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NOTE

Assay of Molybdena–Alumina Catalysts by Oxygen Chemisorption

Parekh and Weller (*1*) adopted a technique devised by Brunauer and Emmett (*2*) to measure the "equivalent molybdena surface area" for reduced molybdena–alumina catalysts. This method contains the implicit assumption that two phases were present, the alumina support and microcrystalline MoO_2, and it was suggested that the low-temperature oxygen chemisorption may be used to measure the surface area of the molybdena phase.

Another view of the molybdena–alumina surface stems from the idea that an epitaxial monolayer of molybdena is formed on the alumina surface in registry with the crystal lattice below, the molybdena complexes replacing the terminal hydroxyl groups of the support (*3–6*). Studies of the reduction process (*7*) have led us to suggest that coordinatively unsaturated sites (CUS = anion vacancies) are introduced into this monolayer as H_2O is formed during the reduction. The CUS should be natural sites for oxygen chemisorption. Moreover, their surface concentration has been shown (*4*, *7*) to be a function of the extent of reduction. Consequently, we have reinvestigated the system with a view to ascertaining whether or not the O_2 chemisorption is site-specific. The catalysts studied by Parekh and Weller (*1*) were extensively reduced (to an average valence state of about Mo^{4+} or $e/Mo = 2.0$ below Mo^{6+}). In the present work the catalyst was reduced to various extents at 500°C using procedures developed in our previous studies (*7*) of the reduction process. Hence, the surfaces of these materials have been characterized as a function of extent of reduction in terms of CUS, surface OH, etc. This has made possible numerical comparisons which have proved enlightening.

The chemisorption technique used by Parekh and Weller (*1*) involved determining an adsorption isotherm on the reduced catalyst at 78 K followed by evacuation at 195 K before redetermining the O_2 isotherm at 78 K; the difference between the first and second isotherms was taken as the amount chemisorbed and as a measure of the extent of the molybdena surface. This technique, while adequate for their large chemisorption, was too inaccurate to use for the small chemisorptions coupled with large physisorptions found for less extensively reduced catalysts. Therefore, we adopted a technique used by Burwell and Stec (*8*) for the present study. Pulses of O_2 were passed over the catalyst in a flowing stream of He until the catalyst was saturated at 78 K; the temperature was then raised to 195 K and the reversible fraction was caught and retained in a silica gel trap at 78 K from which it could be released and determined quantitatively as in glc. In this way, the amount chemisorbed could be evaluated with an accuracy of ± 0.03 cm^3 (STP)/g.

The data for oxygen chemisorption as a function of the extent of reduction are shown in Fig. 1. They also correlated linearly with anion vacancy (CUS) concentration (*7*) as shown in Fig. 2. Interestingly, the line intersects the abscissa

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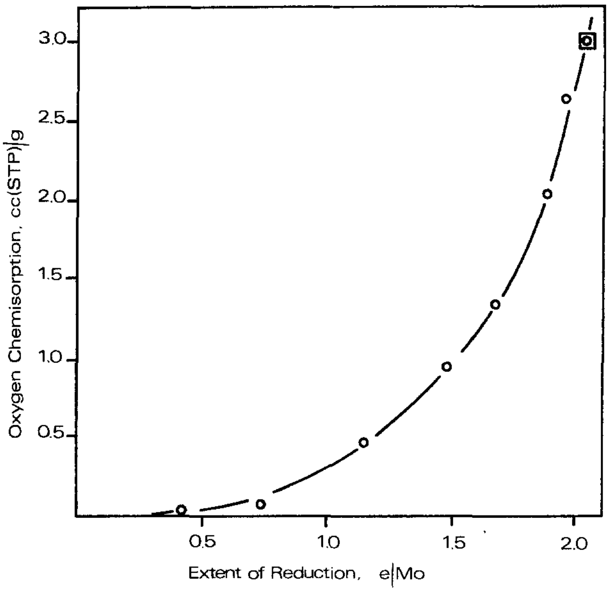

FIG. 1. Relation between oxygen chemisorption and the extent of reduction (*e*/Mo). The former was measured by passing pulses of O_2 over the catalyst at 78 K in a stream of He using the technique of Ref. (*8*). Desorption was effected by raising the temperature to 195 K for about 30 min. The amount desorbed was collected and measured and these two steps were repeated until the amount desorbed at 195 K became equal to the amount adsorbed at 78 K. The extent of reduction was calculated from the amount of H_2 consumed in the reduction as described elsewhere (*7*). The experiment at *e*/Mo = 2.0 was repeated using a BET system, □.

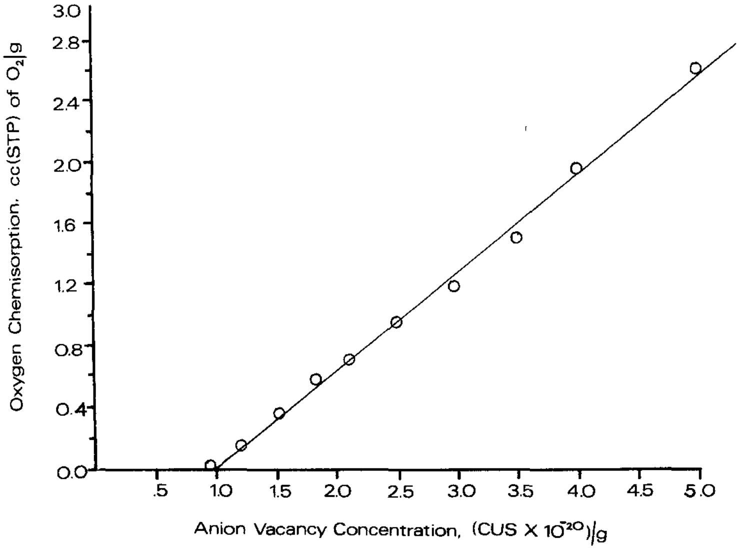

FIG. 2. Correlation of oxygen chemisorption to anion vacancy concentration measured as O atoms removed as H_2O during reduction. Slope corresponds to 0.165 O_2/□ and the maximum chemisorption to 0.175 O_2/Mo.

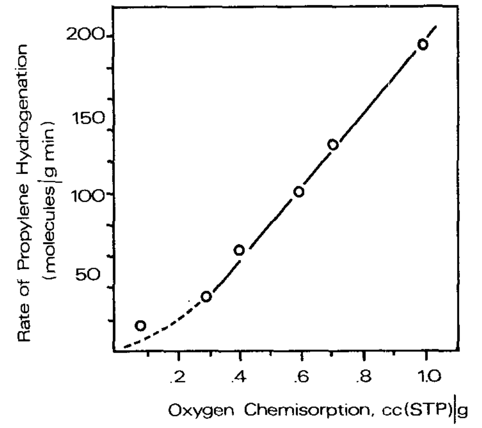

FIG. 3. Catalytic activity for hydrogenation of propylene related to the sites which hold O_2 at 195 K.

suggesting that the first vacancies formed do not function in the chemisorption. This seems reasonable in view of the recent report (*9*) that the same sites which adsorb O_2 also adsorb NO, yielding infrared spectra of a dinitrosyl species. We suppose that this may mean that sites having at least two missing oxygens may be required to hold the chemisorbed oxygen, although other explanations are possible. The slope of Fig. 2 suggests that on the average one O_2 is chemisorbed per six oxygen vacancies. The highest adsorption shown corresponds to 0.17 O_2/Mo. This value is, however, over an order of magnitude larger than the concentrations of the ionic forms (O_2^-, O^-) reported earlier (*10*). The molybdena surface areas estimated by the method of Parekh and Weller are accordingly much smaller than the area of the support, whereas on the basis of the monolayer model about 50% of this area would be covered. This might occur if microcrystals of MoO_2 do indeed form as the reduction approaches its limit (e/Mo $\simeq$ 2), as has been suggested by a number of workers.

The oxygen chemisorption was found to be specific for sites effective for hydrogenation. Figure 3 shows the linear correlations between the propylene hydrogenation rate and the oxygen chemisorption. In fact, we have found (*11*) that the hydrogenation reaction can be completely poisoned by comparable (even smaller) quantities of O_2. This amount is only a small fraction of that removed by reduction. Thus, the low-temperature chemisorption of O_2 appears to measure a property of considerable fundamental significance.

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