A Standard Platinum/Silica Catalyst

A SUMMARY OF THE FIRST REPORT OF THE RESEARCH GROUP ON CATALYSIS OF THE COUNCIL OF EUROPE

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The platinum on silica catalyst designated EUROPT-1 has recently become available as a standard reference catalyst for the scientific communities in academy and industry. The material, which was manufactured by Johnson Matthey, has been characterised by the Council of Europe's Research Group on Catalysis, and the full report of that characterisation study is about to appear in the scientifie literature.

The Research Group on Catalysis of the Council of Europe was formed in 1975 following an initiative by Professor Eric G. Derouane of the University of Namur. The Group is one of several which functions under the aegis of the Council's Committee on Science and Technology. It consists of twenty-four persons with active research interests in heterogeneous catalysis by metals, drawn from laboratories in nineteen universities and research institutes situated in eight European countries.

Early in its life, the Group selected catalyst characterisation as one of its main areas of collaborative work, and its first report, the characterisation of a platinum/silica catalyst code-named EUROPT-1, will shortly appear as five papers in the journal *Applied Catalysis*. The present author was privileged to act as co-ordinator for the scientific programme and as the main author of the Report. This article summarises the main features.

The Project Philosophy

EUROPT-1 was prepared by Johnson Matthey Chemicals under the supervision of Dr. Dennis E. Webster. The order was for 6 kg of catalyst; of this one half was retained as stock for future division into small samples for the benefit of the scientific communities at large, and the remainder was distributed in 200g samples to members for characterisation.

At an early stage the Group had to decide whether they should specify apparatus designs, and experimental procedures and conditions, or whether they should encourage the use of existing apparatus and routines. The latter was deemed acceptable, and each Group member was asked to carry out those measurements for which their laboratory was best equipped. This decision led to a remarkably successful study ranging over the areas of chemical composition, total surface area, the size distribution of the platinum particles, and chemisorption properties.

The specification drawn up by the Group requested the preparation of a reduced silica-supported platinum containing a metal loading of about 6 per cent. This, we appreciated, was an unusually high loading for platinum, but our central intention was to have a catalyst which contained platinum particles of such a size that the majority would be clearly visible by high resolution transmission electron microscopy. This approach has enabled an estimate of metal dispersion to be made by electron microscopy, and this has provided an invaluable reference point against which to interpret the chemisorption properties.

The Catalyst EUROPT-1

The catalyst was prepared by an ion-exchange method; 6 kg of silica (Sorbosil AQ U30 from Crossfield Chemicals) was stirred with 60 litres of 0.01M $Pt(NH_3)_4Cl_2$ solution,

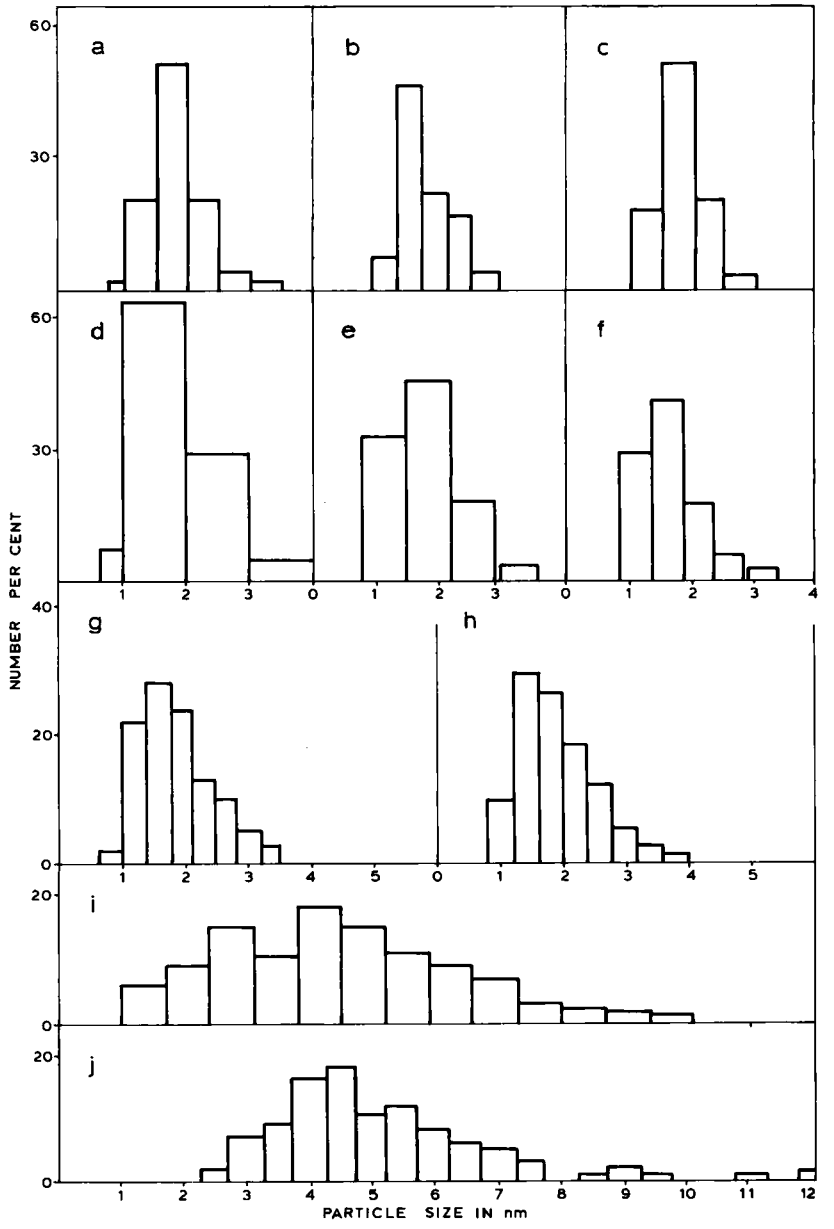

Fig. 1 Size distributions of the platinum-containing particles determined by high resolution transmission electron microscopy. Histograms refer to the following samples: a to e as-received EUROPT-1 as measured in five laboratories; f EUROPT-1 re-reduced in hydrogen at 623 K for 2 hours (zero sintering condition); g to j sintering observed when EUROPT-1 was re-reduced in hydrogen at, respectively, 873 K for 5 hours, 1073 K for 6 hours, 1273 K for 4 hours, and 1273 K for 15 hours as measured in four laboratories

the slurry being kept at pH 8.9 by addition of a basic reagent consisting of 0.01M $Pt(NH_3)_4Cl_2$ and 0.1M $Pt(NH_3)_4(OH)_2$. The material was then filtered, washed, dried, and reduced in hydrogen at 673 K.

Total surface area of as-received EUROPT-1 is 185 ± 5 m^2/g and the metal loading is 6.3 weight per cent. It is well suited for characterisation studies; it is granular and can be easily handled, its weight loss on drying is minimal (0.1 per cent at 473 K), it is suitable for examination by electron microscopy, and so far it has shown no changes with age.

The as-received material has a grain-size distribution and, because the platinum is distributed over the surface of the grains, the larger grains contain a somewhat lower loading of platinum per unit weight. For example, grains of about 500 μm in diameter contain about 5.7 weight per cent platinum.

Trace element analysis showed the presence of aluminium and calcium, each 500 ppm; sodium and titanium, each 400 ppm; magnesium, 200 ppm; potassium, 150 ppm; iron, 90 ppm; chlorine, less than 50 ppm; and chromium, about 10 ppm.

X-ray photoelectron spectroscopy showed the presence of carbon and nitrogen, in addition to the expected platinum, silicon and oxygen. The line-shapes for peaks assigned to platinum suggested incomplete reduction of the metal, and this was clearly demonstrated by application of extended X-ray absorption fine structure (EXAFS) spectroscopy (6) which showed that the majority of platinum atoms in as-received EUROPT-1 have oxygen atoms as nearest neighbours, and not platinum atoms as expected.

Clearly, atmospheric oxidation of the initially reduced platinum occurred after the manufacturer's preparation. However, this was not an impediment to the study, because re-reduction of EUROPT-1 at temperatures below that used in manufacture (673 K) results in no change of the platinum particle size distribution.

The Platinum Particle Size Distribution

Electron micrographs were obtained in seven laboratories with as many electron microscopes. All reported that the silica support was adequately translucent and that the platinum-containing particles were easily visible. The appearance of the micrographs was entirely normal for a material of this type; some of the particle size distributions for as-received EUROPT-1 are shown in Figure 1 (parts **a** to **e**). These histograms differ slightly in appearance because the bands within which particle size was measured differed from one laboratory to another. However, all laboratories report the presence of platinum particles in the range 0.9 to 3.6 nm, there being a maximum in the

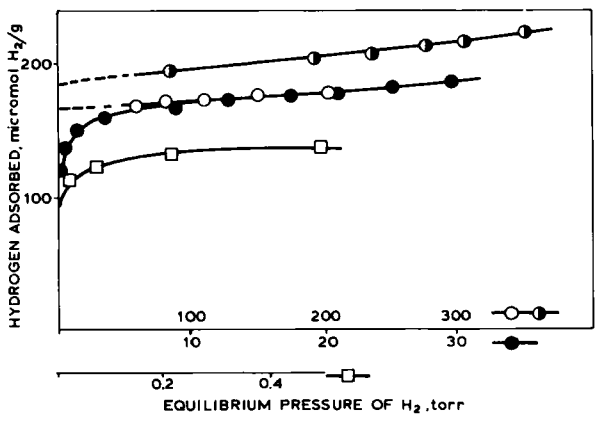

Fig. 2 Isotherms for the adsorption of hydrogen on EUROPT-1 at room temperature as measured in three ranges of pressure in four laboratories

distribution at or a little below 2.0 nm, and about 75 per cent of the particles are less than or equal to 2.0 nm in diameter. This agreement is very gratifying and leads to the conclusion that the platinum particles in EUROPT-1 re-reduced below 673 K have a dispersion close to 60 per cent.

As-received EUROPT-1 showed no change in the particle size distribution of the platinum-containing particles when samples were heated in air at temperatures up to 800 K. Re-reduction in hydrogen at temperatures below 673 K resulted in no sintering (Figure 1**f**), but progressive sintering occurred at 873 K, 1073 K, and 1273 K (Figure 1, parts **g** to **j**). As yet, the details of the sintering process have not been investigated.

The Chemisorption of Hydrogen

It is common practice to calculate a value for the degree of dispersion of platinum in a catalyst by, first, measuring an isotherm for the adsorption of hydrogen on the catalyst at room temperature, second, attributing the "saturation region" to monolayer coverage, and third, assuming that the $H_{adsorbed}$:$Pt_{surface}$ stoichiometry is 1.0:1.0. Our study demonstrates how perilous a procedure that would be if applied uncritically to EUROPT-1.

It is shown in Figure 2 that conventional-looking isotherms are obtained for hydrogen adsorption on EUROPT-1 at room temperature, but that the uptake at the plateau region is pressure dependent. A more extensive study of desorption isotherms at various temperatures shows that, over a wide range of equilibrium pressures (six orders of magnitude at 290 K) the adsorption obeys the Temkin equation. Thus, the plateau regions in Figure 2 are generated by this method of plotting the results, and should not be interpreted as denoting surface saturation or monolayer capacity. Indeed, the condition for full surface coverage is not clearly recognisable from the isotherms, unless it is the value to which the dashed extrapolations of the isotherms at 193, 290, and 373 K converge (see Figure 3). That value is about 200 micromoles H_2 per gram, which exceeds one hydrogen atom per platinum atom present in the adsorbent.

Temperature programmed desorption revealed the presence of four states of adsorbed hydrogen which underwent desorption in the temperature range 100 to 900 K (Figure 4). State **A** hydrogen (T_{max} ~ 200 K) was weakly, perhaps non-dissociatively adsorbed; state **B** hydrogen (T_{max} ~ 400 K) was attributed to hydrogen atoms adsorbed at surface platinum atoms; state **C** hydrogen (T_{max} ~ 550 K) appeared to be the product of reversible processes associated with the supported metal interaction, see the Equation below; and state **D** hydrogen (T_{max} ~ 750 K) was conventional spill-over

$$\equiv \text{Si-O-Pt} + H_2 \rightleftharpoons \equiv \text{Si-OH} + \text{H-Pt}$$

hydrogen which, in the desorption experiment,

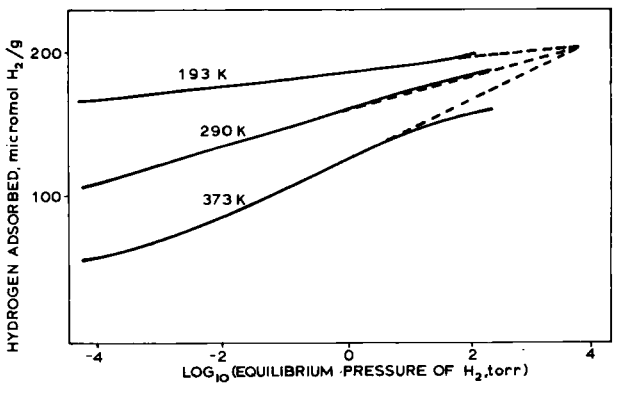

Fig. 3 Isotherms for the desorption of hydrogen on EUROPT-1 at three temperatures over a very wide range of equilibrium pressure as measured in one laboratory

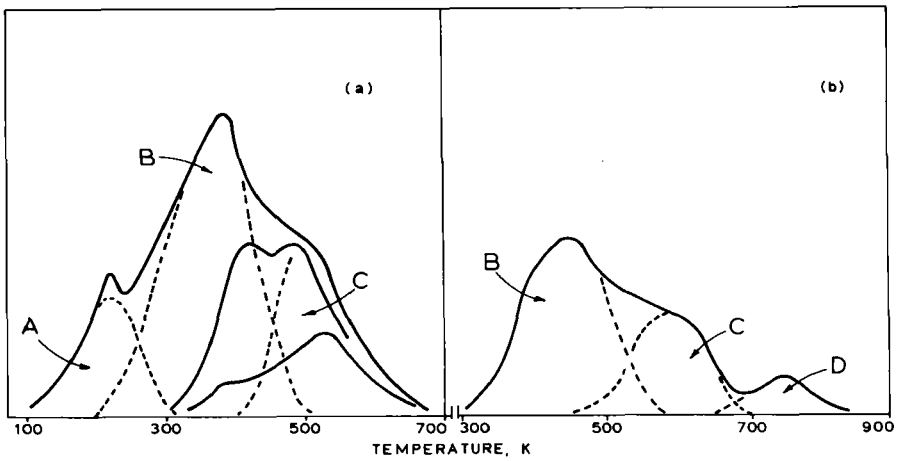

Fig. 4 Profiles for temperature programmed desorption of hydrogen from EUROPT-1 as measured in two laboratories. The four states, A, B, C and D are described in the text. Part (a) shows three profiles, one for each of three extents of initial hydrogen coverage

spills back onto the metallic function and undergoes atom recombination to give gaseous dihydrogen molecules. The population of state **B** hydrogen was such that, if the $H_{adsorbed}$:$Pt_{surface}$ stoichiometry is 1.0:1.0, then the dispersion of the platinum is about 65 per cent, in fair agreement with that obtained by electron microscopy.

Further work is necessary in order to determine whether re-reduction conditions can be found which provide hydrogen mostly in state **B**, with minimal contributions from states **A, C** and **D**.

The Chemisorption of Oxygen and of Carbon Monoxide

Oxygen chemisorption and carbon monoxide chemisorption onto reduced EUROPT-1 at room temperature each gave isotherms of the type shown in Figure 5.

For oxygen chemisorption, extrapolation of the high pressure region of the isotherm to zero pressure gave values of about 86 micromol O_2/g. On the assumptions [i] that this approximates to surface saturation of the exposed platinum atoms by adsorbed oxygen-atoms, and [ii] that the platinum dispersion is 60 per cent, then the $O_{adsorbed}$:$Pt_{surface}$ stoichiometry is 0.9:1.0 at room temperature. This is rather higher than the values obtained from chemisorption studies of oxygen atoms adsorbed on single crystal planes of platinum, and may indicate a special chemistry for oxygen at the surfaces of very small platinum particles. Alternatively, it may indicate that some bulk oxidation occurs. In our study, it was noticed that the extent of oxygen adsorption increased with increasing temperature, and that even at room temperature a slow oxygen uptake followed the fast uptake recorded in the isotherms. Moreover, as noted previously, the as-received EUROPT-1 was substantially oxidised, indicating a considerable sensitivity of the platinum crystallites towards oxygen. Thus, oxygen chemisorption at room temperature appears well-behaved as regards the form of the isotherm, and the number of oxygen atoms adsorbed at a pressure of a few torr appears to "count" the number of surface platinum atoms. There is, however, no firm scientific basis for the use of this measurement as a means of determining dispersion.

Carbon monoxide isotherms were measured at room temperature only. Extrapolations to zero pressure provided values for the uptake of 190 ± 10 micromol CO/g which corresponds to

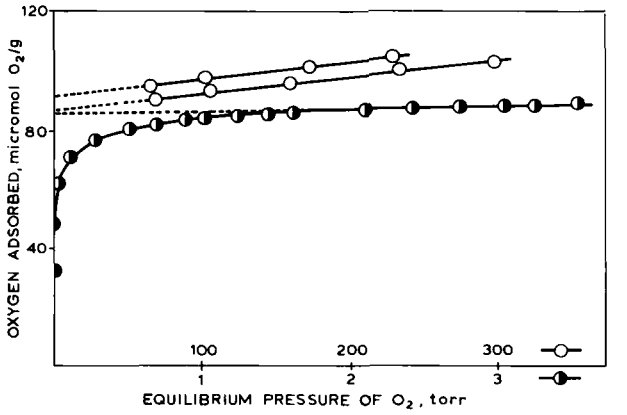

Fig. 5 Isotherms for the adsorption of oxygen on EUROPT-1 at room temperature as measured in two ranges of pressure in three laboratories

$(1.14 \pm 0.06)10^{20}$ CO molecules/g. Thus the ratio $CO_{adsorbed}$:Pt_{total} = 0.6:1.0; and if the dispersion of platinum is indeed 60 per cent as indicated by electron microscopy, then the adsorption stoichiometry ratio $CO_{adsorbed}$:$Pt_{surface}$ must have been close to 1.0:1.0. Infrared spectra (Figure 6) of carbon monoxide supported on reduced EUROPT-1 showed the majority of the molecules to be in the linearly-adsorbed state (ν_{CO} = 2071/cm) but small concentrations of the bridged-species (ν_{CC} = 1843/cm) and of a third species, possibly in a capped configuration (ν_{CO} = 1708/cm), were also formed. The above-mentioned stoichiometries are, again, higher than those observed for carbon monoxide adsorption on close-packed single crystal surfaces of platinum (for example Pt(111)), but they are not inconsistent with the values observed for [a] carbon monoxide adsorption on more open single crystal surfaces (for example Pt(110) for which $CO_{adsorbed}$:$Pt_{surface}$ = 1.0:1.0 (7)) and [b] high nuclearity carbonyl clusters of platinum, for example $Pt_{38}(CO)_{44}^{2-}$ (8).

Main Findings of the Study

The main observations and findings of this characterisation study are set out below; a wealth of greater detail on these and other topics is contained in the original papers.

[1] EUROPT-1 is a 6.3 weight per cent

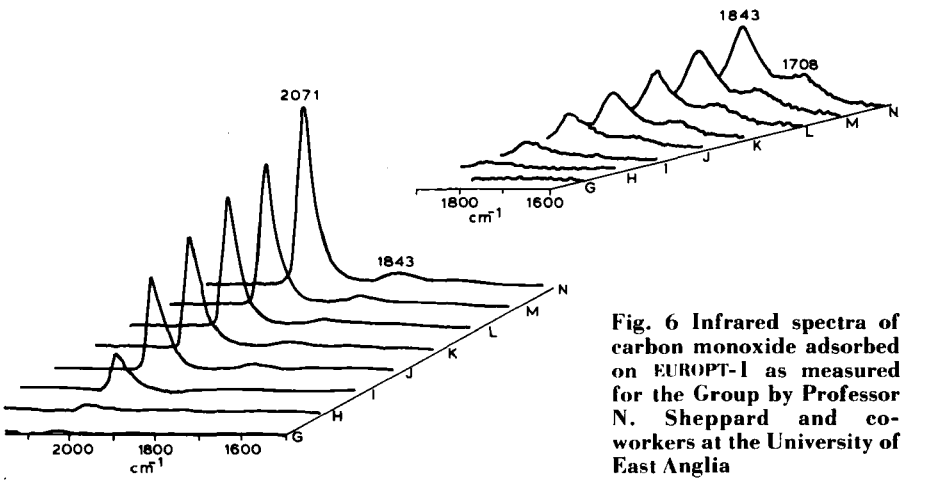

Fig. 6 Infrared spectra of carbon monoxide adsorbed on EUROPT-1 as measured for the Group by Professor N. Sheppard and co-workers at the University of East Anglia

platinum on silica catalyst prepared by Johnson Matthey by an ion-exchange method.

[2] The total surface area is 185 ± 5 m^2/g. The platinum particles, which are substantially oxidised in the as-received material, have a size distribution which ranges from 0.9 to 3.5 nm with a maximum at or a little below 2.0 nm in diameter. 75 per cent of the platinum containing particles are less than or equal to 2.0 nm in diameter.

[3] On re-reduction below 673 K the degree of dispersion of platinum in EUROPT-1 is judged by electron microscopy to be close to 60 per cent.

[4] Isotherms for the adsorption of hydrogen, carbon monoxide and oxygen can be measured with ease in conventional apparatus, and good agreement regarding the extents of adsorption under defined conditions of temperature and pressure have been obtained from a wide range of laboratories (for full details see original papers).

[5] Interpretation of the adsorption isotherms is not straightforward. The extents of adsorption at high coverage exceed "normal" expectations. In the case of hydrogen adosorption, this is attributable to the formation of four adsorbed states only one of which (albeit the most highly populated state) is related directly to the degree of dispersion of the platinum. In the cases of carbon monoxide and oxygen adsorptions, the adsorption stoichiometry at the surface of the small platinum particles appears to be such as to permit a higher extent of adsorption per unit area of surface than the Group originally expected.

Therefore, it appears safer at the present time to use values for the degree of dispersion obtained from electron microscopy to probe the stoichiometry of adsorption for very small metal particles, rather than to assume adsorption stoichiometry in order to determine the degree of dispersion.

In Conclusion

EUROPT-1 has proved very acceptable as a material for this catalyst characterisation exercise. It is the most highly characterised catalyst currently available, and should prove to be of value in many industrial and academic laboratories as a standard against which to test experimental procedures.

Full information is contained in References 1 to 5, to be published shortly, and anyone wishing to obtain a sample should contact the chairman of the Group, Professor V. Ponec (see Appendix for address). Persons wishing to discuss results obtained using EUROPT-1 are welcome to write to the author at the Department of Chemistry, University of Hull, Hull, HU6 7RX, England.

References

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Appendix

Current full members of the Council of Europe Research Group on Catalysis are: **Austria,** H. L. Gruber, Innsbruck; **Belgium,** B. Delmon, Louvain-la-Neuve; E. G. Derouane, Namur; A. Frennet, Brussels; P. A. Jacobs, Leuven; **France,** J. Barbier, Poitiers; G. Leclercq, Lille; G. Maire, Strasbourg; R.Maurel, C. Naccache, J. C. Vedrine, Villeurbanne; **Germany,** G. Ertl, H. Knozinger, Munich; **The Netherlands,** J. W. E. Coenen, Niimegen; J. W. Geus, Utrecht; J. H. C. van Hooff, R. Prins, Eindhoven; V. Ponec, Leiden; **Spain,** G. Munuera, Seville; **Sweden,** R. Larsson, Lund; P. Stenius, Stockholm; **United Kingdom,** G. C. Bond, Uxbridge; P. B. Wells, D. A. Whan, Hull.

Samples of EUROPT-1 can be obtained for research and calibration purposes: persons interested should contact the Group chairman, Professor Vladimir Ponec, Gorlaeus Laboratoria, Rijksuniversiteit te Leiden, Postbus 9502, 2300 RA LEIDEN, The Netherlands.