

Metal-Support and Metal-Additive Effects in Catalysis

A REPORT ON AN INTERNATIONAL SYMPOSIUM

By Professor G. C. Bond

Brunel University, Uxbridge, England

The advantages of using supported metal catalysts in preference to unsupported metals such as colloidal platinum or platinum black have long been appreciated. The support facilitates the formation of extremely small metal particles having a high proportion of their atoms at the surface; the particles have remarkable thermal stability and the presence of the support allows the incorporation of beneficial additives, usually known as promoters. For many years supports were thought to be catalytically inert, except in the special case of bifunctional platinum-alumina catalysts for petroleum reforming. Recently there has arisen evidence that in some systems at least the support can exert a marked influence over the properties of metal particles residing on it. When the platinum metals are supported on titania and reduced in hydrogen at 500°C they lose most of their ability to chemisorb hydrogen and carbon monoxide, and for certain reactions they also lose much of their catalytic activity. This has been attributed to a strong metal-support interaction (SMSI), and its discovery has awakened interest in the whole question of the nature of the interaction of metal particles with the support and with any promoters which may be present.

The first International Symposium devoted specifically to this aspect of catalysis was held at Ecully, near Lyon, from the 14th to the 16th September 1982, and was organised by the Institut de Recherches sur la Catalyse with financial support from the C.N.R.S. It was attended by some 180 persons from a number of countries including the People's Republic of China; six plenary lectures and thirty-five

papers were presented during the three-day meeting. Two of the plenary lectures and at least twelve of the papers bore directly on the SMSI question. Rather than attempt to summarise each paper, it is perhaps better to identify their principal themes and to indicate the current state of understanding of the problem by the use of selective examples.

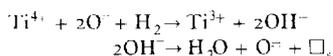
Strong Metal-Support Interactions

As mentioned above, the prime indicator of a SMSI is the loss of the metal's ability to chemisorb molecules which normally react without difficulty at metal surfaces: hydrogen and carbon monoxide are the usual shibboleths. The effect of reduction in hydrogen at about 500°C is not to cause particle growth by sintering, so the loss of chemisorption capacity cannot be attributed to this. However transmission electron microscopy has revealed suggestions of alteration in the morphology of metal particles, as exemplified by the work of R. T. K. Baker at Exxon Corporate Research Science Laboratories with platinum on titania. However the appearance of 'pill-boxes' of metal is not restricted to systems showing SMSI and there is dispute among the experts as to the proper interpretation of what is seen.

Another notable feature of SMSI is that it is reversed by oxidising conditions. Oxygen chemisorption is not suppressed, and any explanation of the effect must take account of this.

It has often been suggested that the origin of the SMSI effect, at least as it applies to titania, lies in a modification of the metal's electronic

character. There is evidence that spillover of hydrogen atoms from the metal to the titania can occur at quite low temperatures, generating first Ti^{3+} and OH^- ions, the latter subsequently forming anion vacancies and water, according to the equations:



where the symbol \square_s indicates a surface anion vacancy. It is then postulated that electron transfer takes place in the sense



As with all explanations of SMSI so far proposed, this idea is not without its critics since the first electron to move to the metal particle will tend to repel others, and so the transfer is thought to be implausible on the grounds of simple electrostatics. Nevertheless small changes in the binding energies of the $4d_{5/2}$ and $4f_{7/2}$ electrons of platinum in the expected sense have been detected by T. Huizinga and R. Prins of the Eindhoven University of Technology using X-ray photoelectron spectroscopy, while the work of J.-M. Herrmann, J. Disdier and P. Pichat at the Institut de Recherches sur la Catalyse, Villeurbanne, on the electrical and photoconductivity of platinum on titania provides supporting evidence.

The response of the specific rates of catalysed reactions to variation in metal particle size, and hence it is thought to variation in surface topography, can be placed in one of two categories. If there is no response, the reaction is said to be structure-insensitive: many simple hydrogenations, for example, of alkenes and of benzene, appear to fall into this class. If there is a response, either positive or negative, the reaction is called structure-sensitive: hydrogenolysis of hydrocarbons, and carbon monoxide methanation and the Fischer-Tropsch reaction, behave in this way, showing higher and lower specific activities, respectively, with increase in the metal dispersion. Now structure-insensitive reactions show relatively small activity changes when the metal moves from the normal to the SMSI state, while hydrogenolysis reactions

generally show very large activity decreases. The work of D. E. Resasco and G. L. Haller, of Yale University, demonstrates that this effect is particularly associated with the smaller metal particle size fraction. The reactions of carbon monoxide proceed if anything more rapidly on metals in the SMSI state, a fact attributed by P. B. Wells, R. B. Moyes, S. R. Morris and R. Whyman at Hull University to the role of the product water in neutralising the SMSI.

Studies on Insulator Supports

The phenomena of SMSI are not confined to titania although most of the work so far carried out has used this oxide as support. According to S. E. Wanke, J. Adamiec, B. Tesche and U. Klengler at the University of Alberta, platinum on magnesia shows similar effects, not yet so deeply studied; ceria behaves analogously, but in these systems the loss of reactivity is more reasonably attributed to the formation of inter-metallic compounds such as Pt_3Ce .

There is still much to learn about the interaction of the platinum metals with insulator oxide supports such as gamma-alumina. E. Lesage, H. Dexpert, E. Freund and J. P. Lynch at the Institut Français du Pétrole presented the results of an elegant study of palladium on this support, showing the occurrence of epitactic growth of the metal, not previously suspected. Transition metal carbides and polyamides as supports for noble metals featured in the plenary lecture by S. J. Teichner, C. Hoang Van and M. Astier, Université Claude Bernard (Lyon I), Villeurbanne.

The second part of the Symposium was concerned with promoters and poisons. Their effects are not easily distinguished, as certain promoters which are used to improve selectivity actually diminish the rate, and are sometimes referred to as selective poisons. This is not a well-charted area, but several of the papers presented at this Symposium threw considerable light on the subject. The synthesis of methanol from hydrogen and carbon monoxide catalysed by supported palladium catalysts under mild conditions is notoriously sensitive to the acidity/basicity balance of the support. Despite

the helpful paper by J. W. Geus, V. Poneč, E. K. Poels and R. Koolstra from the State University Leiden and the State-University Utrecht, the role of the basic element is still far from clear.

There is still considerable interest in improving the selectivity of the partial reduction of alkynes and alkadienes catalysed by palladium. J. P. Boitiaux, J. Cosyns and G. Martino at the Institut Français du Pétrole showed that selective poisons such as carbon monoxide and pyridine are effective in improving the alkene yield from reactants such as acetylene or

isoprene. The selective dechlorination of polychloroanilines to 3,5-dichloroaniline can be controlled by the addition of hydrochloric acid.

The texts of the plenary lectures and papers are now published by Elsevier as Volume 11 of their 'Studies in Surface Science and Catalysis' series. Unfortunately the discussion of the papers could not be incorporated in it, the editors preferring to publish the texts at the earliest opportunity. The volume will however be read with interest by all concerned with the structure and behaviour of supported metal catalysts.

The Recovery of Hydrogen from Waste Gas

Hydrogen can be purified to the very high standard required by the semiconductor and other advanced technology industries by the use of silver-palladium diffusion membranes through which the hydrogen can pass rapidly, while the membranes form a barrier to any other gases present in the input hydrogen. The HM2 diffusion unit illustrated here can produce 28 cubic metres of 99.9995 per cent hydrogen operating at a temperature of 300°C and an input pressure of 21 bars of commercial grade cylinder hydrogen; the electrical control cabinet is not shown, being separate from the hydrogen gas system. Lower outputs result if a reduced input pressure is used or if the feedstock has a lower hydrogen content. In practice hydrogen can be separated from cracked ammonia, cracked methanol or hydrogen-rich hydrocarbon gas streams.

Using a Johnson Matthey Equipment HM4 unit, Texaco U.K. are now recovering hydrogen from a waste stream containing 25 per cent hydrogen and 25 per cent methane, which was formerly vented to the atmosphere during the production of morpholine. The recovered hydrogen is now returned to the process, thus reducing the total hydrogen consumption by 40 per cent.

Because hydrogen is cheap to produce it is often not thought economic to recover and recycle the gas from waste gas streams. However, where hydrogen is delivered to a site from distant sources the transport costs can

be substantial and may alone justify hydrogen extraction. This new application for hydrogen diffusion units in recovering and recycling may well be worthwhile for any chemical or pharmaceutical manufacturer who uses hydrogen as a process material.

In addition to economic considerations, on-site production of hydrogen can be logistically advantageous on isolated sites or when continuity of supply is paramount. At rates of 10 to 100 cubic metres per hour it can be generated efficiently from water and methanol followed by separation through silver-palladium membranes, see *Platinum Metals Rev.*, 1981, 25, (1), 12-13.

