

**Studies in Surface Science and Catalysis**

**Advisory Editors:** B. Delmon and J.T. Yates

**Vol. 107**

## **NATURAL GAS CONVERSION IV**

Proceedings of the 4th International Natural Gas Conversion Symposium,  
Kruger Park, South Africa, November 19-23, 1995

**Editors**

**M. de Pontes**

*CEF(Pty) Ltd., Sandton, South Africa*

**R.L. Espinoza**

*SASTECH R & D, Sasolburg, South Africa*

**C.P. Nicolaidis**

*University of Witwatersrand, Johannesburg, South Africa*

**J.H. Scholtz**

*SASTECH R & D, Sasolburg, South Africa*

**M.S. Scurrall**

*Anglo American Research Laboratories(Pty) Ltd., Crown Mines, South Africa*



**1997**

**ELSEVIER**

**Amsterdam — Lausanne — New York — Oxford — Shannon — Tokyo**

ELSEVIER SCIENCE B.V.  
Sara Burgerhartstraat 25  
P.O. Box 211, 1000 AE Amsterdam, The Netherlands

ISBN 0-444-82352-2

© 1997 Elsevier Science B.V. All rights reserved.

No part of this publication may be reproduced, stored in a retrieval system or transmitted in any form or by any means, electronic, mechanical, photocopying, recording or otherwise, without the prior written permission of the publisher, Elsevier Science B.V., Copyright & Permissions Department, P.O. Box 521, 1000 AM Amsterdam, The Netherlands.

Special regulations for readers in the U.S.A. – This publication has been registered with the Copyright Clearance Center Inc. (CCC), 222 Rosewood Drive, Danvers, MA 01923. Information can be obtained from the CCC about conditions under which photocopies of parts of this publication may be made in the U.S.A. All other copyright questions, including photocopying outside of the U.S.A., should be referred to the copyright owner, Elsevier Science B.V., unless otherwise specified.

No responsibility is assumed by the publisher for any injury and/or damage to persons or property as a matter of products liability, negligence or otherwise, or from any use or operation of any methods, products, instructions or ideas contained in the material herein.

This book is printed on acid-free paper.

Printed in The Netherlands

## TABLE OF CONTENTS

Preface	XV
Organising and Advisory Committee	XVII
Financial Support	XVIII
<b>1. <u>SYNTHESIS OF ALCOHOLS AND OTHER OXYGENATES</u></b>	
THE USE OF A JET-STIRRED CONTINUOUSLY STIRRED TANK REACTOR (CSTR) TO STUDY THE HOMOGENEOUS GAS PHASE PARTIAL OXIDATION OF METHANE TO METHANOL <i>G.A. Foulds, B.G. Charlton, B.T. Le, J.C. Jones and B.F. Gray</i>	3
SYNTHESIS OF ALCOHOLS FROM SYNGAS OVER Ni-BASED CATALYST: COMPARISON WITH THE HYDROFORMYLATION REACTION <i>J. Llorca, P. Ramirez de la Piscina, N. Homs, E. Brum Pereira, P. Moral and G.A. Martin</i>	9
ZIRCONIA MODIFIED Ru/Al <sub>2</sub> O <sub>3</sub> CATALYSTS FOR THE SYNTHESIS OF OXYGENATED PRODUCTS FROM SYNGAS <i>M.R. Goldwasser, M.L. Cubeiro, M.C. Da Silva, M.J. Pérez Zurita, G. Leclercq, L. Leclercq, M. Dufour, L. Gengembre, G.C. Bond and A.D. Hooper</i>	15
PARTIAL OXIDATION OF METHANE TO FORMALDEHYDE ON BULK AND SILICA SUPPORTED MoO <sub>3</sub> AND V <sub>2</sub> O <sub>5</sub> CATALYSTS: SURFACE FEATURES AND REACTION MECHANISM. <i>A. Parmaliana, F. Arena, F. Frusteri, N. Giordano, M.S. Scurrrell and V. Sokolovskii</i>	23
METHANOL SYNTHESIS FROM CO <sub>2</sub> /H <sub>2</sub> OVER Pd-PROMOTED Cu/ZnO/Al <sub>2</sub> O <sub>3</sub> CATALYSTS: KINETICS AND DEACTIVATION <i>M. Sahibzada, D. Chadwick and I.S. Metcalfe</i>	29
ABOUT THE MECHANISM OF METHANOL SYNTHESIS <i>T.M. Yurieva, O.V. Makarova, L.M. Plyasova and T.A. Krieger</i>	35
A NOVEL APPROACH TO THE SCIENTIFIC DESIGN OF OXIDE CATALYSTS FOR THE PARTIAL OXIDATION OF METHANE TO METHANOL <i>G.J. Hutchings, J.S.J. Hargreaves, R.W. Joyner and S.H. Taylor</i>	41

HIGHER ALCOHOL SYNTHESIS ON IRON-COPPER-MOLYBDENUM CONTAINING CATALYSTS <i>A. Barama, M.M. Bettahar and A. Kiennemann</i>	47
LINKS BETWEEN REACTION INTERMEDIATES, ACTIVITY AND/OR SELECTIVITY IN SYNGAS CHEMISTRY <i>A. Kiennemann, P. Chaumette, B. Ernst, J. Saussey and J.C. Lavalley</i>	55
LOW TEMPERATURE DIRECT OXIDATION OF METHANE TO METHANOL <i>K. Fujimoto and Y. Sekine</i>	63
COPPER-COBALT CATALYSTS FOR HIGHER ALCOHOLS SYNTHESIS FROM SYNGAS <i>G.G. Volkova, T.A. Krieger, L.M. Plyasova, V.A. Zaikovskii and T.M. Yurieva</i>	67
CUSTOM MADE CATALYSTS FOR LOW PRESSURE METHANOL SYNTHESIS <i>J. Ladebeck, J.P. Wagner and T. Matsuhisa</i>	73
<b>2. <u>ECONOMICS AND INDUSTRIAL PROCESSES</u></b>	
KEYS TO METHANE CONVERSION TECHNOLOGIES <i>J.-P. Lange, K.P. de Jong, J. Ansorge and P.J.A. Tijm</i>	81
ECONOMIC ROUTE FOR NATURAL GAS CONVERSION TO ETHYLENE AND PROPYLENE <i>B.V. Vora, T.L. Marker, P.T. Barger, H.R. Nilsen, S. Kvisle and T. Fuglerud</i>	87
LARGE-SCALE PRODUCTION OF ALTERNATIVE SYNTHETIC FUELS FROM NATURAL GAS <i>I.Dybkjaer and J.B. Hansen</i>	99
DIMETHYL ETHER: A FUEL FOR THE 21st CENTURY <i>T.H. Fleisch, A. Basu, M.J. Gradassi and J.G. Masin</i>	117
SOFC BASED ON SUPPORTED THICK-FILM Ce(Gd) <sub>2x</sub> ELECTROLYTES <i>K. Zheng, B.C.H. Steele and I.S. Metcalfe</i>	127
USE OF NATURAL GAS IN A CATALYTIC RADIANT BURNER FOR LOW-EMISSION HEAT PRODUCTION <i>P. Bröckerhoff and B. Emonts</i>	133
ETHERMIX PROCESS: SYNTHESIS OF ETHERS FROM CO/H <sub>2</sub> <i>E. Micheli, G.B. Antonelli, D. Sanfilippo, B. Cometa and G.C. Pecci</i>	139

A TECHNICAL AND ECONOMIC COMPARISON OF NATURAL GAS AND COAL FEEDSTOCKS FOR FISCHER-TROPSCH SYNTHESIS <i>D. Gray and G. Tomlinson</i>	145
<b>3. <u>FISCHER-TROPSCH</u></b>	
FISCHER-TROPSCH SYNTHESIS ON COBALT CATALYSTS: STRUCTURAL REQUIREMENTS AND REACTION PATHWAYS <i>E. Iglesia</i>	153
ACTIVITY AND SELECTIVITY OF IRON FISCHER-TROPSCH CATALYSTS IN A STIRRED TANK SLURRY REACTOR <i>D.B. Bukur, X. Lang and L. Nowicki</i>	163
THE ROLE OF CATALYST ACTIVATION ON THE ACTIVITY AND ATTRITION OF PRECIPITATED IRON FISCHER-TROPSCH CATALYSTS <i>A.K. Datye, M.D. Shroff, M.S. Harrington, A.G. Sault and N.B. Jackson</i>	169
ROLE OF CO <sub>2</sub> OXYGENATES AND ALKENES IN THE INITIATION OF CHAIN GROWTH DURING THE FISCHER-TROPSCH SYNTHESIS <i>B.H. Davis, L. Xu and S. Bao</i>	175
KINETIC ANALYSIS OF SLURRY PHASE FISCHER-TROPSCH SYNTHESIS <i>K. Fujimoto, M. Shimose and Y.Z. Han</i>	181
DRIFTS STUDIES ON Co/TiO <sub>2</sub> FISCHER-TROPSCH CATALYSTS <i>B. Mothebe, D.J. Duvenhage, V.D. Sokolovskii and N.J. Coville</i>	187
EFFECT OF WATER PARTIAL PRESSURE ON STEADY STATE FISCHER-TROPSCH ACTIVITY AND SELECTIVITY OF A PROMOTED COBALT CATALYST <i>H. Schulz, M. Claeys and S. Harms</i>	193
POTASSIUM-PROMOTED TITANIA-SUPPORTED NICKEL-IRON CATALYSTS FOR FISCHER-TROPSCH SYNTHESIS <i>J. van de Loosdrecht, A.J. van Dillen, D. Reinders, A.A. van der Horst, E. Boellaard, A.M. van der Kraan and J.W. Geus</i>	201
COBALT AS AN ALTERNATIVE FISCHER-TROPSCH CATALYST TO IRON FOR THE PRODUCTION OF MIDDLE DISTILLATES <i>P.J. van Berge and R.C. Everson</i>	207
SELECTION, DESIGN AND SCALE UP OF THE FISCHER-TROPSCH REACTOR <i>J.W.A. De Swart, R. Krishna and S.T. Sie</i>	213

DEVELOPMENTS IN FISCHER-TROPSCH TECHNOLOGY <i>B. Jager</i>	219
COBALT ON TUNGSTEN-MODIFIED ALUMINA CATALYSTS FOR OLEFIN SYNTHESIS <i>B.G. Baker, S. Thomson and M. Jasieniak</i>	225
HYDROGENATION OF CO AND CO <sub>2</sub> WITH K AND Mn PROMOTED IRON CATALYSTS <i>M.L. Cubeiro, G. Valderrama, M.R. Goldwasser, F. González-Jiménez, M.C. Da Silva and M.J. Pérez-Zurita</i>	231
REOXIDATION OF SUPPORTED COBALT FISCHER-TROPSCH CATALYSTS <i>A.M. Hilmen, D. Schanke and A. Holmen</i>	237
FISCHER-TROPSCH SYNTHESIS: DRIFTS AND SIMS SURFACE INVESTIGATION OF Co AND Co/Ru ON TITANIA SUPPORTS <i>J.G. Price, D. Glasser, D. Hildebrandt and N.J. Coville</i>	243
NASCENT CHARACTERISTICS OF COBALT-BASED FISCHER-TROPSCH CATALYSTS <i>G. Hills, H. Chen and A.A. Adesina</i>	249
<b>4. NOVEL METHANE REACTIONS</b>	
THE CONVERSION OF METHANE TO BENZENE OVER Mo/ZSM-5 ZEOLITES IN THE ABSENCE OF AN OXIDANT <i>J.H. Lunsford, M.P. Rosynek and D. Wang</i>	257
METHANE HOMOLOGATION ON Co SUPPORTED CATALYSTS <i>G. Boskovic, J.S.M. Zadeh and K.J. Smith</i>	263
METHANE TO VINYL CHLORIDE BY "CHLORO-PYROLYSIS" OF METHYL CHLORIDE <i>P.M. Marquaire, M.A. Kazzaz, Y. Muller and J. Saint Just</i>	269
PALLADIUM-CATALYZED ACETIC ACID SYNTHESIS FROM METHANE AND CARBON DIOXIDE <i>Y. Fujiwara, Y. Taniguchi, K. Takaki, M. Kurioka, T. Jintoku and T. Kitamura</i>	275
FORMATION OF ETHANE AND ETHYLENE BY THE REACTION OF METHANE AND CARBON DIOXIDE OVER UNSUPPORTED METAL OXIDES <i>K. Asami, K. Kusakabe, N. Ashi and Y. Ohtsuka</i>	279

REACTION CHARACTERISATION AND MECHANISM FOR THE SELECTIVE REDUCTION OF NITROGEN OXIDES BY METHANE OVER COBALT-CONTAINING MEDIUM PORE ZEOLITES <i>A.D. Cowan and N.W. Cant</i>	285
<b>5. OXIDATIVE COUPLING</b>	
BENEFICIAL EFFECTS OF INORGANIC CHLORINE GRAFTING ON Sm <sub>2</sub> Sn <sub>2</sub> O <sub>7</sub> PYROCHLORE DURING OXIDATIVE COUPLING OF METHANE <i>A.C. Roger, C. Petit, S. Libs, J.F. Koenig and A. Kiennemann</i>	293
DIRECT OXIDATIVE CONVERSION OF METHANE INTO HIGHER HYDROCARBONS AND OXY-PRODUCTS IN THE PRESENCE OF HYDROGEN PEROXIDE <i>I. Eskendirov, N.J. Coville, A. Parmaliana and V.D. Sokolovskii</i>	301
OXIDATIVE COUPLING OF METHANE TO ETHYLENE WITH 85% YIELD IN A GAS RECYCLE ELECTROCATALYTIC OR CATALYTIC REACTOR SEPARATOR <i>I.V. Yentekakis, Y. Jiang, M. Makri and C.G. Vayenas</i>	307
METHANE OXIDATIVE COUPLING OVER METAL OXIDE CATALYSTS <i>Z. Kalenik and E.E. Wolf</i>	313
OXIDATIVE COUPLING OF METHANE OVER NATURAL CALCIUM COMPOUNDS IN FIXED- AND FLUIDIZED-BED REACTORS <i>T. Wakatsuki, M. Yamamura, H. Okado, K. Chaki, S. Okada, K. Inaba, S. Suzuki and T. Yoshinari</i>	319
METHANE OXIDATIVE COUPLING USING POROUS CERAMIC MEMBRANE REACTORS. EFFECT OF AN INCREASED PERMEATION FLUX <i>J. Coronas, M. Menéndez and J. Santamaría</i>	325
COMPARATIVE STUDY ON LOW TEMPERATURE METHANE ACTIVATION OVER COBALT AND RUTHENIUM SUPPORTED ON Al <sub>2</sub> O <sub>3</sub> , SiO <sub>2</sub> AND NaY <i>L. Guzzi, K. V. Sharma, Zs. Koppány, R. Sundararajan and Z. Zsoldos</i>	333
A REACTION-SEPARATION COMBINED OCM PROCESS FOR HIGH C <sub>2</sub> HYDROCARBON YIELDS <i>Y. Jiang, C. Yu, W. Li, J. Yan and Y. Ji</i>	339
STRUCTURE SENSITIVITY OF OXIDATIVE COUPLING OF METHANE AND DEHYDROGENATION OF ETHANE OVER LANTHANA CATALYSTS <i>C. Mirodatos, G. Xu, S. Lacombe, V. Ducarme, W. Li and G.A. Martin</i>	345

KINETIC LIMIT OF C <sub>2</sub> HYDROCARBONS YIELD AT GAS-PHASE OXIDATIVE COUPLING OF METHANE <i>V.S. Arutyunov, V.Ya. Basevich and V.I. Vedeneev</i>	351
MEASUREMENT OF KINETIC ISOTOPE EFFECTS OVER METHANE COUPLING CATALYSTS IN THE PRESENCE OF CARBON DIOXIDE <i>N.W. Cant, P.F. Nelson and B.L. Duffy</i>	355
OXIDATIVE DEHYDROGENATION OF ETHANE AT LOW TEMPERATURE OVER NICKEL CATALYSTS: INFLUENCE OF MORPHOLOGY AND CHEMICAL STATE OF THE SOLID DURING REACTION <i>V. Ducarme, H.M. Swaan, A. Thaib and G.A. Martin</i>	361
DEHYDROGENATIVE COUPLING OF METHANE IN THERMAL DIFFUSION REACTOR WITH PLATINUM IMPREGNATED CARBON ROD AS A PYROGEN <i>K. Onoe, S. Suzuki and T. Yamaguchi</i>	367
OXIDATIVE COUPLING OF METHANE OVER Li/Sn/MgO CATALYSTS. USE OF A FLUIDIZED BED REACTOR AT LOW GAS VELOCITIES <i>A. Santos, M. Menéndez and J. Santamaría</i>	373
OXIDATIVE COUPLING OF METHANE BY WATER <i>X. Li, K. Tomishige and K. Fujimoto</i>	379
EFFECT OF GAS PHASE REACTIONS IN THE OXIDATIVE COUPLING OF METHANE <i>P.M. Marquaire, N. Gueritey, G.-M. Côme and F. Baronnet</i>	383
OXIDATIVE METHANE COUPLING. PROSPECTS AND CONCEPTUAL DESIGN FOR CO-GENERATION OF OLEFINS AND ELECTRIC POWER WITH REDUCED CO <sub>2</sub> EMISSION AND FEED STOCK DEMAND <i>J.M.L. Penninger</i>	389
<b>6. PARTIAL OXIDATION</b>	
HYDROGEN PRODUCTION ON NICKEL-MONOLITH STRUCTURES BY PARTIAL OXIDATION OF METHANE AT HIGH PRESSURE <i>J.P. Gómez, J.M. Jiménez, S. Vic, J. Lezaun, P. Terreros, I. Cabrera, M.A. Peña and J.L.G. Fierro</i>	397
NEW HIGHLY ACTIVE CATALYSTS IN DIRECT PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS <i>A.G. Steghuis, J.G. van Ommen, K. Seshan and J.A. Lercher</i>	403

DEVELOPMENT OF DENSE CERAMIC MEMBRANES FOR METHANE CONVERSION <i>U. Balachandran, J.T. Dusek, P.S. Maiya, B. Ma, R.L. Mieville, M.S. Kleefisch, C.A. Udovich, T.H. Fleisch and A.C. Bose</i>	409
PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS - EXPERIMENTAL AND MODELLING STUDIES <i>K.Heitnes Hofstad, B. Andersson, A. Holmgren, O.A. Rokstad and A. Holmen</i>	415
CATALYTIC PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS - CATALYSIS AND REACTION ENGINEERING <i>M. Baems, O.V. Buyevskaya, L. Mleczko and D. Wolf</i>	421
SYNGAS PRODUCTION BY PARTIAL OXIDATION OF METHANE: DEPENDENCE OF REACTIVITY ON CATALYST PROPERTIES AND CONTACT TIME <i>L. Basini, M. D'Amore, G. Fomasari, D. Matteuzzi, D. Sanfilippo, F. Trifiro and A. Vaccari</i>	429
PARTIAL OXIDATION OF METHANE TO SYNTHESIS GAS OVER SUPPORTED RUTHENIUM CATALYSTS <i>J. Boucouvalas, A.M. Efstathiou, Z.L. Zhang and X.E. Verykios</i>	435
PARTIAL OXIDATION OF METHANE TO SYNGAS OVER NI-LOADED ULTRASTABLE HY ZEOLITE CATALYSTS <i>M.A. Peña, B. Pawelec, P. Terreros, J.L.G. Fierro, J. Lezaun, J.P. Gómez, J.M. Jiménez and S. Vic</i>	441
PARTIAL OXIDATION OF METHANE OVER NICKEL- AND COBALT-BASED CATALYSTS <i>H.M. Swaan, R. Rouanet, P. Widyananda and C. Mirodatos</i>	447
INTERNAL AND EXTERNAL TRANSPORT EFFECTS DURING THE OXIDATIVE REFORMING OF METHANE ON A COMMERCIAL STEAM REFORMING CATALYST <i>J.N. Theron, M.E. Dry, E. van Steen and J.C.Q. Fletcher</i>	455
HIGH YIELD SYNGAS FORMATION BY PARTIAL OXIDATION OF METHANE OVER Co-ALUMINA CATALYSTS <i>V.D. Sokolovskii, J.C. Jeannot, N.J. Coville, D. Glasser, D. Hildebrandt and M. Makoá</i>	461
EFFECT OF La <sub>2</sub> O <sub>3</sub> ADDED TO NiO/Al <sub>2</sub> O <sub>3</sub> CATALYST ON PARTIAL OXIDATION OF METHANE TO SYNGAS <i>L. Cao, Y. Chen and W. Li</i>	467

- THE ROLE OF CATALYSIS IN THE CONVERSION OF NATURAL GAS FOR  
POWER GENERATION 473  
*J.R. Rostrup-Nielsen, K. Aasberg-Petersen and P.S. Schoubye*

## 7. REFORMING

- A COMPARISON OF NICKEL AND RHODIUM CATALYSTS FOR THE  
REFORMING OF METHANE BY CARBON DIOXIDE 491  
*N.W. Cant, R. Dümpelmann and A.M. Maitra*

- THE INFLUENCE OF RARE EARTH OXIDES ON Ni/Al<sub>2</sub>O<sub>3</sub> CATALYSTS  
DURING CO<sub>2</sub> REFORMING OF CH<sub>4</sub> 497  
*Å. Slagtern, U. Olsbye, R. Blom and I.M. Dahl*

- STUDIES ON Ni/Al<sub>2</sub>O<sub>3</sub> CATALYST FOR CO<sub>2</sub> REFORMING OF CH<sub>4</sub> TO  
SYNTHESIS GAS - A COMBINED RESEARCH FOR TPD, TPR AND XPS 503  
*C. Yu, Y. Lu, X. Ding and S. Shen*

- PERFORMANCE OF Ni/La<sub>2</sub>O<sub>3</sub> CATALYST IN CARBON DIOXIDE REFORMING  
OF METHANE TO SYNTHESIS GAS 511  
*Z. Zhang and X. Verykios*

- A NEW ROUTE TO SYNGAS - COMBINED CONVERSION OF CARBON  
DIOXIDE AND ETHANE ON ZEOLITES 517  
*F. Roessner, O. Klepel and A. Hagen*

- REACTION OF CH<sub>4</sub> WITH CO<sub>2</sub> AND H<sub>2</sub>O OVER SUPPORTED Ir CATALYST 525  
*A. Erdőhelyi, K. Fodor and F. Solymosi*

- THE PRODUCTION OF SYNTHESIS GAS BY THE REDOX OF CERIUM  
OXIDE 531  
*K. Otsuka, E. Sunada, T. Ushiyama and I. Yamanaka*

- THE DEVELOPMENT OF PLATINUM-ZIRCONIA CATALYSTS FOR THE CO<sub>2</sub>  
REFORMING OF METHANE 537  
*A.N.J. van Keulen, M.E.S. Hegarty, J.R.H. Ross and P.F. van den  
Oosterkamp*

- LOW-TEMPERATURE SYNGAS FORMATION BY CO<sub>2</sub> REFORMING OF  
METHANE IN A HYDROGEN-PERMSELECTIVE MEMBRANE REACTOR 547  
*E. Kikuchi and Y. Chen*

- CO<sub>2</sub> REFORMING OF METHANE IN A MEMBRANE REACTOR 555  
*A.A. Ponelis and P.G.S. van Zyl*

- MEMBRANE REACTORS - A NEW TECHNOLOGY FOR PRODUCTION OF  
SYNTHESIS GAS BY STEAM REFORMING 561  
*J. Sogge and T. Strøm*

- A GAS-FIRED HEAT-PIPE REFORMER FOR SMALL-SCALE HYDROGEN  
PRODUCTION 567  
*J. T. Richardson*

- AUTHOR INDEX 573

- OTHER VOLUMES IN THE SERIES 577

## PREFACE

---

Following on from the three previous meetings held in New Zealand (1987), Norway (1990) and Australia (1993), South Africa was chosen as the venue for the Fourth International Natural Gas Conversion Symposium. The meeting took place between 19-22 November 1995 at the Berg-en-Dal Camp in the Kruger National Park. With its strong tradition in the commercial application of the Fischer-Tropsch route (SASOL's coal-based plants) and of natural gas conversion (Mossgas plant), South Africa (and the Kruger Park) provided a fitting location for such a Symposium.

The meeting was attended by some 180 delegates from 25 different countries, with an even mix between delegates from academia and industry. About 110 presentations (both oral and poster) were made in the following broad categories:

- Oxidative coupling
- Partial oxidation
- Reforming
- Novel methane reactions
- Fischer-Tropsch synthesis
- Synthesis of alcohols and other oxygenates
- Economics and Industrial Processes.

The opening address was delivered by Mr Roy Pithey, Chairman of South Africa's Central Energy Fund who dealt with the importance and utilisation of natural gas in sub-Saharan Africa.

Plenary lectures were presented by Professors E. Iglesia (Catalyst design and selectivity for F-T Synthesis) and E.E. Wolf (Oxidative Coupling of Methane).

A number of keynote addresses were also delivered.

- Dr T Fleisch (Amoco) described the use of DME as a transport fuel and the work which has been carried out in this area in collaboration with Haldor Topsoe.
- Professor L D Schmidt (University of Minnesota) described his work on the direct conversion of methane at high velocities.
- Dr B Jager (SASTECH R & D) reported on the recent developments in slurry and fluidized bed F-T reactors at SASOL.
- Dr J Rostrup-Nielsen (Haldor Topsoe) discussed the role of catalysis in the conversion of natural gas for power generation.

After three days of presentations of the latest research results in the seven categories given above and the enthusiastic discussions that took place in the setting of the African bush, the concluding remarks were provided by the two plenary speakers who also put forward their view on the future developments in methane conversion and catalysis. It was noted that for methane coupling the science to be developed is centred on the structural aspects of the catalyst whilst the engineering problem to be solved surround novel reactor/separation systems. Areas for further research were: direct conversion of methane to intermediate monomers; methanol conversion to higher alcohols; CO/H<sub>2</sub> conversion in a commercially viable route to higher alcohols; and CO/H<sub>2</sub> conversion to high quality gasoline. Clearly such developments would fit into the energy cycle which has moved from wood, to coal, to oil, to gas, and will most probably move to hydrogen. On this note, the 4th International Natural Gas Conversion Symposium came to a close.

The editors hope that the publishing of these proceedings will help catalyse further developments in this field which could be announced at the 5th International Natural Gas Conversion Symposium to be held in Sicily from 20-25 September 1998.

Lastly, we wish to express our sincere thanks to all our sponsors and especially to SASOL (South Africa) and Süd-Chemie (Germany).

M de Pontes  
R L Espinoza  
C P Nicolaides  
J H Scholtz  
M S Scurrall

---

## ORGANISING AND ADVISORY COMMITTEE

---

### ORGANISING COMMITTEE

M de Pontes	CEF (Pty) Ltd
R L Espinoza	SASTECH (Pty) Ltd
C P Nicolaides	University of the Witwatersrand
J H Scholtz	SASTECH (Pty) Ltd
M S Scurrall	Anglo American Research Laboratories (Pty) Ltd

### ADVISORY COMMITTEE

B Jager	SASTECH (Pty) Ltd
H L Roberts	CEF (Pty) Ltd

### SECRETARIAT

Y Arnold	Mintek
J Martins	Mintek

---



**FINANCIAL SUPPORT**

---

The Organising Committee would like to thank the following organisations for their financial assistance;

AVIS

ROBERTSON

SOUTH AFRICAN AIRWAYS

SASOL (PTY) LTD

SÜD CHEMIE AG

**SYNTHESIS OF ALCOHOLS AND  
OTHER OXYGENATES**

## The Use of a Jet-Stirred Continuously Stirred Tank Reactor (CSTR) to Study the Homogeneous Gas Phase Partial Oxidation of Methane to Methanol.

Gary A. Foulds<sup>a1</sup>, Brian G. Charlton<sup>a</sup>, Buu T. Le<sup>b</sup>, J. Clifford Jones<sup>b</sup> and Brian F. Gray<sup>c</sup>.

<sup>a</sup>C.S.I.R.O. Division of Coal & Energy Technology, Lucas Heights, Menai, N.S.W., Australia.

<sup>b</sup>School of Chemical Engineering and Industrial Chemistry, U.N.S.W., N.S.W., Australia.

<sup>c</sup>School of Mathematics, University of Sydney, Sydney, N.S.W., Australia.

Direct partial oxidation of methane to methanol is a process that has the potential to reduce the energy use and the cost of methanol production by eliminating synthesis gas generation as an intermediate step. This process has been the subject of considerable study, as manifested by the scope of work reported in a number of recent reviews [1-3]. Most of the studies reported have been carried out in tubular flow reactors that were empty or contained inert packing. To complement the experimental studies, theoretical work has been carried out, largely with a view to obtaining a suitably tractable model for computer experiments to be performed, at far less cost and over a greater range of parameter space [1]. It has been pointed out that non-isothermal modelling of tubular reactor systems is not possible without assumptions, as spatial gradients exist and the required transport properties such as diffusion coefficients and thermal conductivities of the numerous transient species involved in the most comprehensive methane oxidation mechanism are not known. However, modelling the reaction in a CSTR is feasible, as spacial effects are absent and the steady state, oscillation and bifurcation behaviour can be clearly seen without physical complications [4]. While the use of a continuously stirred tank reactor (CSTR) for this reaction at high pressure has been suggested by other workers [5], to the best of our knowledge, only one experimental study using a CSTR for this reaction, at pressure, has been reported [6]. However, the equipment used in this study (a commercial, mechanically stirred, cylindrical autoclave with a volume of 240ml) proved less than ideal, due to the substantial thermal resistance of the metal vessel, the glass liner and pocket of air between the two, the uneven heating outside the vessel, and the dissipation of heat along the stirrer shaft. These factors made it impossible to measure the heat transfer coefficient of this vessel, essential for modelling the reaction system.

In our desire to validate the nonisothermal CSTR model experimentally, these factors and the desire to use shorter residence times required by the model, led to the use of a cylindrical jet stirred CSTR, based on the design of David, Houzelot and Villiermaux [7]. In this paper, we report the design and validation of the CSTR, and the results of experimental studies carried out using the reactor. Experiments were carried out using residence times of 10 to 30s, pressures ranging from 1.5 to 5.0 MPa and reactor oven (ambient) temperatures up to 450°C. Results are presented and compared with those predicted by the model, as well as those reported in previous studies.

### 1. EXPERIMENTAL

The design of the CSTR follows the rules established by David and Matras [8], which have been defined and verified for spherical jet reactors incorporating a range of volumes (3ml to 50 000ml). It takes into account the constraints identified by these authors relating to turbulence, sonic velocity and internal recycling limitations. The cylindrical design was based on a reactor made by David, Houzelot and Villiermaux [7], but differs noticeably in volume and the position

---

<sup>1</sup> Present address: BHP Research, Newcastle Laboratories, PO Box 188, Wallsend, Newcastle, NSW, 2287, Australia.

Acknowledgement: We thank K. Wong, D. Chivers, D. Stathers, G.S. Walker for technical assistance and The University of New South Wales and BHP Co. Ltd. for financial support.

of the gas exit port. The cylindrical shape is easier to machine and produce on a larger scale if required. The CSTR was constructed from stainless steel, with a pyrex liner to render the internal surface inert and chain-reflective. Figure 1 is a technical drawing of the vessel. Feed gas injection is through three 1.6 mm o.d. tubes set with a long one in the centre and the two others of the same diameter at 8.0 mm spacing. The outer injection tubes each have one 0.3 mm diameter orifice set halfway into the vessel, acting tangentially and in opposite directions, while in the centre injection tube there are two 0.3 mm diameter orifices, again acting in opposite directions and equidistant from the centre of the vessel. The product gas exit is opposite to injection via a 6.0 mm tube. To render the internal metal parts of the reactor chain-reflective, they were coated with a ceramic material prepared from Fuller's earth as reported by Felton [9]. An 8% by weight suspension of Fuller's earth in water, de-flocculated with 4% by weight of sodium carbonate, was painted onto the metal surfaces and the resultant coating baked at 700°C overnight.

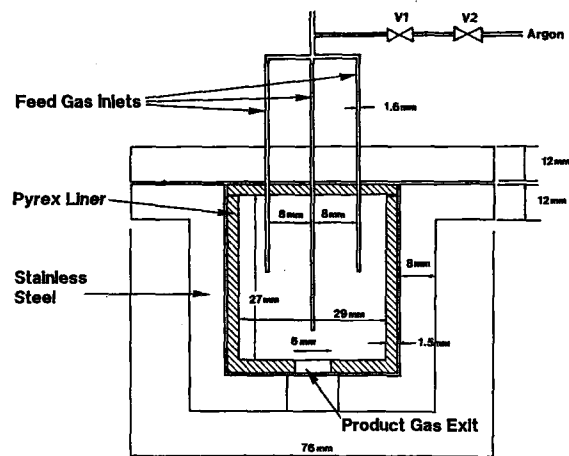


Figure 1. Mechanical design of Jet Stirred Continuously Stirred Tank Reactor

The reaction vessel was contained in a forced-draught oven capable of operating at temperatures up to 500°C. The vessel was incorporated into a super-atmospheric gas handling system, the details of which have been described earlier [10]. Methane (>99.0%) and oxygen (>99.5%), supplied through mass flow controllers to give the desired  $\text{CH}_4/\text{O}_2$  composition, were well mixed before passing through a header to the injection tubes and into the reactor. Product gases exited from the reactor vessel to a water chilled condenser and through a back-pressure regulator, after which the exit flow rate was measured. Gas temperatures ( $T$ ) were measured with a mineral insulated type K thermocouple of 1.5 mm diameter, with the last 10 mm of the thermocouple and the junction bare. The bare portion of the thermocouple was coated with silica using the method described by Felton [9], in which a solution of dimethyl cyclosiloxane (approximately 20 wt%) dissolved in methanol is burnt in a burner with a wick, and the thermocouple is passed through the white smoke apparent above the flame. The even deposition of silica is apparent to the naked eye. A second type K thermocouple was attached to the outside wall of the reaction vessel to measure its wall temperature ( $T_w$ ), while the oven (ambient) temperature ( $T_a$ ) was controlled through a further type K thermocouple set in the forced gas stream. In addition, the oven temperature was also measured independently via the control thermocouple.

Two techniques were used to measure the residence time distribution in the CSTR, pulse injection and step change of input concentration. The equipment was used as in the partial oxidation experiments with only minor modification, as described below. For the pulse injection, a small tube was connected to a tee on the gas inlet line close to the oven inlet. The reactor end of the tube was closed off with a valve (V1) and the other end was connected through a valve (V2) to the injection gas (argon) cylinder (see Figure 1). The amount of argon injected could be

adjusted by varying the tube size or the injection pressure. To operate, V1 was closed and the tube pressurised by opening V2. V2 was then closed and the injection effected by briefly opening V1. For the step change injection, a three-way valve was installed in a side-line, attached to a tee in the gas feed line. A small measured flow of injection gas (approximately 5% of the feed gas flow rate) was established through the three-way valve, passing to atmosphere. The three-way valve was then switched to divert the gas into the feed gas line for injection. A portion of the exit gas from the reactor (15 ml/min NTP) was diverted to a quadrupole mass spectrometer to measure the concentration of the injected gas appearing in the outlet gas stream. The sample take-off point was outside the oven, approximately 180 mm downstream from the reactor exit.

Experiments to determine the overall heat transfer coefficient ( $U$ ) were carried out by passing methane, nitrogen or argon through the vessel at selected pressures and flow rates, while the internal vessel temperature ( $T$ ), vessel wall temperature ( $T_w$ ), oven (ambient) temperature ( $T_a$ ) and influx gas temperature ( $T_i$ ) were measured.

For all reactor runs, ambient temperature was chosen as the preferred or bifurcation parameter i.e. the one which is varied at fixed values of the others (pressure, feed oxygen concentration and residence time), and was varied from 300°C to a maximum of 450°C, above which it has been shown [11] that methanol decomposes in the presence of methane and oxygen. For each of the runs,  $T_a$  was increased (upward traverse) and decreased (downward traverse). NOTE: The high oxygen concentrations used at high pressure are approaching the explosive limit and the reactor was located in an isolated explosion containment area. Product gases were fully analysed using a dual gas chromatographic system as described previously, while oxygen and methane conversion, selectivities and yields, determined on a total product basis, were calculated as described in the same article [10]. Mass balances with respect to C, H and O were determined for each of the runs and were found to be within 5%.

## 2. RESULTS AND DISCUSSION

Residence time distribution studies showed that the vessel behaved as a CSTR over the full range of gas flows and pressures tested. Whilst the shape of the residence time curves showed unequivocally that the system operated as a CSTR, the vessel volume calculated from the results averaged out at 24 ml, compared to the vessel internal volume of 18 ml as determined by measurement. The volume of the tube between the vessel and the sample take-off point was approximately 5 ml. The heat transfer coefficient was determined according to the method described by Caprio et al [12]. A value of  $U = 16.9 \text{ W m}^{-2} \text{ K}^{-1}$  was obtained for the reactor system.

The non-isothermal model predicts a number of significant features including (a) discontinuity in conversion and heat release rate, most significant at high oxygen concentrations and the position of which moves to lower temperature as the system pressure is increased (b) hysteresis, present at 9.5% oxygen in the feed, but not at lower oxygen concentrations, (c) an increase in conversion but decrease in methanol selectivity as feed oxygen concentration is increased, (d) an increase in methanol selectivity as the system pressure is increased, (e) a slight increase in conversion with an associated drop in methanol selectivity at very short residence times, and (f) the presence of oscillations at 9.5% oxygen feed concentration [4].

To illustrate the experimental demonstration of these features we focus on the results obtained at 30 s residence time, 3.0 MPa pressure and 9.5% oxygen in the feed. Figure 2 depicts oxygen and methane conversion as a function of ambient temperature. Both parameters exhibit the discontinuity and hysteresis predicted by the model, with the steeply rising or dropping regions of conversion corresponding to the steeply rising or dropping regions of gas reaction temperature. Note that ignition occurs at a  $T_a$  of approximately 400°C on the upward traverse of temperature, while extinction occurs at a  $T_a$  of 385°C on the downward traverse of temperature, giving a hysteresis width of 15°C. Also confirmed is the fact that the eventual flattening of the reactant temperature at ambient temperatures above the discontinuity is due to complete oxygen consumption, which corresponds to approximately 8% methane conversion at these conditions.

The product spectrum, consists of  $\text{H}_2\text{O}$ ,  $\text{CH}_3\text{OH}$ ,  $\text{CO}$ ,  $\text{CO}_2$ , and trace amounts of  $\text{HCHO}$ ,  $\text{C}_2\text{H}_4$  and  $\text{C}_2\text{H}_6$ . Selectivity to methanol, as illustrated in Figure 2, mirrors the conversion hysteresis and exhibits a maximum of 25% on a region of the curve accessible only on the downward traverse of ambient temperature, as predicted by the model [4].

Methanol yields of up to 1.9% were recorded under these conditions, with the maximum methanol yield once again occurring in a region of ambient temperature only accessible on the downward traverse. Trends exhibited by CO, CO<sub>2</sub> and H<sub>2</sub>O were similar. At high ambient temperatures, CO yields were generally in the region of 4.0%, while CO<sub>2</sub> yields were generally in the region of 2.0% or less. In addition, water yields of over 8.0% were recorded under these conditions.

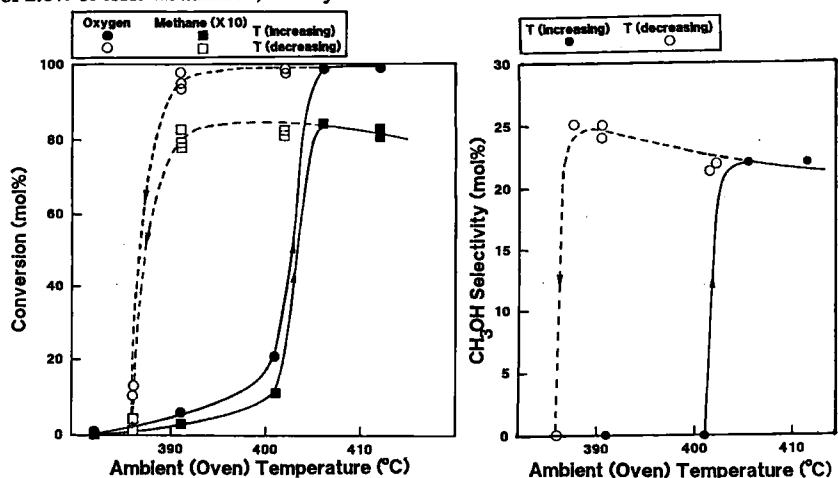


Figure 2. Plots of Oxygen Conversion, Methane Conversion and Methanol Selectivity vs  $T_a$ .

The effect of feed oxygen concentration on the discontinuity and hysteresis is evident from the data listed in Table 1. Semi-quantitative agreement of experimental data with the results predicted by the model is observed, with the important trends predicted by the model clearly in evidence i.e. increasing the feed oxygen concentration causes the discontinuity to move to higher temperature, increases the width of the hysteresis, and increases the discontinuity temperature jump ( $\Delta T$ ).

Table 1. Effect of feed oxygen concentration on discontinuity and hysteresis<sup>a</sup>

Oxygen Conc. (%)	$T_{a,ignition}$ (°C)	$T_{a,extinction}$ (°C)	Hysteresis loop width (°C)	$\Delta T$ (°C)
9.5	411 (381) <sup>*</sup>	381 (376) <sup>*</sup>	30 (5) <sup>*</sup>	60 (110) <sup>*</sup>
7.5	406 (402) <sup>*</sup>	391 (402) <sup>*</sup>	15 (0) <sup>*</sup>	50 (80) <sup>*</sup>
5.0	402 (397) <sup>*</sup>	396 (397) <sup>*</sup>	8 (0) <sup>*</sup>	32 (49) <sup>*</sup>
2.5	401 (397) <sup>*</sup>	398 (397) <sup>*</sup>	3 (0) <sup>*</sup>	10 (20) <sup>*</sup>

<sup>a</sup>-Results obtained using a pressure of 3.0 MPa and a residence time of 20 s; <sup>\*</sup>-Values in parentheses predicted by model [4].

Table 2. lists data relating the effect of residence time on the discontinuity and hysteresis. Once again good semi-quantitative agreement with the model is observed. Clearly, decreasing the residence time results in the discontinuity moving to higher temperature with a concomitant widening of the loop and increase in the temperature jump. This can be explained by the increase in heat release rate as the feed rate to the reactor is increased.

Generally, the experimentally observed hysteresis loops are wider than those predicted by the model and the temperature jumps are larger. This may be due to experimental error in determination of the overall heat transfer coefficient and the surface to volume ratio. The model has shown that hysteresis is extremely sensitive to the product of these two parameters [4].

Table 2. Effect of residence time on discontinuity and hysteresis<sup>a</sup>

Residence Time (s)	$T_{a,ignition}$ (°C)	$T_{a,extinction}$ (°C)	Hysteresis loop width (°C)	$\Delta T$ (°C)
10 (10) <sup>*</sup>	427 (395) <sup>*</sup>	362 (361) <sup>*</sup>	65 (34) <sup>*</sup>	85 (168) <sup>*</sup>
20 (20) <sup>*</sup>	411 (381) <sup>*</sup>	381 (376) <sup>*</sup>	30 (5) <sup>*</sup>	60 (110) <sup>*</sup>
30	405	387	18	40

<sup>a</sup>-Results obtained using a pressure of 3.0 MPa and an oxygen feed concentration of 9.5%; <sup>\*</sup>-Values in parentheses predicted by model [4].

Table 3. summarises the effects of various process parameters on methane conversion and methanol selectivity and yield. Data obtained in other reaction systems have been included for comparison. It should be noted that the methanol selectivities and yields listed correspond to the maximum yield observed experimentally, or quoted in the literature.

Table 3. Comparison of Jet Stirred CSTR results with relevant theoretical and experimental work.

Source of Data	Reactor Design	Temp. (°C)	Res. Time (s)	Oxygen Conc. (mol%)	Press. (MPa)	CH <sub>4</sub> Conv. (mol%)	CH <sub>3</sub> OH Selec. (mol%)	CH <sub>3</sub> OH Yield (mol%)
This Work	Jet Stirred	400	10	9.5	3.0	8.1 (7.0) <sup>*</sup>	18.7 (16) <sup>*</sup>	1.5 (1.1) <sup>*</sup>
		400	20	9.5	3.0	8.0 (7.0) <sup>*</sup>	23.0 (osc) <sup>*</sup>	1.8
		400	30	9.5	3.0	7.7	23.1	1.8
		400	20	7.5	3.0	5.8 (5.0) <sup>*</sup>	28.0 (25.0) <sup>*</sup>	1.6 (1.3) <sup>*</sup>
		400	20	5.0	3.0	4.2 (3.0) <sup>*</sup>	36.0 (34) <sup>*</sup>	1.5 (1.1) <sup>*</sup>
		400	20	2.5	3.0	2.2 (2.0) <sup>*</sup>	45.0 (48.0) <sup>*</sup>	1.0 (1.0) <sup>*</sup>
		432	10 <sup>#</sup>	9.5	1.5	7.5	19.1	1.4
		398	20 <sup>#</sup>	9.5	3.0	7.8	24.0	1.9
		381	33 <sup>#</sup>	9.5	5.0	8.2	26.8	2.2
[6]	mech.CSTR	464		9.5	3.0	8.3	17.0	1.3
[10]	Annular	427		9.5	3.0	8.5	23.0	1.8
[13]	Tubular	455		10.3	3.4	7.5	59.8	4.5
[14]	Tubular	410		9.4	3.3	7.7	16.4	1.3
[5]	Tubular	450		10.0	5.0	12.0	25.0	2.8

<sup>\*</sup>-Values in parentheses predicted by model [4], osc = oscillations predicted; <sup>#</sup>-Note that the residence time has been adjusted to maintain constant flow rate at the different pressures.

Comparison of the experimentally determined results obtained in the jet stirred CSTR shows good semi-quantitative agreement with the non-isothermal model [4]. Increasing feed oxygen concentration results in higher methane conversion and a decrease in methanol selectivity. As predicted by the model, residence time does not affect methanol selectivity or yield, except at the shortest residence time of 10 seconds where they drop from 23% to 18.7% and from 1.8% to 1.5% respectively. Increasing the pressure at constant flow rate results in greater methanol selectivity and yield, a trend which has also been predicted by the model. Instability was observed at 9.5% feed oxygen concentration, as predicted by the model, but the amplitude of the oscillations (approximate period 6/minute) was irregular and thus inconclusive.

Data reported by other workers reveals little difference between the results obtained using the jet stirred CSTR and those obtained using tubular reactors. Similar trends with respect to oxygen concentration and conversion and selectivity are observed. Methanol selectivities vary between 20 and 50% when an oxygen feed concentration in the range of 2.5 to 10% is used. One exception is the work reported by Yarlagadda et al who report methanol selectivities in excess of 60% and yields in excess of 4.5% [13], results which appear not to have been repeated elsewhere [1-3].

### 3. CONCLUSIONS

A newly constructed cylindrical jet stirred reactor, displaying CSTR behaviour at residence times up to 30s, has facilitated the study of the partial oxidation of methane to methanol at pressure. The results obtained over a wide range of process conditions exhibit good semi-quantitative agreement with those predicted by the non-isothermal model [4]. Cool flame phenomena, including discontinuity and hysteresis in heat release rate, were observed. Decreasing the temperature was found to favour methanol production, with the highest yields being observed in the region accessible only on the downward sweep of the hysteresis, a very specific phenomenon predicted by the model. Increasing the oxygen concentration was found to increase conversion and the width of the hysteresis loop, at the expense of methanol selectivity. It is worth noting that the beneficial effect of increasing the pressure is clearer than in previous studies [1], and this may be attributed to its investigation under constant flow conditions. Variation of residence time was found to have little influence, except at the shortest residence time of 10s which resulted in higher methane conversion, an increase in the hysteresis loop, and a decrease in methanol selectivity. Again this trend has been specifically predicted by the non-isothermal modelling studies [4]. The trends and absolute values of methanol yield and selectivity obtained in the CSTR are comparable with those attained, using similar process parameters, in earlier tubular reactor studies. A possible explanation for this is that the fast partial oxidation reaction occurs in a small section of the tubular reactor, with complete consumption of oxygen. The rest of the tubular reactor then functions as a heater keeping the products and unreacted methane at the reactor wall temperature, which has usually been less than 500°C. This type of profile has been observed experimentally in an annular reactor with longitudinal temperature measurement [10]. Methanol would thus be stable under these conditions [11], particularly if negligible back-mixing took place.

If the partial oxidation of methane to methanol is to be of commercial interest, then selectivities, particularly at high conversions, will need to be improved, an indicative target being 77% selectivity at 10% conversion [1]. The results of this study have experimentally verified the value of the non-isothermal model [4], giving confidence in its use to search process parameter space for "windows" of high methanol yield at much less cost and effort than experimental studies. In addition, the model will prove invaluable when used for commercial process design, should commercial targets be achieved.

### REFERENCES

1. G.A. Foulds and B.F. Gray, *Fuel Processing Technology*, 42 (1995) 129.
2. T.J. Hall, J.S.J. Hargraves, G.J. Hutchings, R.W. Joyner and S.H. Taylor, *Fuel Processing Technology*, 42 (1995) 151.
3. S.I. Galanov, L.N. Kurina, A.I. Galanov, V.N. Belovsova and A.A. Davydov, *Catalysis Today*, 24:3 (1995) 293.
4. B.F. Gray, J.F. Griffiths, G.A. Foulds, B.G. Charlton and G.S. Walker, *Ind. Eng. Chem. Res.*, 33 (1994) 1126.
5. D.W. Rytz and A. Baiker, *Ind. Eng. Chem. Res.*, 30 (1990) 2287.
6. B.G. Charlton, G.A. Foulds, G.S. Walker, J.C. Jones and B.F. Gray, *CHEMECA 92, Official Proceedings of the Twentieth Australasian Chemical Engineering Conference, Canberra, Australia*, 1 (1992) 67.
7. R. David, J-L. Houzelot and J. Villiermaux, *Chem. Eng. Sci.*, 34 (1979) 867.
8. R. David and D. Matras, *Canadian J. Chem. Eng.*, 53 (1975) 297.
9. P. Felton, M.Sc. Thesis, Leeds University, 1974.
10. G.A. Foulds, B.F. Gray, S.A. Miller and G.S. Walker, *Ind. Eng. Chem. Res.*, 32 (1993) 780.
11. R. Burch, G.D. Squire and S.C. Tsang, *J. Chem. Soc., Faraday Trans. 1*, 85(10) (1989) 3561.
12. V. Caprio, A. Insoia and P.G. Lignola, *Proceedings of the 16th Symposium (International) on Combustion*, (1977) 1155.
13. P.S. Yarlagadda, L.A. Morton, N.R. Hunter and H.D. Gesser, *Ind. Eng. Chem. Res.*, 27 (1988) 252.
14. H.D. Gesser, N.R. Hunter, L.A. Morton, P.S. Yarlagadda and D.P.C. Fung, *Prepr.-Am. Chem. Soc., Div. Fuel Chem*, 32(3) (1987) 255.

Synthesis of alcohols from syngas over Ni-based catalyst: comparison with the hydroformylation reaction

J. Llorca, P. Ramirez de la Piscina, N. Homs, E. Brum Pereira<sup>1</sup>, P. Moral<sup>1</sup> and G.A. Martin<sup>1</sup>

University of Barcelona, Facultat Quimica, Diagonal 647, 08028 Barcelona, Spain

<sup>1</sup>Institut de Recherches sur la Catalyse - CNRS, 2 avenue A. Einstein, 69626 Villeurbanne, France

The CO hydrogenation reaction into alcohols and the hydroformylation of ethylene have been studied over a series of silica-supported nickel-based catalysts (Ni, Ni-Cu, Li-Ni, Li-Ni-Cu). The oxo selectivity sequence is found to be similar to that of selectivity towards higher alcohols in CO + H<sub>2</sub>, indicating that both reactions share a common path: the migratory insertion of CO into a metal-alkyl bond. In agreement with this view, evidence of a direct relationship between selectivities towards propanol and C<sub>2</sub> hydrocarbons in the CO + H<sub>2</sub> reaction has been observed. This confirms that the concept of metal isolation associated with Lewis acid addition is a fruitful guideline to design new catalysts for both reactions. Sequence comparison suggests that methanol formation proceeds via another route.

### 1. INTRODUCTION

C<sub>1</sub>-C<sub>6</sub> alcohol mixtures from syngas are interesting octane boosters for unleaded gasoline. Today, only a limited amount of oxygenates consisting mainly of ethers are utilized as blend for motor fuel. The demand for oxygenates will probably increase and it could be of interest to diversify their sources. In this context the synthesis of alcohols (methanol, ethanol, mixtures of methanol and higher alcohols) to be added to gasoline, methanol + isobutanol for the production of methyl-tert-butylether) still remains a subject of interest. The catalysts (modified oxides, sulfides or metals) are generally non selective and the factors governing selectivity are not well understood [1]. Alcohol formation is believed to proceed via a CO insertion into an alkyl metal bond, a path which is also shared by the hydroformylation reaction (CH<sub>2</sub> = CH<sub>2</sub> + CO + H<sub>2</sub> = C<sub>2</sub>H<sub>5</sub>CHO). Some limited attempts to compare both reactions have already been carried out [2,3]. This paper reports on a more systematic investigation of the behaviour of a series of nickel-based catalysts towards both reactions.



The number of carbons,  $n$ , in the alkane (alkene) is equal to that of R whilst it equals to  $n + 1$  for the oxygenates.

The methanol (2) and hydroformylation (3) sequences are different, suggesting that methanol formation does not proceed via the previous scheme ( $R = H$ ). It can be argued, however, that copper is also active towards methanol formation; consequently, nickel and nickel-copper catalysts should be compared separately; methanol selectivity has the following characteristics:



They are different from those observed for the hydroformylation activity:



In particular, it can be noticed that lithium addition to nickel results in a limited increase in selectivity towards methanol whilst it increases the hydroformylation activity by two orders of magnitude. It can therefore be concluded that methanol and higher alcohol routes are different, and that methanol formation does not proceed via a CO insertion into a M-H bond to give a formyl species, in agreement with organometallic chemistry which indicates that this insertion reaction does not occur to any appreciable extent for thermodynamic reasons [7].

If scheme (A) is correct, it can be predicted that the selectivity towards  $C_n$  hydrocarbons is related to the selectivity towards  $C_{n+1}$  oxygenates: both selectivities should vary in a parallel way. This is indeed observed when considering the selectivity towards ethane + ethylene and the selectivity towards propanol (Figure 1): various samples were considered, including Li-, Na- and K- promoted Ni/SiO<sub>2</sub> catalysts described elsewhere [4], at different aging time. The slope related to Li-promoted Ni/SiO<sub>2</sub> catalysts seems to be larger than that obtained with Li-Ni-Cu catalysts. This is possibly related to the better hydroformylating properties demonstrated by the latter catalytic system.

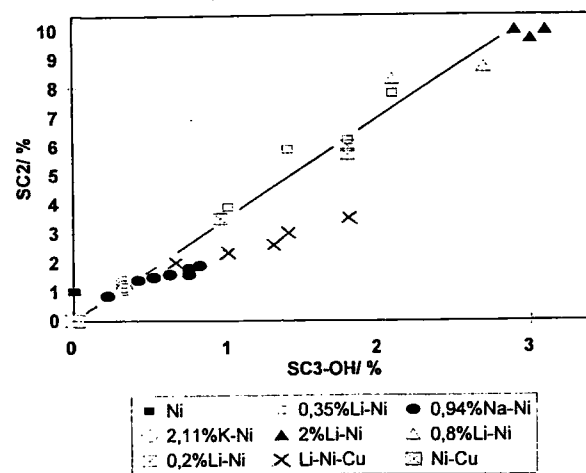


Figure 1: Relationship between selectivity towards  $C_2$  hydrocarbons,  $SC_2$ , and selectivity towards propanol,  $SC_3$  OH for the CO hydrogenation reaction over a series of Ni-based catalysts at different aging time.

Figure 2 shows that the selectivities towards methane and ethanol do not vary in a parallel way, at variance with the previous situation. This may be explained assuming that methane originates from different sources, including a common route to methanol, hydrogenolysis...

Finally another observation deserves some comments: Ni-Cu catalysts demonstrate a certain hydroformylation activity whilst no higher alcohols are formed from CO hydrogenation. This does not discard the CO insertion model but can merely reflect a low concentration of M-R species on the Ni-Cu surface.

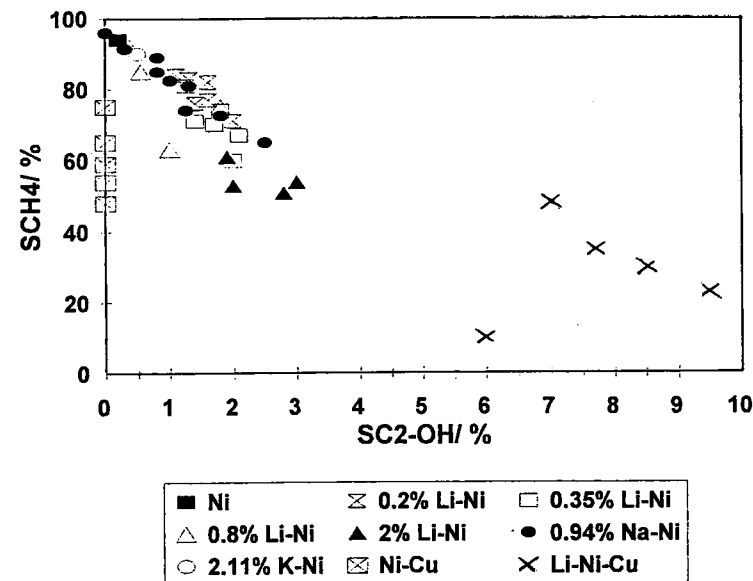


Figure 2: Selectivity towards methane  $SCH_4$  versus selectivity towards ethanol,  $SC_2OH$ .

#### 4. CONCLUSION

It can be concluded from sequence comparison that CO hydrogenation into higher alcohols is closely related to the hydroformylation reaction: both reactions proceed over nickel-based catalysts via a migratory insertion of CO into a metal-alkyl bond, confirming preliminary studies from the literature. This shows that metal isolation associated with Lewis acid addition is a fruitful guideline to design new catalysts more selective into alcohol mixtures. This study has also shown that methanol from CO hydrogenation is likely to proceed via a different mechanism, which does not involve a CO insertion into a M-H bond. Finally, measurement of hydroformylation properties of solids initially designed for CO hydrogenation into alcohol mixtures proves to be useful: it has led to heterogeneous systems which are reasonably selective towards the oxo synthesis (ca 98 %) and which could be of interest with regards to the  $n/iso$  selectivity when higher alkenes are considered.

## ACKNOWLEDGEMENT

The exchange program « Picasso » between France and Spain and CICYT, MAT93-0477 are acknowledged for support.

## REFERENCES

1. For a review, see *Catalysis Today*, 15 (1) (1992).
2. S. Uchiyama, Y. Obayashi, M. Shibata, T. Uchiyama, N. Kawata and T. Konishi, *J. Chem. Soc. Chem. Com.* (1985) 1071.
3. A. Gomez Cobo, N. Mouaddib, J.A. Dalmon, C. Mirodatos, V. Perrichon, M. Primet, P. Chaumette and Ph. Courty, in *Natural Gas Conversion*, A. Holmen et al Eds. 1991, Elsevier, p. 257.
4. E. Brum Pereira and G.A. Martin, in *Natural Gas Conversion II*, H.E. Curry and R.F. Howe Eds. 1994, Elsevier, p. 349.
5. E. Brum Pereira and G.A. Martin, *Appl. Catal. A*, 103 (1993) 291.
6. E. Brum Pereira and G.A. Martin, *Appl. Catal. A*, 115 (1994) 135.
7. W.M.H. Sachtler and M. Ichikawa, *J. Phys. Chem.*, 90 (1986) 4752.

### Zirconia Modified Ru/Al<sub>2</sub>O<sub>3</sub> Catalysts for the Synthesis of Oxygenated Products From Syngas.

M.R. Goldwasser, M.L. Cubeiro, M.C. Da Silva and M.J. Pérez Zurita.  
 Universidad Central de Venezuela, Facultad de Ciencias, Escuela de Química, Apartado Postal 47102, Los Chaguaramos, Caracas, Venezuela.

G. Leclercq, L. Leclercq, M. Dufour and L. Gengembre.  
 Université des Sciences et Technologies de Lille, Laboratoire de Catalyse Hétérogène et Homogène, 59665 Villeneuve D'Ascq, Cedex, France.

G.C. Bond and A.D. Hooper  
 Brunel University, Chemistry Department, Uxbridge, Middlesex, UB8 3PH, U.K.

## Abstract

Modification of Ru/Al<sub>2</sub>O<sub>3</sub> by ZrO<sub>2</sub> has been carried out and tested in syngas conversion. Different coverages of ZrO<sub>2</sub> were attained by means of the controlled hydrolysis of a zirconium alkoxide on the Al<sub>2</sub>O<sub>3</sub> surface. Characterization of the solids by XRD, TEM, TPR, FT-IR and XPS shows that a high dispersion of ZrO<sub>2</sub> over Al<sub>2</sub>O<sub>3</sub> is attained. Impregnation of Ru on these solids gives rise to highly dispersed Ru particles preferentially associated to the ZrO<sub>2</sub> species. Under the reaction conditions ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> solids were almost inactive for syngas conversion. It was established that depending on pre-treatment and/or reaction conditions Ru could leave the surface as Ru carbonyls, the activity/selectivity patterns being dramatically dependent of the protocol followed.

## 1 INTRODUCTION

Growing interest in environmental protection will enforce the use of oxygenates as octane enhancers for automotive fuels. In recent years a significant effort has been devoted to the synthesis of higher alcohols from CO + H<sub>2</sub>. All group VIII metals have the ability to hydrogenate CO, mainly to hydrocarbons, with varying extents of bond formation, chain growth being maximised over Ru. Several approaches have been carried out to improve the formation of C<sub>2</sub> oxygenated products; among them the modification of hydrocarbon forming metals, particularly Ru, by adding components that suppress CO dissociation and stabilise the oxidation products, has recently received a great deal of attention [1-4]. The study reported herein comprises the modification of Ru/Al<sub>2</sub>O<sub>3</sub> by ZrO<sub>2</sub> to produce mixed oxides systems with high component inter-dispersion, to try to understand the influence of its structure in the behaviour of Ru catalysts in syngas conversion.



## 2. EXPERIMENTAL

### 2.1. Catalyst Preparation

The mixed oxides were prepared using the controlled alkoxide hydrolysis method [5] to obtain a well dispersed  $ZrO_2$  which covers the support surface with  $1/4$ ,  $1/2$  and 1 monolayer of  $ZrO_2$ . The desired amount of zirconium(IV)-tert-butoxide (98%, Aldrich), 5 ml of concentrated  $HNO_3$  and 250 ml of n-hexane were added to 10g of the support. The theoretical proportion of  $ZrO_2$  monolayer corresponds to 16.2%. The three  $ZrO_2/Al_2O_3$  solids were impregnated with an aqueous solution of  $RuCl_3 \cdot xH_2O$  (Aldrich) by the incipient wetness method to give a nominal Ru content of 1%. Catalysts are named as  $Ru/ZrO_2(\#)/Al_2O_3$  with number in parenthesis indicating the  $ZrO_2$  monolayer fraction.

### 2.2. Catalyst Characterisation

The catalysts and supports were characterised by chemical analysis, surface area measurements, XRD, TEM-EDX, TGA, TPR, CO adsorption followed by FT-IR and XPS. The Ru and  $ZrO_2$  quantification was followed by ICP argon plasma. The surface areas were measured by a single-point BET procedure using a Flowsorb II 2300 Micromeritics Rapid Surface Area Analyser. The TEM analysis was carried out with an analytical electron microscope Hitachi H-800 coupled with an EDX analyser. The diffraction patterns were obtained with a Phillips PW 1830 diffractometer using  $Cu K\alpha$  radiation. TPR analysis were carried out in a Micromeritics TPD/TPR 2900 apparatus; using ~50mg of the sample in a 10%  $H_2/Ar$  flow at  $10^\circ C/min$ . IR spectra were conducted on a Perkin-Elmer FT-IR 1760 spectrometers with a resolution of  $4\text{ cm}^{-1}$ . The IR cell used has a built-in furnace which was used to pretreat samples in situ at high temperature. Samples were mounted in the cell as wafers having a thickness of approximately  $20\text{ mg/cm}^2$ . Integrated intensities (absorbencies) were normalised to unit wafers thickness ( $mg/cm^2$ ). The protocol followed has been reported elsewhere [6]. The XPS analysis were conducted in a Leybold Heraeus equipment provided with an Al source (K1486.6 eV). All catalysts were studied before and after reduction. For the XPS analysis the reduction treatments were conducted in situ using a 6%  $H_2/N_2$  mixture and were left overnight at  $340^\circ C$ . Different references were used for the analysis of Ru containing solids. For  $Ru/Al_2O_3$  and  $Ru/ZrO_2/Al_2O_3$  the  $Al\ 2p_{3/2}$  at 74.8 eV was used which is equivalent to that of C1s at 285 eV, while for  $Ru/ZrO_2$  the reference used was  $Zr\ 3d_{5/2}$  at  $182.1 \pm 0.1\text{ eV}$ , with C1s at 285 eV.

### 2.3. Catalytic tests

The catalytic tests were performed in a continuous flow system with a fixed-bed reactor at 5.1 MPa, 250-300°C, 6.4 l/g.h.,  $H_2/CO = 2$ ,  $N_2 = 5\%$  (internal standard). The analysis of the reaction products were carried out by gas chromatography using the same conditions as described in Ref.[2].

## 3. RESULTS AND DISCUSSION

### 3.1. Chemical analysis, surface area, XRD and TEM

From the chemical analysis it was observed that, in general, the experimental compositions of the solids were close to nominal values. The BET areas for the solids containing Ru or  $ZrO_2$  were slightly higher than that of the support ( $100\text{ m}^2/g$ ). The diffractograms of the  $ZrO_2/Al_2O_3$  and  $Ru/ZrO_2/Al_2O_3$  solids showed no discernible reflections pertaining to Ru and  $ZrO_2$ , this implies that  $ZrO_2$  and Ru are present either in a highly dispersed or in an amorphous state. However, the first implication seems to be the case since evidence of the good dispersion of  $ZrO_2$  over the alumina matrix was corroborated by TEM as could be seen on Fig.1 for  $Ru/ZrO_2(1)/Al_2O_3$ . Using the dark field technique, the micrograph shows well dispersed solids with particle sizes between 10-20 nm. The EDX analysis for these solids (Fig. 1) show the peaks corresponding to the presence of Al, Zr, and Ru. It is interesting to note that in all the analysed samples the presence of Ru-Zr over the matrix was always simultaneously detected, which seems to indicate a degree of association between these species.

### 3.2. XPS analysis

In the XPS studies the surface composition of the solids were determined to assess the dispersion and degree of reduction of Ru on the supports. For the  $ZrO_2/Al_2O_3$  samples the position and shape of peaks Al 2p and O1s were very similar for all samples, binding energies (BE) corresponding to O1s  $\sim 531.8 \pm 0.1\text{ eV}$  and Al2p = 74.8 eV. On the contrary, a continuous evolution of the Zr 3d signals as the percentage of  $ZrO_2$  increases was observed.

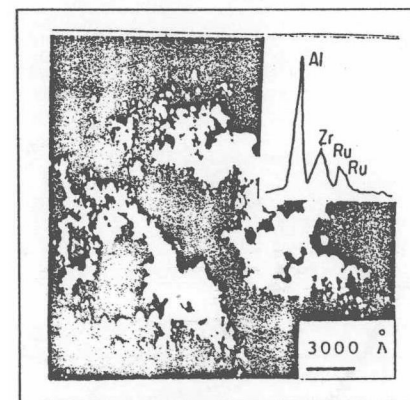


Figure 1. TEM image and STEM-EDX analysis of  $Ru/ZrO_2(1)/Al_2O_3$

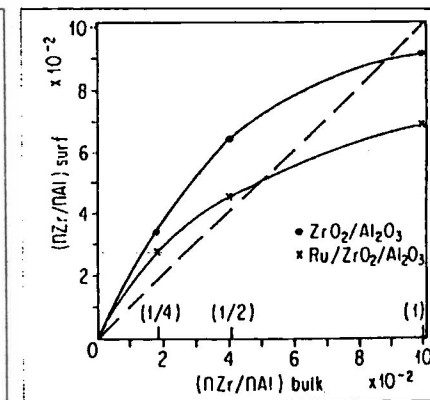


Figure 2. Dependence of surface  $nZr/nAl$  ratio on the bulk ratio for  $ZrO_2/Al_2O_3$  and  $Ru/ZrO_2(1)/Al_2O_3$ .

The shapes of the doublets changed with increasing  $ZrO_2$  loading and they also differed from the  $Zr\ 3d_{5/2}$  and  $Zr\ 3d_{3/2}$  doublets obtained with pure  $ZrO_2$ , which was better defined. The full width at medium height (FWMH) was greater (4.6-4.7 eV) for all  $ZrO_2/Al_2O_3$  samples than