Chemisorption of Carbon Monoxide on Reduced Molybdena

Oxygen chemisorption a low temperatures has been suggested as a method for determining equivalent molybdena area in reduced, supported catalysts (*1*). Liu *et al.* (*2*) report that temperatures of −195 and −78°C, and dynamic as well as static adsorption systems, seem to be equally suitable. Low-temperature O_2 chemisorption was employed very recently by Millman and Hall (*3*) to characterize the sites on incompletely reduced MoO_3/Al_2O_3 active for propylene hydrogenation, and by Tauster *et al.* (*4*) to characterize the sites on MoS_2 active for hydrodesulfurization of dibenzothiophene. On MoO_3/Al_2O_3 containing 12–15 wt% MoO_3, Parekh and Weller, Millman and Hall, and Liu et al. find similar results for the O_2 chemisorption on a well-reduced sample ($e/Mo \simeq 2.0$): the ratio of 0 atoms to total Mo atoms is in the range 0.31–0.35.

Hall and Millman (*5*) are also using the strong chemisorption of H_2 at −195°C on MoO_3/Al_2O_3, reduced to varying extents, to develop correlations with their earlier results on O_2 chemisorption and propylene hydrogenation. Interestingly, the highest value of strong H_2 chemisorption, on the well-reduced catalyst ($e/Mo \simeq 2.0$), was only half that of O_2 chemisorption; the ratio of H atoms to total Mo atoms was 0.154, as compared with the value of 0.34 reported by Millman and Hall for the ratio of O atoms to total Mo atoms.

In view of the potential interest in chemisorption for characterizing reduced MoO_3/Al_2O_3 catalysts, we have studied CO chemisorption at three temperatures (−195, −78, and 0°C) on two samples. One sample was a commercial CoO (3%)–MoO_3 (15%)–Al_2O_3 catalyst (Harshaw 0402T), previously used by Parekh and Weller (*1*) and Liu *et*

al. (*2*). The other was a high-area, unsupported MoO_3 sample prepared by a modification of the alcohol precipitation method of Fransen *et al.* (*6*); its BET surface area, measured after H_2 reduction at 350°C, was 95 m^2/g. Carbon monoxide was generated by reaction of formic and sulfuric acids in a high-vacuum system, followed by passage through Ascarite, Drierite, and a −78°C trap. Details of the preparation of the unsupported MoO_3 and of the CO are given by Ramakrishnan (*7*). CO adsorption isotherms were measured at −195, −78, or 0°C after prereduction in flowing H_2; reduction conditions were 6 h at 500°C for the $CoO–MoO_3–Al_2O_3$ catalyst (+1 hour evacuation at 500°), and 2 h at 350°C for the unsupported MoO_3 +1 hour evacuation at 350°). In each case two isotherms were determined for each adsorption temperature, with intermediate pumping as described in Refs. (*1, 2*). Values for "CO chemisorption" were taken as the vertical difference between the first and second isotherms, which were smooth and parallel. Triplicate experiments on fresh samples were run on different days at each of the three test temperatures, for the $CoO–MoO_3–Al_2O_3$ sample, to estimate the precision. Standard deviation, calculated from the lumped data, was 0.083 ml (STP) CO chemisorbed per gram catalyst.

The chemisorption results are summarized in Table 1. The amount of CO chemisorbed decreases with increasing temperature of adsorption, for both samples. Every use of chemisorption as a titration of surface sites entails an assumption about what sites are being measured. If the interest here were in determining the total number of surface Mo ions on the basis of an assumed 1 : 1 stoichiometry for CO : surface

TABLE 1

Chemisorption of CO on Reduced Samples

Temp. (°C)	CO chemisorbed (ml (STP)/g)	
	Unsupported MoO_3[a]	$CoO/MoO_3/Al_2O_3$[b,c]
−195	2.66	2.44
−78	2.55	2.11
0	2.13	0.96

[a] Prereduced in flowing H_2 for 2 h at 350°C. Surface area (BET) after reduction and determination of CO isotherms was 95 m²/g.

[b] Harshaw 0402T: 15% MoO_3 and 3% CoO on SiO_2-stabilized Al_2O_3. Prereduced in flowing H_2 for 6 h at 500°C.

[c] Averages of triplicate runs on different days. Standard deviation, based on lumped data, was 0.083 ml (STP) CO/g.

Mo, then the observed temperature dependence would convey a lack of reassurance about the absolute count by this method. CO chemisorption appears to be less useful than O_2 chemisorption, therefore, for measurement of specific surface area of the reduced, supported molybdena. Uncertainty about linear vs bridged bonding of the CO would further confound the area measurement by CO adsorption. There is no a priori necessity that the bonding mode for CO should be the same on the supported catalyst as it is on the unsupported molybdena that might be used to establish a "conversion factor" (from gas chemisorbed to molybdena area).

Furthermore, even the highest value of CO chemisorption observed on the supported sample (2.44 ml/g at −195°C) corresponds to much lower coverage by CO molecules than by O atoms during O_2 chemisorption. The ratio of CO molecules to total Mo atoms in this case was 0.105; the ratio of O atoms to total Mo atoms, calculated from the data of Parekh and Weller for the same material, was 0.31.

The average particle diameter and the surface coverage by CO for the unsupported sample are of interest. The BET area, S, of 95 m²/g corresponds to an average particle diameter, $\bar{d}$, of 98 Å (from the formula $\bar{d} = 6/\rho S$, if ρ is taken as 6.47 g/cm³). The maximum CO chemisorption is 2.66 ml (STP)/g at −195°C. This corresponds to 133 Å² per CO molecule adsorbed. Coverage by chemisorbed oxygen is much more complete. For unsupported, reduced molybdena, Parekh and Weller obtained a ratio of 51 Å²/O_2 molecule chemisorbed, or 25.5 Å² per O atom. A more recent study by Garcia Fierro et al. (8), concerning O_2 chemisorption on unsupported, reduced molybdena of area about 55 m²/g, resulted in a similar value, 46.8 Å² per O_2 molecule, or 23.4 Å² per O atom.

The following conclusions may be drawn:

1. Surface coverage of reduced molybdena by chemisorbed CO is substantially lower than the surface coverage by chemisorbed O_2.

2. The surface coverage by chemisorbed CO decreases as the temperature of chemisorption is increased from −195 to 0°C.

3. Chemisorption of O_2 at low temperatures is to be preferred to that of CO as a possible means of measuring the dispersion of reduced molybdena on an alumina support.

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