

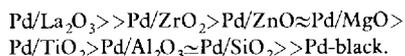
Catalysts for Energy Conversion

A REVIEW FROM THE PEOPLE'S REPUBLIC OF CHINA

The use of catalysts based on platinum group metals featured prominently at a recent conference held at the end of August 1982, at Dalian, Liaoning, in the People's Republic of China. The meeting was a joint China-Japan-U.S.A. symposium organised by an international steering committee and dealt with the use of catalysts in energy conversion processes. The papers presented covered a wide range of topics but the conversion of synthesis gas directly or indirectly via methanol to useful products predominated. Work involving the platinum group metals is reported here.

Methanol Synthesis and Conversion

The conventional methanol synthesis process is based upon zinc-chromium and more recently copper-zinc catalysts but Robert F. Hicks, Qujie Yen and Alexis T. Bell, University of California, U.S.A., have been assessing the use of supported palladium and more particularly the effects of different supports on the selectivity to methanol or hydrocarbons. The specific activity for methanol synthesis decreased in the order:



The catalyst most selective for methanol was palladium supported on lanthanum oxide. This is an unusual choice for a support but in a later paper Xie Youchang, Qian Minxie and Tang Youqi, Peking University, China, found such a support to thermally stabilise nickel crystallites.

Methanol is an important intermediate in the manufacture of high octane gasoline fuels or olefins suitable for use as chemical intermediates. Chen Guoguan and Liang Juan, Chinese Academy of Sciences, have investigated the modification of ZSM-5 type zeolites by introducing into their structure compounds containing such elements as phosphorus, magnesium, zinc and rare earths. In this way they

hoped to enhance the selective formation of light olefins. Moreover, Yuichi Murakami, Tadashi Hattori, Hirofumi Itoh, Carmela V. Hidalgo and Miki Niwa, Nagoya University, Japan, concluded that for unmodified ZSM zeolites the acid activity is critically important. This theme was further exemplified by the work of Makoto Misono, Takuo Hibi, Toshio Okuhara and Yukio Yoneda, University of Tokyo, who studied selective methanol conversion to hydrocarbons with organic salts of heteropoly acids which were found to be highly selective for light olefin conversion.

Fischer-Tropsch Reaction

Synthesis gas can be converted directly into hydrocarbons by means of the well known Fischer-Tropsch process. Several metals have known activity and recent interest has focused on the use of ruthenium for higher molecular weight straight chain paraffins. Liang Dongbai, Lin Liwu, Wu Rongan, Bai Yuheng, Hu Aihua and Han Li, Dalian Institute of Chemical Physics, have re-investigated the synthesis of long chain paraffins over ruthenium supported on alumina and silica. Further indications of carbon monoxide and hydrogen interaction over ruthenium and platinum catalysts were obtained in a kinetic study by Jiang Bingnan (Chiang Pingnan), Liu Weicheng, Huang Shiyu, Wang Hongdao, Guan Yuchun and Fu Chenbi, also of the Dalian Institute of Chemical Physics, who monitored the change in the infrared peaks of linearly absorbed carbon monoxide as it reacted with hydrogen. The results suggest that the adsorbed carbon monoxide species on ruthenium on alumina catalysts react with only one H_{ads} to form C_{ads} as the rate determining step, whereas with a platinum on alumina catalyst every adsorbed carbon monoxide reacts with two H_{ads} species. In an attempt to improve the quality of conventional Fischer-Tropsch products Kaoru

Fujimoto, Osamu Okuda and Hiro-o Tominaga, University of Tokyo, examined the catalytic features of NaY and HY zeolite supported ruthenium-platinum bimetallic clusters. The ratio of branched to straight chain hydrocarbons obtained was up to 18 with a 2 per cent ruthenium-2 per cent platinum on HY zeolite catalyst. Combining a base metal Fischer-Tropsch catalyst with a ZSM-5 zeolite, Guan Yude and Wang Dingzhu, of the Chinese Academia Sinica, attempted to synthesise a high octane gasoline directly. More aromatics were produced but at the expense of a much higher methane yield. Another attempt to overcome this imbalance in reaction conditions was conducted by Tomoyuki Inui and Yoshinobu Takegami, Kyoto University, Japan, who used a less active ZnO-Cr₂O₃ methanol synthesis catalyst which had been modified by the addition of small amounts of copper, palladium, rhodium or ruthenium. The best combination was a thermally treated palladium catalyst but even this was not comparable with the indirect methanol conversion route because of high methane yields.

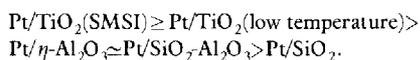
Zheng Lubin, Gu Shijian, Xu Guifen, Yin Guilin and Tao Longxiang, of the Dalian Institute of Chemical Physics, investigated the activity and selectivity of palladium supported on a series of metal exchanged zeolites for carbon monoxide hydrogenation to methanol. The presence of alkali metal ions promoted the methanol synthesis, with the activity of sodium > caesium > potassium > lithium. There was much continued interest in the use of rhodium catalysts for making both C₁ and C₂ alcohols. T. P. Wilson, W. J. Bartley and P. C. Ellgen, Union Carbide Corporation, U.S.A., presented results obtained for the effect of alkali metal promoters on their rhodium-manganese catalyst supported on silica. It was postulated that the alkali metal ions concentrate preferentially on the rhodium metal surface affecting the relative adsorptivity of carbon monoxide and hydrogen. Japanese workers Masaru Ichikawa, Koichi Shikakura and Maki Kawai of the Sagami Chemical Research Centre, in accordance with their previous work on

rhodium supported on a variety of oxides, presented results on rhodium on silica modified with a wide variety of metals. A sharp optimum in activity for ethanol formation occurred with Group IVb and Vb metal oxide additions.

Rather than reducing a rhodium catalyst with hydrogen, Y. Iwasawa, T. Hayasaka, N. Ito and S. Ogasawara, Yokohama National University, Japan, have developed a carbon monoxide/water reduction procedure. This procedure markedly suppresses the formation of methane and results in high selectivities, of approximately 90 per cent, towards C₂-C₄ hydrocarbon formation. The olefin fraction in the C₂-C₃ component was 89.1 per cent. These values were reduced somewhat by the addition of manganese, but the reaction rate accelerated fortyfold. A hydrogen/water reduction procedure enhanced the formation of oxygenated compounds which were further increased by the addition of alkali metals. A supported ruthenium catalyst is also sensitive to the hydrogen/water reduction procedure. S. Naito, S. Kagami, H. Yoshioka, Y. Kobori, T. Onishi and K. Tamaru, University of Tokyo, reported a significant increase in the manufacture of methanol and dimethyl ether after a hydrogen/water pretreatment. These workers also reported results on alkali metal moderated palladium/silica and rhodium/alumina catalysts.

Strong Metal Support Interaction and Infrared Spectroscopy

M. Albert Vannice, Pennsylvania State University, reported further evidence on strong metal support interaction (SMSI) obtained for carbon monoxide hydrogenation over a series of supported platinum catalysts. The activity ranking of these catalysts was:



Under reaction conditions, in situ infrared showed no detectable adsorbed carbon monoxide for the most active catalyst. The higher activity was attributed to a weakened carbon monoxide-metal bond resulting in more competitive hydrogen chemisorption. Another

paper presented by Wang Hongli, Xie Maosong, Wei Zhaobin, Hong Zubei, Wang Xiangzhen, Fu Zugen, Chen Yixuan and Guo Xiexian, Dalian Institute of Chemical Physics, on similar platinum/titania catalysts described the effect of SMSI on the water gas shift reaction which is enhanced by prior high temperature reduction with hydrogen.

Several papers were presented which illustrated the usefulness of infrared spectroscopy for the characterisation of metal-carbon monoxide bonding and the manner in which this changes with metals and metal dispersions. J. B. Peri, Amoco Oil, U.S.A., described the use of computerised dispersive infrared which he finds to be more useful than Fourier Transform infrared when one is interested in limited spectral regions. Such information can add a new dimension to catalyst development and the quality control of commercial catalysts. A detailed infrared investigation of carbon monoxide chemisorption on palladium/alumina catalysts with varying metal concentration and dispersion was discussed by Xu Huizhen, Yin Yuangen and Guo Zhougru, of the Chinese Academia Sinica. An attempt was made to relate infrared results to reactivity of chemisorbed carbon monoxide in the presence of hydrogen. Changes in carbon monoxide bonding on alumina supported platinum and ruthenium catalysts measured

during temperature programmed desorption was discussed by Guo Xiexian and Xin Qin, of the Dalian Institute of Chemical Physics.

Fibrous Alumina Supports

The use of fibrous alumina as a novel catalyst support was illustrated by papers presented by Huang Zhier, Xin Chaifen, Tan Changyn and Peng Shaoyi, and Ge Shiwei, Xiao Dongran, Kang Bingxin and Peng Shaoyi, all of the Academia Sinica. The first of these reported the use of fibrous alumina supported platinum for catalytic combustion. The second paper described the use of palladium supported on a similar material for the selective removal of diolefin by hydrogenation of pyrolysis gasoline. In both cases the activity can be attributed to a reduced mass transfer limitation because of the fine fibre diameter (3 to 5 μm).

The application of heterogenised polynuclear metallic clusters for olefin hydroformylation was covered by two papers from the Academia Sinica. Luo Yuzhong and Fu Hongxiang studied a carbon monoxide carbonyl system supported in a functionalised polystyrene and Su Guiqin, Chen Yuqing, Yang Sukun, Luo Shandao, Xie Wenjuan and Yang Zhenyu investigated cobalt-rhodium mixed metal clusters supported on a phosphinated functionalised silica.

F.K.

J.W.J.

Platinum in Advanced Coatings for Gas Turbines

The use of platinum in corrosion-resistant coatings for the protection of gas turbine blades has been reported in this journal previously (R. G. Wing and I. R. McGill, *Platinum Metals Rev.*, 1981, 25, (3), 94); such coatings are now finding wide application, particularly for aero and marine turbines. More recently, the advantageous use of platinum in ceramic thermal barrier coating systems for advanced gas turbines has been reported at the Third Japan Institute of Metals Symposium on the High Temperature Corrosion of Metals and Alloys, held in November 1982 at Lake Yamanaka, Japan.

Spallation of the ceramic coatings, which are based on stabilised zirconia, arises from the

thermal stresses and the corrosive degradation of the bonding layer between the zirconia barrier and the substrate. At the symposium, H. Takeda, H. Baba, T. Suzuki and K. Shimotori of the Toshiba Corporation reported research where the use of a 1.5 μm layer of platinum between the ceramic layer and the bond layer gave rise to a three-fold increase in life of the coating in hot corrosion tests, and a 20 per cent increase in life in thermal fatigue tests. As yet, no explanation for this major improvement in coating durability has been advanced, but these findings could prove to be a significant breakthrough in the development of commercial thermal barrier coating systems for gas turbines.

C.W.C.