

# Chemisorption and Catalysis

## THE APPLICATION OF MODERN PHYSICAL TECHNIQUES

The platinum metals feature prominently in research on both practical aspects of heterogeneous catalysis and on fundamental aspects of chemisorption processes. Papers read at the recent meeting of the Surface Reactivity and Catalysis Discussion Group of the Faraday Division of The Chemical Society held recently at the University of Nottingham provide evidence of the importance which continues to attach to this group of metals.

After a comprehensive review by Professor D. D. Eley of catalysis by alloys, A. J. Busby and D. L. Trimm of Imperial College summarised their recent work on the application of modern physical techniques, particularly electron spectroscopy, to the activation of platinum-rhodium gauzes for ammonia oxidation. Washing was shown to remove calcium ions introduced in the lubricant used in the drawing operation, while treatment in a hydrogen flame removes carbon and sulphur from the surface. Rhodium enrichment of the surface can occur during activation in consequence of volatilisation of  $\text{PtO}_2$ , but this surface enrichment disappears during use.

The hydrogenation of carbon monoxide to methane and higher hydrocarbons using supported ruthenium-copper alloy catalysts was discussed by Professor G. C. Bond and Dr D. B. Turnham of Brunel University. This alloy system is of interest because although the two components have very limited mutual solubility in the bulk, they nevertheless exhibit clear signs of interaction when in the form of very small particles. The addition of copper was shown to depress the activity of the ruthenium, to alter the kinetics of the reaction and to decrease the formation of ethane and propane.

Dr B. D. McNicol of Shell Research, Thornton, presented a fascinating paper on the temperature-programmed reduction of bimetallic catalysts (Pt-Re and Pt-Ge). This

simple technique permits the progress of the reduction of precursors to supported metal catalysts to be followed: thus, for example, the  $\text{Pt}(\text{NH}_3)_4^{2+}$  ion impregnated on to silica is reduced to platinum in three quite distinct stages. It was possible to demonstrate that under certain conditions the alloying of platinum with rhenium occurs, while reduction in the case of germanium does not proceed past the  $\text{Ge}^{\text{II}}$  stage. Much remains to be learned about the chemical processes occurring in catalyst preparation and reduction.

The process of describing the chemisorbed state of molecules on metal surfaces resembles the peeling of an onion: the removal of each layer of understanding reveals the existence of another underneath. The use of each progressively more refined physical method, while giving new types of information, creates, however, its own problems of interpretation. The application of UV-photoemission permits the determination of the energy levels of molecular orbitals associated with the adsorbed species. For carbon monoxide, bands are observed at 8 and 11 eV: the work presented by D. R. Lloyd, C. M. Quinn and N. V. Richardson from Birmingham University on angular-resolved UV-photoemission of carbon monoxide chemisorbed on low index faces of palladium assigns the 8 eV band to overlapping  $5\sigma$  and  $1\pi$  orbitals, and the 11 eV band to the  $4\sigma$  ionisation.

R. A. Shigeishi and D. A. King of Liverpool University reported results on the application of reflection-absorption infra-red spectroscopy to carbon monoxide chemisorbed on the (111) platinum surface. The results indicated that the molecules do not occupy sites exactly in register with the platinum atoms on the surface, implying perhaps very strong lateral interactions between the adsorbed molecules. Things are becoming "curiouser and curiouser".

G. C. B.