

The State of the Metal Phase in Supported Platinum-Containing Bimetallic Catalysts

EVIDENCE PROVIDED BY HYDROGEN-OXYGEN TITRATION

By Henri Charcosset

Institut de Recherches sur la Catalyse du C.N.R.S., Villeurbanne, France

The catalytic reforming of crude oils has been considerably improved during the last ten years by the addition of a second metal, generally rhenium or iridium, to the small amounts of platinum present in alumina supported catalysts. A most important question, from a scientific point of view, is to differentiate between the various possible states of the metal phase, which may range from a mixture of platinum and the second metal particles to homogeneous bimetallic aggregates. This differentiation is extremely difficult because of the very small size of the metallic particles. It is reported that hydrogen-oxygen titration provides evidence of the presence of small particles of pure rhenium, iridium or ruthenium in platinum bimetallic alumina supported catalysts.

During the last ten years a considerable improvement in the catalytic reforming of crude oils to petrol has resulted from the addition of a second metal, generally rhenium or iridium, to the platinum in the low platinum content alumina supported catalysts. Numerous fundamental research studies have followed the practical application of such catalysts, and, for instance, the oxidation state of rhenium in the platinum-rhenium alumina supported catalysts is the subject of a recent review by Burch (1).

In our Institute, we started to study this sort of catalyst a few years ago with the platinum-rhenium (2, 3, 4) and platinum-iridium (4) systems in collaboration with the Laboratory of Organic Catalysis at the University of Poitiers, and more recently with the platinum-ruthenium system, in collaboration with the French Institute of Petroleum (6). One of our conclusions is that the stabilisation of a significant percentage of the second metal species (rhenium, iridium or ruthenium) in a

degree of oxidation greater than zero is most unlikely, at approximately 500°C and under a hydrogen pressure equal to several atmospheres, over very long periods of time. From this point of view, account should be taken of a possibly large catalytic effect of platinum on the reduction of the second element (MeII) active species (2). From a scientific point of view an important question then arises in differentiating between two extreme cases: the first in which the two metals platinum and MeII exist as separate particles, and a second where they coexist as bimetallic aggregates of constant composition. Of course many possibilities for intermediate situations occur.

There does not exist at this moment any method of physical analysis which would make it possible to determine the composition of a (Pt, MeII) aggregate smaller than approximately 20Å in size. However, we have found that hydrogen-oxygen titrations performed either at room temperature and/or at a linearly increasing temperature, do give very strong

evidence for the presence of pure rhenium, or iridium, or ruthenium particles inside a bimetallic catalyst. It is the purpose of the present article to report on the principle of the method, its possible extension and also its limitations.

The hydrogen-oxygen titration method is currently used to determine the percentage of the platinum atoms exposed to the gaseous environment in supported platinum monometallic catalysts. It is convenient to carry out the experiments at room temperature, and volumetry or gravimetry or thermal conductivity may be used as well. In the last case we think the differential frontal sorption method, used by Fuhrman and Parravano (7) is advantageous compared to the more usual pulse methods.

The oxygen titration of prechemisorbed hydrogen by an oxygen-helium mixture, and the hydrogen titration of prechemisorbed oxygen by a hydrogen-nitrogen mixture, may be performed successively. Using the currently accepted stoichiometries of 1 hydrogen atom and 1 oxygen atom chemisorbed per platinum surface (Pt_s) leads to reasonable values for the per cent dispersion of platinum, whichever type of apparatus is used.

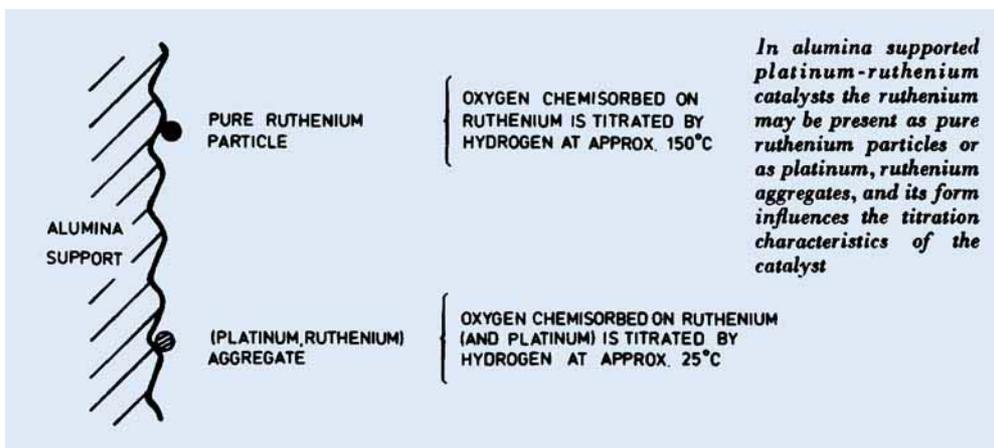
On the other hand, the hydrogen titration of oxygen chemisorbed on supported rhenium particles is very slow at room temperature; for instance only approximately 10 per cent of the oxygen is titrated after 30 minutes, when $p(\text{H}_2)$ is approximately 100 torr (3). This does not mean that hydrogen-oxygen titrations may not be used to measure the per cent dispersion of rhenium, but the hydrogen titration has to be performed above room temperature, as suggested previously in (3), in agreement with Kubicka (8).

Rhenium Bimetallic Aggregates

The main point, with regard to the subject of the present article, is that the reducibility of the oxygen chemisorbed onto rhenium is considerably improved, that is the rate of reduction is increased, when rhenium is in the form of (Pt, Re) bimetallic aggregates. It

follows that hydrogen-oxygen titrations performed at room temperature, according to the sequence (hydrogen-oxygen-hydrogen-oxygen) will give rise to approximately equal values for the first and second oxygen titrations only when all of the rhenium is in the form of (Pt, Re) aggregates. On the other hand, the value for the second oxygen titration is lower than for the first oxygen titration when a significant percentage of the ($\text{Pt}_s + \text{Re}_s$) atoms are present as Re_s of pure rhenium particles. In this way we have found that, depending on the activation procedure for the bimetallic catalysts, either nearly all of the rhenium is combined with platinum in the form of (Pt, Re) aggregates, or only part of the rhenium gives rise to (Pt, Re) aggregates while the balance of the rhenium exists as highly dispersed pure rhenium particles (5). The fact that a variation in the activation procedure alone will result in either all of the Re_sO or only a small per cent of the Re_sO being reducible by hydrogen at approximately 25°C supports the idea that the improvement in reducibility of Re_sO results mainly from the formation of bimetallic aggregates rather than from hydrogen spillover, that is migration of active hydrogen species which may be formed on the surface of platinum particles (9). Nevertheless we cannot actually exclude the possibility of some participation by hydrogen spillover—for example if the distance between the pure platinum and the pure rhenium particles is sufficiently small. Unfortunately, spillover effects in these hydrogen-oxygen titrations over bimetallic catalysts seem to be extremely difficult to prove unambiguously.

The platinum-ruthenium system, studied with a thermal conductivity cell instead of a thermobalance as in the platinum-rhenium system, has corroborated the usefulness of this method. When the hydrogen titrations are performed at a linearly increasing temperature, the oxygen chemisorbed by the platinum is titrated at room temperature, the oxygen chemisorbed by the alumina supported pure ruthenium particles at approximately



150°C (see the above Figure), and the oxygen chemisorbed by the ruthenium in the surface of (Pt, Ru) aggregates is also titrated at room temperature, then the presence of a hydrogen titration peak near 150°C is characteristic of a catalyst in which pure ruthenium particles coexist with pure platinum and/or with (platinum, ruthenium) particles. We have further found that the increase in the reducibility of oxygen chemisorbed by ruthenium most probably results from the formation of bimetallic aggregates, while no definite evidence for any hydrogen spillover effect has been observed under the conditions of these hydrogen-oxygen titrations.

The platinum-iridium system has been investigated similarly to the platinum-ruthenium system but arriving at definite conclusions has been more difficult. This is due to the smaller difference in the reducibility of the oxygen chemisorbed onto pure iridium, or pure platinum, compared to the platinum-ruthenium and platinum-ruthenium systems. Taking account of some variations in the kinetics of the hydrogen titration reaction, we nevertheless have arrived at the conclusion that a relatively homogeneous bimetallic platinum-iridium phase is difficult to obtain on a large specific surface area alumina when the relative percentage of iridium to platinum plus iridium is more than a few per cent. The platinum-iridium and platinum-

ruthenium systems have been found to show similarities, with regard to the difficulty in obtaining bimetallic aggregates at least relatively homogeneous in composition. The bimetallic (Pt, Re) aggregates have been found to be more easily obtained on the same alumina support, provided the conditions of activation allow the rhenium species sufficient mobility during the reduction step (5).

Limitations and Possible Extension of the Method

Clearly, the hydrogen-oxygen titrations as performed over bimetallic catalysts give valuable information not only about the overall dispersion of the (Pt + MeII) metal phase but also about the interactions between platinum and MeII. We should now comment on the possible extension, and on the limitations, of this type of approach. Obviously the method should not be confined to platinum bimetallic catalysts and has a broader field of applicability; the necessary requirement being a sufficient difference in the reducibility of the oxygen chemisorbed on the two metal components when studied separately. With regard to further limitations:

- (i) Note that a small number of say, Ru_s , corresponding to pure ruthenium particles may be interpreted as the absence of any pure ruthenium particles, or to the presence of very coarse pure

ruthenium particles (6). Electron microscopy and eventually X-ray diffraction analysis will allow us to confirm or reject the latter possibility.

- (ii) In a bimetallic catalyst, once the absence of any significant amount of pure particles of say ruthenium, has been established, it follows that all, or almost all, of the ruthenium is present as

(Pt, Ru) bimetallic aggregates. However, this does not necessarily mean that the bimetallic phase has a narrow particle composition distribution. We are now working on methods which could give further insight into the (in)homogeneity in composition from one particle to another, in very small (Pt, MeII) aggregates.

References

- 1 R. Burch, *Platinum Metals Rev.*, 1978, **22**, (2), 57
- 2 C. Bolivar, H. Charcosset, R. Frety, M. Primet, L. Tournayan, C. Betizeau, G. Leclercq and R. Maurel, *J. Catalysis*, 1975, **39**, (2), 249
- 3 C. Bolivar, H. Charcosset, R. Frety, M. Primet, L. Tournayan, C. Betizeau, G. Leclercq and R. Maurel, *J. Catalysis*, 1976, **45**, (2), 163
- 4 C. Betizeau, G. Leclercq, R. Maurel, C. Bolivar, H. Charcosset, R. Frety and L. Tournayan, *J. Catalysis*, 1976, **45**, (2), 179
- 5 L. Tournayan, J. Barbier, H. Charcosset, R. Frety, C. Leclercq and P. Turlier, *Thermo-chim. Acta*, in press
- 6 G. Blanchard, H. Charcosset, M. T. Chenebaux and M. Primet, Second Intern. Symposium: Scientific Bases for the Preparation of Heterogenous Catalysts, Sept. 4-6, 1978, Louvain-la-Neuve, Belgium, Paper B8
- 7 Z. A. Furhman and G. Parravano, *Proc. of the Sixth Int. Congr. on Catalysis*, London, July 1976, Chem. Soc., London, 1977, 686
- 8 H. Kubicka, *Roczniki Chemii*, 1973, **47**, (3), 599
- 9 For review articles on hydrogen spillover, see P. A. Sermon and G. C. Bond, *Catalysis Rev.*, 1973, **8**, 211; H. Charcosset and B. Delmon, *Ind. Chim. Belge*, 1973, **38**, (5), 481

New Platinum Cluster Catalysts

A new way of preparing platinum cluster catalysts using a photocatalytic deposition method has been described recently by Bernhard Kraeutler and Allen J. Bard of the University of Texas (*J. Am. Chem. Soc.*, 1978, **100**, (13), 4317-4318).

A semiconducting lightly doped anatase phase of TiO_2 was suspended under nitrogen in 0.1M $\text{H}_2\text{PtCl}_6/0.1\text{M}$ HCl which had been treated successively with sodium carbonate and acetic acid to give a pH of 4; and then irradiated with a mercury-xenon lamp. Carbon dioxide is evolved and is carried away in the nitrogen stream. Chemical analysis by electron spectroscopy showed that the dark deposits on the TiO_2 powder were entirely Pt(0); and this platinum was fairly uniform—no agglomerates were detected by scanning electron microscopy.

The procedure also works with undoped TiO_2 , and platinum deposits from homogeneous solution when irradiated in this way, but these processes are not as efficient as on the semiconducting oxide. The proposed mechanism involves the oxidation of acetate via a photogenerated hole while the photogenerated electron leads to reduction of the platinum complex. The oxidative decarboxy-

lation is irreversible and this prevents any back reaction between the reduced metal species and the oxidation product. This suggests that carboxylic acids are ideal choices as electron donors for heterogeneous photo-reductions.

The method described thus enables the preparation of a catalyst with a high dispersion of small clusters of platinum atoms on the support surface. Metal deposition probably only occurs near sites where photons strike the surface and the light flux can be made very small. The low temperature of the photo-decomposition (55°C) also minimises surface diffusion of metal atoms and prevents the formation of large aggregates. The extent to which a range of metals may be photo-deposited on to semiconducting powders is now being investigated.

Both platinised TiO_2 and WO_3 powders have shown high activity in the catalytic hydrogenation of both neat benzene and cyclohexene to cyclohexane at temperatures of 80°C and below. Similarly, the platinised anatase powders promoted the efficient photocatalytic decarboxylation of saturated carboxylic acids.

D. T. F.