

# Preparation of Heterogeneous Catalysts

## A REVIEW OF A SECOND INTERNATIONAL SYMPOSIUM

By Paul A. Sermon

School of Chemistry, Brunel University, Uxbridge, England

*Over three hundred participants met in Louvain-la-Neuve, Belgium, at the beginning of September 1978 to attend a Second International Symposium, sponsored by the International Union of Pure and Applied Chemistry and the Division de Catalyse of the Société Chimique de Belgique, to discuss the scientific bases for the preparation of heterogeneous catalysts. Papers described the preparation of active oxides, carbides and metals; a considerable fraction concerned the platinum group metals and a brief review of some of these is now presented.*

In his introductory address, Professor D. L. Trimm of the University of Trondheim reflected on the growing realisation of the importance of catalyst preparation and how this might be improved by scientific study. E. G. Derouane of the University of Namur, Belgium; L. Moscou of Akzo-Chemie Nederland, A. H. Neal of Exxon Corporation, Baton Rouge, and K. S. W. Sing of Brunel University, England, described the extensive international collaboration taking place on standardising such catalyst preparation and characterisation. A review of chemisorption methods for determining the surface areas of metals, by J. J. F. Scholten of Dutch State Mines, showed how several phenomena could complicate such measurements.

Several papers concerned the adsorption of platinum metal salts onto alumina supports. E. R. Becker and T. A. Nuttall, C.S.I.R., South Africa, reported studies of the simultaneous adsorption of  $\text{PtCl}_6^{2-}$  and citric acid upon alumina pellets, with subsequent reduction of wet pellets using hydrazine vapour. Radial platinum concentrations were measured by electron microprobe analysis. The depth of platinum deposition below the surface increased with increasing concentra-

tion of citric acid. Unfortunately, the effect of citric acid on platinum particle size was not known. A paper by S. Sivasanker, A. V. Ramaswamy and P. Ratnasamy, of the Indian Institute of Petroleum, indicated that hydrochloric acid adsorbed upon  $\gamma$ -alumina, replacing up to one tenth of the surface hydroxyl groups, reduced the simultaneous adsorption of  $\text{PtCl}_6^{2-}$ . However this was not the case for  $\eta$ -alumina. The adsorption of  $\text{PtCl}_6^{2-}$  upon  $\gamma$ -alumina was also considered in a paper by G. H. Van den Berg and H. Th. Rijnten, Akzo-Chemie Nederland, who showed that simultaneous adsorption of chloride ions increased the depth of penetration of pellets by platinum but also reduced the extent of  $\text{PtCl}_6^{2-}$  adsorption. This was probably as a result of competitive adsorption upon the same basic sites. L. L. Hegedus, T. S. Chou, J. C. Summers and N. M. Potter, General Motors, U.S.A., presented a theoretical model for chromatographic processes during the simultaneous adsorption of rhodium salts and hydrofluoric acid upon  $\gamma$ -alumina.

A paper by G. Blanchard, H. Charcosset, M. T. Chenebaux and M. Primet, C.N.R.S., France, described work on supported Pt-Ru bimetallic catalysts carried out at C.N.R.S.,

Villeurbanne. Upon silica, poorly dispersed but homogeneous Pt-Ru particles were produced, but upon  $\gamma$ -alumina, heterogeneous and segregated metal particles resulted during the impregnation step. L. L. Murrell and D. J. C. Yates, Exxon Research and Engineering Co., reported work on the preparation of highly dispersed Ru/MgO. Such ruthenium is stabilised against oxidation and is selective for conversion of nitric oxide to dinitrogen. Aqueous solutions of 0.06M  $\text{RuCl}_3$  have a pH of 1.5, and precipitation occurs at  $\text{pH}=1.7$ . Since water above alumina is buffered at pH 4.2 by hydrolysis, ruthenium precipitates when aqueous  $\text{RuCl}_3$  solutions are added to alumina. Equally, magnesia hydrolysis in aqueous impregnating solutions may result in poor ruthenium dispersions. A. Bossi, F. Garbassi, A. Orlandi, G. Petrini and L. Zanderighi, Montedison S.p.A., Italy, noted that  $\text{RuCl}_3$  was precipitated as black oxy-chlorides or hydroxides at basic sites on alumina and that pre-acidifying reduced this interaction and increased ruthenium penetration and dispersion. However, the use of aprotic anhydrous solvents, for example acetone, for  $\text{RuCl}_3$  was reported by L. L. Murrell and D. J. C. Yates to prevent this hydrolysis and allow selective adsorption of  $\text{RuCl}_3$ . Unusually, the dispersion of ruthenium upon magnesia was well estimated by both carbon monoxide and hydrogen chemisorption; a fact attributed to strong Ru-MgO interaction retarding multiple CO chemisorption. The preparation of highly dispersed Ru/ $\text{SiO}_2$  was described in a paper by L. Guzzi, K. Matusek, I. Manninger, J. Kiraly and M. Eszterle, Institute of Isotopes, Hungary. Hydrogen adsorbed in excess of monolayer coverage upon this ruthenium, which the authors believed was beneath the metal surface, was only desorbed on heating to about 773K. Hydrogen-oxygen treatment increased the surface area and catalytic activity of the ruthenium, and also removed this sub-surface hydrogen.

The activity of ruthenium is good in ammonia synthesis and may be increased by

added electron donors such as potassium. A. Ozaki, K. Urabe, K. Shimazaki and S. Sumiya, Tokyo Institute of Technology, reported the preparation of 2 per cent Ru/ $\text{Al}_2\text{O}_3$  catalysts by impregnating with  $\text{RuCl}_3 + \text{KNO}_3$  or  $\text{K}_4\text{Ru}(\text{CN})_6$ . The former route yielded the more active catalysts. L. Leclercq, K. Imura, S. Yoshida, T. Barbee and M. Boudart of Stanford University, described the preparation of molybdenum oxycarbides of approximately the same specific activity as supported ruthenium in the Fischer-Tropsch synthesis, but having only a fraction of its useful surface area and with lower stability.

In the future, it seems that preparative processes will be optimised to modify further the location, dispersion, activity and selectivity of supported metals.

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## Platinum Sputtered Coatings for Scanning Electron Microscopy

The high electron emission and resistance to corrosion of thin noble metal films make them eminently suitable as conductive coatings on scanning electron microscope (S.E.M.) specimens. Gold and its alloys with palladium are most frequently used for this purpose but at the Ninth International Congress on Electron Microscopy held in August, 1978 at Toronto, Canada, a display presentation by I. M. Watt of the Johnson Matthey Research Centre compared coatings of these established materials with those of platinum. Simple sputter coaters, only recently commercially available, and advances in platinum plating technology have now made it practicable to coat S.E.M. specimens with platinum as conveniently as with gold.

A suitable platinum coating needs to be only half the thickness required for gold, resulting in less specimen distortion and giving superior peak-to-background ratio in X-ray analysis. In addition, the lower atomic mobility of newly condensed platinum atoms results in a coating having a finer microstructure which is less influenced by temperature changes and substrate composition.