

# An Exchange of Ideas on Catalysis

## Homogeneous and Heterogeneous Catalysis

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When catalyst scientists gather together the platinum group metals are generally a prominent feature of their discussions. The "Fifth International Symposium on Relations between Homogeneous and Heterogeneous Catalysis", held at Novosibirsk in July of last year, proved to be no exception.

The recently published proceedings of this important meeting contain the full collection of some 39 invited guest lectures and a representative 27 of the 267 poster communications which were also presented. Since most of the invited speakers reviewed their own areas of expertise, the information in this volume is very concentrated, giving an in-depth and up-to-date picture of practically the whole of catalysis, viewed from the aspect of organometallic surface intermediates.

The rationale behind this particular series of meetings was aptly expressed earlier in the series when it was noted that "new departures in science and technology often originate at the boundaries between separate but related areas of enquiry". This point of view is reiterated in the foreword to this volume which lists "one of the main tasks of these symposia—to create an opportunity of a meeting of specialists from different areas of catalysis for an exchange of ideas and a redistribution of experience from some areas of research into others". In keeping with these overall objectives, it is particularly useful that this volume should begin by listing the subjects and titles of presentations given at earlier symposia in this series. This serves to put into historic perspective how far the subject has progressed since the first symposium was held in Brussels in 1974.

Here the presentations are considered in three roughly equal sections.

The first section emphasises the relationships between homogeneous and heterogeneous catalysis, and it is here that the power of

analogy in opening up new lines of thought and enquiry becomes most evident.

One of the visions of the future, probably held by all who work with catalysts, is the possibility of being able to duplicate or even simulate the activity and selectivity of biological enzyme systems. Several papers obviously had this as their theme, notably a paper by A. E. Shilov of the Institute of Chemical Physics, U.S.S.R. Academy of Sciences, on organised molecular assemblies in catalysis. This included results using micelles, microemulsions and lipid vesicles.

Another of the themes of much current work is the nature of the active site itself, in particular the nuclearity and effects of the localised charge distribution.

Earlier symposia had discussed catalytic and chemical properties of metals quenched in a matrix. Such studies have now been extended into the gas phase. The low temperature oxidative addition of various hydrocarbons to transition metal atoms and ions leads to the formation of organometallic intermediates. Thus the reaction of  $Rh^+$  with hydrocarbons in a mass spectrometer results in all the reactions and products more normally associated with metallic surfaces, and which are usually interpreted by multicentre mechanisms. In the same paper, by B. A. Dolgoplosk and I. A. Oreshlin of the A. V. Topchiev Institute of Petrochemical Synthesis, Moscow, interesting information resulting from the decomposition of the organometallic compounds produced by the reaction of  $CH_3Li$  with platinum group metal halides is given.

Another paper which seemed to embody the essence of the series was entitled "Multiple Roles of Palladium in Liquid Phase Oxidation" by J. E. Lyons, G. Suld and C.-Y. Hsu of the Sun Refining and Marketing Company. Homogeneous catalytic oxidations with palladium and

a copper co-catalyst (Wacker) are generally associated with the vinylic oxidation of olefinic substrates, which arises from nucleophilic attack on a palladium(II) olefinic  $\pi$ -complex. The authors point out however that olefins can also co-ordinate with metals (or palladium(II) with electrophilic ligands) to form  $\pi$ -allylic complexes. They show that these can then undergo nucleophilic attack giving allylic products. These types of catalytic systems have been operated homogeneously and heterogeneously—thus the commercially important oxidation of ethylene to acetaldehyde was initially carried out with a heterogeneous catalyst and is now practised in a homogeneous system, whereas the equally important oxidation of ethylene to vinyl acetate was first practised in a homogeneous system but now uses a supported catalyst.

This paper also shows how one may control allylic/vinylic oxidation, as in the case of propylene, and discusses the palladium catalysed acetoxylation of aromatics. This reaction yields phenylene diacetates and diacetoxy biphenyls, and these provide a route to dihydroxy aromatics of commercial importance.

Palladium catalysed oxidation of a somewhat different kind, carbon monoxide to carbon dioxide with oxygen at low temperatures, was given in a paper by a large group of workers from the Novosibirsk Institute of Catalysis. This reaction is catalysed by conventional homogeneous  $\text{PdCl}_2 + \text{CuCl}_2$  (Wacker) catalytic systems but the problems associated with the corrosivity and volatility of HCl led them to try other co-oxidants and also attempt to heterogenise the catalyst. One advantage of the palladium catalyst, in contrast to the well-known low temperature Hopcalite catalyst, is its water tolerance. The catalytic system was varied, by varying the co-oxidant used. For this purpose a wide range of mixed metal heteropolyphosphorus complexes based upon molybdenum, vanadium and tungsten were prepared and characterised. With such compounds the redox potential of the co-oxidant could be systematically varied. The rate of carbon monoxide oxidation proves to be very sen-

sitive to these oxidation potentials and shows a marked optimum at an intermediate level which is pH dependent. They went on to study silica, alumina and titania supported catalysts with palladium and the same series of heteropoly metal complexes.

This section of the symposium was concluded by a paper from the University of Utrecht which illustrates yet another variant of the homogeneous-heterogeneous theme. Epoxidation of cyclohexene by oxygen was the reaction studied, and this time the oxidation co-catalyst was a heterogeneous platinum on silica catalyst—or preferably a platinum-silver alloy catalyst—operated in conjunction with a homogeneous manganese tetraphenylporphyrin oxidation catalyst. Silver was added to inhibit the direct hydrogen/oxygen reaction and thereby increase the oxygen conversion efficiency.

### Immobilised Metal Complexes

Much of the second section was taken up with discussions of Ziegler-Natta and nickel catalysed polymerisation reactions, and olefin metathesis reactions using base metal catalyst systems. Any hopes that the reader may find here the answer to the problem of catalyst stability and leaching of conventionally anchored homogeneous catalysts are not to be satisfied. Indeed there seems to be a growing awareness that the essential lability of conventional soft ligands to hydrolytic and thermal degradation may mean that the problem has no solution when attempted along these lines, and alternative approaches are now being explored.

One of these is the use of ligands with more polar bonding and the use of polydentate ligands. M. Čapka from the Czechoslovak Academy of Sciences studied neutral rhodium(I) complexes with bi-dentate phosphines and cationic rhodium(I) complexes with monodentate phosphines, both bonded to silica gel. Catalysts were characterised with regard to selectivity and stability in the hydrogenation of cyclooctadiene, 1-heptyne and 1-heptene. Much better results are obtained by a procedure which entails forming the rhodium complex in solution using a silyl

substituted alkyl-diphenyl-phosphine and grafting this onto the silica rather than the more conventional approach of first functionalising the silica with the phosphinated anchoring ligand. Better results than when using the homogeneous catalyst alone are claimed.

Another approach to heterogenising catalysts is to use supported liquid phase systems having low volatility. J. Hjortkjaer from the Technical University of Denmark has been using solutions of  $\text{HRh}(\text{CO})(\text{PPh}_3)_3$  in phenyl-dibenzophosphole supported on silica for propylene hydroformylation. However the results would appear to be inferior to the more conventional homogeneous catalytic system.

Carbon supported platinum group metals are being used at the University of Tokyo for the carbonylation of methanol. The order of activity for the supported metals was  $\text{Rh} > \text{Ir} > \text{Ni} > \text{Pd} > \text{Co} > \text{Ru} > \text{Fe}$ . Methyl iodide is used as promoter in a vapour phase reaction at around  $300^\circ\text{C}$ . The use of nickel is somewhat surprising in view of the known methanation activity of nickel catalysts, as indeed was found to be the case here when nickel was used on silica or alumina supports.

Several papers also deal with novel ligand systems including organic azo dyes at the Bulgarian Academy of Sciences and macrocyclic ligands prepared in situ in conjunction with alumino-silica supports at the I. M. Gubkin Institute of the Petrochemical and Gas Industry in Moscow.

### **Catalysis by Metal Clusters and Dispersed Metal Particles**

Much of this section is concerned with the use of organometallic and carbonyl cluster compounds in the preparation of supported catalysts. The potential advantage of these systems arises from the fact that in principle the catalytic site is well defined, and that analogous polymetallic species can also be prepared whose structure can be well characterised.

M. Ichikawa from the Research Institute for Catalysis at Hokkaido University has studied rhodium-cobalt and rhodium-iron bimetallic cluster catalysts for hydroformylation and has

characterised them by using a combination of EXAFS, HREM and Mössbauer spectroscopy.

Work at Bristol University on chemical transformations associated with a tri-ruthenium carbonyl cluster is discussed by S. A. R. Knox, and osmium carbonyl clusters also come in for their share of attention from P. B. Wells of Hull University and D. K. Chakrabarty and co-workers at the Indian Institute of Technology, among others.

French workers report some rather dramatic effects on the selectivity for syngas conversion to methanol for platinum on silica catalysts to which chromia and molybdena have been added. Possibly related effects on modified rhodium on silica catalysts used for  $\text{C}_2$  oxygenate formation are discussed by H. Knözinger of the University of Munich in a general discussion of the analogies between metal carbonyls and surface chemisorbed carbon monoxide.

Strong metal support interactions (SMSI), a favourite topic at present for workers with heterogeneous catalysts, did not receive much attention at this conference. One notable exception was the paper by Yu. I. Yermakov and Yu. A. Ryndin which discussed the effects of supports and metal promoters on platinum. This discussion included not only conventional supports but also the surprisingly large differences which were found among the rare earth oxide supports. They conclude, after discussing the possible reasons for the chemical effects associated with SMSI, which they also define, that there can be significant catalytic effects due to interaction between the active metal and the promoter in an ionic form.

Perhaps the final say on the subject of metal clusters and dispersed metal particles should have been given to P. Gallezot at the French CNRS catalyst laboratories who demonstrated that he can reversibly interchange platinum carbonyl clusters of high nuclearity and platinum crystal aggregates, all when contained within the cages of a zeolite support. He showed that oxidation destroyed the metal-metal bonds but did not change the nuclearity, and this conversion is reversible. He extended this work to

supported rhodium aggregates but here carbonylation led to a break-up of the aggregate and the formation of mobile mono-nuclear carbonyl species.

## Conclusions

Here it has only been possible to cover a small part of the work reported which, as remarked on earlier, is very concentrated. Many of the other papers are interesting inasmuch as they suggest new techniques, and by analogy, new possibilities for following new directions in

research. All papers are of a very high standard, and the comprehensiveness makes this a valuable source of up-to-date reference material.

After five conferences in this series on homogeneous and heterogeneous catalysis it is clear that the discussions engendered are very fruitful. This area of study is still expanding and developing, but there is clearly a long way to go before man can even start to approach nature's enzymes in their efficiency and selectivity.

J.W.J.

## Corrosion in Nitric Acid Plants

The use of stainless steels for the heat exchangers in nitric acid plants is widespread, although nickel based alloys are finding application in the newer plants. These steels are subject to corrosion by the reaction products, mainly nitric acid, which are produced during the oxidation of ammonia over platinum-rhodium catalyst gauzes. Such corrosion can lead to premature failure of components, resulting in unscheduled plant shut down and reduced production of nitric acid.

In practice, this corrosion is particularly prevalent on parts subjected to tensional stresses and, in an attempt to understand the factors that contribute to this enhanced corrosion, S. Ž. Kostić of Hemijska Industrija Pančevo, Yugoslavia, has examined the behaviour of two typical stainless steels in boiling nitric acid; in particular the influence of cold work and of galvanic coupling on the corrosion rate (*Br. Corros. J.*, 1987, 22, (1), 53-55).

Kostić believes that galvanic coupling can result from the deposition of platinum-rhodium particles from the catalyst gauzes onto the stainless steel tubes. The loss of platinum from such catalysts during service is well known, of course, and has a significant impact on the process economics.

Samples of two steels, AISI 304L (18Cr-8Ni) and 2RE10 (25Cr-20Ni), in strained and unstrained conditions, some in contact with platinum-rhodium, were exposed to boiling nitric acid (42-65% vol.), and corrosion rates and electrochemical corrosion potentials measured. The results for the 2RE10 steel indicate that the corrosion rate after 240 hours exposure is substantially increased when the steels are in the strained condition, and that galvanic coupling with platinum-rhodium leads to a

dramatic increase in the rate of corrosion. However, these latter results are calculated on the basis of only 24 hours exposure and thus may give a distorted picture.

Anodic polarisation curves in 42 vol. per cent nitric acid measured on AISI 304L steel samples taken from damaged tube elbows, which have a surface deposit containing about 1wt. per cent platinum, show corrosion potentials in the range 1200-1700mV, approximately 300-800mV higher than the same steel before service exposure. The corrosion potential of the latter, typically 900mV, lies within the passive region of the anodic polarisation curve, while that of the "damaged" steel lies in the transpassive region of the curve. Kostić attributes the nobler electrode potential to the establishment of a mixed potential between the steel and platinum-rhodium in the surface deposit. Metallographic examination of "damaged" components and laboratory samples shows corrosion to be intercrystalline, attack being concentrated at chromium carbides in the grain boundaries.

The implication of these results for commercial practice is that the deposition of platinum-rhodium particles onto such stainless steel surfaces should be avoided, if possible, in order to inhibit enhanced corrosion and premature failure. Clearly the use of catchment systems would be beneficial here, since their prime purpose is to trap much of the platinum emitted from the catalyst during service, primarily to improve process economics. Such catchment systems have been shown to be very effective (see, for example, A. E. Heywood, *Platinum Metals Rev.*, 1982, 26, (1), 28-32) and are being increasingly specified by major nitric acid producers.

C.W.C.