 14, Baku, Azerbaijan Republic,
akhmed26@yahoo.com
[2]Petroleum & Petrochemicals Research Institute, King Abdulaziz City for Science andTechnology, P.O.Box 6086, Riyadh-11442,
Saudi Arabia, e-mail: *abagabas@hotmail.com*

Methane reacts with the most of Metal-Vapor prepared nano-structured catalysts (MVM) under mild conditions (normal pressure, 450-570K). In the first stage of interaction, methane forms CHx species on the catalyst surface, which can be condensed into C_2-C_6 alkanes at the same temperature range by hydrogen treatment. Increasing the reaction temperature up to 973-1073°K causes the one stage catalytic conversion of methane to the aromatics. In this case, benzene was the main reaction product (85-95%) along with small amounts of ethylene, ethane, and toluene.

P88
(106)

Induction period observation in the conversion of C1-derivatives to light olefins

Yingxu Wei[a], Dazhi Zhang[a], Fuxiang Chang[a], **Bao-lian Su**[a,b,c], **Zhongmin Liua**
[a]Dalian National Laboratory for Clean Energy, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, P. O. Box 110,
116023 Dalian, P. R. China; Tel:+ 86-411-84685510; Fax:+ 86-411-84691570, e-mail: *liuzm@dicp.ac.cn*
[b]Laboratoire de Chimie des Matériaux Inorganiques (CMI), The University of Namur (FUNDP), B-5000 Namur, Belgium; Tel:
3281724531; Fax: 3281725414, e-mail: *bao-lian.su@fundp.ac.be*
[c]State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, 430070,
Wuhan, Hubei, P. R. China.

The initial transformations of methanol or chloromethane over SAPO-34 and ZSM-5 catalyst were investigated by a consecutive pulse reaction system. The induction period, in which an organic-free catalyst could be transferred to a working catalyst, was directly observed. By varing the catalyst-reactant contact time, the performances present the character of induction period and steady-state reactions. The duration of induction period could be determined in this way.

P89
(117)

Selective propylene production in the MTO process

E. Epelde, A.T. Aguayo, M. Gamero, A.G. Gayubo, J. Bilbao
Departamento de Ingeniería Química, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

The selective transformation of methanol into propylene has been studied on different catalysts based on different microporous acid phases (HZSM-5, SAPO-34 and SAPO-18). An analysis is made of the influence of their proper ties (micropore diameter, total acidity and acid strength) on the kinetic behaviour of the catalysts (propylene yield, propylene/ethylene ratio and deactivation rate). SAPO-18 has resulted to be a suitable catalyst, as high propylene yields (42.5 % at 550°C) and P/E ratios (3.2 at 550°C) are obtained. Moreover, SAPO-18 presents a significantly lower deactivation rate than SAPO-34 which is the one industrially used in the MTO process.

P90
(132)

A VOx/Meso-TiO_2 catalyst for methanol oxidation to dimethoxymethane

Ensheng Zhan, Yong Li, Junlong Liu, Xiumin Huang, **Wenjie Shen**
State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China,
shen98@dicp.ac.cn

Mesoporous TiO_2 was prepared by simply controlling the hydrolysis of $Ti(OBu)_4$ with the help of acetic acid. The mesoporous TiO_2 had a well-crystallized anatase phase and a high surface area of 290 $m^2 \cdot g^{-1}$ with a pore size of about 4 nm.The anatase phase and the mesoporous structure were maintained in the VOx/TiO_2 catalyst with a monolayer dispersion of V_2O_5, however, the surface area decreased to 126 $m^2 \cdot g^{-1}$. The catalyst was highly active and selective for methanol oxidation, giving about 55% conversion of methanol and 85% selectivity to dimethoxymethane at 423 K.

P91
(148)

Pt, ReO_x/Al_2O_3 as active catalyst for methane conversion into benzene

D. Tagiye, S. Abasov, F. Babayeva
Institute of Petrochemical Processes Azerbaijan NAS, 30, Khocaly ave, AZ1025, Baku, Azerbaijan, *dtagiyev@hotmail.com*

Pt, ReO_x/Al_2O_3 catalyst prepared by adsorption method and having a high activity in the methane conversion into benzene contains platinum in a high dispersion state. Due to the interaction between platinum and rhenium oxide the bound oxygen obtains non-homogeneous reactivity and these properties are transferred to oxygen of Re oxide. During methane activation Pt,ReO_x/Al_2O_3 catalyst undergoes a partial reduction and becomes covered by carbon deposits. The bound oxygen takes part in C_2H_y intermediates formation, and the carbon deposits participate in their subsequent oligomerization and dehydrocyclization.

P92
(166)

Comparative study of unsupported and Al_2O_3-supported MoV and MoVP catalysts in the oxidative dehydrogenation of ethane to ethylene.

N. Haddad[a], E. Bordes-Richard[b] and **A. Barama**[a]
[a]Laboratoire des Matériaux Catalytiques & Catalyse en Chimie Organique, Faculté de Chimie, USTHB, BP32 El Alia,
16111 Bab Ezzouar, Alger, Algerie. Fax: 213 21 24 80 08. *a_barama@yahoo.fr*

Unsupported and Al_2O_3-supported MoV and MoVP catalysts (Mo/V=11, V/P=1 and 15% of active phase) were prepared, characterized using XRD, LRS, TGA, HT-XRD, HT-XPS and TPR techniques and tested in the oxidative dehydrogenation of ethane to ethylene at 550°C. The results indicated that the catalytic properties were significantly affected by the catalyst content. Activity results, in C_2H_6+O_2 reaction, revealed that the series ofthe supported catalysts have better catalytic performance than the unsupported ones. The addition of vanadium and phosphorus has significant influence on improving both the activity and ethylene selectivity of the Mo catalysts.

P93
(172)

Characterization of the surface chemistry of platinum promoted molybdenum carbide-zeolites for the direct aromatization of methane and natural gas

M.S.Scurrell[1] , T. Tshabalala[1] and J. A. Anderson[2]
[1]Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa,
michael.scurell@wits.ac.za
[2]University of Aberdeen, Scotland

The modification of molybdenum carbide-pentasil zeolites by platinum for use in the direct aromatization of methane and natural gas under dioxygen-free conditions, has been assessed using FTIR measurements of the chemisorbed carbon monoxide. Distinct sites have been identified, together with evidence of the manner in which Pt and Mo interactions can be manipulated. Implications for catalysis are discussed.

P94
(176)

Experimental evidence for the formation of alkyl-gallium species in propane aromatization reactions.

A. C. Faro Júnior, V. O. Rodrigues
Instituto de Química - Universidade Federal do Rio de Janeiro (UFRJ), Av. Athos da Silveira Ramos, 149 – CT/Bl. A Sala 302,
Rio de Janeiro, RJ, Brazil. *farojr@iq.ufrj.br*

Gallium modified H-ZSM5 catalysts prepared by incipient wetness impregnation and submitted to two reduction-oxidation cycles were studied by *in situ* DRIFTS and aromatization reaction in a batch reactor. Data obtained through these techniques suggest that gallium hydride species are not stable under reaction conditions with propane at the temperature of 703 K. Also the deficit of methane observed at the beginning of the reaction, together with the detection of irreversibly adsorbed alkyl species in gallium modified ZSM-5 catalysts suggest that the active species may be an alkyl-gallium species.

P95
(182)

Experimental Investigation and Microkinetic Modeling of Methane Oxidative Coupling

B. Bolado Escudero[1], **J. W. Thybaut**[1], G. B. Marin[1], L. Olivier[2], C. **Mirodatos**[2], A. C. van Veen[2]
[1]Laboratory or Chemical Technology, Ghent University, Krijgslaan 281-S5, B-9000 Ghent, Belgium. *Joris.Thybaut@UGent.be*
[2]Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON), UMR 5256 CNRS - Université de Lyon,
2, av. A. Einstein, 69626 Villeurbanne cedex, France. *cmiro@ircelyon.fr*

Experiments on methane oxidative coupling reaction over La-Sr/CaO catalyst were carried out in a high-throughput reactor setup and simulated by means of a 1-D heterogeneous model that accounted for the irreducible mass transport limitations caused by the fast radical chain reactions occurring inside the catalyst pellets. The microkinetic model used includes catalyst descriptors, directly related to physical and chemical properties of the catalyst in interaction with the reactive species. The catalyst descriptors allow extraction of fundamental kinetic knowledge and a rational optimization of the catalyst behavior in terms of activity, selectivity or yield.

P96
(224)

At Time-resolved spectroscopic and steady-state catalytic analysis of coke formation during methanol functionalization over molecular sieves

E.V. Kondratenko[1], D. Linke[1], and C. Ferrini[2]
Leibniz Institute for Catalysis at the University of Rostock, Albert-Einstein-Str., 29A, 18059 Rostock, Germany
evgenii.kondratenko@catalysis.de

Methanol conversion to dimethyl ether (DME) and to olefins (MTO) over SAPO-34 has been investigated under industrially relevant conditions with simultaneous time-resolved in situ UV/Vis catalyst characterization during the reactions and oxidative regeneration. Depending on reaction temperature and time on stream, the spectrum of products is changed from DME to olefins and back to DME. The nature of carbon-containing species depends also on these process characteristics. Coke formed below 260°C is easily oxidized below 400°C, while the coke formed during MTO is oxidized at higher temperatures and should be of aromatic and polyaromatic/graphitic nature.

P194
(259)

In situ ESR, XRD/GC-MS Study of Oxidative Conversion of Methane over $YBa_{2-x}Sr_xCu_3O_{7-\delta}$

E. Ismailov, G. Martinova, Y. Abbasov, M. Maharramov R. Zarbaliyev, H. Alimardanov, S. Abasov, M. Rustamov
Scientific Research and Project Institute of Oil an Gas, State Oil Company of Azerbaijan
Institute of Petrochemical Processes of ANAS, Baku, Azerbaijan, e-mail: *mammad-maharramov@rambler.ru*

ESR, XRD technique in combination with GC/MS are used to examine the copper state, phase transitions and gas phase products in the reaction of methane with $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ ceramics at the temperature 423–973°K. The formation of CO and CO_2 as the major products and small amount of C_2 hydrocarbons (ethane + ethane) is shown. The increase of C_2–selectivity of oxidative conversion of methane over $YBa_{2-x}Sr_xCu_3O_{7-\delta}$ samples after interaction of CH_4 with the samples under UV–irradiation is established and the lattice oxygen in the form O- of the chain –Cu-O-Cu-as the active centre of the oxidative conversion of methane to C_2 hydrocarbons is suggested.

P195
(266)

Partial oxidation of methane to oxygenate compounds

L. Travalloni, A.B. Gaspar, **M.A.P. da Silva**
Escola de Química/UFRJ, Centro de Tecnologia, Bloco E, Ilha do Fundão, Rio de Janeiro, RJ, 21949-909, Brazil,
Tel. (+55)(21)2562-7419, Fax (+55)(21)2562-7637, e-mail: *monica@eq.ufrj.br*

Catalysts of Fe incorporated in ZSM-5 or MCM-41 by hydrothermal synthesis or wet impregnation were prepared. Catalysts were characterized by XRD, TGA, XRF, DRS, TPR-H_2, N_2 physisorption, FTIR of adsorbed pyridine, and evaluated for their performance in methane partial oxidation (CH_4/O_2 molar ratio of 6) at atmospheric pressure and 200-700°C. The main reaction product was CO_x, but traces of oxygenate compounds and hydrocarbons were also detected. The MCM-41 based catalysts provided the largest formation of formaldehyde, probably due to a higher density of isolated Fe^{3+} species.

P196
(270)

Partial oxidation of propane-butane to acetone and acetaldehyde

S.A. Tungatarova, K. Dossumov, B.K. Massalimova
D.V. Sokolsky Institute of Organic Catalysis and Electrochemistry, 142, D. Kunaev str., Almaty, 050010, Kazakhstan.
tungatarova58@mail.ru

Oxidative conversion of liquefied oil gas (propane-butane mixture) by air into O_2-containing compositions was carried out in reaction mixtures with the maintenance of propane-butane from 14 up to 80 % and oxygen from 4 up to 18 % at T = 300-600°C and W = 330-15000 h-1. Investigation of 1, 5 and 10% MoCrGa/NWC has shown that 5% sample is active in forming of ketones (acetone, methyl ethyl ketone), 10% - acetaldehyde and 1% - ethylene. 50,9% of acetone was produced on 5% MoCrGa/NWC catalyst at 550oC, W = 450 h^{-1}, C_3-C_4:O_2:N_2:Ar = 5:1:4:5. 41,0% of acetaldehyde - on 10% MoCrGa/NWC catalyst at 450°C, W = 450 h^{-1}, C_3-C_4:O_2:N_2:Ar = 5:1:4:5.

P197
(285)

Characterization of $H_{3+x}PMo_{12-x}V_xO_{40}$ heteropolyacids supported on mesoporous molecular sieve hms and their catalytic performance in propylene oxidation

S. Benadji, P. Eloy, A. Leonard, B.L. Su, K. Bachari, C. Rabia and E.M. Gaigneaux
Laboratoire de Chimie du Gaz Naturel, Faculté de Chimie, Université des Sciences et de la Technologie Houari Boumediene
(U.S.T.H.B.), B.P: 32 El-Alia, 16111 Bab-Ezzouar, Alger, Algeria, e-mail: *c_rabia@yahoo.fr*

Keggin heteropolyacids (HPAs), $H_{3+x}PMo_{12-x}V_xO_{40}$ with x = 0–3 (10–50wt.%) were supported on mesoporous HMS by dry impregnation method and characterized by XRD, FT-IR, DRIFT, Raman, XPS, nitrogen physisorption and TG-DTA and tested in the propylene oxidation reaction by molecular oxygen at 350°C. The HPAs species have been found to be finely dispersed on HMS in form ($\equiv SiOH_2^+$)($H_{2+x}PMo_{12-x}V_xO_{40}^-$). HPA/HMS catalysts appear more active and selective in propylene oxidation compared to the bulk heteropolyacids.

Keywords : Heteropolyacid (HPA); Mesoporous materials; Propylene oxidation, Spectroscopies.

P198
(303)

LSCF 6428 hollow-fibre membrane for the production of syngas through the partial oxidation of methane

Luiz Carlos L. Santos[1], C. Moraes[2], R. Hughes[3], Ian S. Metcalfe[4]
[1]Federal University of Bahia, Escola Politécnica, DCTM, Rua Professor Aristides Novis 02, 3º Andar, Federação, CEP 40210-630, Salvador/BA, Brazil. *lclsantos@ufba.br,* [2]Federal University of Rio de Janeiro, DEQ Av Horácio Macedo 2030, Rio de Janeiro/RJ, Brazil, [3]University of Staford, Greater Manschester, M5 4WT, UK, [4]School of Chemical Engineering and advanced Materials, Newcastle University, NE1 7RU, UK

A ceramic membrane reactor operating at high temperatures (> 650°C) was used to study the syngas production of the LSCF 6428 hollow-fibre membranes. The experiments were done by using air and a mixture of 5% methane diluted in helium as inlet gases in a co-current flow. The results showed that by using 5% methane diluted in helium the main reaction is the total oxidation. This was probably due to the high oxygen content, supplied by the membrane, related to methane. It was also observed that although the LSCF 6428 presents some catalytic activity, a catalyst might improve the partial oxidation reaction.

P199
(309)

A novel three step low temperature method for direct and selective conversion of methane into methanol

M. Stratmann, P. Yang, C.B. Schneider, C. Breitkopf, **R. Olindo**, J. A. Lercher
Technische Universität München, Department of Chemistry, Lichtenbergstr. 4, 85747 Garching, Germany, *roberta.olindo@mytum.de*

A method for direct and selective conversion of methane into methanol has been successfully developed and optimized in laboratory scale. Methanol is obtained in the gas phase with selectivity reaching 100% under optimized conditions. Methane, oxygen and water are the only reactants used and mild operative conditions are involved. The process is catalyzed by redox metal-exchanged zeolites following a Mars-van-Krevelen mechanism. A proposal for the active species has been formulated and a mechanistic route suggested.

P200
(310)

Nanometric ZrO_2-CeO_2 Catalyst Doped with Ca for the Oxidative Dehydrogenation of Ethane with CO_2

P. Navarro[1], A.P. de Melo Monteiro[2], A. Gómez[3], V. Cortés Corberán[1].
[1]Institute of Catalysis and Petroleumchemistry (ICP), CSIC, Madrid, Spain. e-mail: *vcortes@icp.csic.es*
[2]Institute of Chemistry, Federal University of Bahia (UFBA). Salvador, Bahia, Brazil.
[3]Institute of Materials Science of University of Valencia (ICMUV), Valencia, Spain

The oxidative dehydrogenation of ethane (ODE) with CO_2 is a potential direct way to produce high purity ethene. We study here the effect of calcium incorporation into $(Zr_{0.7}Ce_{0.3})_{1-x}Ca_xO_2$ solid solution catalysts, prepared by the freeze-drying method, on their performance for this reaction. The nature of the products (CO , C_2H_4, H_2O and traces of CH_4) involves two catalytic reactions: ODE to ethane and ethane oxidation to CO. The incorporation of Ca atoms into the ZrO_2-CeO_2 network reduces surface area, does not modify phase composition, but improves both activity and selectivity to C_2H_4, up to an optimum content of Ca (5-10%). The further addition of Ca is detrimental.

P201
(314)

Nickel-iron oxides for methane oxidative transformation

R. Benrabaa, H. Boukhlouf, and A. Barama
Laboratoire des Matériaux Catalytiques & Catalyse en Chimie Organique, Faculté de Chimie, USTHB, BP32 El Alia,
16111 Bab Ezzouar, Alger, Algérie. Fax: 2132124 80 08, *a_barama@yahoo.fr*

Activity and selectivity of nano-sized nickel ferrite $NiFe_2O_4$ have been studied for hydrogen and synthesis gas production via the methane oxidative transformation (MOT). The materials were prepared by co-precipitation (CP) and hydrothermal (HT) methods and characterized by XRD, BET, LRS, DSC, FT-IR, TPR and surface acid-base measurements performed by 2-propanol decomposition. HT- $NiFe_2O_4$ sample showed a basic character and a good catalytic performance in MOT at 450°C. The influence of the preparation method, on the catalytic behavior of Ni-Fe samples, is established. The surface acid-base properties seem to play an important role in MOT reactions.

P202
(315)

Production of light olefins from methanol using MeAPSO-34

L. A. Torres, A. B. Gaspar, **M. A. P. da Silva**
Escola de Química, UFRJ, Centro de Tecnologia, Bl.E, Ilha do Fundão, Rio de Janeiro, RJ 21941-909 (Brazil). *monica@eq.ufrj.br*

SAPO-34 and MeAPSO-34 (Me=Ni, Co, Mn, K or Cs) catalysts were synthesized by different techniques and characterized. The effects of using two templates (morpholine and tetraethylammonium hydroxide – TEAOH), temperature, time on stream and WHSV, and the incorporation of metals to SAPO-34 on catalytic performance were analyzed. SAPO-34 based on TEAOH and MnAPSO-34 were the most selective to ethene and propene and more stable at 400°C and at WHSV of 0.94^{h-1}, whereas NiAPSO-34 showed the opposite behaviour. The type of template influences the acid properties and the catalytic performance.

P203
(326)

The nature of active sites in Pt nanoparticles for Propane Dehydrogenation

Jun Zhu[1], **De Chen**[1], Magnus Rønning[1], Yingda Yu[2], Anders Holmen[1]
[1]Department of Chemical Engineering, [2]Department of Materials Technology, Norwegian University of Science and Technology,
NO-7491 Trondheim, Norway. *de.chen@chemeng.ntnu.no*

We have prepared Pt nanoparticles of different size and shape, which have different ratio of surface sites on the surface and varied in the orientations of the surface such as {111} and {100}. The different surface sites of Pt nanoparticles on the activity, selectivity and coking in propane dehydrogenation (DHP) have been investigated. The results indicate that hydrolysis and coking mainly takes place on the low coordinate atoms located at steps and kinks of the Pt nanoparticles, while the dehydrogenation reactions mainly takes place on the facets. Furthermore, the {111} facets have higher propylene selectivity than the {100} facets.

P204
(333)

CH_3OH decomposition and C_2 Formation Over Alkali Promoted Cu-MgO

Shahin Goodarznia, and **Kevin J. Smith**
Department of Chemical & Biological Engineering, University of British Columbia, 2360 East Mall, Vancouver, BC, Canada, V631Z3, e-mail: *kjs@interchange.ubc.ca*

The decomposition of CH_3OH in the presence of CO has been investigated over MgO, Cu-MgO, K-Cu-MgO and Cs-Cu-MgO catalysts. Results revealed that methyl formate was a primary product of CH_3OH decomposition, whereas CO was a secondary product. Although selectivity to C_2 species (ethanol and acetic acid) was low (< 5 C-atom %) at atmospheric pressure, there was an optimum intrinsic basicity (9.5 μmol $CO_2.m^{-2}$) at which the selectivity to C_2 species and methyl formate reached a maximum. The role of catalyst basicity and Cu dispersion on the formation of methyl formate from CH_3OH will be discussed.

P205
(335)

Effect of acid amount on external surface of nano-crystalline ZSM-5 for neat-DTO reaction

Y. Yamazaki, K. Omata, M. Yamada, **A. Muramatsu**
IMRAM Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan, e-mail: *mura@tagen.tohoku.ac.jp*

Recently, the synthesis of light olefins from dimethyl ether (the reaction of Dimethyl ether To Olefin, abbreviated as DTO) on zeolite-catalyst is feasible as an olefin synthesis process. Catalyst lifetime seems shorter due to deposition of coke on catalyst, when dimethyl ether (DME) used us not diluted. So, a noble catalyst stable under neat-DME supply is desired. In the present study, we discussed the desirable characters of ZSM-5 for long catalyst lifetime on neat-DTO reaction. In conclusion, the low amount of strong acid near external surface and small crystalline diameter are important characteristics for long catalyst lifetime.

P206
(342)

Investigation of the supported $H_3PMo_{12}O_{40}$ catalysts of oxidative conversion of alkanes

S.A. Tungatarova
D.V. Sokolsky Institute of Organic Catalysis and Electrochemistry, 142, D. Kunaev str., Almaty, 050010, Kazakhstan.
tungatarova58@mail.ru

Reversible cycle of structural and phase transformations of HPA under influence of environment and temperature at investigation of structural changes of HPA in 30%$H_5PV_2Mo_{10}O_{40}/SiO_2$ and 30%$H_3PMo_{12}O_{40}/SiO_2$ catalysts by TPR TPO, IR, and XRD methods at stages of their step-by-step reduction, subsequent oxidation at 773-1273 K and processing by water (298 K, superheated steam) are demonstrated. Obtained data indicate on lability of HPA/SiO_2 system in oxidation-reduction conditions and influence of water at temperatures close to temperatures of the reaction of partial oxidation and oxidative dehydrogenation of alkanes.

P207
(343)

The acid-catalyzed dehydration of glycerol into acrolein: the control of selectivity with sulphated-zirconia catalysts

F. Cavani, S. Guidetti, L. Marinelli, M. Signoretto
Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna, Italy. *fabrizio.cavani@unibo.it*

Sulphated zirconia catalysts were used for the dehydration of glycerol to acrolein, both in the absence and in the presence of oxygen. It was found that the reaction network includes both parallel and consecutive reactions, leading to acrolein, several C_2 and C_3 by-products, and heavy compounds. The higher selectivity to acrolein was obtained after a careful control of the reaction parameters, e.g., temperature and feed inlet flow. The acidity of the catalyst was affected by the presence of sulphate self-reduction phenomena that preferably occurred under anaerobic conditions with catalysts having the greater amount of S loading.

P208
(344)

Rutile-type Ga/V/Sb mixed oxides, catalysts for propane ammoxidation: the role of catalyst composition on reactivity

F. Cavani, A. Castelli, F. Trifirò
Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna, Italy. *fabrizio.cavani@unibo.it*

Rutile-type Ga/V/Sb mixed oxides were studied as catalysts for the gas-phase ammoxidation of propane to acrylonitrile. The incorporation of V and of excess Sb in the rutile Ga antimonate provided the active sites for an efficient oxidative dehydrogenation of the alkane and for the transformation of the intermediately formed olefin into acrylonitrile. Moreover, the incorporation of V led to the generation of cationic vacancies that play an important role in the activation of the alkane. The best yield to acrylonitrile was shown by the catalyst with composition (atomic ratios) Ga/V/Sb 1/0.4/3.

P209
(345)

Kinetics of Oxidative Coupling of Methane: Towards a Non-Contradictory and Comprehensible Description

V. Lomonosov, Yu. Gordienko, Z. Fattakhova, M. Sinev
ZAO "SCHAG" Company, Arbat Business Center, office 501a, 9 Karmanitskiy per., Moscow 119002, Russia,
vlomonosov@schag.ru

A detailed description of oxidative coupling of methane (OCM) includes several hundred elementary reactions proceeding both in gas phase and on the catalyst surface. Corresponding kinetic schemes are very useful for the studies of reaction mechanism. However, they are hardly applicable to quantitative description and scaling-up of OCM process. On the other hand, an empirical kinetic description may suffer from a poor validity and low predictive power beyond relatively narrow limits of reaction parameters. An approach to non-contradictory description of OCM kinetics is proposed and discussed.

P210
(347)

Highly dispersed Fe_2O_3 on carbon nanofibers for the Fischer-Tropsch synthesis of lower olefins

Hirsa M. Torres Galvis, Johannes H. Bitter, **Krijn P. de Jong**
Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, 3584 CA, Utrecht, The Netherlands.
K.P.dejong@uu.nl

Supported Fe-based catalysts were prepared by means of a colloidal route using carbon nanofibers (CNF) as support. These catalysts were tested in the Fischer-Tropsch reaction under high temperatures (350°C) to direct product selectivity to shorter hydrocarbon chains. At high temperatures, undesired side reactions such as methanation and carbon deposition are favoured. In comparison with bulk iron catalysts, Fe_2O_3/CNF catalysts not only exhibited an enhancement of catalytic activity and stability but also a reduction of the extent of the methanation reaction and higher selectivities towards lower olefins were observed.

P211
(360)

Influence of the preparation method on the catalyst performance of Ni-W-O catalysts in the oxidative dehydrogenation of ethane

J.M. López Nieto, B. Solsona, F. Ivars, A. Dejoz, M.I. Vázquez, P. Concepción.
Instituto de Tecnología Química (UPV-CSIC), Avda. Naranjos s/n, 46022 Valencia, Spain, *jmlopez@itq.upv.es*

Ni-W-O catalysts are active and selective towards ethylene in the oxidation of ethane. At this work several Ni-W-O catalysts presenting a previously optimised composition (Ni/(Ni+W) = 0.3 at. ratio) have been prepared and tested in the oxidative dehydrogenation of ethane. From the results obtained it can be concluded that the preparation method clearly determines the catalytic behaviour of the catalysts. The catalysts have been widely characterized by several techniques and a correlation between the catalytic results and the characterization results has been proposed.

P315
(363)

IR study on the reaction mechanism for the selective oxidation of propane to acrolein over $MoPO/SiO_2$ and $MoPTeO/SiO_2$ catalysts

Xiaodong Yi, Rongchun Li, Hong Ling, Chuanjing Huang, Weizheng Weng, **Huilin Wan**
State Key Laboratory for Physical Chemistry of the Solid Surfaces. Chemistry Department, College of Chemistry and Chemical Engineering, Xiamen University, Xiamen, 361005, P. R. China,
e-mail: *xdyi@xmu.edu.cn* (Xiaodong Yi); *hlwan@xmu.edu.cn* (Huilin Wan)

The effect of Te on the catalytic behavior of $MoPO/SiO_2$ catalyst for selective oxidation of propane to acrolein has been performed. The catalysts have been characterized by BET, XRD, Raman, H_2-TPR, NH_3-TPD, Py-IR and XPS. The surface species formed by adsorption of propene and isopropanol on the catalysts and the transformation of these species at elevated temperature under vacuum or under O_2/He atmosphere were studied by IR spectroscopy. The results showed that the addition of Te to $MoPO/SiO_2$ improved the reducibility of the catalyst and enhanced conversion of propene intermediate to acrolein, thus improving the acrolein selectivity and yields.

P316
(366)

Nonoxidative Conversion of Methane into Aromatic Hydrocarbons on Ag–Mo/ZSM-5 Catalysts

A.V. Vosmerikov[1], V.I. Zaikovskii[2], L.L. Korobitsyna[1], N.V. Arbuzova[1], V.V. Kozlov[1], Ya.E. Barbashin[1] and S.P. Zhuravkov[3]
[1]Institute of Petroleum Chemistry SB RAS, 3, Akademichesky Avenue, 634021, Tomsk, Russia, e-mail: *pika@ipc.tsc.ru*
[2]Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
[3]Research Institute of High-Voltage Equipment, Tomsk Polytechnic University, Tomsk, Russia

The nonoxidative conversion of methane into aromatic hydrocarbons on high-silica zeolites ZSM-5 containing nanosized powders of molybdenum (4.0 wt %) and silver (0.1–2.0 wt %) was studied. Data on the acid characteristics of the catalysts and the nature and amount of coke deposits formed on the surface of the catalysts were obtained using the thermal desorption of ammonia and thermal analysis. The microstructure and composition of Ag–Mo/ZSM-5 catalysts were studied by high-resolution transmission electron microscopy and energy-dispersive X-ray analysis.

P317
(368)

Comparison of J_2 and KBr catalysts for methane oxidation in oleum

B. Michalkiewicz
Institute of Chemical and Environment Engineering, West Pomeranian University of Technology, ul. Pulaskiego 10,
70-322 Szczecin, Poland. *beata.michalkiewicz@zut.edu.pl*

The methane can be transformed to methanol by a new method wherein alcohol is produced via the formation, and subsequent hydrolysis, of methyl bisulfate formed by catalytic oxidation of the hydrocarbon in a oleum. A comparison between J_2 and KBr catalyst of the methane oxidation was described. The influence of methane partial pressure, sulphur trioxide and temperature on the methyl bisulphate yield was investigated. To the best of my knowledge this is a first report on the KBr use as catalyst for conversion of methane to methyl bisulfate in oleum and on the methane oxidation to methyl bisulfate in concentrated sulfuric acid (100 wt%) with J_2.

P318
(409)

Efficient Transformation Of Natural Gas Using Light Gasoline As Co-Reactant Into Aromatic Hydrocarbons On Zn/H-ZSM-11

Oscar A. Anunziata, Andrea R. Beltramone and Froilan A. Luna D'amicis
Grupo de Fisicoquímica de Nuevos Materiales-FRC-UTN, M. López y Cruz Roja Argentina. *oanunziata@scdt.frc.utn.edu.ar*

The catalytic conversion of Natural Gas (NG) to aromatic hydrocarbons, over a Zn/H-ZSM-11 catalyst using Light Gasoline (LG) as co-reactant was studied. The aromatic hydrocarbon (AH) yield reached more than 60 mol% C at 500°C,W/F= $70 g.h.mol^{-1}$ and molar fractions of NG=0.15-0.20. The NG transformation in these conditions, using the methane conversion as reference, was as higher as 50 mol% C, over a Zn/H-ZSM-11 with 2.11 mol of Zn^{2+} per unit cell. The catalytic activity using NG+LG at total pressure of 1 atm over H-ZSM-11 and Zn/H-ZSM-11 catalysts, showed the efficiency of the Zn^{2+} species to make active NG obtaining higher Aromatics production.

P319 (413)

Simultaneous Optimization of Methane Conversion and Aromatic Yields by Catalytic Activation with Ethane

Jorgelina Cussa and **Oscar A. Anunziata**
Grupo de Fisicoquímica de Nuevos Materiales-FRC-UTN, M. López y Cruz Roja Argentina. *oanunziata@scdt.frc.utn.edu.ar*

Response Surface Methodology (RSM) is used to model and to optimize the activation of Methane (C1) using Ethane (C2) as co-reactant into higher hydrocarbons, over Zn-containing zeolite catalyst. The application of this methodology leads a better understanding of the influence of the different factors on two responses simultaneously: C1 Conversion and Aromatic Hydrocarbons Yield. Applying the statistic methodology, the higher levels of the two objective function operation conditions obtained were C1 conversion of 50 mol% C and aromatic hydrocarbons yield of 47.2 mol%.

P320 (438)

The Comprehensive Modification of ZSM-5 for Catalyzing shape-selective Alkylation of Methanol and Toluene to para-Xylene

Zhirong Zhu[1], Can Li[2]
[1]Department of Chemistry, Tongji University, Siping Road 1239, Shanghai 200092, China, e-mail: *zhuzhirong@mail.tongji.edu.cn*
[2]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics ,Chinese Academy of Sciences, 457 Zhongshan Road, Dalian 116023, China.

Zeolite ZSM-5, for catalyzing shape-selective alkylation of methanol and to toluene produce *para*-xylene, was investigated by modification of chemical deposition of silica, loading metallic oxides and nonmetallic oxides. The results show that ZSM-5 modified by silica chemical deposition has better reactive than loading metallic oxides and nonmetallic oxides, due to less lose of acidic sites in ZSM-5 pores. As a result, ZSM-5 modified by both chemical deposition of 8 wt% silica and loading of 4 wt% Fe_2O_3 shows an acceptable stability and 90 % *para*-xylene selectivity under 28 % toluene conversion.

P321
(453)

Effect of operational conditions over methane dehydroaromatization reaction with ru-mo/hzsm-5 catalyst

Valderio O. Cavalcanti-Filho, Mohand Benachour, Cesar A. Moraes de Abreu
Laboratório de Processos Catalíticos, Departamento de Engenharia Química, Universidade Federal de Pernambuco, Rua Prof. Arthur de Sá, S/N, Cidade Universitária, 50.741-200, Recife, PE, e-mail: *mbena@ufpe.br*

Methane direct conversion to valuable liquid products is still recognized as a challenge to catalysis engineering. The last decade has witnessed an increasing interest in methane dehydroaromatization (MDA) over molybdenum supported in zeolites such as HZSM-5, HMCM-49 and HMCM-22. Instead of high selectivity to aromatics, mainly benzene, and hydrogen co-production, this reaction is thermodynamically constrained to conversion as low as 5% at 873K and is severely limited due to heavy coke deposition. In the present work, 0.5%Ru-3.0%Mo/HZSM-5 catalyst was synthesized and an evaluation study of operational variable effects over the methane dehydroaromatization was developed Steady state values of methane conversion, benzene yield, product selectivities and coke composition were quantified.

The catalyst 0.5%Ru-3.0%Mo/HZSM-5 was prepared by wet co-impregnation method with excess of solvent of the ammonium form of the commercial support ZSM-5 (Si/Al =26, 450m^2/g, Zeolyst Int.) using the required amounts of ruthenium chloride ($RuCl_3$) and ammonium heptamolibdate ($(NH_4)_6Mo_7O_{24}.4H_2O$). The catalytic tests were performed in a quartz differential reactor with 8mm inner diameter loaded with ca 1g of the fresh catalyst. All the catalytic tests were developed at 973K, under atmospheric pressure with contact time (τ_W) between 2639 and 5624 g.h/m^3. Feeding methane molar fraction (Y_{A0}) was varied between 0.2 and 0.8. The gaseous reaction products were analyzed by a gas chromatography (Ultra Trace GC, Thermo Corporation) equipped with a six-way heated valve heated and a column Porapak S (4mm x 1m) using a thermal conductivity detector (TCD) and flame ionization detector (FID).

The results of the influence of operational conditions over methane dehydroaromatization using 0.5%Ru-3.0%Mo/HZSM-5 catalyst suggested that: Operations with high contact times promoted increase in methane conversion but disfavoured selectivity to benzene; Feeding methane molar fraction exhibited a minor effect over methane and methane-to-benzene steady-state conversions; Analysis based on coke composition indicated a possible content of polyaromatics, these results occurred in operations with higher contact times and higher hydrogen productions.

P322
(459)

Activity evolution study of the Co-ZSM-5 catalyst in ethane ammoxidation

H. Ben Boubaker and A. Ghorbel
Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis, Campus Universtaire 2092 Tunis, Tunisie. *hbenboubaker@yahoo.fr*

The activity evolution of ethane ammoxidation is studied on Co-ZSM-5 catalysts prepared by impregnation. The catalytic results show an increase of global and acetonitrile activities with time. According to the TPR and the XPS measurements, the transformation of cobalt silicate species to other cobalt species reducible above 900°C could be the reason. Moreover, nitrogen with a considerable amount is detected on the tested Co-ZSM-5 solid.This result suggests the adsorption of a nitrogen compound during reaction. Which may causes the activity enhancement under reaction mixture.

P323 (465)

Ammoxidation of ethylene to acetonitrile over Cr-ZSM-5 catalysts prepared by different methods

F. Ayari[1], M. Mhamdi[1], A.R.G. Ruiz[2], G. Delahay[3], A. Ghorbel[1]
Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis, Campus Universitaire Tunis ElManar 2092 Tunis-Tunisie, *lcmc_fa@yahoo.fr*

Cr-ZSM-5 catalysts prepared by different methods were tested in the ethylene ammoxidation to acetonitrile in the temperature range 425-500°C. Whatever the preparation method, all the catalysts are active and selective toward acetonitrile. Catalyst issued from impregnation using chromium acetate as precursor exhibits the best catalytic activity when compared to other samples. From physico-chemical and catalytic results, it seems that a high oxidation state of chromium is requested in the ammoxidation of ethylene to acetonitrile but Cr_2O_3 enhances the deep oxidation of hydrocarbon to CO_2.

P324 (471)

Methane dehydroaromatization over Mo/HZSM-5 at severe conditions

Y. Xu, Y. Suzuki, **Z.-G. Zhang**
National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki-ken 305-8569, Japan.
z.zhang@aist.go.jp

The methane dehydroaromatization tests in periodic CH_4-H_2 switching operation mode were conducted at the severe conditions of 1073-1173K and 10000 ml/g/h. The results revealed that the reaction at 1123 K provided a relatively higher conversion, larger benzene formation rate, better stability and the highest benzene selectivity as approximately 70%. At 1173 K methane decomposition to carbon became more competitive and accelerated the catalyst deactivation and reduced largely the selectivity to aromatics.

P325 (482)

Fe-doped La_2O_3 catalyst for oxidative coupling of methane

K. Tanaka, **Y. Sekine**, M. Matsukata, E. Kikuchi
Department of Applied Chemistry, School of Science and Engineering, Waseda University,
Okubo, Shinjuku, Tokyo 169-8555, Japan. *ysekine@waseda.jp*

Oxidative coupling of methane (OCM) is attractive for C2 hydrocarbon production from natural gas. We have attempted to develop effective catalysts for the OCM reaction, and found that Fe-doped La_2O_3 catalyst showed higher activity for C2 production. $LaFeO_3$ in the catalyst was associated with effective O_2 activation, and La_2O_3 in the catalyst played an important role for C2 production. Derived from these two phases, Fe-doped La_2O_3 catalyst showed both high O_2 conversion and C2 selectivity. At La/Fe=20, this catalyst exhibited the highest C2 yield due to the most effective balance of $LaFeO_3$ and La_2O_3 in the catalyst.

P326
(486)

Understanding the reactivity of high valence metal oxides

G. Fu, R.M. Yuan, **X. Xu**, **H. L. Wan**
State Key Laboratory for Physical Chemistry of Solid Surfaces; College of Chemistry & Chemical Engineering,

Here, we will establish the structure-function relationship of selective oxidation of light alkane over high valence metal oxides. Our calculations demonstrate that the activation barriers of light alkanes are closely related with the strength of O-H bond, the ΔE_{ST} of M=O as well as HOMO /LUMO gap. However, the reactivity of H_2 does not correlate well with that of alkanes, downplaying the role of H_2 TPR in determining the reducibility of metal oxide. In addition, we show that (2+4) mechanism can be an alternative pathway for the cleavage of the allylic C-H bond. This indicates that more acidic oxide, such as Mo, is a key element for activation of allylic C-H bond.

P327
(496)

Investigation of parameters impacting on oxidative methane coupling over La-Sr/CaO catalysts

L. Olivier, A.C. van Veen, **C. Mirodatos**
Institut de Recherches sur la Catalyse et l’Environnement de Lyon (IRCELYON), UMR 5256 CNRS - Université de Lyon,
2, av. A. Einstein, 69626 Villeurbanne cedex, France. *claude.mirodatos@ircelyon.univ-lyon1.fr*

The direct conversion of methane to C_2-products via oxidative coupling of methane involves a complex network of elementary steps involving homogeneous and heterogeneous reactions. Parameters susceptible to influence performances in this process can be divided into three interconnected categories related to: i) intrinsic catalyst properties, ii) reaction kinetics and iii) reactor dimensioning. To explore all these parameters, a parallel high throughput approach has been followed, with the ultimate objective to establish reliable structure-activity relationships to predict performances from measurable or computable system descriptors.

P328
(500)

Methane valorisation reactions investigated with a novel microstructured reactor

Sylvain Bosquain[1], Louis Olivier[1], Helmut Pennemann[2], André van Veen[1,3], **Claude Mirodatos**[1]
[1]Institut de Recherches sur la Catalyse et l’Environnement de Lyon(IRCELYON), UMR 5256 CNRS - Université de Lyon,
2, av. A. Einstein, 69626 Villeurbanne cedex, France. *claude.mirodatos@ircelyon.univ-lyon1.fr*
[2]Institut für Mikrotechnik Mainz GmbH, Carl-Zeiss-Straße 18-20, 55129 Mainz, Germany
[3]Ruhr-University Bochum, Laboratory of Industrial Chemistry, Office NC 5/69, Universitätsstraße 150, 44780 Bochum, Germany

Direct conversion of methane to added value products like ethylene or methanol is highly desirable to by-pass the costly intermediate syngas production. La-based catalysts were studied in the oxidative coupling of methane using a novel 6-fold parallel microstructured reactor for further process intensification. The reactor configuration was found to affect the catalyst ranking compared to primary screening in a fixed bed reactor. Direct partial oxidation to methanol was also investigated. Both reactions should benefit from this new reactor, which ensures a better heat management (less hot spots) and works more safely due its flame arrestor capabilities.

P329
(506)

Conversion of methane to C_2-hydrocarbons over tungsten oxides

D. Yamaguchi, N. Burke, D. Trimm, **K. Chiang**
Division of Petroleum Resources, The Commonwealth Scientific and Industrial Research Organisation (CSIRO),
Clayton, VIC 3168, Australia, e-mail: *ken.chiang@csiro.au*

Methane (CH_4) coupling reaction was conducted in a fixed bed quartz reactor at 950°C over pure and ZrO_2-modified tungsten oxides. The oxide samples were prepared by urea precipitation. The addition of ZrO_2 effectively contributed to the selective conversion of CH_4 into C_2-hydrocarbons and suppressed the reactions of CH_4 via oxidation and thermal decomposition pathways. It enhanced the production of C_2H_2 and C_2H_4 yielding a maximum C_2 selectivity of 98 %.

P330
(523)

Catalytic performance of Cu-Fe-pyrophosphates modified by glycols in the direct oxidation of methane to formaldehyde

R. Polnišer, **M. Štolcová**, M. Hronec
Slovak University of Technology, Radlinského 9, 81237 Bratislava, Slovakia, *magdalena.stolcova@stuba.sk*

Cu-Fe-pyrophosphate catalysts synthesized in the presence of triethylene glycol (TEG) by hydrothermal method were tested in the partial oxidation of methane to formaldehyde at atmospheric pressure and in the temperature of 900 K. The XRD analysis confirmed the presence of crystalline $Cu^{II}Fe^{III}_2(P_2O_7)_2$ and $Fe^{II}Fe^{III}_2(P_2O_7)_2$ phases formation in the catalysts. Activity and selectivity of the catalysts is roughly correlated with the presence of crystalline phases and the using of TEG during the catalysts preparation. Over the "$Cu^{II}Fe^{III}_2(P_2O_7)_2$" catalyst modified with TEG the formaldehyde selectivity of 63 % at about 3 % of methane conversion was obtained.

P331
(539)

High porous monolithic alumina and carbon as catalysts for conversion of propane into ethylene

Krasilnikova O.K[1]., Serov Ju.M[2]., Markova E.B[2]., Pogosian A.S.[1]
[1]A.N.Frumkin Institute of Physical Chemistry and Electrochemistry of Russian Academy of Sciences, Leninsky prospect 31, Moscow GSP-1, 119991. Russia, e-mail: *albert-voloshchuk@rambler.ru*
[2]Peoples' Friendship University of Russia, Miklukho-Maklaya str 6, Moscow, 117198. Russia, e-mail: *JSerov@sci.pfu.edu.ru*

The comparison of activity and selectivity of conversion of propane into ethylene for commercial Pt/Al_2O_3, and synthesized in this work porous monolithic alumina (PMOA) and Fe/C are considered. The effect of temperature in range 673 – 1073 K and properties of catalyst on the activity and selectivity were studied and the results were compared with thermal cracking of propane. The activity and selectivity are increased in an orderly sequence – thermal cracking < commercial Pt/Al_2O_3 < Fe/C < porous monolithic alumina (PMOA). The maximum selectivity of ethylene are 62% at 830 K for PMOA and 63% at 890 K for Fe/C catalyst.

P332 (549)

Chloromethane conversion to hydrocarbons over bifunctional metal/silica-alumina catalysts

A L. O. Alcázar R., J. C. Nascimento, J. A. C. Ruiz, J. F. de Sousa
A CTGAS-ER, Av. Capitão Mor Gouveia 1480 – Lagoa Nova, Natal RN. CEP 59063-400. *leopoldo@ctgas.com.b*

Amorphous silica alumina support modified by metals (Zn, Cr) were tested in the reaction of chloromethane condensation. TPD studies for chloromethane were also performed. Oxide end reduce metal material s were tested. Activity was observed in the range of 623 a 673 K. Above coke production is promoted. The materials shown inactive at low temperatures. The materials that presented the strongest adsorption bonding with chloromethane showed to be the more active. Amorphous silica alumina can be used to activate chloromethane tunning certains parameters as adsorption activation energy.

P333 (557)

Conversion of individual components at oxidation of complex hydrocarbon mixtures

Fokin I.G., Arutyunov V.S., Rudakov V.M., Savchenko V.I.
Institute of Problems of Chemical Physics, Russ. Acad. Sci., Chernogolovka, Moscow region, 142432, Russia,
ilia@icp.ac.ru

Direct oxidative conversion of oil associated gas into more valuable and easily transportable products is a very promising route to stop its flaring. But due to the significant difference in reactivity of individual hydrocarbons and intensive interconnection between stable and unstable products during oxidation, the kinetics and products yield is a very complex function of gas composition and process parameters. The investigation of high pressure oxidation of mixtures that imitate real hydrocarbon gases lets to obtain dependences of conversion of individual hydrocarbons and the yield of main products on gas composition and process parameters.

P334 (569)

New approach to conversion of natural gas to fuels and chemicals

M. Glushenkov, T. Roestenberg, M. Sprenkeler, **A. Kronberg**
Encontech B.V. CTW/ThW, P.O. Box 217, 7500 AE Enschede, The Netherlands. *a.e.kronberg@utwente.nl*

Theoretically the rapid, near isentropic compression-expansion process is the most energy effective method of gas heating and subsequent cooling. This method is implemented in the pulsed compression reactor which opens new routs to direct non-catalytic conversion of natural gas to ethylene, acetylene and hydrogen and eventually to production of fuels and chemicals. The reactor allows using any energy source such as residual heat, biomass, and solar energy for endothermic methane pyrolysis at temperatures up to 4000 K. The reactor is very attractive as it combines minimal capital/operating costs and the smallest footprint with maximum energy efficiency.

P335
(571)

Methane and Propane Selective oxidation in aqueous media using Fenton like catalysts

C. Espro, S. Marini[1], F. Frusteri[2], S. Perathoner[1] and G. Centi1
[1]Dept. of Industrial Chemistry and Material Engineering, University of Messina,
Via Ferdinando Stagno D'Alcontres, 31, I-98166, Messina, Italy,
[2]Institute CNR-ITAE, Via S. Lúcia 5, 98126, Messina, Italy

This report refers on then recent results of our R&D activity aimed to exploit innovative systems for enhancing the performance of the Fenton catalyst in the selective oxidation of methane and light alkanes. The activity of a series of acid supported catalytic systems, in the selective partial oxidation of methane to methanol, using H_2O_2 (1% vol/vol) as oxidant in presence of Fe^{2+} (10-350 μmol/l) has been evaluated. The immobilization of Fe^{2+} ions on the Nafion/SiO_2 promoter, resulting in a partial heterogenization of the Fenton system, induces a remarkable enhancing effect on reaction rate.

P336
(572)

VOx/SBA15 and VOx/TiO_2/SBA15 catalysts in Oxidative Dehydrogenation of Propane (ODP). A Critical Review and Kinetic Study.

C. Carrero, T. Wolfram, K. Friedel, A. Dinse, O. Ovsitser, R. Schögl, R.Schomäcker
Departament of Chemestry, TU-Berlin, Strasse des 17 Juni 124, D-10623, Berlin, Germany, *asfalteno@yahoo.com*

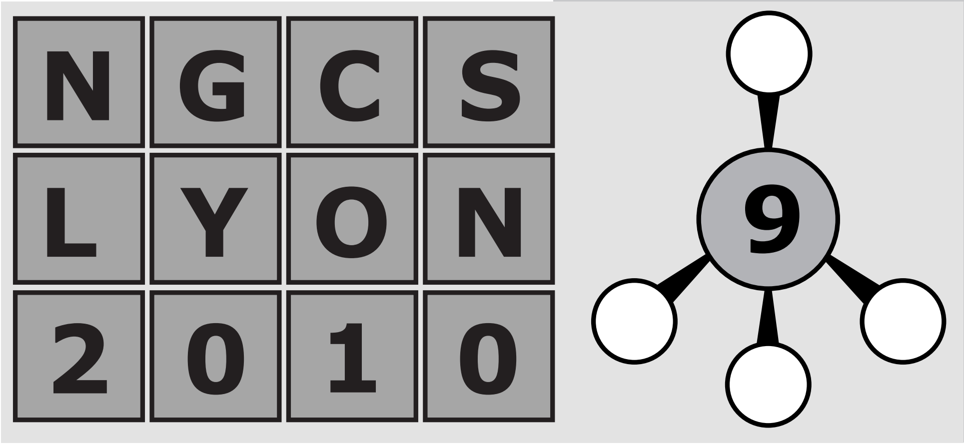
The ODP reaction on a variety of supported vanadia catalysts, and under oxidizing atmosphere, has yielded promising results, but the propylene yield of these processes remains insufficient for industrial application. VOx/TiO_2/SBA15 catalysts have showed excellent catalytic performance for different selective oxidative reactions. In this work, vanadia loaded on SBA15 and TiO_2/SBA15 as supports, have been employed to correlate catalyst structure data with experimental kinetic parameters, thereby attempting to establish a molecular structure-activity-selectivity relationship. Additionally, a critical review was done focused on kinetic parameters.

P337
(576)

Oxygen defect formation in VO_x-catalysts – a support effect

M. Harth, C. Carrero, R. Mitdank, H. Schubert
Institut für Werkstoffwissenschaften und –technologien – Technische Universität Berlin, Englische Straße 20, 10587 Berlin, Germany,
harth@ms.tu-berlin.de

Conductivity measurements via impedance spectroscopic experiments on supported VO_x catalysts for the ODP gave evidence for an oxygen defect formation starting at the onset point of propane conversion. Furthermore, the enthalpy of oxygen defect formation was determined and a strong support effect was found. The enthalpy is connected to the activation energy of propane conversion. Catalysts releasing oxygen more readily exhibit lower propane activation energy. This correlation shows the connection between solid state aspects and catalysis.



Session V - Energy

(IGCC, catalytic combustion, hydrogen production from C_1-C_4 gases) and novel concepts for feedstock activation (plasma, dense membrane, etc)

P97
(32)

Metal oxide redox systems for the production of pure hydrogen from natural gas

D. Trimm, A. Sim and N. Cant
CSIRO Petroleum, Clayton South, Vic 3169, Australia, e-mail: *David.Trimm@csiro.au*

The use of the steam iron redox process for the production of hydrogen from gasified coke is well established. Thermodynamic analyses have suggested that several metal-metal oxide redox couples could be suitable for the conversion of methane to pure hydrogen. Experimental testing has confirmed that ceria-zirconia doped catalysts based on iron and tungsten perform well. Careful control of the oxidation states is essential to avoid sintering and formation of coke and carbon oxides.

P98
(34)

New processes for associated oil gas pre-treatment for its use in gas-fueled piston and turbine engines

Arutyunov V.S., Shmelev V.M., Sinev M.Yu.
Semenov Institute of Chemical Physics, Russ. Acad. Sci., Kosygina 4, Moscow, 119991, Russia. *arutyunov@center.chph.ras.ru*

The new technology aimed at the increase of gas suitability for its utilization in gas-fueled piston engines is suggested. It consists in a non-catalytic selective conversion of heavy C_6+ components of associated oil gas. The process is based on the difference in reactivity of various hydrocarbons at their homogeneous oxidation. For gas turbine engines the conversion of associated oil gas into syngas by direct partial oxidation in 3D matrix burners is more preferable. The same process can be applied to low-scale production of syngas or (if coupled with water-gas shift reaction and CO_2 sequestration) hydrogen.

P99
(49)

Hydrogenation of Succinic acid to 1,4-Butanediol over Heterogeneous Copper-based Catalysts

Young-Moo Park1, Sang-Ho Chung[1], Hee-Jun Eom[1], Min-Sung Kim[1], Yoon-Ki Hong[1], Kwan-Young Lee[1]
[1]Department of Chemical and Biological Engineering, Korea University, 5-1, Anam-dong, Sungbuk-ku, Seoul 136-701, Korea.
kylee@korea.ac.kr

1,4-Butanediol produced by hydrogenation of succinic acid has become more attractive recently because of its environmental benefits and the fact that it is made from renewable resources. In this work, the production of 1,4-butanediol from succinic acid has been developed in liquid-phase reaction medium by heterogeneous copper-based catalysts. By comparing the activities of the several copper-based catalysts, we developed CuZn/MCM-41 catalyst as a highly active for the reaction. The characterization of copper-based catalysts was performed by XRD, TEM, ICP, BET and XPS analysis.

P100
(56)

Selective oxidation of methanol to hydrogen over gold catalysts promoted by alkaline-earth-metal and lanthanum oxides

B. P. C. Hereijgers and B. M. Weckhuysen
Inorganic Chemistry and Catalysis group, Sorbonnelaan 16, 3508 TB Utrecht, the Netherlands. *b.p.c.hereijgers@uu.nl*

The partial oxidation of methanol to CO-poor hydrogen for fuel cell application was studied over gold-based catalysts. Promoting alumina supported gold catalysts with alkaline earth metal and lanthanum oxides significantly improved the selectivity towards hydrogen and CO_2 and suppressed undesired side reactions and CO-formation. Superior results were obtained using a Au/La_2O_3 catalyst, yielding 80% H_2 selectivity, with a CO-formation as low as 2.1%. It is proposed that the acid/ base properties of the support are crucial in directing the gold-catalyzed oxidation reaction.

P101
(70)

Steam Reforming of DME over a Mixed Catalyst of γ-Al_2O_3 and CuO/CeO_2 Prepared by Urea Combustion

Xiaoyan Zhou, Xingang Li, **Ming Meng**
Tianjin Key Laboratory of Applied Catalysis Science and Engineering, School of Chemical Engineering and Technology,
Tianjin University, Tianjin 300072, P. R. China. *mengm@tju.edu.cn*

Recently, dimethyl ether (DME) is considered as an ideal carrier for hydrogen. In this work hydrogen production from steam reforming (SR) of DME was tested over CuO/CeO_2+γ-Al_2O_3. The catalyst CuO/CeO_2 was prepared by two different methods of urea combustion (UC) and coprecipitation (CP). The catalyst prepared by UC exhibits much higher DME conversion, H_2 yield and CO_2 selectivity than that prepared by CP. The particle size of copper species seems not related to the catalytic performance, while the contents of surface reducible copper species and surface adsorbed oxygen species are the determining factor on the DME SR activity of the catalysts.

P102
(73)

Hybrid Catalytic Combustion for Radiant Gas Burners

S. Cimino, G. Russo, C. Accordini and G. Toniato
Istituto Ricerche sulla Combustione – CNR – P.le Tecchio 80 Napoli –Italy. *stefano.cimino@cnr.it*

A prototype hybrid catalytic radiant gas burner suitable was developed based on the novel concept of rich-catalytic homogeneous combustion with interstage heat removal. An extensive experimental campaign was carried out to characterize of the operating features of the prototype burner with special focus on the catalytic partial oxidation reactor which simultaneously acts as a radiant element. Methane combustion tests were conducted also in direct comparison with two low-NOx forced air commercial systems. The novel burner shows improved performance with regards to heat transfer efficiency, pollutants emissions, stability, rangeability and safety of operation.

P103
(90)

A Novel Approach to the Synthesize of Highly Selective Pt /Mg(Al)(Ga)O and Pt /Mg(Al)(In)O Catalysts for H_2 and Alkene Production by Alkane Dehydrogenation

P. Sun, G. Siddiqi, **Alexis. Bell**
Department of Chemical Engineering, UC Berkeley, Berkeley, CA 94720, USA, *bell@cchem.berkeley.edu*

Modified platinum dehydrogenation catalysts are achieved by an innovative synthesis, combining support preparation with modifying element addition. Impregnation of Pt onto the support creates a catalyst with excellent activity, selectivity and stability for the dehydrogenation of ethane and propane. The catalyst properties are a function of Ga/Pt or In/Pt ratio. The characterization of the metallic phase by EXAFS and STEM confirms the presence of Pt-Ga and Pt-In alloys, which are hypothesized to be the cause of the high alkene and hydrogen production and selectivity.

P104
(105)

Catalytic conversion of methane for hydrogen and carbon production

K. L. Salipira, P. Ndlovu, **M. S. Scurrell** and N. J. Coville
Molecular Sciences Institute, School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa.
Michael.scurrell@wits.ac.za

Three different approaches have been used for the decomposition of methane : Thermal decomposition,, floating catalyzed methods, in which decomposable organometallic compounds are introduced into a hot zone with the methane, and heterogenously catalyzed systems in which the methane decomposition takes place on an appropriate solid surface. The carbons obtainedd have been characterized.

P105
(118)

Optimization of the preparation method of a bifunctional Cu and a modified ZSM-5 zeolite catalyst for dymethyl ether steam reforming

J. Vicente, A. Remiro, B. Valle, J. Ereña, A.G. Gayubo
Dpto. Ingeniería Química, Universidad del País Vasco, Apartado 644, 48080 Bilbao, Spain

Steam reforming of dimethyl ether was carried out over bifunctional catalysts ($Cu/ZnO/Al_2O_3$ and HZSM-5 zeolite modified by moderate alkaline treatment) prepared by different methods. A catalyst prepared by wet physical mixture (suspension) containing equal mass amount of the metal and acid functions produces high hydrogen production and selectivity (0.71 mol H_2 (respect to the stoichiometric value) / mol DME_0 and 95 %, respectively) and has good stability for DME SR. Lower activity for H_2 production is obtained by impregnation and coprecipitation methods, due to an inappropriate incorporation of the metal phase and to a lower copper dispersion.

P106
(131)

Hydrogen production via oxidative steam reforming over Ir/CeO_2 catalysts: influence of particle sizes

Weijie Cai[1,2] , Fagen Wang[1], Tana[1], **Wenjie Shen**[1], C. Mirodatos[2], A.C. Van Veen[2], H. Provendier[2]
[1]State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China.
shen98@dicp.ac.cn
[2]University of Lyon; Institut de Recherches sur la Catalyse et l'Environnement de Lyon (IRCELYON, UMR 5256, CNRS;
Université Claude Bernard Lyon 1), 69626 Villeurbanne Cedex, France

The catalytic activity of ethanol reforming strongly depends on the interaction between Ir particles and ceria support, which is determined by the ceria particle size. The catalyst with ceria size of 6-8 nm exhibited the strong metal-support interaction and resulted in the promising activity and stability. When ceria size was larger than 20 nm, large amounts of coke was formed on the catalysts. It seems that ceria particle in the range of 6-10 nm provides a sufficient Ir-CeO_2 interfacial perimeter, which favors activation of water and/or oxygen and transfer of oxygen species to Ir particles, promoting carbon removal.

P107
(137)

Effect of the zirconium precursor nature on the behaviour of Pd/Al_2O_3-ZrO_2 catalysts in methane combustion

C. Amairia, S. Fessi, A.Rîves and A. Ghorbel
Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis,
Campus Universitaire 1092 Tunis, Tunisie.
[2]Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181 USTL - Bâtiment C3, 59655 Villeneuve d'Ascq Cedex - France

In recent years, Al_2O_3-ZrO_2 based materials have been employed as catalysts in numerous catalytic applications. In this work, we are interested in the preparation of Pd/Al_2O_3-ZrO_2 via sol gel method as an attractive route to control the properties of mixed oxides to be tested in methane combustion. We are particularly focused in the study of the effect of the zirconium precursor used to promote Pd/Al_2O_3 system with Zr. For this aim, $Zr(OC_4H_9)_4$ and $Zr(C_5H_7O_2)_4$ have been used to have Zr loading between 2 and 15 wt.-%. N_2 physisorption, H_2 chemisorption, NH_3 TPD, Scanning Electronic Microscopy (SEM) and XRD are the main techniques used.

P108
(139)

Decomposition of ethanol and methanol over tungsten carbides supported by carbon Norit

Ákos Koós, Aleksander Széchenyi and **Frigyes Solymosi**
Reaction Kinetics Research Group, Chemical Research Centre of the Hungarian Academy of Sciences, Department of Physical
Chemistry and Materials Science, University of Szeged, P.O.Box 168, H-6701 Szeged, Hungary, *fsolym@chem.u-szeged.hu*

The primary aim of this work is to synthesize a new active and stable catalyst for the production of hydrogen from alcohols. W_2C was prepared by the reaction of WO_3 with carbon Norit in the presence of hydrogen. XPS studies revealed that the formation of W_2C started above 873 K and completed at 1073 K. The dehydrogenation of ethanol over 5% W_2C/Norit reached a conversion of 90% at 723 K. The yield of H_2 formation was 35%. The conversion of methanol decomposition on this catalyst was 90% at 823 K with a ~90% selectivity of H_2. The W_2C/C catalyst exhibited a high stability.

P109
(141)

Ethanol reforming in a microreactor: heat effects and production rate

A.M. Anzola, Y. M. Bruschi, N. S. Schbib, M. N. Pedernera, D. O. Borio
PLAPIQUI (UNS-CONICET), Camino La Carrindanga Km. 7, 8000 Bahía Blanca, Argentina.
aanzola@plapiqui.edu.ar

Hydrogen production from ethanol steam reforming over catalytic washcoated microreactors is an efficient process in terms of the high heat requirements. The simulation of a microreactor is carried out using a 1-D mathematical model. The system can be represented by foils through which the reactant mixture and flue gas flow alternatively. The hydrogen production rate and the thermal effects are studied for both diluted and concentrated reactant feeds. For the case of concentrated feed streams, the temperature drop along the microchannels limits the hydrogen production rate.

P110
(143)

Preferential CO Oxidation over Ru Catalysts Supported on Alumina with Different Crystalline Phases

Yun Ha Kim, **Eun Duck Park**
Division of Energy Systems Research and Division of Chemical Engineering and Materials Engineering, Ajou University,
Wonchun-Dong Yeongtong-Gu Suwon , 443-749, Republic of Korea. *edpark@ajou.ac.kr*

We prepared Ru catalysts supported on alumina with different crystalline phases such as α-Al_2O_3, κ-Al_2O_3, γ-Al_2O_3, η-Al_2O_3, δ-Al_2O_3 and θ-Al_2O_3 with an incipient wetness method and applied them to the PROX in a hydrogen-rich stream. Among them, Ru/ α-Al_2O_3 showed the highest CO conversion especially at low temperatures. Several measurements: BET, ICP-AES, XRD, the CO chemisorptions, TPO, TPR, TPD of CO_2 with mass spectroscopy and TEM were conducted to characterize the catalysts. Ru/α-Al_2O_3 can reduce the high inlet CO concentration to be less than 10 ppm even in the presence of H_2O and CO_2 over a wide temperature range.

P111
(162)

Catalytic combustion of methane over thermally stable $La_xSr_{1-x}MnAl_{11}O_{19}$ in simulated PSA tail gas

S. Kim, J. Y. Lee, H.-J. Eom, H. J. Lee, D.-W. Lee, M.-J. Kim, **K.-Y. Lee**
Chemical and Biological Engineering, Korea University, Seoul, Republic of Korea, *kylee@korea.ac.kr*

To operate the integrated systmes efficiently which have PSA unit, PSA tial gas, containing CH_4, H_2, CO, H_2O and CO_2, is used as a fuel. Catalytic combustor was applied because of two reasons, low Nox emmision and high fuel efficiency. La-Sr-Mn hexaauminate was synthesized by $(NH_4)_2CO_3$ co-precipitation method after calcinations at 1200°C for 5 h. Partial substitution of Sr in Mn-substituted La-hexaaluminate increased the surface area 25 m^2/g and 23 m^2/g in case of x= 0.8, 0.6. Under simulated PSA tail gas condition, $La_{0.6}Sr_{0.4}MnAl_{11}O_{19}$ performed good oxidation ability for methane and had a good thermal stability.

P112
(168)

Catalytic oxidation of liquid and gaseous fuels on ceramometal-based catalytic packages with fluidized heat transfer material

N.A. Yazykov, A.D.Simonov, **S.F.Tikhov**, V.V.Usoltsev, R.V.Bunina, V.A.Sadykov, V.N.Parmon
Boreskov Institute of Catalysis SB RAS, av.Lavrentieva, 630090, Novosibirsk, Russia, *tikhov@catalysis.ru*

The reactions of catalytic oxidation of diesel oil, octane and methane on the porous FeAl and CrAl-based cermet catalysts with CuO as active component were studied. These cermets have hierarchical porous structure with mesoporous alumina encapsulated in utramacropores and high attrition resistance.The increase of alumina content in the cermet support improves performance due to increase of CuO content in the catalysts. These cermet catalysts shaped as honeycombs with large channels are promising for the fuel combustion in a fluidized bed of inert materials transferring heat from the catalyst to the heat exchanger.

P113
(170)

Foam-supported catalysts tailored for industrial steam reforming processes

Faure, R., Basile, F., Bersani, I., Chartier, T., Cuni, A., Cornillac, M., Del Gallo, P., Etchegoyen, G., Gary, D., Rossignol, F., Vaccari, A.
SPCTS, UMR CNRS 6638, ENSCI, 47-73 avenue Albert THOMAS, 87065 Limoges, France. *raphael.faure@etu.unilim.fr*

Our work is focused on the elaboration of foam-supported catalysts for steam reforming processes (ESR, SMR). Considering industrial requirements (temperature, pressure, hydrothermal atmosphere, catalytic activity) and existing issues of such processes (overheating, pressure drop, catalyst deactivation), catalysts produced must have controlled macrostructures and microstructures. Supports of different sizes and shapes are produced by impregnation of PU foam templates. Ceramic foams produced are coated either with sols or with slurries containing optimized active phases. Catalytic tests are performed on ESR pilots and on industrial SMR units.

P114
(193)

Methane steam reforming behaviour in packed bed membrane reactor at moderate temperature and pressure

Lemnouer Chibane, Brahim Djellouli, François Garin
Laboratoire de Génie des Procédés Chimiques (LGPC), Université Ferhat ABBAS, 19000, Sétif, Algéri. *lchibane@yahoo.com*

Steam reforming of methane was carried out in a reactor containing a hydrogen permeable membrane, made of a thin palladium film supported on porous stainless steel. An isothermal one-dimensional model was developed to simulate the operating parameters in the reactor. The reaction showed some limitations at 500°C in terms of methane conversion and a high H_2/CO ratio. The methane conversion is significantly enhanced by the removal of hydrogen from the reaction side under temperatures: 580-600°C, pressures: 300-600kPa, steam to methane ratio=3 and sweep gas ratio=3. The H_2/CO ratio obtained is satisfactory and highly hydrogen recovery was achieved.

P115
(199)

Propane Combustion over Pt Catalysts Supported on Various Zeolites

Min Kyu Kim[a], Yun Ha Kim[a], Kwang Sup Song[b], **Eun Duck Park**[a]
[a]Division of Energy Systems Research and Division of Chemical Engineering and Materials Engineering, Ajou University, Wonchun-Dong Yeongtong-Gu, Suwon , 443-749, Republic of Korea.
[b]Korea Institute of Energy Research, 102 Gajeong-ro, Yuseong-gu, Daejeon, 305-343, Republic of Korea. *edpark@ajou.ac.kr*

We prepared Pt catalysts supported on various zeolites such as H-ZSM-5, Na-ZSM-5, H-mordenite, Na-mordenite, H-ferrierite, H-Y, Na-Y and H-BEA and applied them to the propane combustion. Pt catalysts prepared from $Pt(NH_3)_4(NO_3)_2$ had higher activity than that from H_2PtCl_6. Among the supported Pt catalysts, Pt/H-BEA showed the highest catalytic activity for propane combustion. The catalytic activity of H-ZSM-5 increased with increasing SiO_2/Al_2O_3 ratios and reached the maximum value at SiO_2/Al_2O_3 ratio of 150 and decreased with further increasing SiO_2/Al_2O_3 ratios.

P116
(202)

Influences of CaO-Al_2O_3 Interaction on Coke Resistance of CaO Modified Pt/Al_2O_3 Catalyst

Jiafeng Yu, **Qingjie Ge**,, Wen Fang and **Hengyong Xu**,
Laboratory of Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
xuhy@dicp.ac.cn (Xu); *geqj@dicp.ac.cn* (Ge)

Influences of CaO-Al_2O_3 interaction on catalyst coke resistance were studied by adjusting calcination temperatures. The catalyst calcined at 600°C exhibits the worst, while the one calcined at 800°C shows the best coke resistance among the catalysts calcined at different temperatures. High activity (86 %) and high stability for cyclohexane dehydrogenation during 220 h investigation are obtained. This is attributed to strong Ca-Al interaction and relatively large CaO particles, which lead to more dispersed Pt and larger amount of spilt-over H_2. Models of Ca-Al interactions are established, exhibiting the variations of CaO particles and the formation of calcium aluminates.

P117
(213)

CuO/CeO_2 catalysts for PROX reaction: synthesis and characterizations

L. S. Neiva[1], M. A. Ribeiro[1], **L. Gama**[1]
[1]Federal University of Campina Grande, Academic Unit of Engineering Materials, Avenue Aprígio Veloso – 882, Bodocongó, 58109 – 970, Campina Grande – PB, Brazil, e-mail: *lucianna@dema.ufcg.edu.br*

This work report the development of CuO/CeO_2 catalysts to be applied in to reaction of preferential oxidation of CO (PROX). The CuO/CeO_2 catalysts was synthetized by means combustion reaction method and also by Pechini method. The CuO/CeO_2 catalytic systems was characterized by XRD, SEM, textural complete analysis by BET method, size agglomerates distribution analysis and was also characterized by test catalytic in the preferential oxidation of CO in H_2 rich streams was tested in the 75-180°C temperature range.

P118
(217)

A model of rinsing solvent influences on NiO for methane decomposition to carbon nanofibers

Wei Zhang, **Qingjie Ge**, and **Hengyong Xu**
Laboratory of Applied Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China
Tel: 86-411-84581234 (Xu); 86-411-84379229 (Ge); *xuhy@dicp.ac.cn*; *geqj@dicp.ac.cn*

Effects of NiO preparation conditions on methane decomposition have been investigated in this study. Rinsing solvents played crucial roles in determining the catalytic properties of the corresponding Ni catalysts. Models for elucidating the effect of rinsing solvents on the morphology of NiO samples were proposed. Ni catalyst could exhibit a good methane decomposition performance at 500°C with GHSV of 45,000 mL/ (gcat h). Reduction temperature had a limited effect on the activity Ni catalyst toward methane decomposition. Graphitic carbon in deposited carbon nanofibers would increase with the time of methane decomposition.

P119
(221)

Chemical CO_2 Valorization: CO_2 to Methanol

Veronika Gronemann, Marius Hackel, N.N., **Martin Rothaemel**
Lurgi GmbH, Lurgiallee 5, 60439 Frankfurt (Germany)

An interesting approach to mitigate the increasing CO_2 concentrations in the atmosphere is the chemical valorization of CO_2 by conversion into methanol. First studies appeared in the mid-90s; however, this technology lay dormant in the years after. New tests were carried out by Lurgi in a polytropic fixed-bed reactor revealing that very high CO_2 conversions (>95%), stable catalyst operation and very high crude methanol purity (lower distillation effort) can be achieved.

P120
(229)

Combined Experimental and Theoretical Investigation of the CO_2 Adsorption on $LaMnO_{3+y}$ Perovskite Oxide

Ramzi Hammami[1,2], Habib. Batis[2], Christian Minot[1]
[1]Laboratoire de Chimie théorique, Université Pierre & Marie Curie, Paris 6, CNRS, UMR7616, Case 137,
4 place Jussieu, Paris, F-75252 Cedex France
[2]Unité de Recherche d'Elaboration de Nanomatériaux et leurs Applications (URENMA), Faculté des Sciences de Tunis,
Campus Universitaire-2092 ManarII, Tunis, Tunisia

The surface interaction of CO_2 with perovskite-type oxide $LaMnO_{3+y}$ has been investigated by means of density functional theory calculations and experimental measurements of adsorption isotherms in the temperature range 298-473K. A (100) oriented slab of the cubic structure was used for modeling CO_2 adsorption. Analysis of isosteric heat revealed an energetically heterogeneous character for the surface. Considering theoretical calculations and thermodynamical approaches, two types of active sites were found to be responsible for irreversible and reversible adsorption of CO_2 as a function of surface coverage and O_2 treatment.

**P212
(238)**

Water assisted synthesis of single-walled carbon nanotubes over Co-Mo/MgO catalysts

G.W. Wang, **Y.D. Li**
Tianjin Key Laboratory of Applied Catalysis Science and Technology and State Key Laboratory of Chemical Engineering (Tianjin University), School of Chemical Engineering, Tianjin University, Tianjin 300072, China. *ydli@tju.edu.cn*

Water assisted CVD yields pure single-walled nanotube (SWNTs) and is thought to be a milestone towards the production of pure SWNTs with high efficiency. However, the role of water has not yet been fully understood. In this work, we have studied the role of water in the catalytic decomposition of methane over Co-Mo/MgO catalyst in a controlled mixture of CH_4 and Ar. Water vapor was introduced into the reactor by a small part of Ar going through a water saturator. A growth mechanism of CNTs is presented.

**P213
(239)**

The mechanical properties of FeCrAlloy foil used as the monolithic support for catalytic combustion

L.H. Zhang, D. Zhang, **Y.D. Li**
Tianjin Key Laboratory of Applied Catalysis Science and Technology and State Key Laboratory of Chemical Engineering (Tianjin University), School of Chemical Engineering, Tianjin University, Tianjin 300072, China. *ydli@tju.edu.cn*

The mechanical properties and thermal stability of the FeCrAlloy used as the monolithic catalyst support are examined by tensile test, dynamic mechanical analysis (DMA) and thermal shock test. The results show that DMA show clearly the change of the mechanical properties of the alloy with temperature. The plasticity of the alloy is enhanced not only by increasing measurement temperature, but also by rising the oxidation temperature. Those have great significance for the release of the residual stress of the alumina layer on the surface of the FeCrAlloy and improve the thermal stability of the alloy monolithic catalyst.

**P214
(261)**

Energy integration of a sorption enhanced steam reforming process

R. Murillo, T. García, G. Grasa, J.C. Abanades
Instituto de Carboquímica, CSIC, Miguel Luesma Castán 4, 50008 Zaragoza, Spain, e-mail: *ramonm@icb.csic.es*

In this work the energy integration of a sorption enhanced methane steam reforming is described. Hydrogen is produced in a catalytic reactor where the CO_2 is continuously removed from the reforming reaction products by absorption with CaO. This sorbent is produced in a limestone calciner operated under oxy-combustion conditions so that the supply of pure oxygen is necessary to run this reactor. In addition, the generated CO_2 has to be compressed up to the appropriate conditions for permanent geological storage. Therefore, the energy integration of this process is necessary to take advantage of all the energy fluxes and to minimise the CH_4 consumption.

P215 (269)

Ni/Al_2O_3 catalysts: the effect of support promoters on steam and oxidative reforming of methane

T. F.Silva[1], A. F. Lucrédio[2], E. M. Assaf[2], J. M. Assaf[1]
[1]Laboratório de Catálise – Departamento de Engenharia Química – Universidade Federal de São Carlos, Rodovia Washington Luiz, Km 235 13565-905 – Brazil. *tatianaufv@yahoo.com.br*
[2]Universidade de São Paulo, Instituto de Química de São Carlos, CEP 13560-970, São Carlos, SP, Brazil

The catalysts were prepared by wet impregnation on γ-Al_2O_3 with 10% by weight of support promoters (La_2O_3, La_2O_3-CeO_2, La_2O_3-ZrO_2) and 15% Ni. The samples were characterized by EDX, X-ray diffraction, TPR with 5% H_2-N_2 mixture, TPD-H_2, surface area determination and *in situ* Energy-dispersive H_2-TPR/XANES and oxidative reforming/XANES in the Ni K- edge, performed in the transmission mode. All the promoted catalysts showed higher conversions compared to the non-promoted in both the reactions. Through XANES analysis, the NiLaAl catalyst was the only one who did not show oxidation of nickel even with the addition of O_2 in the reaction.

P216 (289)

Methane conversion to hydrogen and carbon nanotubes on Ni/Pt catalysts supported over spinel $MgAl_2O_4$

Giselle De B. Nuernberg[1] , Edson Foletto[2], **Luiz F. D. Probst**[1], Jöel Barrault[3]
[1]Laboratório de Catálise Heterogênea – Dept. de Química, Universidade Federal de Santa Catarina, 88040-900, Florianópolis, SC, Brazil. *luiz.probst@univ-poitiers.fr*

The aim of the present work consists in the study of the catalytic properties of Ni-Pt supported over spinel $MgAl_2O_4$ for the selective conversion of methane into hydrogen and carbon nanotubes. All the samples were characterized from XRD, TPR, BET, SEM, TEM and hydrogen adsorption. The methane conversion was studied in a fixed-bed quartz reactor at 550°C using 100 mg of catalyst with a reactants feed N_2:CH_4 of 7:1 or 2:6 and a total flow of 80 mLmin^{-1}. The addition of a small amount of Pt to a Nickel-$MgAl_2O_4$ catalyst promotes the formation of carbon nanotubes with a significant selectivity to SWCNT.

P217 (311)

Highly active Cu/Ce, Cu/Al and Cu/Ce/Al catalysts for H_2 production via steam reforming of methanol reaction

Mary Mrad, Cédric Gennequin, **Edmond Abi-Aad**, Antoine Aboukaïs
LCE, MREI, F-59140 Dunkerque, France. Cor. author: e-mail : *abiaad@univ-littoral.fr*

The performances of different, Cu/Ce, and Cu/Al pelletized catalysts were investigated in the steam reforming of methanol (SRM). The addition of Cu on CeO_2 and/or Al_2O_3 supports shows better results than in the case of CeO_2 and Al_2O_3 alone. The catalytic activity was found to be strongly dependent on the copper loading and on the nature of the support. Pelletized catalysts show characteristics that permit to avoid its prereductive step. Cu/Ce catalysts with high copper content were evidenced as the most active solids due to a synergistic effect between Cu and Ce. At a low copper content Cu/Ce/Al are more performed catalysts due to the highly dispersed Cu species.

P218
(313)

Fuel Gas Generation from Pyrolysis and Gasification of Crude Glycerol Mixed with Biomass Wastes

V. Sricharoenchaikul and **D. Atong**
National Metal and Materials Technology Center, Thailand Science Park, Pathumthani 12120 Thailand. *duangdua@mtec.or.th*

Thermal conversion of extracted physic nut and palm shell mixed with glycerol waste was carried out using a tubular reactor at 700-900°C. When temperature increased, CO_2 decreased while yields of CO, CH_4 and H_2 increased. Greater conversion to CO_2, CO, H_2 with air factor increased from 0.0 to 0.3. Higher air factor resulted in lesser CO and H_2. C_xH_y decreased when air factor changed from 0.0 to 0.6. The maximum gas LHV's are 3.48 MJ/m^3 and 2.27 MJ/m^3 for glycerol waste mixed with physic nut waste and palm shell waste, respectively. The maximum of mole ratio of H_2 to CO obtained is 0.59 for physic nut and 0.37 for palm shell mixed wastes.

P219
(322)

New calcium-based mixed oxide sorbents for CO_2 capture in sorption enhanced steam methane reforming

Saima Sultana Kazi, Li He,Tiejun Zhao, Siri Albertsen Fagerbekk, Anna Lind, Magnus Ronning and De Chen
Department of Chemical Engineering, Norwegian University of Science and Technology, Sem
Sælands vei 4, NO-7491 Trondheim, (Norway), e-mail: *saima.kazi@chemeng.ntnu.no*

Sorption enhanced steam methane reforming (SESMR) is an alternative to the traditional steam reforming process (SMR) for the hydrogen production from fossil fuels at low temperatures with *in situ* CO_2 capture. Present work aims to develop new calcium based synthetic sorbents and test their stability both in dry and wet conditions. Synthetic mixed oxide sorbents, CaCeZr (10:1:1) and CaZr (8:1) provide stable CO_2 capture capacity in dry condition compared to natural sorbents, such as dolomite. Experiments in real SESMR condition clearly show a significant enhancement of H_2 production and relatively good stability of the CaCeZr sorbent.

P220
(323)

Lanthanum manganites prepared by one-step combustion synthesis: Catalytic performances in deep oxidation of methane

H. Najjar[1,2], H. Batis[2], O. Mentré[1], J.F. Lamonier[1], J.M. Giraudon[1]
[1]Unité de Catalyse et de Chimie du Solide (UCCS), UMR 8181 CNRS - Université des Sciences et de Technologies de Lille,
Cité scientifique, 59655 Villeneuve d'ASCQ cedex, France
[2]Unité de Recherche d'Elaboration de Nanomatériaux et leurs Applications (URENMA), Faculté des Sciences de Tunis,
Campus Universitaire-2092 ManarII, Tunis, Tunisia

The present work deals with the study of physico-chemical and catalytic properties in deep CH_4 oxidation of a series of $LaMnO_3$ perovskite-type prepared by one-step combustion method by varying five glycinel/nitrate ratios (r) from 0.32 to 0.8. XRD patterns show a single phase perovskite type oxide when r is above 0.37. Surface areas in the range of 18-37m^2/g were obtained. Higher SSA values were attributed to powders prepared with rich-fuel conditions. Content of Mn^{4+} was related to the synthesis conditions determined by glycine/nitrate ratios. The activity of these catalysts in term of 50% of methane con version was related to their specific areas.

P221
(324)

Mechanochemical treatment as a method of Cu-based catalyst synthesis for steam reforming of methanol

J. Nizioł, J. Rakoczy, K. Wieczorek-Ciurowa
Faculty of Chemical Engineering and Technology, Cracow University of Technology,
Warszawska 24, 31-155 Cracow, Poland. *jniziol@chemia.pk.edu.pl*

Characterization of catalytic properties of products after 5 and 10 hours milling as the effect of aluminothermic reactions in the CuO-Al system is presented.Catalytic tests were analyzed by a gas chromatographic method. High yield of hydrogen production by steam reforming of methanol using copper-based catalyst has been obtained. The results show also high activity and stability of used CuO-Al system.

P222
(341)

A cycle redox approach for the production of H_2 by methanol reforming over Co/Fe spinel-type mixed oxides: the role of spinel crystallinity on reactivity

F. Cavani, S. Cocchi, M. Comito, S.Passeri
Dipartimento di Chimica Industriale e dei Materiali, Viale Risorgimento 4, 40136 Bologna, Italy. *fabrizio.cavani@unibo.it*

This work reports about a study on the reactivity of spinel-type Co/Fe mixed oxides in methanol reforming under cycle conditions, that is, by alternating the feed of methanol and the feed of steam. During the first step, the spinel is reduced to Co/Fe metallic compound and methanol is oxidized, whereas during the second step, steam oxidizes the solid with production of hydrogen. The effect of spinel crystallinity on the initial (first cycle) reactivity was studied. Moreover, the effect of various reaction parameters on the reduction process and on coke accumulation were investigated, with the aim of finding conditions at which the formation of coke is minimal.

P223
(353)

Steam methane reforming and carbon formation on Ni surface alloying catalysts prepared by surface redox reaction

Anh Hoang Dam, H. M. Wang, Anders Holmen and Chen De
Department of Chemical Engineering, Norwegian University of Science and Technology, N-7491 Trondheim, Norway
anhhoang@chemeng.ntnu.no

The bimetallic Ni(M)/HT catalysts supported on hydrotalcite-like material (HT) were prepared with various M/Ni ratios on the surfaces of Ni nanoparticles (M: Ag, Pt, Pd, Ru, Re, or Rh) using surface redox method which provides a precisely control of the surface composition. Surface alloying of M with Ni influenced both the activity and the activation energy in the CH_4 steam reforming reaction, and these changes were the function of the surface M/Ni ratio. The addition of the second noble metal M significantly suppressed the carbon formation.

P224
(354)

The effects of Pd and Fe added on alumina-supported Pt catalyst for the treatment of diesel exhaust gas

Yeon-Su Kim[1], Yong Kwon Chung[1], Sun Ju Lim[1], Jin Ha Lee[2], **Ho-In Lee**[1]
[1]School of Chemical and Biological Engineering and Research Center for Energy Conversion and Storage,
Seoul National University, Seoul 151-744, Korea
[2]Emission Research Team, Hyundai Eco-Technology Research Institute, Hyundai-Motors Company, Yongin 446-912, Korea
hilee@snu.ac.kr

Catalysts with various weight ratios of Pt to Pd were prepared by incipient wetness method to investigate synergistic effects on the diesel oxidation catalysts. The effect of the Pd addition to the Pt catalyst on the activity was evaluated in a simulated gas mixture of diesel engine. Although 4Pt1Pd catalyst exhibited the lowest light-off temperature due to less phase transition of Al_2O_3 to $Al_2(SO_4)_3$ which blocks the active sites, it showed drastic decreases of CO conversion in some temperature range. Iron was added to the 4Pt1Pd catalyst to have sulfur resistance. Consequently, 2 wt% Fe-added catalyst had a considerably good activity without drastic decrease range.

P225
(357)

Hydrogen production by oxidative steam reforming of n-propanol over new Ni/Y_2O_3-ZrO_2 catalysts

L. Yermán, N. Homs, **P. Ramírez de la Piscina**
Departament de Química Inorgànica and Institut de Nanociència i Nanotecnología, Universitat de Barcelona, Martí i Franquès 1-11,
08028, Barcelona, Spain. *pilar.piscina@qi.ub.es*

Biomass-derived resources can be considered as alternative feedstock for hydrogen production. Alcohols as propanol can be produced from sugary biomass. Catalysts of Ni over Y_2O_3-ZrO_2 with different Y content were prepared and tested in the oxidative steam reforming of propanol. The results contribute to the knowledge of the reforming of C2 to C4 bio-alcohols. All catalysts prepared were active in the reaction, and those supported on the new Y_2O_3-ZrO_2 materials showed less selectivity towards CO than those prepared using commercial supports. This is important for fuel cells applications, where a CO-free hydrogen flow is highly desirable.

P226
(374)

Steady state isotopic transient kinetic analysis of the complete methane oxidation over Pd-Pt/Al_2O_3 catalysts

Marek Rotko, Andrzej Machocki, Beata Stasińska
University of Maria Curie-Skłodowska, Faculty of Chemistry, Department of Chemical Technology, 3 Maria Curie-Skłowska Square,
20-031 Lublin, Poland, e-mail: *marekrotko@poczta.onet.pl*

The methane oxidation on Pd-Pt/Al_2O_3 catalysts was studied by the SSITKA method. The isotopic switches from $^{16}O_2$ to $^{18}O_2$, and from $^{12}CH_4$ to $^{13}CH_4$ were carried out. The average surface life-time and surface concentration of the intermediates leading to the formation of carbon dioxide on the surface of Pd-Pt/Al_2O_3 catalysts prepared by the incipient wetness impregnation (IWI) and by the ion exchange (IE) are different, and also change with temperature. The activity of Pd-Pt-IE and Pd-Pt-IWI catalysts is very similar. However, on the Pd-Pt-IE catalyst there are more intermediates and active centres than on Pd-Pt-IWI catalysts, but the reaction rate is slower.

P227
(380)

Catalytic decomposition of simulated natural gas

I. Suelves, J.L. Pinilla, M.J. Lázaro, R. Moliner, J.M. Palacios
1Instituto de Carboquímica. CSIC. Miguel Luesma Castán 4. 50018 Zaragoza, Spain; *isuelves@icb.csic.es*

In the present work, the decomposition of ternary mixtures of methane-ethane-propane was studied using a $NiCu/Al_2O_3$ catalyst, in order to investigate the effect of the minor hydrocarbons present in natural gas on the catalytic decomposition of methane (CDM). Additionally, the textural and structural properties of the filamentous carbon produced have been studied by means of SEM, XRD and N_2 adsorption.

P228
(382)

Effect of the reduction conditions on Fe_2O_3/MgO and Fe_2O_3/Al_2O_3 catalysts used in the methane decomposition reaction

J.L. Pinilla, R. Utrilla, I. Suelves , M.J. Lázaro,R. Moliner, J.M. Palacios
Instituto de Carboquímica. CSIC. Miguel Luesma Castán 4. 50018 Zaragoza, Spain; *jlpinilla@icb.csic.es*

The Catalytic Decomposition of Methane (CDM) into hydrogen and carbon is an interesting alternative to other conventional hydrogen production methods without CO_2 emissions. The present work deals with the study of the influence of the reduction stage (RP) on the iron oxide based catalysts performance. This reduction stage is necessary to obtain iron reduced species which are catalytically active towards the CDM reaction. The influence of the RP on the resulting iron crystal domain size calculated by means of XRD, and on the hydrogen produced in a typical CDM test, is here presented.

P229
(385)

Steam Reforming of Diesel Fuel over Ca Modified Ni-Based Catalysts

Sojung Kim[a,b], Seung-hwan Lee[a], Byung Gwon Lee[a], **Sang Deuk Lee**[a] and **Dong Ju Moon**[a,b]
[a]Clean Energy Research Center, Korea Institute of Science & Technology, Seoul, Korea,
sdlee@kist.re.kr and *djmoon@kist.re.kr*
[b]Clean Energy & Chemical Engineering, UST, Daejeon, Korea

Steam reforming of n-hexadecane over Ni-based hydrotalcite catalysts were carried out in a temperature range of 700~950°C, at atmospheric pressure with a space velocity of 10,000 h^{-1} and feed molar ratio of H_2O/C in the range of 1.0~3.0. Ni-based catalysts were characterized by N_2-physisorption, TPR, XRD, TEM and SEM techniques. It was found that low concentration **Ca-modified** Ni/MgAl catalyst showed higher catalytic stability and inhibition of carbon formation then the Ni/MgAl under the tested conditions.

P338
(390)

Synthesis and Characterization of Ni Hydrotalcite Catalyst for Hydrogen Production from Steam methane Reforming

Tayyaba Noor[a], Anna Lind[b], Anders Holmen[a], De Chen[a]
[a]Department of Chemical Engineering, Norwegian University of Science & Technology, (NTNU), 7491, Trondheim, Norway
[b]SINTEF, Department of Chemical Engineering, NTNU, Trondheim, Norway
tayyaba.noor@chemeng.ntnu.no

Hydrotalcite is an anionic clay mineral and is a hydroxycarbonate of magnesium and aluminium that occurs in nature containing exchangeable anions. Hydrotalcite have been used as diverse range catalyst for various organic reactions. In addition for reactions like SMR, the hydrotalcite derived catalysts have shown to be more resistant to coke formation and sintering than other alumina supported catalysts. The hydrotalcite has a general formula $[M^{2+}_{n}M^{3+}_{m}(OH)_{2(n+m)}]^{m+}(A^{x-}_{m/x})^{*}\ yH_2O$. Considering Nickel Cobalt hydrotalcite, after calcination the catalyst will consist of CoO /MgO/Al2O that after reduction goes to Co/Ni/MgO/Al_2O_3. It is reduce form which determines the composition of hydrotalcite.

In the present study hydrotalcite catalyst with different Ni loading were prepared by employing three different methods, which are co precipitation, spray drying and microemulsion method and comparative study was made for shape of catalyst, particle size, surface area, prosity.

Later on the catalyst was tested for hydrogen production from natural gas using steam methane reforimg reaction. The catalyst showed high selectivity and reactivity towards hydrogen production reaction.

P339
(404)

Enhanced performance in catalytic combustion of propane and DME over PdO-CeO_2 surface superstructure

S. Colussi, A. Gayen, J.Llorca, A. Trovarelli
Dipartimento di Scienze e Tecnologie Chimiche, Università di Udine, 33100 Udine, Italy. *sara.colussi@uniud.it*

Catalytic combustion is an efficient technology for emission prevention, due to ultra-low NO_x formation, and for exhausts aftetreatment. In this work we compare the catalytic activity of Pd-based catalysts prepared by impregnation or by solution combustion synthesis supported on CeO_2 and Al_2O_3 for the combustion of propane and dimethyl ether. The results strongly suggest a relationship between the presence of a stable, ordered Pd-O-Ce surface superstructure in Pd/CeO_2 catalysts made by SCS and their higher activity for catalytic combustion compared to traditional impregnated samples.

P340
(414)

Steam reforming of methanol over PtInAl catalysts

Y. Men, G. Kolb, R. Zapf, M. O'Connell, A. Ziogas
Institut fürMikrotechnik Mainz GmbH, Carl Zeiss Str. 18-20,D-55129 Mainz,Germany. *men@imm-mainz.de*

A novel PtInAl type catalyst was found to exhibit excellent methanol steam reforming activity, selectivity, and stability. The effect of reaction temperature, metal loading, and space velocity on the methanol steam micro-structured reformer performance is presented in terms of catalytic activity, selectivity, and hydrogen production rate. High CO_2 selectivity has been ascribed to the active PtIn alloy phase. This result demonstrates that the PtInAl catalyst is very efficient and also highly selective and, therefore, is a promising candidate for use in methanol reforming applications.

P341 (415)

Steam Reforming of Glycerol over Ni-Based Catalysts

Eun Hur[1,2], Yun Ju Lee[1], So Jung Kim[1,2], Ji Sik Choi[1] and **Dong Ju Moon**[1,2]
[1]Clean Energy Center, Korea Institute of Science & Technology, Seoul, Korea, *djmoon@kist.re.kr*
[2]Clean Energy & Chemical Engineering, UST, Daejeon, Korea

Steam Reforming (SR) of glycerol over Ni-based hydrotalcite catalyst was performed. in this work, SR of glycerol was carried in a temperature range of 700~850°C, at atmospheric pressure with a space velocity of 10,000 h^{-1} and feed molar ratio of H_2O(steam)/C=3.0, it means that water to glycerol ratio was 9/1. Ni-based catalyst was characterized by CO-chemisorption, N_2 physisorption, TPR, SEM, TEM and XRD techniques. It was found that $Ni_{0.5}/Mg_{2.5}Al_{1.0}$ catalyst in the lower temperature condition showed lower H_2 conversion result.

P342 (416)

Hydrogen and methane storage in microporous materials

A. Gil, S.A. Korili, A. Vallone, A.A. García Blanco, K. Sapag
Department of Applied Chemistry, Los Acebos Building, Public University of Navarra, Campus of Arrosadia,
E-31006 Pamplona, Spain, e-mail: *andoni@unavarra.es*

Hydrogen and methane storage capacities of several microporous materials have been studied using volumetric adsorption measurements up to 4 MPa. Activated carbons, MOFs, pillared clays and zeolites have been considered in this study. The results of the adsorption indicate that there is a relation between the gas uptake and the microporous volume of the materials. Equilibrium adsorption data were analysed using isotherm models, in order to investigate the adsorbed phase densities of the materials.

P343 (421)

Low temperature hydrogen production from ethanol over cerium and nickel based oxyhydrides

L. Jalowiecki-Duhamel, C. Pirez, M. Capron, F. Dumeignil, H. Jobic, E. Payen.
Unité de Catalyse et de Chimie du Solide, UMR CNRS 8181, Bât. C3, Université des Sciences et Technologies de Lille.
59655 Villeneuve d'Ascq Cedex, France. *Louise.Duhamel@univ-lille1.fr*

Steam reforming and oxidative steam reforming of ethanol were studied over $CeNi_XO_Y$ catalysts ($0 < x \leq 5$). 100% of ethanol conversion is obtained at 400°C. However, at 200°C a high activity i.e. ethanol conversion and H_2 selectivity can be obtained when the solid is previously in-situ treated in H_2 at 250°C i.e. in the oxyhydride form. Different physicochemical techniques, including Inelastic Neutron Scattering (INS), XPS, ion sputtering, XRD, TPR, TGA were used to characterize the catalysts. An active site based on the formation of anionic vacancies and a mechanism involving a heterolytic abstraction of a hydride species from ethanol are envisaged.

P344
(432)

Catalytic Partial Oxidation of Methane on Rh-ZrO_2 systems

I. Pettiti, D. Pietrogiacomi, D. Gazzoli, G. Ferraris, M. C. Campa, S. De Rossi
Dipartimento di Chimica, Sapienza Università di Roma, P.le A. Moro 5, 00185 Roma, Italy, *ida.pettiti@uniroma1.it*

Rh-ZrO_2 catalysts (Rh content 0.1-2.0 wt%) were characterized by XRD, H_2 chemisorption, XPS analysis, Raman, FTIR spectroscopy with probe molecules and investigated for methane catalytic partial oxidation (CPO) in a flow apparatus at 300-750°C, 9x10^5 NL Kg$_{cat}^{-1}$ h^{-1} space velocity. A Rh amount of 0.5 wt% on ZrO_2 was enough for high activity and selectivity; higher Rh loading did not improve the catalytic properties. Turnover frequency values suggest that, on Rh-ZrO_2 system, the reaction is demanding, requiring a specific Rh site, whose content was not proportional to the exposed Rh atoms. A Rh-α -Al_2O_3 reference catalyst was slightly more selective.

P345
(440)

Propane Oxidative dehydrogenation over ZSM-5 modified with Cr, Mg, Ni and V

C. M. Escobar, A. Santa, J. Arboleda, A. Echavarría
Grupo Catalizadores y Adsorbentes, Universidad de Antioquia, Calle 67 No. 53-108, Medellín, (Ant.), Colombia.
Ciudad Universitaria, Oficina: 1-317. Teléfono: (574) 2195667. *aechavar@udea.edu.co*

In this research, zeolite ZSM-5 was modified with four metals (Cr, Mg, Ni by ion exchange and V by impregnation techniques) and studied as catalysts in propane oxidative dehydrogenation (ODH). Catalysts were characterized with XRD and atomic absorption (AA). Catalytic tests were carried out at temperatures ranging from 250°C to 600°C at intervals of 50°C and constant space velocity of 50 mL/(g.min). Propane conversions were obtained up to 43.7% using Ni at 600°C and selectivities to propylene of 84.9% with V at 350°C.

P346
(441)

Propane oxidative dehydrogenation over Mn, Ni, and V mixed oxides from novel layered precursors

D. Gómez, J. Arboleda, C. Manrique, **A. Echavarría**
Grupo Catalizadores y Adsorbentes, Universidad de Antioquia, Calle 67 N° 53-108 Oficina: 1-317, Medellín, Colombia.
aechavar@udea.edu.co

Three new layered precursors with $(NH_4)Mn_2V_2O_7(OH).H_2O$, $(NH4)_{3/2}Ni_2V_2O_7(OH)_{3/2}.1/5H_2O$ and $(NH4)_{1/2}MnNi_{3/2}V_2O_7(OH)_{3/2}.H_2O$ formulas were synthesized by hydrothermal method. The characterization was performed by X-ray Diffraction, X-ray Fluorescence, CHN analysis, Thermogravimetric Analysis and Differential Scanning Calorimetry. The mixed oxides catalysts obtained after calcination were identified and tested in propane oxidative dehydrogenation reaction. An outstanding performance (9.3%) was obtained with MnVc600 which showed a great stability during 50 h under reaction, and exhibited an increase to olefins yield close to 16%.

P347
(444)

Kinetic study of the catalytic combustion of CH_4 and CH_4-H_2 mixtures at variable pressure

P. S. Barbato, **G. Landi, R**. Pirone, G. Russo
Istituto di Ricerche sulla Combustione – CNR, P.le Tecchio 80 80125 Naples (ITALY), *g.landi@irc.cnr.it*

Combustion of CH_4 and CH_4-H_2 mixtures was studied over platelet catalysts (Pd, Pt, $LaMnO_3$, Pt-$LaMnO_3$) under isothermal conditions. Experimental conditions were chosen in order to reduce temperature profiles inside the catalytic reactor and avoid mass transfer limitations. The effects of pressure, temperature, CH_4 concentration and H_2 co-feeding were investigated. Kinetic parameters were calculated by a dedicated software. Results revealed that CH_4 reaction rate only depends on fuel partial pressure; moreover reaction rate is limited by adsorption phenomena. H_2 addition does not improve CH_4 reaction rate, burning according a parallel reaction scheme.

P348
(448)

A comparison of 254 nm, 365 nm and 400 nm excitation of Ag/TiO_2 in CO_2 photocatalytic reduction

K. Kočí, L. Obalová, S. Krejčíková, Z. Lacný, D. Plachá, O. Šolcová
Technical University of Ostrava, 17. listopadu 15, Ostrava, Czech Republic, e-mail: *kamila.koci@vsb.cz*

The reduction of CO_2 by photocatalysts is one of the most promising methods since CO_2 can be reduced to useful compounds. Pure TiO_2 and variously silver-enriched TiO_2 powders were prepared by the sol-gel process controlled in the reverse micellar environment and characterized by XRD, BET surface area measurement, UV-vis and SEM. Methane and methanol were the main reduction products. The shorter wavelength 254 nm radiation is significantly more effective in promoting CO_2 photoreduction than 365 nm and 400 nm radiation d. However, even with 365 nm radiation CO_2 photoreduction with Ag/TiO_2 is possible but with 400 nm not.

P349
(450)

Insights into the reactivity of $La_{1-x}Sr_xMnO_3$ mixed oxides in catalytic methane combustion

D. Ivanov, L. Pinaeva, E. Sadovskaya, L. Isupova
Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, pr. Acad. Lavrentieva 5,
630090 Novosibirsk, Russia, *ivanov@catalysis.ru*

Investigation of oxygen isotope exchange revealed a clear view on the mechanism of oxygen mobility in $La_{1-x}Sr_xMn(Fe)O_3$ mixed oxides and enabled to establish a correlation between the oxygen mobility and catalytic activity in methane combustion. Sr promotion resulted in the appearance of the fast pathway of oxygen diffusion in the bulk through oxygen vacancies. High reactivity of multiphase samples correlated well with the appearance of highly defective layer-structured $(La_{1-y}Sr_y)_2Mn(Fe)O_4$ perovskites on the surface which makes layer-structured phases promising catalysts for methane combustion.

P350
(454)

Improved Pd/Al_2O_3-SiO_2 catalysts for methane combustion prepared by sol-gel synthesis combined to solid exchange method as a new alternative process

S. Fessi[1], A. Ghorbel[1], A. Rives[2] and R. Hubaut[2]
[1]Laboratoire de Chimie des Matériaux et Catalyse, Département de Chimie, Faculté des Sciences de Tunis, Campus Universtaire 2092
Tunis, Tunisie

In this work, an attempt to prepare Pd/Al_2O_3-SiO_2 solids by combining the sol-gel process with the solid exchange method is tried as a new synthesis route. The improvement of the catalytic activity in methane combustion on the Pd/Al_2O_3-SiO_2 sample is correlated to the increase of metal dispersion and PdO reducibility which seem to be influenced by acidity, support texture and PdO interaction nature. In fact, the mesoporosity size control via the hydrolysis ratio variation limits the palladium migration on the support surface. In addition, as it is shown by the XPS measurements, stronger PdO interaction with the support is obtained on the Pd/Al_2O_3-SiO_2 catalysts.

P351
(466)

Pd and Pt catalysts supported on α-Si_3N_4 by MOCVD method for total oxidation of methane

G. García Cervantes, P. D. Díaz Herrera, S. Pondigo Sosa, and J. Bonis.
Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada, CICATA-IPN Unidad Altamira, Km. 14.5 Carretera Tampico-Puerto Industrial, C.P. 89600, Altamira, Tamaulipas. México, e-mail: *ggarciace@ipn.mx*

Silicon nitride presents better properties (thermal conductivity, calorific capacity, chemical inertia, mechanical properties etc.) than oxides like SiO_2 and Al_2O_3, making it a good support for catalysts in high temperature reactions. Pd/α-Si_3N_4 catalysts have been synthesized by MOCVD and impregnation techniques to study the preparation method influence on their catalytic properties in methane total oxidation. MOCVD has not been very studied in this area, but recent results have shown that it is a very good option to obtain highly effective catalysts. Moreover MOCVD does not use pollutant organic solvents and requires less time compared to other methods.

P352
(499)

Decomposition of Methane over Ceria Promoted Iron Catalyst

L.G. Tang, D. Yamaguchi, W.J. Lee, N. Burke, D. Trimm, **K. Chiang**
Division of Petroleum Resources, The Commonwealth Scientific and Industrial Research Organisation (CSIRO),
Clayton, VIC 3168, Australia, e-mail: *ken.chiang@csiro.au*

The use of methane decomposition to produce CO_2 free H_2 is of practical importance. Pure and CeO_2-modified Fe_2O_3 samples as prepared by urea precipitation were assessed. The activity and stability of Fe_2O_3 on CH_4 decomposition was significantly improved by the addition of CeO_2. CeO_2 supported Fe_2O_3 also showed a lower degree of deactivation and enhanced the conversion of CH_4. It is proposed that the formation of well-dispersed Fe and Ce centres and the high surface area were responsible for the improvement.

P353 (504)

In-situ investigation of alcohol reactions to H_2 production: the support effect on zinc catalysts

N. S. Resende1, D. V. Cesar, V. Salim
Federal University of Rio de Janeiro - Programa de Engenharia Química / COPPE, av. Horacio Macedo, 2030, Centro de Tecnologia, bloco G/115, Cidade Universitária, 21941-914 Rio de Janeiro - RJ, Brazil. *neuman@ufrj.br*

A combination of surface characterization techniques (pulse TPSR-MeOH) and *in-situ* diffuse reflectance infrared Fourier transformed spectroscopy (DRIFTS) and X-ray diffraction (XRD) data was employed to further understand how the surface properties are affected by the support on the zinc oxide based catalysts. Special attention is given to intermediate species formation, surface activity and mechanism involving surface species after methanol and ethanol adsorption, as well as the role of Zn incorporation into the Hap structure. Zinc catalysts over Hap and TiO_2 supports presented surface activity for the steam reforming of methanol reaction with high H_2/CO_2 ratio.

P354 (522)

Effect of CeO_2-ZrO_2-Al_2O_3 and carbonnanotube support on catalytic performance of Ni catalyst in catalytic partial oxidation of methane to syngas

M.Alaittin Hastao lu[1], **Eyüp im ek**[2],Özgün Yücel[3],Ali Ata[1], Gül ah Ozan[4],Saadet K.Beyaz[4],Nalan Tekin[4], Farida D.Lamari[5]
[1]Gebze Inst. of Tech., [2]Material Sci. and Eng. [3]Energy Systems, Istanbul Cad. No:110, 41400 Cayırova/Kocaeli,Turkey,
e-mail: *eyupsimsek@gmail.com*, [4]University of Kocaeli, Umuttepe Yerlesksi, Faculty Art. and Sci., Chem. dept, 41380 Izmit, Turkey,
[5]LIMHP Univ. Paris 13 CNRS UPR1311, Institut Galilée, 99 av. Clément, 93430 Villetaneuse, France

The purpose of this study is to investigate the effect of support material of Ni based catalyst on hydrogen production by partial oxidation (POX) of methane. In addition, the effect of temp. on the POX experiments will be performed. Two different Ni based catalyst group supported by carbon nanotube (CNT) and CeO_2-ZrO_2-Al_2O_3. Catalysts for POX experiments were prepared by imp. method. CNT support material was prepared by Chemical Vapor Deposition (CVD) technique. Catalysts were characterized by SEM, TEM and XRD. The results of catalysts will be discussed with the ones in literature, in terms of catalytic activity, selectivity and coke deposition.

P355 (533)

Nanocrystalline $Ce_{0.9}Zr_{0.1}O_2$ highly active in combustion of methane

M.G. Zimicz, P. Núñez, D.G. Lamas and S.A. Larrondo
Departamento de Ingeniería Química, Facultad de Ingeniería Universidad de Buenos Aires, Ciudad Universitaria, (1428)
Buenos Aires, Argentina, *susana@di.fcen.uba.ar*

In this work we present the catalytic behavior of $Ce_{0.9}Zr_{0.1}O_2$ synthesized by a-aminoacid/nitrate combustion processes, through stoichiometric routes, in order to see the effect of the a-aminoacid used in the synthesis on the characteristics of the solids It can be concluded that selecting different a-aminoacid, makes it possible to get materials with tailored properties for catalytic applications. In this work, the $Ce_{0.9}Zr_{0.1}O_2$ catalyst synthesized by the a-aminoacid/nitrate combustion method following a stoichiometric route with glycine showed the best performance.

P356 (534)

Ni/$Ce_{0.9}Zr_{0.1}O_2$ catalysts for methane partial oxidation

M G. Zimicz, S.A. Larrondo and D.G. Lamas
CINSO (Centro de Investigaciones en Sólidos) CONICET – CITEFA, J.B. de La Salle 4397 (1603) Villa Martelli, Pcia. De Buenos Aires, Argentina, *mzimicz@citefa.gov.ar*

The aim of this work is to analyze the potential use of Ni/$Ce_{0.9}Zr_{0.1}O_2$ as anode materials for SC-SOFCs operated in mixtures of CH_4 and air. All catalysts have shown excellent conversion levels and high stability at 600ºC. At 700ºC, carbon deposition was observed, but after a treatment in oxidizing atmosphere the carbonaceous species can be removed recovering the activity of the catalysts. The combination of a high nickel content and high calcination temperature leads to the reduction of Ni and $Ce_{0.9}Zr_{0.1}O_2$ contact areas, diminishing the capacity of carbon removal. Therefore, these solids could be used as anode materials for intermediate temperature SC-SOFCs (500-600°C).

P357 (535)

COPROX Fixed Bed Reactor. Heat transfer schemes

P. Giunta, N. Amadeo, **M. Laborde**
Laboratorio de Procesos Catalíticos. Facultad de Ingeniería, Universidad de Buenos Aires. Pabellón de Industrias, Ciudad Universitaria, 1428 Buenos Aires, Argentina. *miguel@di.fcen.uba.ar*

Preferential oxidation of CO (COPROX) is used as the last stage to eliminate CO in the hydrogen stream, when it is used as feed for a PEM fuel-cell. A typical problem of this reactor is the temperature increase due to the exothermicity of the reactions. In this work different schemes of heat transfer in a COPROX fixed bed reactor are analyzed.

P358 (546)

Effect of the preparation Pd-LUS catalyst for methane combustion

A. Gannouni, M. Said Zina, B. Albela, L. Bonneviot, A. Ghorbel
Laboratoire de Chimie des Matériaux et Catalyse Faculté des Sciences de Tunis, Université El-Manar, 2092 Campus Universitaire, Tunisie. *anis.gannouni@ens-lyon.fr* or *anis4543@live.fr*

This work presents preliminary results on the catalytic methane combustion on palladium particles supported on LUS, a MCM-41 type of mesoporous material. The Pd element was introduced as a bisacetylacetonate palladium (II) complex using two methods: either by impregnation of LUS where the surfactant has been partially removed at different ratios or by direct hydrothermal synthesis. These materials are characterized using XRD , N_2 adsorption-desorption measurements and solid state ^{27}Al MAS- NMR, then the catalytic activity was evaluated in the combustion of methane.

P359
(556)

Synergetic hydrogen production and CO_2 separation via sorption enhanced reforming of methane

C. Martavaltzi, E.S. Korkakaki, E.P. Pampaka, **A.A. Lemonidou**
Department of Chemical Engineering, Aristotle University of Thessaloniki, University Campus GR 54 124, Thessaloniki, Greece,
alemonidou@cheng.auth.gr

This study examines the sorption-enhanced production of hydrogen via steam-methane reforming process over a mixed bed of a commercial nickel based catalyst and a novel CO_2 sorbent, $CaO\text{-}Ca_{12}Al_{14}O_{33}$. Hydrogen concentration higher than 92%, on a dry basis, was reached at 650°C, 1atm and for steam to methane ratio equal to 3.4 instead of 77% produced under the same conditions via the conventional steam reforming. The concentration of the gases in the reactor outlet and the production time during the prebreakthrough and breakthrough periods remained unaffected after thirteen reforming-regeneration cycles revealing the stability of the sorbing material.

P360
(586)

Advanced High-Temperature Air Combustion Technology (HiCOT) for Steam Reformer Furnace

Tomoyuki Mikuriya, **Toshiaki Yoshioka** and Toshihisa Tanaka
Chiyoda Corporation, 2-12-1 Tsurumichuo, Tsurumi-ku, Yokohama 230-8601, Japan
tyoshioka@ykh.chiyoda.co.jp

High temperature air combustion technology (HiCOT) is innovative technology which utilizes new combustion region of high combustion air temp. and lean oxygen content. Chiyoda has developed HiCOT for steam reformer furnace with Nippon Furnace Co., Ltd. It was confirmed that the HiCOT Steam Reformer increases in combustion efficiency, reduction in CO_2 and NOx emission and also achieves optimized heat flux profile in comparison with the conventional technology. HiCOT Combustion Technology is going to be optimized and integrated by Haldor Topsoe A/S with their extensive tubular steam reforming technologies.

P364
(255)

CuO_x/CeO_2 catalysts for preferential oxidation of CO: influence of the preparation methods

C. G. Maciel[1] L. P. R. Profeti[2], E. M. Assaf[2], J. M. Assaf[1]
[1]Universidade Federal de São Carlos, Departamento de Engenharia Química, Via Washington Luiz, Km 235 - São Carlos - SP, Brasil,
CEP: 13565-905, Fax: + 55 (16) 3351-8266, e-mail: *mansur@ufscar.br*
[2]Universidade de São Paulo, Departamento de Físico-Química, Avenida Trabalhador São Carlense 400, São Carlos - SP, Brasil.
CEP:13560-970, Fax: + 55 (16) 3373- 990

Catalysts $CuO_x\text{-}CeO_2$ was prepared by impregnation, co-precipitation, citrate and deposition-precipitation methods. Those catalysts were characterized and tested in PROX-CO reaction. The results indicated that solids prepared by impregnation and citrate are most active and selective in the reaction, especially at lower temperatures. The characterization techniques showed that the active metals of these samples were well dispersed and presenting small particle size that in the solids prepared by co-precipitation and deposition-precipitation that are very important characteristics for the enhance the synergistic interaction between CuO_x and CeO_2.

Session VI - Technical-economical studies, technology demonstration, industrial processes and plant operation

P230
(9)

Prospect of Natural Gas Industry in Iran

Hedayat Omidvar
Member of IGU Marketing Committee, Head of Communication Affairs with Science & Research Centers,
Research & Technology Dept., National Iranian Gas Company, No.77-Southern Aban St. - Karimkhan Ave.-Tehran-1598753113-Iran,
e-mail: omidvar@nigc.ir

Gas has been recognizing as the fuel for the future. This is entirely evident as a result of decreasing global resources due to environmental considerations. According to IEA estimates, in year 2015, oil demand will reach 93 million barrels and natural gas demand will reach 64 million barrels of oil equivalent. This in effect is a 20% increase for oil and 45% for gas in regard to current figures in conclusion. It could be stated that more than ever before, gas has gained significance and is the leading basis for modern services in energy, and in the long term is considered a bridge towards a hydrogen resource based economy. Gas as a new fuel, provides the modern technology of fuel cell construction for vehicles possible. To portray the enormity of Iran gas reserves it is enough to consider that Iran's natural gas reserves alone exceeds the total volume of natural gas reserves in USA, Canada, Europe and the entire Asia pacific.

P231
(30)

Carbon Dioxide Removal from Natural Gas by Pressure Swing Adsorption (PSA): a Feasibility Study

A.Cianca, **E. F. Gambarotta**, V. Piccolo, C. Rizzo, M. Tagliabue
Eni S.p.A. Refining & Marketing Division, Via Maritano 26, San Donato Milanese, I-27100 Milano, Italy. *enrico.gambarotta@eni.it*

Pressure Swing Adsorption (PSA) separation systems appear to be interesting technologies in the natural gas treatment because of their high flexibility, low energy intensity and eco-compatibility. In this study is evaluated the potentiality of a commercial adsorbent in the removal of carbon dioxide from a natural gas stream by a PSA based process. The evaluation, carried out as comparison with a consolidated amine technology, was realized with the help of the commercial software: ASPEN ADSIM, that combined with a process simulator allowed to evaluate the consumptions and the sizing of the main process equipments.

P232
(89)

Influence of the activation of carbons on the natural gas storage by compression and adsorption

D. C. S. Sales[1], R. G. Martins[1], A. Knoechelmann[1], E. F. Jaguaribe[2], C. A. M. Abreu[1]
[1]Departamento de Engenharia Química, Universidade Federal de Pernambuco, Recife – PE,50740-520, Brazil,
deivsoncesar@yahoo.com.br
[2]Departamento de Engenharia Mecânica, Universidade Federal da Paraíba, João Pessoa – PB, 58051-900, Brazil.

In view of the transporting are proposed ways to improve the natural gas storage by compression and adsorption, with the use of adsorbents in fixed bed. In this work, activated carbons were produced from precursor coconut shell, by chemical activation with phosphoric acid (CAQ1) and zinc chloride (CAQ2), and had measured its specific heats, absolutes densities and textural characteristics. Were observed higher area and density for CAQ1 compared with CAQ2, which in turn had higher specific heat and micropore volume, beyond increases in the volumetric storage capacity of 300% and 85% for CAQ1 and CAQ2, respectively.

P233
(181)

Economical comparison of natural gas exportation methods (LNG, GTL and pipeline)

M. Sarmad[1], A. Zamaniyan[1], A. Fazeli[1], R. Behradi yekta[1], A. Ghozatloo1, A. Mousaei[1]
[1]Research institute of petroleum industry, West Blvd., Near Azadi Sports Complex, Tehran, Iran, *sarmadm@ripi.ir*

This paper explains the software which has been developed to compare three different methods for natural gas exportation, including LNG, GTL and Pipeline simultaneously so to find the most economically efficient one. The effective parameters such as feed price, selling price, capital investment and exploitation duration, have been considered strictly in this study. The resulting parameters, CAPEX, NPV, IRR and pay back, have been calculated for economic analysis. Having the world's second greatest natural gas reservoirs, Iran was selected as a case study.

P234
(218)

Industrial gas cleaning system using the electrostatic filter

Evgen Lunev, Alexey Kapustin
Priazovskiy State Technical University, Mariupol, 87500 Ukrain, *lunev.ea@gmail.com*

Industrial cleaning system of the gas flow with a decrease in the concentration of dust to the given parameters using the electrostatic corona discharge from the fields capture different fractions of dust.

P235
(219)

Industrial gas cleaning system with scrubber and electrostatic precipitator

Vasiliy Babich, Alexey Kapustin
Priazovskiy State Technical University, Mariupol, 87500 Ukrain, *babich.vn@tdru.com.ua*

This paper presents the technological characteristics of the industrial gas purification system, which includes scrubber and electrostatic precipitator, as well as control systems and discusses the features of work under various operating conditions.

P236
(262)

Economic Investigation of Natural Gas Conversion to Liquid Fuels via Non-FT GTL

L. Shirazi, H. Manafi, N. Fatourehchi
Research Institute of Petroleum Institute (RIPI), P.O. Box 18745/4163, Tehran, Iran, *shirazil@ripi.ir*

Natural gas is converted to fuel and petrochemical products which have a higher value added than natural gas but there are many challenges in technology and capital cost to make it as commercial process. RIPI has been at the forefront of gas conversion technology development with great emphasis on Non-FT routes in the last few years. This process has great flexibility to produce products with a range of gasoline/diesel ratios, depending on the operating conditions and processes used. In this paper, challenges and advantages of introducing Non-FT GTL as a new rout in Iran have been discussed and the economical study of a Non-FT GTL plant has been investigated.

P237
(379)

Performance of a commercial WGS catalyst using industrial coal derived syngas

A.R. de la Osa, P. Sánchez, A. De Lucas, A. Romero, F. García Peña, P.Casero, I. Monteagudo, J.L. Valverde.
Departamento de Ingeniería Química, Facultad de Ciencias Químicas, Universidad de
Castilla-La Mancha. Avenida Camilo José Cela 12, 13005 Ciudad Real, Spain. *AnaRaquel.Osa@uclm.es*

The optimization of the reaction conditions (reaction temperature, H_2O_v/CO molar ratio and GHSV) of WGS reaction was carried out in a bench scale plant, using a commercial sulfur resistant catalyst and an industrial coal-derived feeding in order to scale it up for industrial applications. Catalytic activity showed an important dependence on reaction temperature and space velocity but remained almost constant with increasing H_2O_v/CO molar ratios. It was also study the resistance of this commercial catalyst to a certain amount of H_2S and COS in the feed stream, providing good catalytic results for the maximum level of these poisons.

P238
(426)

Modelling of an integrated gas-chemical to produce methanol, ammonia, hydrogen and ethylene

Tatiana Magalhães Gerosa, Patricia Helena Lara dos Santos
Instituto de Eletrotécnica e Energia da Universidade de São Paulo; Avenida Professor Luciano Gualberto, 1289, 05508-900,
São Paulo-SP-Brazil. *tatiana.gerosa@iee.usp.br*

The target of this work is modelling of an integrated gas-chemical plant through the versatility of the use of natural gas as a raw material for the chemical industry, aiming the production of methanol, ammonia and hydrogen, from the fraction methane, as well as in the petrochemical industry, the attainment of ethylene from the ethane fraction. It to Brazil that the diversification of the supplies happens in order to produce ethylene. Based in a market research, it was determined that among the products to be obtained from methane, methanol is the product that presents the most critical internal scenario. The new discoveries of oil and gas in Brazil can be contributed to this project.

P239 (505)

Optimum structure for multi metallic catalysts in propane dehydrogenation

Abedeh Gholidoust[1], Maryam Saeedizad[2], Saeed Sahebdelfar[2], Mohammad Rahmani[1], Abbas Naderifar[1]
[1]Department of Chemical engineering, Faculty of engineering, Amirkabir university of technology, Tehran, Iran, *gholidoost@aut.ac.ir*
[2]Catalysis Research group, Tehran center, Petrochemical Research &Technology Company NPC, P.O.Box 14965-115, Tehran, Iran

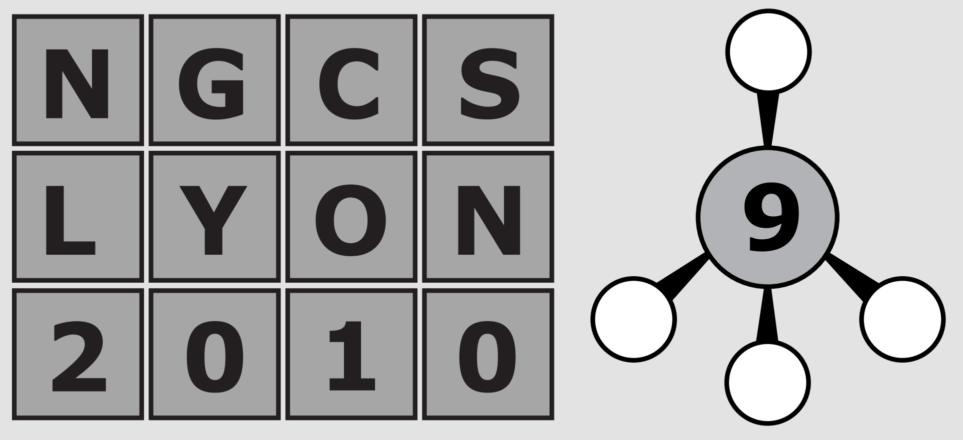
Different thin-step type of Three-metallic (Pt-Sn-K) catalysts based on Pt and supported on different materials (γ-Al_2O_3, θ-Al_2O_3) were tested in the propane dehydrogenation reaction (in fixed-bed reactor).
Results show that the non-uniform catalysts on θ-Al_2O_3 has a better performance in propane dehydrogenation (high yield to propylene and low coke deposition), than the uniform systems. Thus, the use of an adequate support (θ-Al_2O_3) in combination with non-uniform system enhances the catalytic performance.

P240 (583)

Energy Research Faster & Better by Automated High-Output Solutions – Catalyst Impregnation

Olaf Köhler
Chemspeed Technologies, Rheinstr. 32, CH-4302 Augst, Switzerland, *olaf.koehler@chemspeed.com*

Most chemicals have their origin in fossil energy resources and require catalysis based refining. Heterogeneous catalysts are the most abundant catalysts. Their most common preparation is the incipient wetness impregnation. In this poster we will describe the fully automated high-output incipient wetness impregnation of 48 heterogeneous catalysts in a 2.5 g scale carried out with one of our partners.



Novel Gas Conversion Symposium
C1-C4 chemistry: from fossil to bio resources

AUTHORS INDEX

Instruction

AR - Award Recipient
PL - Plenary Lectures
KN - Keynote Presentations
O - Oral Presentations
P- Poster Presentations

NGCS
LYON
2010

9

Novel Gas Conversion Symposium
C1-C4 chemistry: from fossil to bio resources

PLENARIES, KEYNOTES, ORAL AND POSTERS INDEX

INDEX ACCORDING TO NUMBERS

AWARD RECIPIENT

PLENARY LECTURES

KEYNOTE PRESENTATIONS

ORAL PRESENTATIONS

POSTER PRESENTATIONS

Avantium Chemicals

Since its foundation in 2000, Avantium has been providing research services and stand alone research equipment to many of the world's largest global (petro) chemical and refining companies (e.g. BP, Sasol, Shell, and Chevron). The company's dedicated Chemicals team has acquired an extensive track record in assisting companies in search of new products and process optimization. In numerous customer service projects Avantium has developed broad expertise in the use of high-throughput technologies to increase customers' catalysis, formulation and corrosion.
Avantium's high-throughput technology, fixed bed as well as batch, is based around 16 up till 96 isothermal micro reactors running in parallel.
Temperature can be varied up to 850°C and we are able to operate at pressures reaching 200 bar. Using our services will allow you to simultaneously study a broad range of temperatures, pressures and catalysts. Using both your knowledge of the application and our experience in the area of high throughput will allow you to quickly find the best catalyst at optimal operating conditions.
Next to its Services and Systems business, Avantium develops and commercializes Furanics, a next generation of biobased fuels and plastics.

You are invited to visit our booth at the exhibition stand for more information and a real Dutch treat; the 'stroopwafel'.

AVANTIUM

Zekeringstraat 29 - 1014 BV Amsterdam - The Netherlands
tel. +31 20 5860154 (office) - fax. +31 20 5868085
www.avantium.com

OCMOL - Oxidative Coupling of Methane followed by Oligomerization to Liquids. Taking advantage of resources

A European Integrated Project supported through the Seventh Framework Programme for Research and Technological Development. September 2009 - August 2014

As the global energy demand and crude oil price rise, alternative production routes for the same hydrocarbon products are becoming more and more economically attractive. The OCMOL project (www.ocmol.eu) aims at developing an innovative chemical route adapted to the exploitation of small gas reservoirs from both a technical and economic point of view. The corresponding process is, among others, based on oxidative coupling of methane followed by its subsequent oligomerization to liquids. OCMOL, which gathers 17 entities coming from 8 European countries and 1 non-European country, is coordinated by Ghent University with the support of Alma Consulting Group (www.lmacg.com). Alma Consulting Group offers unique expertise in determining all research and innovation financing possibilities on a European, national and regional scale (seeking and obtaining public financing - competitive clusters, National Research bodies, EUREKA, EUROSTARS, 7th EU Commission Framework Programme- and managing collaborative research projects).

ocmöl
Taking advantage of resources

ALMA
Consulting Group

Maquette et mise en page
Pascale Sentenac/Sitbon et associés
Tél. +33 (0)4 37 85 11 22
69140 Rillieux-la-Pape

Crédit photographique
Yves Neyrolles

Imprimé par
ALAIN GILLES GROUP LYON
Tél. +33 (0)4 37 24 21 50