

A Potential Opportunity for Platinum Group Metals Catalysts

New Developments in Selective Oxidation, Studies in Surface Science and Catalysis, 55

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With the exception of a few important examples platinum group metals catalysts have found little utility in commercial selective oxidation processes. This is because the high specific activity of platinum group metals catalysts tends to make them highly efficient for deep oxidation, hence their widespread use in pollution control. In the process chemical industry the requirement is for the high value intermediate, and this prompts the question "Is it likely that there will be an expanded role for platinum group metals catalysts in this area in future years?"

The international symposium held in Rimini, Italy, from 18th to 22nd September 1989, considered the whole field of selective oxidation, and so the recently published proceedings enables an assessment to be made of both current research activity and the future potential for platinum group metals catalysts in this area. From the point of view of the number of papers presented at the conference concerning these materials the question may seem rhetorical. Even if silver and gold are included with the platinum group metals no more than 15 per cent of the papers reported studies using such materials as selective oxidation catalysts. However, in recent times there has been an increasing interest in their use, particularly in the liquid phase, especially since the successful commercialisation of Wacker chemistry and alkene acetoxylation, both using palladium catalysts. Papers were presented not only on the use of palladium but also of platinum and ruthenium catalyst systems in liquid phase selective oxidation processes.

A paper by G. Strukul, A. Zanardo and F. Pinna describes a well exemplified case of bifunctional catalysis involving two platinum

group metal centres in the oxidation of olefins to ketones using hydrogen peroxide. Kinetic studies established that the oxygen transfer step is a bimolecular process involving nucleophilic attack of a PtOOH species on an olefin activated at a separate, distinct platinum group metal centre. Thus in the presence of a 1:1 [(dppe)Pd(CF₃)(CH₂Cl₂)]⁺ and (diphoe)-Pt(CF₃)(OH) catalyst mixture a variety of olefins were oxidised to the corresponding ketones, with up to 38 per cent yield in the case of butylvinyl ether; (dppe = 1,2-diphenylphosphinoethane, diphoe = *cis*-1,2-diphenylphosphinoethylene).

Homogeneous bimolecular action was also inferred by N. I. Kuznetsova, A. S. Lisitsyn, A. I. Boronin and V. A. Likholobov who used platinum and palladium catalysts for the epoxidation of cyclo-hexene by molecular oxygen in the presence of hydrogen. They suggest the in-situ formation of hydrogen peroxide over Pt⁰ followed by interaction of peroxide and olefin over a platinum group metal ion. Thus mixtures of K₂PtCl₆ and H₂PdCl₄/SiO₂ or (CH₃CN)₂PdCl₂ converted 63 per cent cyclo-hexene at up to 24 per cent yield to epoxide.

Another interesting paper in the related area of co-catalysis was provided by N. H. Kiers, B. L. Feringa and P. W. N. M. van Leeuwen who used chemistry with a distinct analogy to Wacker technology to oxidise olefins to aldehydes over (CH₃CN)₂PdClNO₂/CuCl₂ co-catalyst systems using molecular oxygen.

Papers dealing with heterogeneous oxidations in the liquid phase using platinum group metals included that by P. Vinke, H. E. van Dam and H. van Bekkum who used Pt/Al₂O₃ to oxidise 5-hydroxymethylfurfural to the dicarboxylic acid using molecular oxygen. The objective

here was to oxidise materials obtained from renewables, rather than oil derived chemicals, to yield existing or new products; in this case a product was obtained with potential as feedstock for new polymers. Another interesting feature is the use of supported platinum to selectively oxidise the substrate.

For the oxidation of hydrocarbons and alcohols M. Hronec, Z. Cvangrosova, J. Tuleja and J. Ilavsky found that promotion of Pt/C and Pd/C by base metals gave higher catalytic activity and higher resistance against deactivation. Thus the incorporation of cobalt, bismuth, cadmium, zinc, or manganese into the catalyst systems improved performance in the oxidations of numerous olefins, for example α -pinene, to alcohols and ketones.

The use of a tri-metallic Pd-Pt-Bi/C catalyst to oxidise glucose to gluconic acid with high selectivity and space time yield was described by B. M. Despeyroux, K. Deller and E. Peldszus. Yields approaching 100 per cent at 4000g/g/h were achieved. Platinum was shown to boost activity while bismuth improved selectivity.

In recent years there has been interest in biomimetic systems, particularly in attempts to use laboratory analogues of such enzymes as the monooxygenase Cytochrome P450 which promotes a range of oxidations in biological systems with very high efficiency. A paper by

N. Rajapakse, B. R. James and D. Dolphin describes the use of dioxo(porphyrinato)-ruthenium(VI) species to oxidise thioether and olefinic substrates using molecular oxygen. Thus the complex *trans*-Ru(porp)O₂ was shown to transfer oxygen cleanly or remove hydrogen from several such substrates, albeit slowly, (porp = dianion of 5,10,15,20-tetramesitylporphyrin).

An interesting paper by M. Bressan and A. Morvillo demonstrates that aliphatic acyclic and cyclic hydrocarbons can be oxidised in good yield from hydrocarbon substrates using homogeneous catalysts. [Ru^{II}Cl(DPP)₂]PF₆ and *trans*-[Ru^{II}Cl₂(DPP)₂] were effective for the oxidation of cyclo-octane, cyclo-hexane and *n*-hexane to the corresponding alcohols and ketones, using sodium hypochlorite as oxidant (DPP = 1,3-bis(diphenylphosphino)propane).

In summary those papers dealing with the use of platinum group metals catalysts for selective oxidation reactions demonstrate a growing awareness of the applicability of these elements to this important field. The selective oxidation of commercially important substrates using cheap oxidants such as air or hydrogen peroxide and platinum group metals catalysts is the goal, and it is likely that in the future new processes incorporating such technology will emerge to augment the few examples currently being operated on a commercial scale. E.S.

Automobile Emissions Control Catalysts

Now utilising more than one third of the Western World's demand for platinum, it is interesting to recall that the use of platinum metals catalysts to control the emissions from gasoline fuelled, spark ignition engines has only arisen in the last twenty years. A concise account of the major technical and scientific advances made during this time has recently been given by Kathleen C. Taylor, of the General Motors Research Laboratories (*Chemtech.*, 1990, 20, (9), 551-555).

Initially the control of carbon monoxide and gaseous hydrocarbons was achieved by the use of platinum and palladium. After 1981 more stringent standards were introduced, including a new requirement to decrease nitrogen oxides emissions. The approach adopted was to

oxidise the first two components while simultaneously reducing the latter. Including rhodium in the catalyst formulation enables this to be achieved. Cerium oxide additions also improve the performance of these "three-way" catalysts, while engine controls ensure that the air-to-fuel ratio is maintained at the stoichiometric composition, where platinum-rhodium catalysts promote the conversion of the three major pollutants simultaneously.

Further work is still required, for example, to improve catalyst activity under cold-start conditions and tolerance of high temperatures. The development of catalytic converters has already contributed to significantly lower vehicle emissions and improved air quality, and to our knowledge of platinum metals catalysis.