

# The Sixth International Congress on Catalysis

## OUTSTANDING IMPORTANCE OF THE PLATINUM METALS

*The four-yearly International Congress on Catalysis provides an opportunity to survey the dominating importance of the platinum metals in catalysis and to sense the major areas of growth and interest. This article reviews some of the papers relevant to the platinum metals that were presented.*

The Sixth International Congress on Catalysis took place at Imperial College, London, in the week of 12 July 1976. It was attended by almost a thousand full participants from over forty countries. Of the 101 papers presented, more than a third were concerned with the adsorptive and catalytic properties of the platinum group metals, either as heterogeneous or homogeneous catalysts. Some of the more significant of these papers are reviewed here.

### Characterisation of Supported Catalysts

Advanced spectroscopic techniques have been applied to the characterisation of silica-supported platinum. X-ray photoelectron spectroscopy (XPS) can be used to estimate the degree of dispersion ( $\alpha$ ) of the metal (Angevine, Delgass and Vartuli): nuclear magnetic resonance (NMR) spectroscopy has been directed for the first time to examining adsorbed hydrogen, and interstitial H atoms have been distinguished from surface H atoms (Bonardet, Fraissard and de Menorval). By the use of XPS it has also been shown that the cations of palladium and platinum in dehydrated zeolites form nearly pure ionic bonds with the zeolite framework (Minachev, Antoshin, Shpiro and Yusifov).

### Hydrogenation and Hydrogenolysis over Monometallic Catalysts

A number of papers were addressed to the problems of mechanisms in reaction of hydro-

carbons with hydrogen catalysed by the platinum metals. The competitive hydrogenation of pairs of unsaturated hydrocarbons was used by Burwell, Kung and Pellet as a sensitive indicator of specific particle size effects ( $\alpha$ ): the interesting conclusion was reached that chemisorption of an acetylenic hydrocarbon may cause metal atoms to be raised outwards from the catalyst surface. The phenomenon of "hydrogen spillover" also received attention: when platinum on alumina was diluted with more alumina, catalytic activity for the hydrogenation of cyclopropane increased considerably, and this was attributed by Compagnon, Hoang-Van and Teichner to the participation in the reaction of hydrogen which had migrated from the catalyst to the alumina.

The mechanism of hydrogenation of allene over the platinum metals was discussed by Khulbe and Mann, who used infrared spectroscopy to investigate the structure of adsorbed intermediates. Silica-supported catalysts prepared by simultaneous impregnation by solutions of allyl complexes of platinum and tungsten were reported to be more active for benzene hydrogenation and for ethane hydrogenolysis than similar catalysts not containing tungsten (Ioffe, Kuznetsov, Ryndin and Yermakov): the tungsten was thought to be in the +2 oxidation state in the active catalysts.

The chemisorption of acetylene on palladium produces a "surface template" which modifies subsequent reaction behaviour of

other substances (Inoue, Kojima, Moriki and Yasumori): this effect should be capable of development to produce highly specific catalysts.

The selectivity of hydrogenation of acetylene to ethylene is greater over  $\alpha$ -PdH than over palladium itself, and is less over  $\beta$ -PdH (Borodziński, Duś, Frańk, Janko and Palczewska). Very small palladium particles were found to be unable to form the  $\beta$ -PdH phase.

### Bimetallic Catalysts

There have been highly significant developments in catalysts for petroleum reforming during the past decade. The introduction of one or more other elements besides platinum has produced catalysts much less prone to deactivation by carbon deposition, and of greater specificity. This has led to a great deal of continuing research both in academic and industrial laboratories, partly aimed at understanding the phenomena and partly designed to explore the application of bimetallic catalysts in other areas.

The addition of copper causes a drastic decrease in the activity of iridium for *n*-pentane hydrogenolysis, while increasing its isomerisation and cyclisation selectivity; the addition of rhenium however increases its hydrogenolysis activity (Brunelle, Montarnal and Sugier). Iridium added to platinum has a similar effect, but hydrogenolysis activity (which is normally undesired) may be poisoned by sulphiding (Ramaswamy, Ratnasamy, Sivasanker and Leonard). The addition of copper to platinum causes a decrease in isomerisation selectivity, but an increase in dehydrocyclisation selectivity (Jongste, Kuijers and Poneč). Van Keulen presented a kinetic model to describe the loss of selectivity of platinum-rhenium catalysts, and used it in accelerated life tests. Menon and Prasad examined and accounted for the greater sensitivity of platinum-rhenium catalysts to sulphur. Alloys of palladium with nickel, ruthenium and platinum all demonstrate an activity maximum for dehydrogenation of

cyclohexane at some composition (Gryaznov, Smirnov and Slin'ko).

### Supported Complexes

The notion of chemically linking inorganic complexes active as homogeneous catalysts on to supports such as silica or synthetic polymers, and of using them as heterogeneous catalysts, was a most attractive one, and a number of papers in this Congress reported studies on such systems. It is however fair to say that, with a few notable exceptions, they have not fulfilled their early promise.

The kinetics of ethylene hydroformylation by a rhodium complex adsorbed on  $\gamma$ -alumina were reported by Tjan and Scholten, while the same reaction with propylene using a rhodium-polymer catalyst was investigated by Batchelder, Gates and Kuijpers. Interaction of rhodium trichloride with polymeric diphenylbenzylphosphine leads to a rhodium(II) complex active for the hydrogenation of a number of olefins (Imanaka, Kaneda, Teranishi and Terasawa), and ruthenium complexes linked to polymeric carboxylic acids are also active for olefin hydrogenation and isomerisation (Braca, Carlini, Ciardelli and Sbrana). A new method for heterogenising catalytically active homogeneous complexes, involving radiation grafting, was described by Garnett and his associates.

### Conclusion

The large proportion of papers presented at the Sixth International Congress on Catalysis concerned with one or more of the platinum group metals is a continuing witness of their importance as catalytic agents of immense practical value. The development and application of bimetallic catalysts is undoubtedly one of the major growth points, and their extension into other areas besides petroleum reforming may be confidently expected.

G. C. B.

### Reference

- 1 G. C. Bond, *Platinum Metals Rev.*, 1975, **19**, (4), 126