

Reply to "Interpretation of Temperature-Programmed Reduction (TPR) Experiments of Platinum-Iridium Catalysts"

In a recent note (1) we presented evidence from temperature-programmed reduction (TPR) experiments for the existence of bimetallic clusters in the reduced state of highly dispersed Pt-Ir/ γ -Al₂O₃ catalysts, and suggested that intimacy between the metal species was retained after oxidation in O₂/He mixtures at 350°C. After such treatments, a single TPR reduction peak was observed with a maximum at 105°C, the size of which indicated an average metal oxidation state of 3. This suggested, but did not prove, that individual oxidation states of Pt(2) and Ir(4) were present, as found for the alumina-supported metals separately. Foger and Jaeger (2) dispute these conclusions on the basis of their own investigations of Pt-Ir/Al₂O₃ and Pt-Ir/SiO₂ systems using TPR, X-ray diffraction (XRD), transmission electron microscopy (TEM), and selected-area electron diffraction (SAED). They comment that there are dangers in the use of TPR experiments in isolation to determine the structure of bimetallic catalysts, since interpretation is not necessarily unambiguous.

While we agree that care should be taken when interpreting TPR results, we believe that the discrepancies between Foger and Jaeger's work and our own lie in the fact that the size of the metal or metal oxide particles was significantly greater in Foger and Jaeger's work. Our reasoning is as follows:

1. Although superficially the TPR profiles published by both groups resemble one another, closer inspection reveals large differences.

First, the average oxidation state of the metals after oxidation of a Pt-Ir/Al₂O₃ cat-

alyst at 350°C was found in our work to be 3, from the TPR peak area. Foger and Jaeger propose oxidation states of 0 (Pt) and 2 (Ir). This means that their TPR peak at 80-90°C must be smaller by a factor of 2-3 than our peak at 105°C, the area under the peak corresponding to the total hydrogen consumption for reduction of the oxidic species. Since there is a single peak after the oxidation treatment at 350°C, we cannot unambiguously assign individual oxidation states, but if the platinum was zero valent, as Foger and Jaeger suggest, then our TPR hydrogen consumption would indicate that iridium was present as Ir(VI), which seems very unlikely.

Second, the difference in the reported temperature of the peak maximum may well be significant. The lower temperature found by Foger and Jaeger is consistent with a lower degree of interaction between the metal species and the carrier. This argues that the particle size of the metal species was indeed greater in that case.

2. Although Foger and Jaeger do not give details of the actual particle diameters determined in their study, the very fact that they were able to use techniques such as XRD shows that theirs was a less highly dispersed state of the catalyst than that examined in our TPR work. It has been our intention, in the work on both Pt-Ir and Pt-Re (3) systems, to investigate the structure of metal clusters smaller than 1 nm in diameter. Such particles are not susceptible to study by XRD or even TEM. Foger and Jaeger's catalysts must contain particles of diameter greater than 3 nm for the XRD technique to be applicable.

As a check on dispersion, dissociative adsorption of hydrogen was used to charac-

terize our Pt-Ir/Al₂O₃ catalyst and its monometallic counterparts. In all cases H/metal atomic ratios close to unity were found for the catalysts in the reduced state, indicating excellent dispersions. For catalysts containing particles visible by XRD and TEM, much lower H/metal ratios are determined. Not only the hydrogen adsorption titer, but the reduction profile itself, is affected by the metal particle size. In the case of platinum certainly, agglomerates of the zero-valent metal yield considerably diminished TRP signals, and determination of oxidation states becomes subject to considerable ambiguity. Under these circumstances other techniques are more suitable, as Foger and Jaeger's work has demonstrated.

3. Foger and Jaeger base their conclusions largely on their studies with a Pt-Ir/SiO₂ catalyst. While the behavior of this system apparently bears a superficial resemblance to that of its alumina-supported counterpart, we feel that it is dangerous to make comparisons between the two. In particular, the absence of any contribution from platinum species to the reduction profiles of the silica-supported catalyst suggests a very poor dispersion of the metal, as indeed indicated by the XRD results. The small amount of oxygen likely to be chemisorbed on the platinum particles found in Foger and Jaeger's catalyst would perhaps not be expected to give rise to much signal in a TPR profile. This situation cannot be

considered typical of that applying to a highly dispersed, alumina-supported catalyst, in which the entire complement of the metal can take part in chemisorption/reduction phenomena. Nor would we necessarily expect the species present in the two systems to be the same.

Thus, we suggest that the structure found by Foger and Jaeger for their catalysts is probably inherent to the state of the metal particles present, specifically their dispersion. Taking their results together with our own on more highly dispersed metal clusters, it appears that caution is needed in generalizing the behavior of supported metal species over a wide range of particle sizes, especially with respect to bimetallic interaction and alloying phenomena.

REFERENCES

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