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Surface Reaction for Measurement of Metal Dispersion

In Ref. (*1*) the authors discourse on the use of the surface reaction

$$O(s) + 2CO(g) \longrightarrow CO(s) + CO_2(g) \quad (1)$$

for the measurement of surface-areas of dispersed platinum (*2*). Specifically they speculate that the stoichiometry of the reaction may be a function of temperature and of metal crystallite size. In response we wish to point out that the surface titration O(s)/CO is carried out at room temperature at which the surface coverage with oxygen adatoms has been found to be nearly equal to that of the two strongly bound CO states on a polycrystalline Pt surface (*3*), as well as on a number of individual crystal planes of Pt (*4–6*). Furthermore the experimentally determined ratio of CO reacted to CO_2 formed, which exhibits a constant value of 2.00 ± 0.05 for a number of Pt-dispersions examined by the O(s)/CO titration technique, tends to support the stoichiometry specified by reaction (1). Thus during surface titration a one-for-one replacement takes the place of a chemisorbed oxygen atom by a CO-molecule.

As for variations of surface-coverage with crystallite size there is no reason, a priori, to assume that the adsorption characteristics would be a function of the number of metal atoms in the crystallite for the size range under discussion (> 25 Å). More likely the crystal orientation on the surface of the cluster is responsible for the variations reported. A case in point is the absence of oxygen chemisorption (*5*) on Pt(100) and its low rate of adsorption (*7*) on Pt(111) in the absence of stepped surface structures. In addition, surface reconstruction has been recognized to be associated with exothermic surface reactions such as chemisorption of oxygen and hydrogen on Pt (*8*,*9*). As suggested in Ref. (*2*), this phenomenon of surface rearrangement during the redox cycle of the O(s)/CO titration procedure offers an alternate and more satisfactory interpretation of the apparent change in surface area exhibited by the Pt/Al_2O_3 catalyst, than the room-temperature formation of different oxygen species (including an ionic compound) with different reactivities favored by Flynn and Wanke (*1*).

With regard to oxygen uptake as a measure of metal surface area of supported Pt catalysts, this parameter, due to oxygen interaction with the carrier, is less reliable than the mass of CO reacted during the titration. Thus the surface-area results reported are based on the CO consumed, in view of the oxygen loss to such supports as carbon and alumina, noted in our work (*2*).

In an extension of the O(s)/CO titration technique to the Pd-system (*10*) we employ a conventional pulsed-flow reactor/gas-chromatographic technique to monitor the CO consumed and the CO_2 formed after exposure of the catalyst to oxygen. The results demonstrate a surface reaction stoichiometry identical to that of Pt, and, by comparison with other surface-area measurements, the suitability of the technique to the determination of dispersed Pd in the presence or absence of different support materials.

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