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NOTES

On the Temperature-Programmed Reduction of Pt–Ir/γ-Al_2O_3 Catalysts

The accompanying paper (*1*) from this laboratory described the temperature-programmed reduction (TPR) of Pt–Re/γ-Al_2O_3 catalysts which yielded strong evidence for the existence of Pt–Re clusters in the reduced state of the catalyst. An intriguing feature of the results was the segregation of Pt and Re oxides observed after oxidation of the bimetallic clusters at temperatures above about 200°C. Evidently the oxide moieties are immiscible on the scale of the small clusters (up to 10–15 atoms) in the case of these metals. In general, the phenomena should vary from one metal to another, and comparison of the behavior of different bimetallic combinations should assist in understanding the principles underlying metals interaction and segregation on supports. The present results for Pt–Ir/γ-Al_2O_3 represent an example of a supported, highly dispersed system in which the intimacy of the metals remains intact even after fairly severe oxidation treatments.

Catalysts were prepared by (co-)impregnation of H_2PtCl_6 and H_2IrCl_6 onto pure alumina of reforming grade quality (specific surface area 180 m^2/g, pore volume 0.9 ml/g, Cl content 0.45 wt%) in the form of 1.7-mm-diameter spheres. The catalysts were dried at 120°C in an oven and calcined in circulating air to 500°C, this end temperature being maintained for 1 hr. TPR runs were carried out as previously described (*1*).

The TPR profile of fresh, calcined 0.375 wt% Pt/0.37 wt% Ir/Cl/Al_2O_3 showed a sharp reduction peak at 235°C with a small tail extending to 500°C. This was expected since both calcined Pt/Al_2O_3 and Ir/Al_2O_3 are fully reduced in this temperature region with a sharp peak in the region between 200 and 250°C. The "overlap" means that TPR cannot be used here as a diagnostic test for bimetallic interaction.

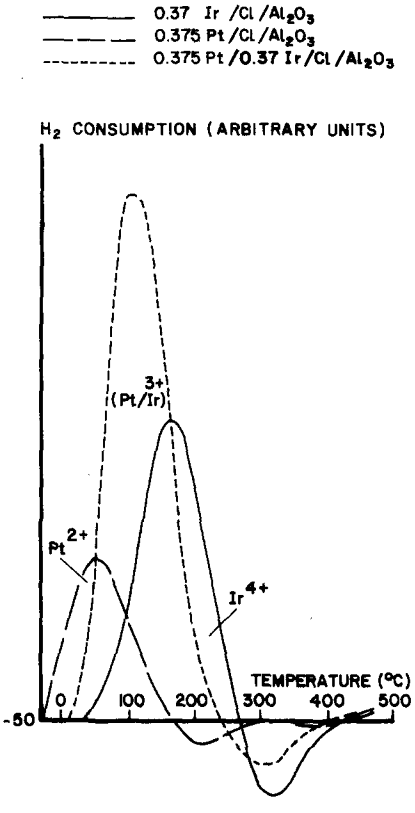

FIG. 1. TPR reduction profile for prereduced catalysts reoxidized at 350°C.

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The situation after reoxidation for 1 hr at 350°C (Fig. 1) reveals much more. The Pt–Ir bimetallic catalyst shows a unique reduction peak at 105°C, almost exactly the middle point between the peaks for Pt/Al_2O_3 and Ir/Al_2O_3 treated identically. The peak intensity amounts to the sum of the separate peak intensities for the individual monometallic systems, the average oxidation state being 3 for the metal atoms in the bimetallic catalyst, 4 for Ir/Al_2O_3, and 2 for Pt/Al_2O_3. (N.B. The peak intensities can be directly related to oxidation states since the atomic weights of Pt and Ir differ very little.) This suggests that the individual oxidation states of Pt(2) and Ir(4) are retained in the bimetallic catalyst.

The unique reduction peak at 105°C in the Pt–Ir catalyst constitutes, in our opinion, evidence for the existence of bimetallic alloy clusters in this catalyst system in its reduced form. A particularly interesting feature is that the intimacy of the metals is apparently not destroyed by the fairly severe oxidation treatment (at 350°C). This is in marked contrast to the situation with $Pt–Re/Al_2O_3$ catalysts, in which we found oxide segregation to be well advanced after such oxidation treatments. Study of other bimetallic systems on alumina by TPR should yield further valuable information on this interesting aspect of metal cluster behavior.

REFERENCE

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