

LETTERS TO THE EDITORS

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

Comments to a Note by Wagstaff and Prins

Recently Wagstaff and Prins (1) have published temperature-programmed reduction (TPR) profiles from the hydrogen reduction of Pt-Ir(50/50)/ γ -Al₂O₃ catalysts which had been reoxidized at 350°C in 5% O₂ in He. They observed a single TPR peak with a maximum at 105°C and assigned this peak to the reduction of Pt(II)-oxide and Ir(IV)-oxide in intimate contact. They suggested that the appearance of a single peak indicated that the catalysts consisted of bimetallic clusters. We believe it is dangerous to use TPR experiments in isolation to determine the structure of bimetallic catalysts, since, in the absence of additional data, TPR results are not necessarily open to unambiguous interpretation. Therefore, using Pt-Ir(50/50)/ γ -Al₂O₃ and Pt-Ir(50/50)/SiO₂ catalysts, which had been oxidized at various temperatures, we have studied catalyst structure by combining the techniques of TPR, transmission electron microscopy (TEM), selected-area electron diffraction (SAED), and X-ray diffraction (XRD).

A 2 wt% Pt-Ir(50/50)/ γ -Al₂O₃ catalyst was prepared by impregnation of γ -Al₂O₃ (Woelm W200) with a solution of H₂PtCl₆ and H₂IrCl₆ by the method of incipient wetness. After drying in air the catalyst was reduced in H₂ at 400°C for 15 hr. The particle size distribution determined from TEM images showed a spread between <1 and 7 nm with an average value of 2 nm. Before TPR the catalyst was oxidized for 30 min in 1% O₂ in He at selected temperatures (T_{ox}) in the range 300 to 550°C. TPR experiments were carried

out in 3% H₂ in N₂ in the range 25 to 350°C at 5°C min⁻¹.

As illustrated in Fig. 1 we obtained a single peak in the TPR profile with a maximum at 80–90°C if T_{ox} was below 400°C, but a fairly sharp second peak with a maximum at 210–230°C appeared if T_{ox} was above 400°C. Increasing T_{ox} caused a continuous increase of the narrow high-temperature TPR peak and a decrease of the broader low-temperature peak.

No marked changes were detected with XRD and TEM if the catalyst was exposed to O₂ at $T_{ox} < 400^\circ\text{C}$, but for $T_{ox} > 400^\circ\text{C}$ TEM images revealed thin needles and lamellar growths besides metallic particles. SAED showed that those needles and lamellae were IrO₂ and/or PtO₂. The presence of oxide was further substantiated by XRD. At T_{ox} about 400°C most of the oxide was still attached to metal particles, but at $T_{ox} > 500^\circ\text{C}$ separate oxide and metal particles were frequently observed.

A distinction between IrO₂ and PtO₂ is not possible because the oxide diffraction patterns differ markedly only in the vicinity of the Pt-Ir alloy (111) reflection. In addition, preferential oxidation of one of the metals cannot be deduced from the shift of the (111) alloy peak because it coincides with a fairly strong γ -Al₂O₃ peak.

More information about the system may be obtained from a comparison between Pt, Ir and Pt-Ir(50/50) catalysts supported on SiO₂ (Aerosil, Degussa)

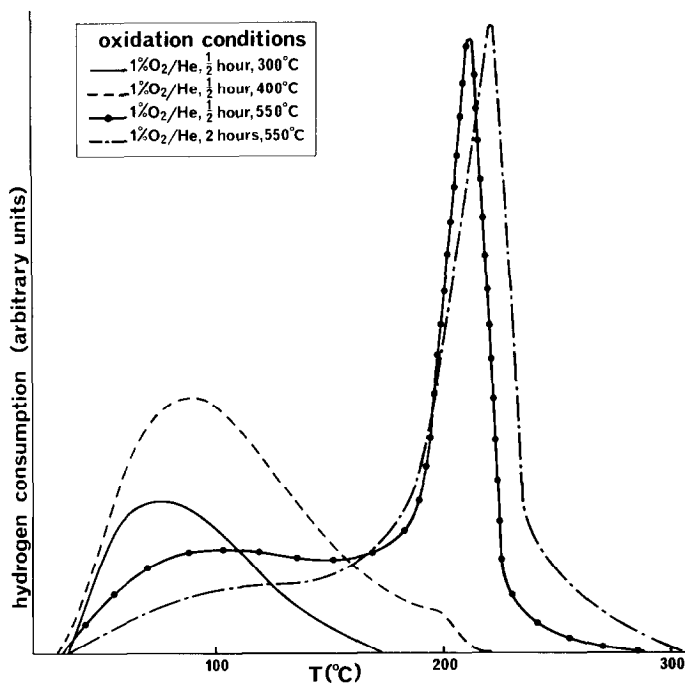


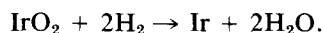
FIG. 1. TPR profiles for a prerduced 2 wt% Pt-Ir/ γ -Al₂O₃ catalyst reoxidized under the conditions indicated.

since in this case the support does not exhibit any diffraction peaks in the region of interest. The results of an extensive study, which we have carried out on such catalysts with TPR, XRD, and TEM (2, 3) showed that only iridium oxides contributed to the TPR profiles between 25 and 350°C. Bulk IrO₂ was present at $T_{\text{ox}} > 300^\circ\text{C}$ and a surface oxide Ir₃O at $T_{\text{ox}} < 300^\circ\text{C}$. This is supported by the following observations:

1. Catalysts containing only Pt did not exhibit any TPR peaks after exposure to O₂ at any value of T_{ox} in the range 100–700°C, nor was any bulk oxide detected with either TEM or XRD. The reduction of chemisorbed oxygen or surface Pt oxide would be complete already at 25°C and therefore would not contribute a peak to the TPR profiles in the temperature range 25 to 350°C studied in this case.

2. When Ir catalysts were heated in O₂ at increasing T_{ox} above 300°C, reflections due to IrO₂ became prominent with both

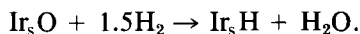
XRD and SAED while Ir metal reflections eventually disappeared and separate IrO₂ crystals became increasingly obvious in TEM images. In addition, TPR profiles of Ir catalysts oxidized at $T_{\text{ox}} \geq 300^\circ\text{C}$ showed two peaks with maxima above 200°C and below 100°C. When T_{ox} was increased further the maximum above 200°C increased while that below 100°C decreased (in a similar manner as shown in Fig. 1) and disappeared altogether at $T_{\text{ox}} \geq 550^\circ\text{C}$. At this stage Ir metal was also no longer detectable with diffraction. By analogy with the reduction of other Ir(IV) compounds the TPR peak maximum at 200°C is expected for the reduction of IrO₂, which proceeds according to the equation



3. Before oxidation XRD traces of Pt-Ir(50/50) catalysts revealed symmetrical metal peaks at positions intermediate between those for pure Pt and Ir catalysts, as is expected for fcc bimetallic particles. Ox-

idizing Pt–Ir(50/50) catalysts at increasing T_{ox} above 300°C produced the same results as for Ir catalysts with respect to the TPR profiles and with respect for the detection of oxide by TEM and XRD. In this case, however, metal particles were detected by TEM, SAED, and XRD even if T_{ox} was as high as 700°C. Furthermore, the alloy XRD peaks shifted toward the Pt positions and when samples oxidized at $T_{\text{ox}} \geq 400^\circ\text{C}$ were examined after TPR, additional Ir metal peaks were observed. This showed that Ir is preferentially oxidized and that the alloy is eventually destroyed.

4. When Ir or Pt–Ir(50/50) catalysts were oxidized at $T_{\text{ox}} < 300^\circ\text{C}$, no marked changes were observed with TEM or XRD, but the TPR profiles now exhibited single peaks with maxima at 90 and 60°C for Ir and Pt–Ir(50/50) catalysts, respectively. On Ir catalysts it was established that the oxide was reduced according to the equation



Repeated TPR runs showed on Pt–Ir(50/50) the preferential formation of one type of surface oxide and hydrocarbon reactions carried out immediately after TPR of a Pt–Ir(50/50) catalyst oxidized below 300°C indicated a more iridium-like behavior compared to the platinum-like behavior of the as-prepared catalyst. However, extensive heating in H_2 at 400°C restored the selectivities observed before oxidation. These observations strongly suggest that the TPR peak, maximum at 60°C, obtained on Pt–Ir(50/50) is also caused by the reduction of Ir_5O and that the platinum present on the oxidized surface lowers the peak maximum from 90°C for pure Ir to 60°C. This presumably involves spillover of adsorbed hydrogen from the platinum.

If we compare the oxidation behavior of Pt–Ir(50/50) on SiO_2 with that of Pt–Ir on $\gamma\text{-Al}_2\text{O}_3$ it appears that on $\gamma\text{-Al}_2\text{O}_3$ the reactivity of the metal particles is markedly reduced. This finding is not unexpected, since it is well known that metal–substrate inter-

actions are much stronger on Al_2O_3 than on SiO_2 .

Our results on Pt–Ir(50/50)/ $\gamma\text{-Al}_2\text{O}_3$ and Pt, Ir and Pt–Ir(50/50)/ SiO_2 are in conflict with the observation by Wagstaff and Prins that, after oxidation treatment, Pt on Al_2O_3 produced an appreciable TPR peak at 50°C. When we examined Pt–Ir(50/50)/ $\gamma\text{-Al}_2\text{O}_3$ after oxidation, substantial metal particles were present at all temperatures. From our observations on SiO_2 (see observations 1–3 above) we conclude that at $T_{\text{ox}} > 500^\circ\text{C}$ such metal particles are nearly pure Pt and that Pt is not oxidized to any appreciable extent on either SiO_2 or Al_2O_3 substrates.

With regard to the TPR profile for Pt–Ir(50/50) our observations are in essential agreement with those of Wagstaff and Prins. However, taking all the available evidence into consideration we suggest that the oxide which causes the TPR peak, maximum at 90°C, when Pt–Ir(50/50) on $\gamma\text{-Al}_2\text{O}_3$ is exposed to O_2 at T_{ox} below 400°C is the surface oxide Ir_5O in intimate contact with metallic Pt. Since Wagstaff and Prins start their TPR run at -50°C , the TPR profile may well contain a contribution from chemisorbed oxygen on Pt, but our study clearly showed that Ir(IV) oxide is certainly not present to any appreciable extent at that stage of oxidation.

REFERENCES

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