Second European Congress on Catalysis

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The second European Congress on Catalysis (EUROPACAT-II) was held in the MECC Centre, Maastricht, The Netherlands, from 3rd to 8th September, 1995, and was attended by more than 750 participants. There were 13 separate symposia, covering all aspects of catalysis, with three running simultaneously. Two poster sessions contained a large number of presentations. This report covers aspects of the work presented featuring the platinum group metals.

As usual the metals of the platinum group featured prominently as catalysts in many of the sections. In this short report the contributions presented in the three most relevant symposia are highlighted; and a few important papers given in other symposia will be mentioned.

Catalysis and Catalytic Processes to Abate Environmental Damage

The reactions occurring in simulated vehicle exhaust continue to excite considerable attention; however, in practice, the number of chemical species present is such that for fundamental work it is necessary to use simpler systems. Thus, for example, for a $Pt-Rh/Al_2O_3$ three-way catalyst, the addition of 1 to 12 per cent water vapour increases the rate of carbon monoxide oxidation by 2 to 6 times, respectively, and the presence of ceria also enhances the oxidation rate. By using isotopically-labelled oxygen ($^{18}O_2$) it was found, surprisingly, that the main source of the oxygen used to form the carbon dioxide was in fact water, and not molecular oxygen (1).

From a broadly-based kinetic modelling study of NO + CO and CO + O_2 reactions, it was concluded that nitrous oxide is formed as an intermediate product in the former reaction (2). Because of the continuously-changing conditions that the actual catalyst has to endure, the transient-response technique is particularly suitable for providing information on reaction kinetics. Consequences of the step-changes applied to a conventional three-way catalyst were analysed on a time-scale of about 2 minutes, and showed that for the NO + CO reaction there was a time-delay before nitrogen appeared (3).

There still remains some scope for improving the performance of the catalysts used for vehicle exhaust treatment by altering the nature of the support. Solid solutions of CeO_2 + ZrO_2 are in some ways superior to ceria by itself, and in particular they have a very high oxygen storage capacity at low temperatures (4).

The continuing use of palladium as the active component in exhaust gas treatment catalysts has stimulated a comparison between the decomposition of nitric oxide, and its reaction with hydrogen and with carbon monoxide, on single crystal surfaces of palladium and of rhodium. The decomposition of nitric oxide requires a higher temperature on palladium than on rhodium, and on palladium affords some nitrous oxide, whereas on rhodium the only product is nitrogen (5).

A comprehensive study of the oxidation of a number of different hydrocarbons on a Pt/Al_2O_3 catalyst was reported (6). Alkyl-substituted benzenes are less easily oxidised than benzene itself, because the substituents release negative charge to the aromatic ring, which is consequently more strongly adsorbed on the catalyst and less reactive. Bicyclic C_{10} molecules, such as naphthalene, decalin and tetralin, are less reactive than n-decane, again because of adsorption through the ring structures.

Catalysis of (Pseudo) Metals

The somewhat strange title of this symposia was intended as a short way to show that compounds such as the carbides of molybdenum

and of tungsten, which show catalytic properties similar to those of metals, were within the remit of the symposium. Papers dealing with them are not however covered here.

The reason for the enhancement of activity during the hydrogenation of 2,4-dinitrotoluene on adding iron to Pd/SiO_2 was examined by studying the IR spectra of chemisorbed carbon monoxide and nitric oxide. It was concluded that on chemisorption nitric oxide oxidises Fe^0 to Fe^{2+}, which in turn can chemisorb nitric oxide, but carbon monoxide is only adsorbed on palladium surface atoms; the two species are interspersed at an atomic level (7).

The structures and properties of some other bimetallic systems were reported. A series of alumina-supported RuGe catalysts were described: Ge^0 is not incorporated in the ruthenium particles except at the highest germanium:ruthenium ratio; however, according to EXAFS spectra, it exists as GeO_2 'molecules' on the surface (8).

One of the best methods for investigating the surface composition of bimetallic catalysts is low-energy ion scattering (LEIS), which is a strictly surface-sensitive technique. By its use it was shown that platinum-palladium particles on alumina are enriched in platinum after a treatment in hydrogen at 300°C, while at lower temperatures bulk and surface compositions were about the same (9). A number of different types of metallic particles are formed by platinum and copper on and in the zeolite ZSM-5; the combined use of EXAFS, of FTIR using carbon monoxide, and of XPS, leads to the identification of five different kinds of particle or surface (10).

Straightforward methods of catalyst preparation are still capable of producing surprises. The use of acetylacetonates in non-hydroxylic solvents as impregnating solutions is well established; however, it could not be predicted that the hydrogenation activity of the catalyst resulting from using palladium acetylacetonate in benzene depended on whether (i) there were multiple impregnations with dilute solutions or (ii) there was a single impregnation with a concentrated solution, although the particle sizes

were in the same range (4 to 6 nm) in each case. An explanation was suggested based on a difference in binding energy of the palladium $3d$ core level (11). One factor that can affect the activity of palladium catalysts in hydrogenation reactions is the dissolved hydrogen content, which is known to decrease as the particle size becomes smaller. There is, in fact, a linear relation between x in β-PdH_x and dispersion, and between x and the temperature at which the hydride decomposes (~ 70°C). No hydride is formed when the dispersion exceeds 80 per cent, for then the particles have almost no middle. However, for dispersions over 45 per cent (where XRD ceases to be effective) the decomposition temperature can be used to estimate the degree of dispersion (12).

Ruthenium for Ammonia Synthesis

Carbon-supported ruthenium catalysts promoted with barium or caesium are effective catalysts for ammonia synthesis. Systematic studies are in progress, aimed at understanding how ruthenium differs from iron, and to this end the ruthenium (0001) surface, polycrystalline ruthenium and ruthenium on magnesia and on alumina, both unpromoted and promoted by potassium and caesium, are being examined by a variety of techniques. It appears that the Ru(0001) surface has a very low sticking coefficient for nitrogen, and that in the supported catalysts only a small fraction of the surface is active; the active sites in the caesium-promoted Ru/MgO catalyst are associated with the presence of the alkali (13).

Finally, two contributions of a more fundamental kind will be mentioned from this symposium. Many of the most important catalytic reactions of the platinum group metals involve hydrogen, and detailed studies of its chemisorption on EUROPT-1 (Pt/SiO_2), and on Rh/Al_2O_3 and Pd/SiO_2, show that under all conditions of measurement it is the change in Gibbs free energy, G, and not kinetic factors, that controls what takes place (14).

The importance of equilibrium constants for the adsorption of reactants was also stressed, using alkane hydrogenolysis on Ru/Al_2O_3

catalysts as the example: differences in activity caused by changing the particle size or surface morphology have been traced to thermodynamic factors, rather than to geometric (that is the ensemble size) factors (15).

Research on Model Catalysts

In recent years interest has grown in the preparation of 'model' catalysts that simulate the structure and properties of supported metals, but because they are made on flat surfaces under UHV conditions, they can be investigated by methods of characterisation that are not usually suitable for powdered materials. In a careful study of ethene oxidation on platinum foils, thick platinum films and model Pt/SiO$_2$ catalyst, it was found that the oxidation rates were proportional to the metal area only when the ethene:oxygen ratio was low. It was concluded that the support takes an active part in the reaction when the platinum surface is covered by hydrocarbon species (16).

Another example of support involvement is provided by the sulphur dioxide-assisted oxidation of propane catalysed by the Pt(111) surface, which when partially covered by a disordered aluminium oxide layer gives a rate that is much greater than on the uncoated metal surface. It is thought that adsorption of SO$_4^{2-}$ groups on the support allows an increased uptake of hydrocarbons (17).

Characterisation of Model Catalysts

New and sensitive techniques, such as scanning tunnelling microscopy (STM) and atomic force microscopy (AFM), as well as EXAFS, are being applied to the characterisation of model catalysts. The rate and selectivity shown in the hydrogenation of 1,3-butadiene depend on the microstructure of palladium-graphite films: the structure of which can be changed by altering the hydrogen:hydrocarbon ratio (18). These observations are relevant for understanding the strange behaviour of palladium catalysts prepared from acetylacetonate, as mentioned above (11). Particle growth of IrFe/SiO$_2$ bimetallic model catalysts after oxidation has been followed both by EXAFS and TEM (19).

It is now possible to monitor catalytic reactions on single crystal metal surfaces over a wide pressure range, and, although such surfaces do not precisely mimic technical catalysts, the added advantages – in terms of the applicable techniques for study – more than compensate for this limitation. So, for example, the cause of the oscillatory behaviour in carbon monoxide oxidation on Pd(110) and Pt(210) surfaces is suggested to be subsurface oxygen (20). This form of adsorbed oxygen also features in the interpretation of the results of the NO + CO reaction on iridium (21). Oscillation is also shown in the reaction of NO + H$_2$ on the stepped Rh(533) surface at 470 K and 10^{-6} mbar, but not on Rh(100) (22).

A new technique in the study of adsorbed species is Temperature Programmed Static Secondary-Ion Mass-Spectrometry (TPSSIMS), which together with the more traditional TPD has been used to investigate the conversion of chemisorbed ethene to ethylidyne, and its further decomposition at higher temperatures, on the Rh(111) surface (23).

Another novel and powerful method for examining adsorbed species, Sum Frequency Generation Vibrational Spectroscopy, was described by G. A. Somorjai in his plenary lecture. It has the advantage over conventional infrared spectroscopy by having no interference from gaseous molecules.

Contributions to Other Symposia

It is not only the metallic states of the platinum metals that are catalytically active. However, few of the platinum group metal compounds are stable under the conditions that are required for use in industrial processes; the sulphide may be such a compound. Ruthenium sulphide displays very high activity for hydrotreating processes, especially for hydrodesulphurisation (HDS) and can moreover be prepared in various states of dispersion depending on whether it is supported or not (24).

Metals of the platinum group are also highly effective oxidation catalysts. The use of Pd/Al$_2$O$_3$ for the catalysed complete oxidation of methane allows heat generation at a lower temperature

than does non-catalysed combustion, and thereby reduces the extent of nitrogen oxides formation. Water, being a product, does however act as an inhibitor (25) (see also (16) and (17)). The possibility of reforming methane with carbon dioxide, that is

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2$$
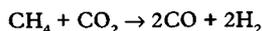
has recently attracted attention, and alumina-supported ruthenium, rhodium, iridium and platinum catalysts all show comparable behaviour for this process (26). In the partial oxidation of methane to synthesis gas, that is

$$CH_4 + 1/2 \, O_2 \rightarrow CO + 2H_2$$
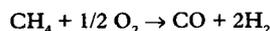
the methane is in fact initially oxidised non-selectively until all the oxygen has disappeared, after which it reacts with either carbon dioxide or with water:

$$CH_4 + H_2O \rightarrow CO + 3H_2$$
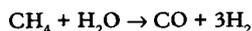
Concluding Remarks

The arrangement of three parallel sessions, together with the very large number of posters available for inspection, made it virtually impossible to absorb and retain all the information. This however reflects the healthy state of the subject, and the great effort that European scientists are devoting to its development. Platinum group metals retain their foremost position in the field of metal catalysis, from which they are unlikely to be moved in the foreseeable future.

EUROPACAT-III will take place in Cracow in 1997. It is a beautiful city: try to be there.

Speakers

1 M. A. J. Campman, J. H. B. J. Hoebink and G. B. Marin, Eindhoven University of Technology, The Netherlands

2 G. Leclercq, P. Granger, J. J. Lecomte, C. Dathy, L. Leclercq, G. Mabilon and M. Prigent, Université des Sciences et Technologies de Lille and Institut Français du Pétrole, France

3 J. Ahola, T. Maunula, H. Haario, T. Salmi, M. Härkönen, M. Luoma and V. J. Pohola, Kemira Metalcat and Åbo Akademi, Finland

4 J. Kašpar, P. Fornasiero, G. Balducci and M. Graziani, Università di Trieste, Italy

5 M. Bowker and R. Sharpe, Reading University, U.K.

6 F. Deihl, G. Mabilon and I. Guibard, Institut Français du Pétrole, France

7 F. Boccuzzi, E. Guglielminotti, F. Pinna and M. Signoretto, Università di Torino and Università di Venezia, Italy

8 B. S. Clausen, C. V. Ovensen, J. Schiøtz, J.K. Nørskov and H. Topsøe, Haldor Topsøe Research Labs., Lyngby, Denmark

9 L. C. A. van den Oetelaar, O. W. Nooij, A. W. Denier van der Gon, H. Brongersma, A. G. Rosenbrand and J. A. R. van Veen, Eindhoven University of Technology and Koninklijke/Shell Laboratorium, Amsterdam, The Netherlands

10 E. S. Shpiro, O. P. Tkachenko, R. W. Joyner, M. R. H. Siddiqi, N. I. Jaeger and G. Schulz-Ekloff, Zelinksy Institute of Organic Chemistry, Moscow, University of Liverpool and Universität Bremen, Germany

11 J. Goetz, M. A. Volpe, A. M. Sica, C. E. Cigola and R. Touroude, Université Louis Pasteur, Strasbourg, and U.N.S.-Conicet, Bahia Blanca, Argentina

12 G. Fagherazzi, A. Benedetti, S. Polizzi, A. di Mario, F. Pinna, M. Signoretto and N. Pernicone, Università di Venezia and Montecatini-Technologie, Novara, Italy

13 M. Mühler, F. Rosowski, O. Hinischen and G. Ertl, Fritz-Haber Institut, Berlin

14. A. Frennet and C. Hubert, Université libre de Bruxelles, Belgium

15 G. C. Bond and J. C. Slaa, Brunel University, Uxbridge, U.K.

16 L.-G. Petersson, L. R. Wallenberg and U. Ackelid, Linköping University, and Chemical Center, Lund, Sweden

17 K. Wilson, C. Hardacre and R. M. Lambert, Cambridge, University

18 K. Catani, K.-H. Lee and E. E. Wolf, University of Notre Dame, Indiana, USA

19 R. Zanoni, M. Bellatreccia, R. Psaro, C. Dossi, S. Calmotti, R. Della Pergola, S. Bertoni and S. Marengo, Università di Milano and Istituto G. Donegani, ENICHEM, Novara, Italy

20 M. Berdau, S. Moldenhauer, A. Hammoudeh, K. Christmann and (the late) J. H. Block, Fritz-Haber Institut and Freie Universität, Berlin.

21 A. I. Boronin, V. I. Elokhin and E. A. Ivanov, Boreskov Institute of Catalysis, Novosibirsk, Russia

22 N. M. H. Jassen, P. D. Cobden, B. E. Nieuwenhuys, M. Ikai and K. Tanaka, Rijksuniversiteit Leiden, The Netherlands, and University of Tokyo

23 H. J. Borg, R. M. van Hardeveld and J. W. Niemantsverdriet, Eindhoven University of Technology, The Netherlands

24 M. Lacroix, M. Breysse, H. Jobic, V. Kougionas and J. L. Portefaix, Institut de Recherches sur la Catalyse, Villeurbanne, France

25 J. C. van Giezen, A. J. van Dillen and J. W. Geus, Utrecht University, The Netherlands

26 H. Papp and Q. Zhuang, Universität Leipzig, Germany