

LETTERS TO THE EDITORS

Comments on CO Titration

A method for determining metal surface areas of bulk and supported platinum by means of CO titration of preadsorbed oxygen was recently described by Wentrcek, Kimoto and Wise (1). Although this method may be an alternative to the more commonly employed H₂ and CO adsorption and O₂-H₂ titration methods, the interactions of O₂-CO with supported platinum are complex; the adsorption and surface reaction stoichiometries for the O₂-CO supported Pt system are not well defined.

In general, caution must be used in postulating integral stoichiometries for replacement of one adsorbed species by another following titration reactions such as CO-O₂ or H₂-O₂. Inspection of oxygen, hydrogen, and carbon monoxide isobars [e.g., Refs. (2-5)] suggests that a "clean" catalyst surface adsorbs different amounts of these gases at room temperature. At a given temperature, which depends in part on the catalyst and the measuring system, the metal surface will adsorb equal amounts of CO and oxygen (or hydrogen and oxygen); however, the ratio of oxygen to hydrogen or carbon monoxide uptakes is always temperature sensitive since oxygen uptake increases with increasing temperature while hydrogen and CO uptakes decrease with increasing temperature. Thus there is no reason *a priori* to anticipate a one for one replacement of one adsorbed species by another in a titration reaction at room temperature. An additional complicating factor is the dependence of the gas uptakes relative to each other on the metal particle size (or disper-

sion). Several authors (5-7) have noted a decrease in oxygen uptake relative to hydrogen uptake as particle size decreases, while Gruber (8) also noted that CO uptake decreases relative to hydrogen uptake as particle size decreases. Hence titration stoichiometries would appear to be far more complex than postulated integral stoichiometries suggest [e.g., Refs. (9-11)]; stoichiometries can be expected to be sensitive to both temperature and dispersion.

Wentrcek, Kimoto and Wise (1), in order to explain their results, postulated that the CO adsorption stoichiometry during CO titration was significantly different than the CO adsorption stoichiometry for CO adsorption on a "clean" surface and that during multiple O₂-CO titration cycles the platinum surface areas increased. An explanation of the cause for the change in CO adsorption stoichiometry was not given, nor was the observation that oxygen adsorption uptake remained constant during multiple titration cycles reconciled with the postulated Pt surface area increase. We would like to present an explanation for the above observations which can account for the change in the CO adsorption stoichiometry and the increase in CO uptake with multiple titration cycles without requiring an increase in Pt surface area. (Atomic rearrangement of Pt surface atoms under different environments is possible, but we do not believe that one gets a cumulative increase in Pt area with cyclical O₂-CO treatment, particularly since no significant increase in O₂ uptake was observed during titration.)

Infrared studies of O_2 -CO interactions with supported metal catalysts at room temperature (5,12,13) have shown that if CO is introduced to a Pt surface onto which oxygen has been adsorbed a CO adsorption band, which is not present when CO is adsorbed on a "clean" Pt surface, results. This new CO species is attributed to adsorption of CO on a Pt^{2+} (12) or a PtO (13) surface species. [Heyne and Tompkins (12) also found evidence for another weakly adsorbed CO species which they ascribed to CO adsorption on the O^{2-} associated with the Pt^{2+} .] Hence, in the O_2 -CO-Pt system there exist at least two types of adsorbed oxygen: O^I the species formed during adsorption of O_2 on freshly reduced Pt, and O^{II} the species formed during the interaction of CO with O^I [it should be noted that O^{II} can also be formed by oxygen adsorption at elevated temperatures (5,12)]. In addition, there are at least three types of adsorbed CO; $(CO)^I$ attributed to linear adsorbed CO, $(CO)^{II}$ attributed to bridged adsorbed CO, and $(CO)^{III}$ attributed to CO adsorbed on Pt- O^{II} . Infrared studies (5,13) have shown that repetitive O_2 -CO titration cycles result in an accumulation of O^{II} . After the first titration cycle the intensity of the CO^I adsorption band remains constant or increases slightly relative to the band observed for CO adsorption on the fresh catalyst. However, this band starts to decrease with subsequent O_2 -CO cycles. The relative amounts of $(CO)^{II}$ during cyclic O_2 -CO titrations cannot readily be determined by ir since the CO_2 formed during titration partially adsorbs on the Al_2O_3 support resulting in a broad adsorption band in the 1800 cm^{-1} region which interferes with the $(CO)^{II}$ band.

We believe that the results presented by Wentrcek, Kimoto and Wise (1) can be explained by the cumulative formation of O^{II} . The increased CO uptake with increasing number of CO titration, according to this explanation, is caused by

the increase in O^{II} sites which are not reduced by CO (gas) at room temperature, and are only partially desorbed by evacuation at 620 K. In order for the oxygen adsorption uptakes to remain relatively constant over the first several cycles, it is necessary that the O^{II} sites do not interfere with the formation of O^I . According to this description, the oxygen adsorption uptakes should start to decrease once a sizable fraction of the surface is covered by O^{II} which begins to interfere with O^I adsorption. This could be checked experimentally by carrying out a large number of O_2 -CO cycles and evacuating at lower temperatures.

Another aspect of the results of Wentrcek, Kimoto and Wise is not explained by the authors' stoichiometry is the measured ratio of carbon monoxide titration to oxygen adsorption uptake (molecules CO per atom of oxygen) of ~ 1.6 for the Pt/ Al_2O_3 catalyst. According to their proposed reaction and adsorption stoichiometries (1), i.e., $1O(s) + 2CO(g) \rightarrow 1CO_2(g) + 1CO(s)$, $CO/O = 2.0$ should be obtained. The low CO/O ratio can be explained by oxygen adsorption on the support, but this does not explain the increase in the CO/O ratio with a number of titrations. The presence of O^{II} sites, however, can also account for a CO/O ratio less than 2 if, on the average, less than one CO molecule adsorbs per O^{II} site. We postulate that the observed CO/O ratio of 1.6 for the supported Pt catalysts, which increases with titration cycles, may be due to this nonintegral stoichiometry.

An additional factor may also be cited in accounting for the increase in CO uptake observed during titration. Enhancement of hydrogen following the O_2 - H_2 titration reaction has already been noted (5,14). Recent studies (5) suggest that the enhancement may be due to an alteration of the metal-adsorbate interaction arising from the titration reaction product (H_2O). Since the $CO-O_2$ titration reaction generates

CO₂ in the region of the metal particle, changes in CO uptakes of the order of 10% observed by Wentrcek, Kimoto and Wise (1) may well be attributed to the effect of CO₂ on the metal-adsorbate interaction.

Given these considerations, we suggest that attributing the observed increase in CO uptake to "an apparent increase in Pt dispersion caused most likely by crystal reorientation" is somewhat premature.

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