

# International Congress on Catalysis

## NEW HORIZONS IN CATALYSIS BY THE PLATINUM METALS

*At four yearly intervals the International Congress on Catalysis provides an opportunity to identify the major areas of growth and importance in catalysis, particularly where the noble metals are involved. This article reviews some of the many papers on catalysis by the platinum metals that were presented at the latest congress.*

The Seventh International Congress on Catalysis took place in Tokyo, during the week of 30th June 1980. It was attended by over a thousand participants from thirty eight countries. The theme of the Congress was "New Horizons in Catalysis", which recognised the fact that the future of mankind is heavily dependent on the progress of catalysis, particularly in the areas of pollution control, natural resources and energy conservation. The importance of the role of platinum metals was emphasised by their inclusion in 52 of the 168 papers and communications presented.

### Characterisation of Catalysts

A number of recently developed techniques have been applied to the characterisation of noble metal catalyst systems. X-ray absorption spectroscopy (EXAFS) has been used by T. Fukushima and J. R. Katzer of the University of Delaware and D. E. Sayers and J. Cook of North Carolina State University, U.S.A., to study the adsorption of oxygen, hydrogen and carbon monoxide on alumina supported platinum. Adsorption of oxygen at room temperature was shown to cause structural disruption of platinum crystallites. The catalytic decomposition of methanol on palladium foils has been investigated using molecular beam relaxation spectroscopy and a mechanism initiated by the non-dissociative adsorption of methanol was proposed by F. Steinbach, H.-J. Spengler, H.-J. Bohlmann and J. Hynding of Universität Hamburg. X-ray photoelectron spectroscopy (XPS) has been used to demonstrate that the electronic properties of

supported metals are quite different from those of the bulk metals. The results were interpreted by G. V. Antoshin, E. S. Shpiro, O. P. Tkachenko and S. B. Nikishenko, of the U.S.S.R. Academy of Sciences, Moscow, in terms of a metal-support interaction, and XPS shifts were shown to decrease in the order zeolite >  $\gamma$ -alumina > silica for the supports studied.

### Metal Support Interactions

The interaction of noble metals with support materials is of increasing concern since both selectivity and activity can be affected significantly where strong interactions occur. A number of papers and communications dealt with the interaction of rhodium with support materials such as silica, alumina and titania. In the rhodium/titania system the metal support interaction increases as the hydrogen reduction temperature, during preparation, increases. The nature of the interaction also influences reaction selectivity, for example in the carbon monoxide hydrogenation reaction rhodium on alumina produces primarily hydrocarbons, whereas rhodium on titania produces significant quantities of alcohols, reported P. Gajardo, E. F. Gleason, J. R. Katzer and A. W. Sleight of the University of Delaware, U.S.A. P. Meriaudeau, of the Université Claude Bernard, and H. Ellestad and C. Naccache of Institut de Recherches sur la Catalyse, Villeurbanne, France, have interpreted the rhodium/titania system in terms of a metal-semiconductor interaction model. L. L. Murrell and D. J. C. Yates of Exxon Research and Engineering, Linden, U.S.A., have also found evidence for a

strong rhodium/titania interaction which affects the ability of rhodium to adsorb hydrogen and carbon monoxide.

The interaction of rhodium with alumina in auto-exhaust catalysts is of great concern in that this is one of the primary modes of catalyst deactivation. H. C. Yao and M. Shelef of the Ford Motor Co., U.S.A., have identified a disproportionation reaction involving the production of  $\text{Rh}^{2+}$  and  $\text{Rh}^{4+}$  species from  $\text{Rh}^{3+}$  in a well dispersed system on  $\gamma$ -alumina. Only the  $\text{Rh}^{2+}$  ions in the dispersed phase are active, but unfortunately  $\text{Rh}^{2+}$  diffuses into the alumina support and becomes inactive. The interaction between rhodium and alumina is influenced by rhodium precursor, calcination atmosphere and temperature. The effect of catalyst ageing atmosphere is also important in relation to realistic auto-catalyst applications, since this has a profound effect on rhodium dispersion. B. Harrison, J. P. Heffer and F. King of the Johnson Matthey Research Centre, England, reported that the rhodium precursor can also affect the depth of impregnation of the noble metal.

### Catalysts for Hydrogenation Hydrogenolysis and Isomerisation

The isomerisation of hydrocarbons and their interaction with hydrogen over both mono-metallic and bimetallic catalysts was discussed in a number of papers. The catalytic activation of rhodium catalysts for ethylene hydrogenation has been investigated by A. Amariglio, M. Lakhdar and H. Amariglio of the Université de Nancy I, France, who reported that activation was accomplished by pre-treatment of the catalyst with oxygen. During the hydrogenation reaction, oxygen was removed from the catalyst surface by hydrogen thus producing active centres. The active sites were regenerated by diffusion of further oxygen from the bulk of the catalyst to the surface. M. Lacroix, G. Pajonk and S. J. Teichner of the Université Claude Bernard, France, investigated the activation of a silica aerogel by hydrogen spilled over from a platinum on alumina catalyst. The silica was converted into a catalyst active in the

hydrogenation, hydrogenolysis, cyclisation and cracking of hydrocarbons at moderate temperatures of 170 to 270°C.

The interest in bimetallic catalyst systems remains high, especially in the area of petroleum reforming. The addition of a second element to platinum metal systems often results in catalysts of greater stability, activity and selectivity. Much of the recent research has been aimed at gaining a better understanding of the mechanisms by which bimetallic catalysts work and, in particular, in identifying the reasons for selectivity changes.

In the copper-platinum system, copper rich alloys cause a significant reduction in the selectivity for n-pentane isomerisation while increasing hydrogenolysis selectivity. The mechanism is explained in terms of single and multi-site adsorbed intermediates, the presence of which is influenced by platinum ensemble size. H. C. de Jongste and V. Ponc, of the State University of Leiden, Netherlands, reported that adding copper to platinum causes this to decrease in size, and hence changes the mechanistic path. French industrial and academic researchers from the Université L. Pasteur and the Centre de Recherches, C.F.R., reported that the addition of tin to platinum enhances platinum dispersion and at low tin concentrations (platinum:tin up to 7:1) the reaction mechanisms for hexane isomerisation and hydrogenolysis of methyl-cyclo-pentane (MCP) were the same as for highly dispersed pure platinum systems. At higher tin contents (up to platinum:tin, 3:1), part of the tin is alloyed with platinum which produces a dilution effect and favours a non-selective cyclic type isomerisation of hexanes and non-selective hydrogenolysis of MCP; (the late) F. G. Gault, O. Zahraa, J. M. Dartigues, G. Maire, M. Peyrot, E. Weisang and P. A. Engelhardt. Platinum-nickel alloys have been investigated by A. J. Renouprez, B. Moraweck, B. Imelik, V. Perrichon, J. M. Domingez-Esquivel and J. Jablonski of the French Institut de Recherches sur la Catalyse and the Université Paris-Sud. The compositions  $\text{Pt}_{10}\text{Ni}_{90}$  and  $\text{Pt}_{85}\text{Ni}_{15}$  were shown to be particularly interesting in that the

former increases the rate of hydrogenolysis of n-pentane by two orders of magnitude compared to pure nickel, and the latter significantly increases the rate of n-pentane isomerisation compared to pure platinum. The results are explained in terms of electronic modifications of the metals at these compositions. J. R. Bernard and J. L. Bousquet, of the Société Nationale Elf Aquitaine, and P. Turlier, Institut de Recherches sur la Catalyse, investigated the selective hydrogenolysis of alkanes to ethane over platinum-iridium catalysts. The subsequent steam cracking of ethane to ethylene is thought to result in much higher yields than conventional pyrolysis of the same alkane feedstock would produce.

### Methanation/Fischer-Tropsch Synthesis

An increased interest in alternative energy sources and the expected shortage of natural gas has led to a renewal of interest in methanation and the Fischer-Tropsch synthesis. The distribution of products in this synthesis over cobalt, iron and ruthenium catalysts has been studied by R. B. Pannell, C. L. Kibby and T. P. Kobylinski of Gulf Research and Development, U.S.A. The turnover number on ruthenium was found to be substantially higher than on cobalt and both catalyst systems produced decreased olefin content, lower average carbon number and increased chain branching with increasing hydrogen:carbon monoxide ratio. The methanation of carbon dioxide over rhodium on alumina catalysts revealed that this reaction proceeds eight times faster on this catalyst than the methanation of carbon monoxide and the activation energy is also lower. The influence of support was examined by F. Solymosi and A. Erdöhelyi of The University, Szeged, Hungary, and titania was identified as the most, and silica the least, effective.

The individual steps occurring in the methanation of carbon monoxide have been analysed by D. L. Trimm and E. R. Karal of the Technical University of Norway with the aim of designing catalysts to accelerate the reactions involved. A large number of catalysts were

tested and several were found to be superior to a commercial methanation catalyst. One of the best catalysts was a nickel-chromium system promoted with rhodium and platinum.

### Conclusion

The outstanding importance of the platinum metals in catalysis was once again confirmed by the number of papers which described their use. There is a growing awareness regarding the interaction of noble metals with support materials which can modify the activity and selectivity of catalysts. Interest remains high in catalysts for hydrogenation, hydrogenolysis and isomerisation reactions in the petrochemical industry where bimetallic catalysts are now well established. There is also a growing interest in catalysts for the production of synthetic petrochemicals. One of the major growth areas in catalysis is in the anti-pollution area, especially with regard to automobiles, and this was reflected by the presentation of several papers on this topic.

B.H.

### The Niobium-Palladium System

The production of accurate alloy constitution data is not generally considered to be a popular pursuit at present. It is therefore all the more commendable to see that the extended collaborative study under way on alloys of the Group V transition metals with some of the platinum group is continuing to produce valuable information. The latest phase diagram published (B. C. Giessen, N. J. Grant, D. P. Parker, R. C. Manuszewski and R. M. Waterstrat, *Metall. Trans.*, 1980, **11A**, (5), 709-715) is concerned with the niobium-palladium system over the full range of compositions. Terminal solubilities are reported to be high, with a maximum of 36 atomic per cent palladium in  $\alpha$ -niobium at 1520°C and 31 atomic per cent niobium in  $\alpha$ -palladium at 1610°C. The presence of three intermediate phases is confirmed in the system, NbPd<sub>2</sub>,  $\alpha$ -NbPd<sub>3</sub> and  $\beta$ -NbPd<sub>3</sub>. Full crystallographic and lattice spacing data are given for these phases. A further phase NbPd was found at high temperatures only, and is possibly an extension of the  $\alpha$ -palladium cubic solid solution. Discrepancies between this and previous work on the intermediate phases in the system are now largely resolved.