

Platinum Metals in Catalysis

A REVIEW OF SOME OF THE PAPERS PRESENTED AT THE TENTH INTERNATIONAL CONGRESS ON CATALYSIS

The 10th International Congress on Catalysis, arranged by an Organising Committee chaired by Professor L. Guzzi (and sponsored by the International Union of Pure and Applied Chemistry, the Chemistry Section of the Hungarian Academy of Sciences, the Federation of European Chemical Societies and the Hungarian Chemical Society), took place in Budapest from 19th to 24th July, 1992. It was attended by about 1000 persons; more than 100 papers were presented and over 350 posters were available for inspection. With such rich fare, it is impossible to do justice to all the contributions relating to catalysis by the platinum group metals. Reluctantly, therefore, attention is confined to the orally presented papers, and within this group almost one-third referred to platinum group metals.

Catalysis on Single Crystal Surfaces

Many powerful techniques are now available for the study of molecules chemisorbed on single-crystal metal surfaces, and important extensions now permit catalytic interactions between adsorbed molecules to be examined. It is however necessary to remember that there will be differences as well as similarities between these systems and the small supported metal particles found in practical catalysts. These factors are well illustrated by a group of papers discussed at the Congress.

It is now firmly established that some catalysed oxidation reactions, particularly the carbon monoxide-oxygen reaction, can under certain conditions exhibit oscillation. Use of photoemission electron microscopy, which senses the work function variation over the surface, showed that on Pd(110) various travelling waves and spatial patterns were formed in consequence of "gas-phase communication" (M. Ehsasi, M. Berdau, A. Karpowicz, K. Christmann and J. H. Bloch, Fritz-Haber Institut and Freie

Universität, Berlin). Clearly such waves and patterns cannot exist on very small metal particles, but supported metals also show oscillatory phenomena, presumably because gas-phase communication is also possible there.

The trimerisation of ethyne to benzene is another reaction which has been well studied on palladium catalysts. C. J. Baddeley, R. M. Ormerod and R. M. Lambert (Cambridge University) reported that simultaneous adsorption of nitric oxide on Pd(111) caused compression of the adsorbed ethyne phase, with a consequent increase in rate. Palladium on alumina catalysts are also active in this reaction, and the use of bimetallic palladium-gold catalysts, formed by evaporating palladium onto Au(111), showed the extreme structure-sensitivity of the reaction.

The way in which the inert partner in a bimetallic catalyst affects the behaviour of the active one has been debated for many years, the consensus now being that it merely serves to reduce the mean ensemble size of the active element. However when palladium is deposited by evaporation onto tantalum, tungsten, rhenium and ruthenium surfaces, there are distinct differences in the palladium 3d binding energy observed in XPS, and in the temperatures at which adsorbed carbon monoxide desorbs (R. A. Campbell, J. A. Rodriguez and D. W. Goodman, Texas A and M University). This betokens some electronic modification, but, as the subsequent discussion showed, the interpretation is still controversial.

Noble Metals in Zeolites

Turning now to metals in a highly dispersed form, several papers presented results on small noble metal particles in zeolite cavities. The discovery, reported in 1980, that platinum particles in the non-acidic L-zeolite were highly selective in dehydrocyclisation of *n*-hexane to

benzene has generated a number of further studies of this system, some of which were reported at this Congress. E. Iglesia and J. E. Baumgartner (Exxon Research and Engineering Co.) discussed the reaction mechanism in terms of inhibited deactivation of platinum sites within zeolite channels, while the effects of sulphur on platinum/KL-zeolite (J. L. Kao, G. B. McVicker, M. M. J. Treacy, S. B. Rice, J. L. Robbins, W. E. Gates, J. J. Ziemniak, V. R. Cross and T. H. Vanderspurt from the same organisation) and of the type of cation on *n*-heptane aromatisation (R. F. Hicks, W.-J. Han and A. B. Kooh, University of California) were also described. G. Larsen and G. L. Haller (Yale University) prepared and studied palladium/L-zeolite catalysts made both by impregnation and ion exchange, and M. Vaarkamp, J. T. Miller, F. S. Modica; G. S. Lane and D. C. Koningsberger (Eindhoven University) used the intensities of the white lines at the L_{II} and L_{III} X-ray absorption edges to determine the local density of states. They concluded that platinum particles on acidic supports were more electron-deficient than those on neutral supports.

Two studies were reported of bimetallic particles in the cavities of Y zeolite. W. M. H. Sachtler, Z. Zhang, A. Yu. Stakheev and J. S. Feeley (Northwestern University, Evanston) examined palladium-nickel/Y-zeolite catalysts using XRD and EXAFS, and found that during carbon monoxide hydrogenation there was a pronounced metal redistribution at the macroscopic level. O Bong Yang and Seong Ihl Woo (Korea Advanced Institute of Science and Technology) prepared platinum-iridium particles in NaY-zeolite and found that they were more active and stable in *n*-heptane reforming than the monometallic platinum analogue.

Supported Metal Catalysts

Zeolites represent a somewhat special class of supports for metals, with their regular pore structure and facility for acid/base control. Interest continues at a high level in dispersed metals on more usual supports such as silica and alumina; the applicability of catalysts of this type in petroleum reforming clearly influ-

ences the kind of work performed. However, the interpretation of the behaviour of bimetallic catalysts continues to be the subject of debate, but in the cases of platinum-rhenium and platinum-tin reforming catalysts there are questions concerning the interaction of the second element with the support. G. Munuera, P. Malet and A. Caballero (Seville Institute of Science of Materials) explored the effect of Cl⁻ in stabilising the interaction of Re⁴⁺ with the alumina support, while G. C. Bond, R. H. Cunningham and E. L. Short (Brunel University, U.K.) determined the kinetics of hydrogenolysis of the lower alkanes on typical reforming catalysts which were either clean or partially coked. Disagreement still continues concerning the role of tin in platinum-tin reforming catalysts; J. Schwank, K. Balakrishnan and A. Sachdev (University of Michigan) concluded that most of the platinum was in a monometallic form, but that the particles were in contact with ionic tin (2+ or 4+) associated with the alumina support. B. H. Davis (University of Kentucky) on the other hand detected platinum-tin alloys, with the role of the tin depending on the acidity of the support. Clearly more research is needed to resolve these conflicting findings.

Other techniques of great potential usefulness in the characterisation of catalysts and their precursors were described. Scanning tunnelling microscopy (STM) permits the creation of images of surfaces with a resolution approaching the atomic scale, and M. Komiyama and M. Kirino (Yamanashi University, Japan) reported topographic and barrier-height images of platinum particles vacuum-deposited on thick silica films. The resolution is however not yet sufficient to afford information of great value. Laser Raman spectroscopy (LRS) on the other hand can sensitively detect oxides of the platinum group metals (rhodium, iridium and platinum) attached to ceria microphases in ceria-alumina mixed oxide supports (L. L. Murrell, S. J. Tauster and D. R. Anderson, Engelhard Corporation).

The use of a neutral zeolitic support, as described above, is not essential for the effective

conversion of linear alkanes to aromatics. E. G. Derouane, V. Jullien-Lardot, R. J. Davis, N. Blom and P. E. Højlund-Nielsen (Facultés Universitaires, Namur) have demonstrated that palladium on alumina-stabilised magnesia affords high selectivities in conversion of *n*-hexane to benzene. They used ²⁷Al magic-angle spinning NMR to show that Al³⁺ ions occupied both tetrahedral and octahedral holes in the magnetic structure.

Syngas Reactions

The popularity of syngas reactions as a subject for research is now much diminished, and only three contributions to the Congress dealt with the role of the platinum metals as catalysts for these reactions. Rhodium is well-known for its ability to give higher oxygenates, especially ethanol, and A. L. Borer and R. Prins (Federal Institute of Technology, Zürich) confirmed previous findings on the promoting effect of lanthana on rhodium on silica catalysts. They showed moreover that the order in which the components are introduced to the support is important, higher dispersions of rhodium being obtained when lanthanum is applied first to the

silica. Higher oxygenates can also be produced when carbon monoxide reacts on rhodium catalysts with adsorbed species formed from chlorinated molecules and alkenes (M. W. Balakos, S. S. C. Chuang, R. Krishnamurthy and G. Srinivas, University of Akron). K. R. Krishna and A. T. Bell (University of California, Lawrence Berkeley Laboratory) applied transient-response isotopic tracer methods to follow chain-growth during Fischer-Tropsch synthesis on ruthenium upon titania catalysts. The chain-growth probability, α , decreases with temperature because the activation energy for termination exceeds that for propagation.

Conclusion

The 10th International Congress on Catalysis proved a most stimulating and enjoyable occasion, and the organisation was faultless. The posters, as well as the papers presented orally, confirmed the pre-eminent role of the metals of the platinum group in the field of heterogeneous catalysis. The proceedings will be published in the first half of 1993. The 11th Congress will take place in Baltimore, Maryland, U.S.A, in 1996. G.C.B.

Progress in Palladium Membrane Catalysis

In the April 1992 issue of this journal two papers from Russia were concerned with palladium alloy membrane technology (1, 2). Now this topic has again been featured, in a useful review of high temperature membrane catalysis by John N. Armor of Air Products & Chemicals, Inc., Allentown, Pennsylvania (3).

High temperature membranes are those that can be used at temperatures above 200°C, and suitable materials include: inorganic oxides, carbon, palladium and its alloys, and composites. While the use of palladium-based membranes is limited to reactions that involve hydrogen, the high solubility of hydrogen in palladium and the fact that it is currently being fabricated into thin foils makes it particularly suitable for these reactions. To avoid problems associated with the α/β phase transformation, the operating temperature should be above 310°C.

The benefits that are encountered when palladium is alloyed with silver, ruthenium, rhodium and rare earths, are considered, as are the

limitations of such membranes. For the future, the potential for commercial exploitation is seen to be with catalytic materials deposited on monomodal sub-8 Å inorganic membranes, and with thin metal alloy coatings on mesoporous supports. Already studies have been made of composite membranes consisting of palladium and silver-palladium deposited on the outer surface of porous glass tubes and porous alumina cylinders by electroless plating techniques.

While many problems have still to be overcome, it is concluded that the progress made to-date in membrane catalysis encourages further fundamental research on the topic.

References

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- 2 V. Z. Mordkovich, Yu. K. Baichtock and M. H. Sosna, *ibid.*, 90-97
- 3 J. N. Armor, *Chemtech*, 1992, 22, (9), 557-563