

# First Paul Sabatier Conference

## EUROPEAN MEETING HELPS TO BRIDGE THE GAP BETWEEN MODEL AND INDUSTRIAL CATALYSTS

The first European Conference on Catalysis named after the French chemist Paul Sabatier, who won a Nobel Prize in 1912 for his work on catalytic hydrogenation, was held in Liebfrauenberg, France, during the week of 21st September 1987, and was attended by 90 participants from 16 countries. Seventeen papers and a number of posters were presented, the main themes being the reactions on metals, the surface chemistry of catalysts and the surface characterisation of catalysts. Many were concerned with the platinum group metal systems, and a selection are reviewed here.

### Reactions on Metals

Several of the papers describing reactions on metals involved their application in actual industrial processes. In particular, a detailed description of industrial catalytic hydrogenation processes was given by J.-P. Boitiaux of the Institut Français du Pétrole, France, who compared and contrasted the activity and selectivity of palladium, platinum and rhodium catalysts, and reviewed the influence of metal particle size and metal-support interaction. The importance of combining fundamental catalyst design and characterisation with kinetic experimentation was emphasised.

The use of radiotracer techniques in metal-catalysed hydrogenation reactions, which enable the direct observation of adsorbed species under reaction conditions, was described by G. Webb of the University of Glasgow. The hydrogenation of acetylene and ethylene over the EURONI-1 and EUROPT-1 catalysts was considered in terms of reaction mechanisms and intermediates. It was proposed that the surface of the catalyst becomes covered by hydrocarbonaceous species which may act as soft landing sites for adsorbing molecules.

The coking of platinum-based reforming catalysts was considered by J. Barbier of the

Université de Poitiers, France, who explained the role of the catalyst support. It was concluded that, for a platinum/alumina catalyst, coke is more readily removed from the metal than from the support in an oxidative regeneration process. If acidic sites on the support are neutralised, coking of the support is lessened. The inclusion of iridium and rhenium in reforming catalysts also reduces the rate of catalyst coking by promoting the formation of less toxic, graphitic coke.

The rôle of the support was also emphasised by H. Knözinger of the Institut für Physikalische Chemie der Universität München, Germany. During the hydrogenation of carbon monoxide on rhodium catalysts, silica and  $\gamma$ -alumina supports favour hydrocarbon formation, while zinc oxide, magnesia and calcium oxide favour oxygenates. The mechanism of carbon monoxide adsorption was explained in terms of the metal-support interface, particle morphology and Lewis acidity.

J. K. Nørskov of Haldor Topsøe, Denmark, used the ammonia synthesis reaction to demonstrate how the gap between surface science and real industrial catalysis can be bridged. The process was described in relation to adsorption and dissociation processes defined from electronic structure calculations. The relationship between measurements from ultrahigh vacuum techniques and the kinetics of the high pressure synthesis reaction over an industrial catalyst was described. Vehicle emission control catalysts account for the biggest use of platinum and rhodium in industrial catalysis, and B. Harrison of Johnson Matthey Technology Centre, presented data on the rôle of ceria in stabilising and promoting rhodium in such catalysts. Ceria promotes the water gas shift reaction under rich engine conditions and assists rhodium in retaining its redox characteristics under transient conditions. Also

it can store sulphur dioxide as sulphate. This topic will be addressed in a subsequent issue of this journal.

### Surface Chemistry of Catalysts

Interactions between molecules and surfaces were classified by G. Ertl of the Fritz-Haber Institut der Max-Planck-Gesellschaft, Berlin, into three groups. These are direct-inelastic scattering, in which the incoming molecule undergoes a single collision with the surface and is reflected back into the gas phase; trapping/desorption in which the incoming molecule adsorbs, but leaves again intact after a period of time; and reactive scattering in which the molecule undergoes chemical bond changes. These processes were illustrated with examples which included nitrogen oxide adsorbed on Pt(111), hydrogen adsorbed on Ni(110) and the oxidation of carbon monoxide on Pt(110). The influence of surface morphology on the adsorption process was explained and the surface reconstruction that takes place in the presence of adsorbed species, even at temperatures as low as 100K, was described. D. Spanjaard of the Université de Paris-Sud, Orsay, France, also discussed surface reconstruction in transition metal catalysts, invoking tight binding theory to explain observed effects. This theory predicts compaction of the surface layer of a metal catalyst because of the lower than normal co-ordination number of surface atoms. Surface reconstruction was identified for body centred cubic metals, and for face centred cubic metals, such as Ir, Pt, Au (100 or 110). An adsorbate increases the co-ordination of surface atoms and hence can cause the surface to relax.

During a study aimed at bridging the gap between surface science and organometallic cluster chemistry, A. Masson of E. N. S. C. de Paris, France, considered the properties of small metal particles in relation to model catalysts produced by atomic beam techniques. X-ray photoelectron spectrometry (XPS), synchrotron techniques and adsorption of carbon monoxide were used as physical or chemical probes for particle size determination of noble and transition metal systems. Model catalysts

involving transition metal aggregates or clusters of platinum, palladium and nickel on alumina and silica were characterised using XPS by P. Légaré of the Université Louis Pasteur, Strasbourg. New valence states belonging neither to the support nor to the metal were proposed, based upon shifts in the binding energy of the metal or oxygen from the support. The relationship between the evolution of aggregates and the mechanism of the methylcyclopentane hydrogenolysis reaction was described for an iridium/alumina model catalyst.

The nickel-copper and platinum-rhenium alloy systems were used by V. Ponc of Leiden University, The Netherlands, to illustrate the influence of catalyst structure on reaction mechanism. Reactions were classified into those which are sensitive to ensembles of active atoms and those which are insensitive. For the former, reaction activity and selectivity can be related essentially to the presence or absence of ensembles rather than to any electronic interaction between the alloying metals.

### Surface Characterisation of Catalysts

The rôle of hydrogen chemisorption in catalysis by metals was reviewed by A. Frennet of the Université Libre de Bruxelles, Belgium. The advantages and disadvantages of hydrogen chemisorption for characterising the surface area of metal catalysts were presented, the principal disadvantages being spillover from the metal to the support, impurity reduction and molecular adsorption on the support at low temperature. In the second part of the paper the effect of hydrogen chemisorption on the kinetics of reactions involving hydrocarbons was discussed. Ethane hydrogenolysis on a rhodium catalyst was used to show that hydrogen pressure did not affect the amount of hydrogen adsorbed significantly, but did inhibit the rate of hydrocarbon adsorption. The effects were explained in terms of hydrogen coverage and the free surface available for multisite hydrocarbon adsorption.

The use of electronic techniques for catalyst characterisation was reviewed by P. Gallezot of

C. N. R. S., Villeurbanne, France. In particular, macroscopic techniques such as Extended X-ray Adsorption Edge Fine Structure (EXAFS) and Radial Electron Distribution (RED) were compared and contrasted. While EXAFS has been used to determine metal aggregate morphology in catalysts, RED has been used to show the flexibility of aggregates in the presence of adsorbates. This was illustrated for the adsorption of hydrogen and oxygen on platinum aggregates on graphite. Field-Emission Gun Scanning Transmission Electron Microscopy (FEG-STEM) equipped with Electron Energy Loss Spectrometry (EELS) can be used to probe the nanostructure of catalysts. The application of EXAFS was expanded upon by R. Prins of the Technical University of Eindhoven, The Netherlands, specifically in the characterisation of metal-support interactions. The importance of the method of data analysis was stressed and exemplified by the study of the strong metal support interaction (SMSI) of rhodium on titania. It was concluded that, in the SMSI state, the rhodium particles rest on a reduced suboxide of titania. Oxygen admission at 100K resulted in adsorption on, but not oxidation of, rhodium, in contrast to the rhodium/alumina system where rhodium was oxidised. It was concluded that the electronic

influence from the titania support was responsible for the properties of rhodium in the SMSI state. The use of surface EXAFS to aid comparison of the C-C distances in acetylene, ethylene and ethane in the gas phase, and when adsorbed on a Pt(111) surface, was described by D. Chandresis of the Université de Paris-Sud, Orsay, France.

## Conclusions

Much of the discussion during the conference was concerned with bridging the gap between surface physics/chemistry and "real" catalysis. The debate was, perhaps, best summarised by R. Burch of the University of Reading, England, who reviewed the relationship between high-vacuum low-temperature techniques and industrial processes, which often occur at high temperature and pressure. The rôle of ensembles in structure sensitive reactions and the influence of electronic effects were discussed in relation to catalyst additives, promoters and poisons.

It is clear that much still needs to be done in reconciling studies on "model" catalysts with those on "working" catalysts. It is also clear that meetings such as this Paul Sabatier Conference provide a valuable forum for catalysing this process.

B.H.

## Palladium in Low Alloy Steels

Palladium has been examined as a possible alloying addition to various grades of iron-based alloys, particularly medium strength non-stainless ferritic steels, to decrease susceptibility to hydrogen embrittlement. Although the mechanism by which palladium alters the characteristics of these materials is still uncertain, the benefits achieved by this alloying technique have been observed recently in high strength steels, and reported by B. E. Wilde, I. Chatteraj and T. A. Mozhi of the Fontana Corrosion Centre, Ohio State University ("The Influence of Palladium on the Resistance of Low Alloy Steels to Hydrogen Embrittlement", *Scr. Metall.*, 1987, 21, (10), 1369-1373), their work receiving financial support from the General Motor Corporation and Sandia National Laboratory.

In the case of high strength low alloy steels,

resistance to hydrogen embrittlement can be achieved with quite low levels of palladium addition and in less severe hydrogen charging environments. A particular application for such improved material is said to be for automobile spring fasteners, where failures caused by hydrogen embrittlement from corrosion in de-icing salts can be a problem.

The introduction of palladium into the surface of heat treated steel by ion implantation also resulted in the elimination of hydrogen embrittlement, when 6.5 atomic per cent palladium was implanted to a depth of 11 nm below the surface. Clearly this developing technology could have major implications on the performance of other steel structures. Further studies are being undertaken to provide information on the palladium/hydrogen interaction at the atomic level.

I.R.M.