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Studies of Molybdena–Alumina Catalysts

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MoO_3–Al_2O_3 catalysts over the loading range 3.9 to 14.9 wt% MoO_3 have been studied. Although the BET surface areas in the higher valent (MoO_3) form are compatible with a monolayer model, the areas after H_2 reduction at 500°C are not; the appropriate model would be porous or finely crystalline MoO_2 produced by reduction. For reduced catalysts, the curve for O_2 chemisorption (at −78°C) vs molybdena loading is concave upwards. The origin of this behavior seems to be incomplete reduction (of MoO_3 to MoO_2, after 6 hr at 500°C in flowing H_2) for catalysts containing less than about 11 wt% MoO_3. If correction is made for the actual extent of reduction at 500°C, then O_2 chemisorption vs loading is essentially a straight line through the origin. Activity for cyclohexane dehydrogenation at 500°C vs molybdena loading is also a curve concave upward; again, correction for the actual amount of MoO_3 reduced during prereduction changes the curve to one that is slightly convex upward. The sites responsible for both O_2 chemisorption and cyclohexane dehydrogenation may correspond to surface Mo^{4+} ions, but this is not proven.

INTRODUCTION

Consensus exists that in MoO_3–Al_2O_3 catalysts, MoO_3 occurs as a monolayer on the Al_2O_3 surface provided that the loading does not exceed ca. 1.5 mg MoO_3/m^2 Al_2O_3 surface (*1, 2*). There is disagreement about the nature of the catalyst after reduction, however; suggested models range from monolayer MoO_2 (*3*), to interrupted monolayer (*4*), to small crystallites (*5*).

Measurements of total surface area (BET) are useful in discriminating between models. For molybdena monolayers, addition of molybdena to a fixed weight of alumina will result in constant surface area per gram of alumina, but decreased surface area per gram of catalyst. For small molybdena crystallites possessing intrinsic porosity and surface area, addition of molybdena to a fixed weight of alumina will result in increased surface area per gram of alumina, and a surface area per gram of catalyst which may even remain constant, if the intrinsic surface area per gram of molybdena chanced to be as large as that of the alumina support.

This criterion has been used for catalysts in the oxidized state (MoO_3–Al_2O_3) but not for those after H_2 reduction at elevated temperature. Giordano *et al.* (*6*) measured surface areas for MoO_3–Al_2O_3 preparations over the range 0–30% MoO_3. They showed that the areas decreased linearly with increased loading up to 15–20% MoO_3, in the manner expected if only the alumina contributed, i.e., for MoO_3 monolayer coverage. Massoth (*7*), in a reexamination of the surface area data of Giordano *et al.* (*6*) and of de Beer *et al.* (*8*), has similarly concluded that a monolayer model is appropriate for a number of oxide and sulfide catalysts.

The present paper contains a study of MoO_3–Al_2O_3 catalysts over the loading range of 3.9 to 14.9 wt% MoO_3. Measurements have been made of: (1) surface area both in the oxidized condition and after reduction in H_2 at 500°C; (2) H_2 and O_2 consumption in redox experiments at 500°C; (3) O_2 chemisorption at −78°C after reduction at 500°C; and (4) activity for dehydrogenation of cyclohexane at 500°C after reduction at 500°C.

EXPERIMENTAL METHODS

Materials and equipment. Catalysts were

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prepared by impregnation of 60- to 80-mesh alumina with aqueous ammonium molybdate, by the "no excess solution" technique. The alumina was Houdry (Air Products) Type 200S, having a measured area of 144 m^2/g and pore volume 0.415 ml/g. The concentration of impregnating solution was chosen to give the desired MoO_3 loading after vacuum drying at 110°C and calcination at 500°C for 12 hr in air. The range of loading was 3.9 to 14.9 wt% MoO_3 in the finished catalyst.

The low-temperature adsorption and 500°C redox studies were conducted in a standard, gas volumetric, glass high-vacuum system equipped with a recirculation pump and in-line cold trap. Details of the system have been published (*5*). About 1 g of catalyst was used in each experiment.

Oxygen chemisorption. Chemisorption of O_2 was determined as the difference between two O_2 adsorption isotherms at −78°C (*9*). Prior to the first isotherm, the catalyst was prereduced for 6 hr at 500°C in flowing H_2 (40 cm^3/min), pumped for 1 hr at 500°C, and cooled under vacuum. Between the first and second O_2 isotherms the sample was pumped for 1 hr at −78°C. The BET surface area of the reduced catalyst was determined after completion of the chemisorption experiment.

Redox studies at 500°C. Details of the procedure have been published (*5*). A known initial volume of H_2 was circulated through the sample and in-line cold (−195°C) trap. H_2 consumption during 6 hr at 500°C was determined through measurement of the pressure decrease in the closed system. After this reduction treatment, the sample was evacuated for 1 hr at 500°C and then exposed to a known amount of O_2 at 500°C. The cold trap was held at −78°C during this reoxidation treatment.

Cyclohexane dehydrogenation. A pulsed microcatalytic reactor was used to study the conversion of cyclohexane to benzene at 500°C. The reactor was a stainless-steel tube of 0.25-in. i.d. (0.18-in. o.d.); the catalyst charge was 0.400 g in each experiment. Standard prereduction (*in situ*) was in flowing H_2 (40 cm^3/min) for 6 hr, followed by a He purge overnight. Each experiment consisted of ten pulses of cyclohexane, each pulse being 1 μl (9.2 μmole) of liquid feed. The injection port was kept at 170°C and connecting lines were kept at 200°C. Upstream pressure was 32 psia. He carrier gas was kept at a flow rate of 35 cm^3/min. Gas analysis, after cooling of the effluent stream to 100°C, was by gas chromatography with a column of 20% BMEA on 60- to 80-mesh Chromosorb P. The column and detector were kept at 120°C.

No sign of deactivation was observed during the brief on-stream period of ten pulses. The activity, calculated from the steady-state value of benzene produced during this period, has been expressed be-

TABLE 1

BET Area of Oxidized and Reduced MoO_3–Al_2O_3 Catalysts

wt% MoO_3	Oxidized MoO_3/Al_2O_3		Reduced MoO_3/Al_2O_3	
	BET area (m^2/g cat.)	BET area (m^2/g Al_2O_3)	BET area (m^2/g cat.)	BET area (m^2/g Al_2O_3)
0.0	—	144	—	—
3.9	136	141	142	148
5.7	—	—	147	156
7.5	137	148	147	159
10.8	—	—	144	161
11.4	128	145	146	163
13.2	—	—	143	165
14.9	124	146	141	166

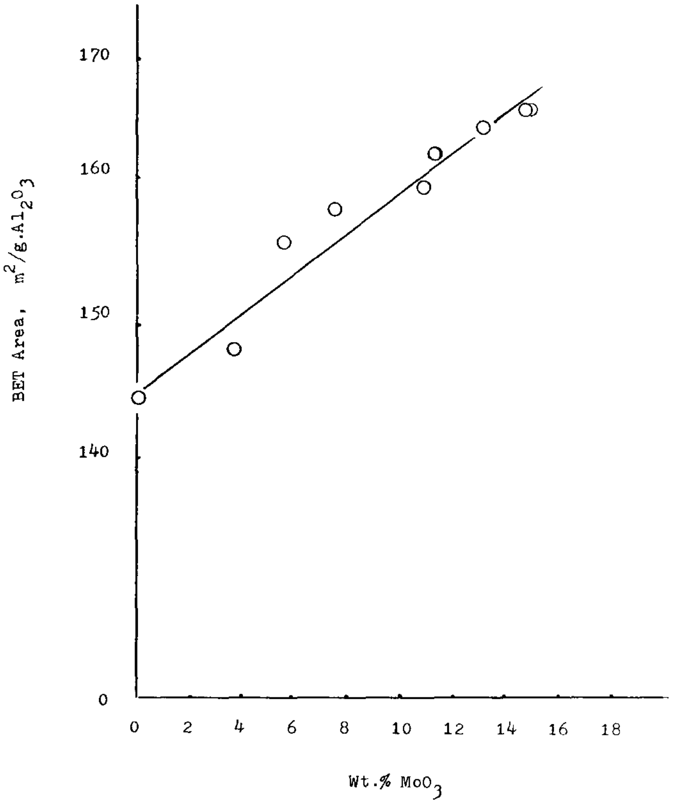

FIG. 1. BET area of reduced MoO_3–Al_2O_3 vs MoO_3 loading in unreduced catalyst.

low as moles of benzene produced per mole of cyclohexane injected. Since the cyclohexane injected in each pulse was held constant, this measure gives information about the fractional conversion in each pulse as well as the relative activities of different catalysts under the standardized test conditions.

RESULTS AND DISCUSSION

The results of surface area measurements on the oxidized and on the reduced (H_2, 6 hr, 500°C) samples are given in Table 1. Areas are expressed on two bases: square meters per gram catalyst and square meters per gram Al_2O_3 in the catalyst. For samples in the oxidized condition, the area per gram

TABLE 2

Redox Study of MoO_3–Al_2O_3 Catalysts

wt% MoO_3	H_2 consumed [ml (STP)/g cat.]	Theoretical H_2 for $MoO_3 \rightarrow MoO_2$	O_2 consumed [ml (STP)/g cat.]	Theoretical O_2 for $MoO_2 \rightarrow MoO_3$	"Extent of reduction"[a]
14.9	28.52	23.19	12.48	11.59	1.08
11.4	18.01	17.74	7.34	8.87	0.83
7.5	10.55	11.67	4.55	5.84	0.78
3.9	4.61	6.07	1.67	3.03	0.55

[a] "Extent of reduction" ≡ O_2 consumed (actual)/O_2 consumed (theoretical) = atomic ratio of actual O_2 consumed/total Mo in sample.

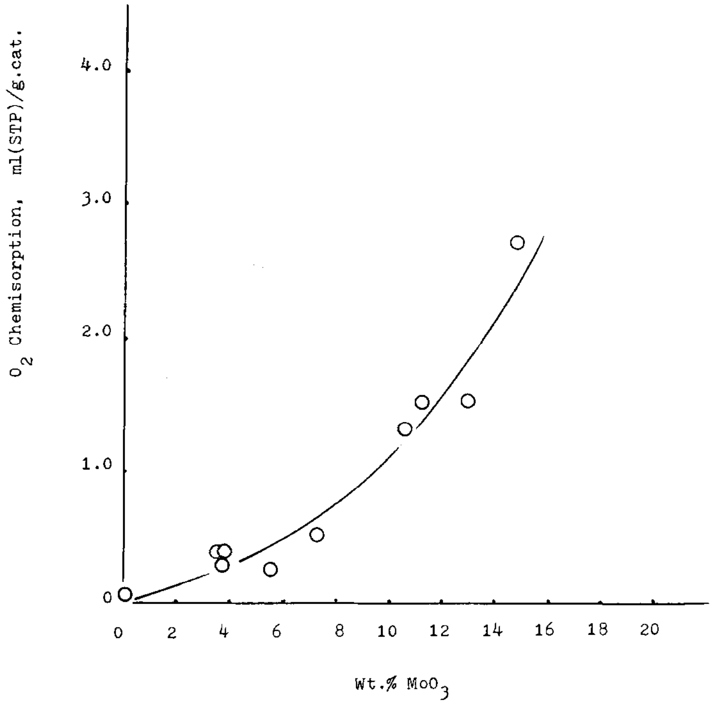

FIG. 2. O_2 chemisorption at −78°C on reduced MoO_3–Al_2O_3 vs MoO_3 loading in unreduced catalyst.

catalyst decreases with increasing loading of MoO_3, but the area per gram Al_2O_3 remains constant. (The highest loading, 14.9% MoO_3, corresponds to 1.2 mg MoO_3/m^2 Al_2O_3.) These results are consistent with the data and conclusions of Giordano *et al.* (*6*) and of Massoth (*7*) about a monolayer of MoO_3 on Al_2O_3.

The reduced catalysts present a different picture. The area per gram catalyst remains essentially constant over the loading range, and the area per gram Al_2O_3 increases almost linearly with loading. This behavior is shown more clearly in Fig. 1. It is not consistent with any monolayer model for the reduced catalyst. It would be consistent with the existence of small crystallites of molybdena in the reduced catalyst, if the crystallites were sufficiently small (or sufficiently porous) to possess surface area comparable with that of the alumina support. Such a model has been previously suggested for MoO_2–Al_2O_3 (*5*).

Measurements of O_2 chemisorption at −78°C were then used to estimate the relative surface areas of the reduced molybdena in catalysts after 500°C reduction. The results are shown in Fig. 2. The shape of the curve was somewhat puzzling. O_2 chemisorption may be a measure of the specific surface area of the MoO_2 formed by reduction, in the same way as H_2 chemisorption is used to measure the specific surface area (or dispersion) of Pt in Pt–Al_2O_3. Since the dispersion in supported catalysts is normally highest with low loading, the curve for O_2 chemisorption vs MoO_2 loading might be expected to be linear or convex upward. The actual curve is concave upward.

A partial explanation was found in redox studies at 500°C, the results of which are summarized in Table 2. H_2 and O_2 consumption for the 14.9% MoO_3 sample are in close agreement with those reported by Parekh and Weller (*5*) for a 15.0% MoO_3 sample. For this sample, the difference between the total H_2 consumed and that required for $MoO_3 + H_2 \rightarrow MoO_2 + H_2O$ was attributed by Parekh and Weller to either the total H_2 chemisorbed on MoO_2 or, alternately, the partial reduction of Mo beyond the Mo^{IV} stage. The difference in this case between the total O_2 consumed on reoxidation and that required for $MoO_2 + \frac{1}{2}O_2 \rightarrow MoO_3$ is attributed to oxidation of irreversibly adsorbed hydrogen which is retained after evacuation at 500° [cf. Massoth (*11*), Hall and Massoth (*12*), and Parekh and Weller (*5*)] or, alternately, to reoxidation of any Mo that had been reduced beyond Mo^{IV}. These alternatives are not distinguished by the present redox experiments. The last column in Table 2 is the atomic ratio of oxygen consumed on 500°C reoxidation to total molybdenum in the sample; for any given sample, this ratio is taken as a measure of the extent of reduction of MoO_3 to MoO_2. The ratio is 1.08 for the 14.9% MoO_3 sample.

The situation is different for the samples with lower loading of MoO_3. For the 11.4% MoO_3 sample, the total H_2 uptake is still slightly in excess of the theoretical for $MoO_3 \rightarrow MoO_2$, but the subsequent O_2 uptake is significantly less than theoretical for $MoO_2 \rightarrow MoO_3$. The extent of reduction, calculated from O_2 uptake, is only 0.83 (Table 2). On the basis of this interpretation, the excess H_2 consumption [18.01 − 2(7.34)] for this sample is attributed to reversible H_2 adsorption accompanying the reduction process.

Measured in this way, the extent of reduction after 6 hr in flowing H_2 at 500°C is 0.78 for the 7.5% MoO_3 sample and 0.55 for the 3.9% MoO_3 sample. Whatever the reason may be for this incomplete reduction, it is plausible to associate the values for O_2 chemisorption at −78°C (Fig. 2) with the actual amount of reduced molybdena, rather than with the total MoO_3 loading as in Fig. 2. Figure 3 is a replot of Fig. 2 for the four samples listed in Table 2, where the abscissa for each point is not the MoO_3 loading in the unreduced catalyst, but that loading corrected for the extent of reduction given in the final column of Table 2.

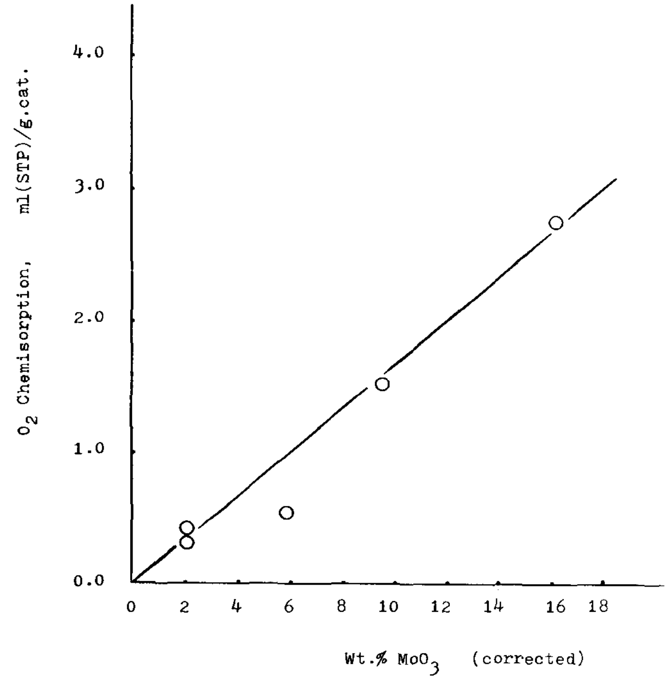

FIG. 3. O_2 chemisorption vs MoO_3 loading, corrected for extent of reduction.

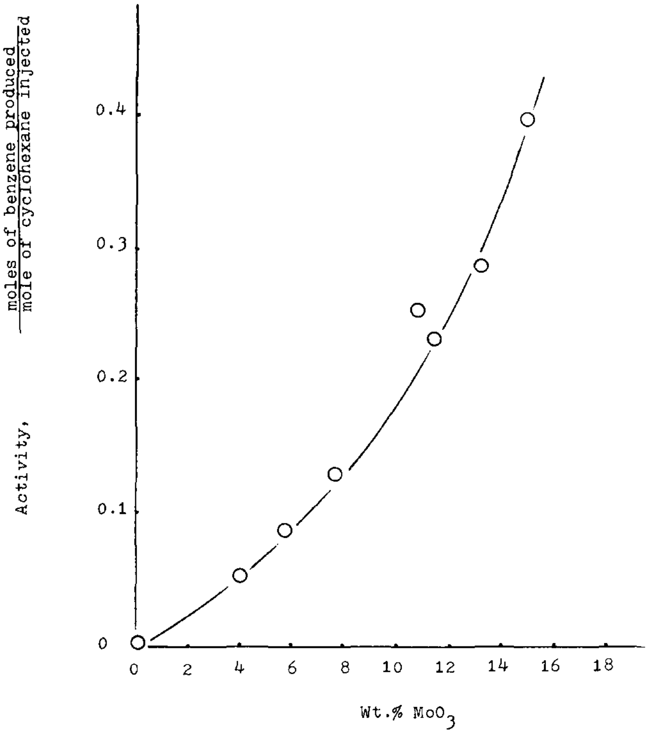

FIG. 4. Activity of reduced MoO_3–Al_2O_3 vs MoO_3 loading in unreduced catalyst.

With the exception of one point, the values now fall almost on a straight line through the origin, suggesting a dispersion of the MoO_2 that is independent of loading.

The reason for incomplete reduction at low MoO_3 loading is unclear. Much has been made of the stabilization of MoO_3 by reason of chemical interaction with an Al_2O_3 surface. The data in Table 2 are compatible with this but imply a more complex model. Complete reduction (to MoO_2) is possible in 6 hr at 500°C with 15% MoO_3–Al_2O_3 but not with 11% MoO_3 or lower, although all the MoO_3 loadings should fall within the limits of monolayer coverage.

Differences in reduction behavior at low loading of MoO_3 on Al_2O_3 have been previously reported by Kabe *et al.* (*13*) and by Massoth (*11*); both followed the course of reduction gravimetrically. Kabe *et al.* studied loadings of 5, 12.5, and 27% MoO_3 at 550°C. Catalysts with lower MoO_3 reduced more slowly, but at 550°C reduction proceeded past the MoO_2 stage in all cases after 5 hr. At 500°C, in contrast, the 12.5% MoO_3 sample appeared to be reduced to about MoO_2, even after 20 hr. Lower loading was not studied at 500°C, and the sensitivity to temperature makes it difficult to compare our results with theirs. Massoth studied catalysts containing 2 to 25% Mo. A 10% Mo (15% MoO_3) catalyst was reduced to ca. MoO_2 in 2 hr at 500°C. However, the extent of reduction of a 6% Mo (9% MoO_3) catalyst was only ca. 0.50 after 2 hr at 500°C (based on MoO_2; 0.17 based on reduction from MoO_3 to Mo), and the corresponding value for a 2% Mo (3% MoO_3) catalyst was ca. 0.20 (or 0.07, based on reduction to Mo). The data in Table 2 for 6-hr reductions are roughly compatible with those of Massoth.

Our sample of 3.9% MoO_3–Al_2O_3 was analyzed by a solution–titration method to confirm that the expected amount of Mo was present in the finished catalyst; it was. Another experiment was made to see if the low O_2 chemisorption (Fig. 2) was simply the result of unusually slow reduction at 500°C. One sample of this material was subjected to the standard prereduction of 6 hr in flowing H_2 at 500°C and then used for O_2 chemisorption at −78°C. After the chemisorption, the same sample was again reduced for a second 6 hr in flowing H_2 at 500°C and again used for O_2 chemisorption at −78°C. The O_2 chemisorption value was the same after 12 hr of reduction as after 6 hr.

The catalytic activity of each MoO_3–Al_2O_3 catalyst was measured, after a 6-hr prereduction in flowing H_2, for the dehydrogenation of cyclohexane to benzene at 500°C. Pulses of 1 μl of cyclohexane were injected into a He carrier stream flowing at the rate of 35 ml/min through 0.400 g of catalyst. The activity, as measured by the benzene production, was essentially constant in a series of ten pulses for each catalyst sample. No deactivation was observed.

Figure 4 shows the activity (expressed as moles of benzene produced per mole of cyclohexane injected) for the prereduced samples, plotted against the gross composition (weight percentage MoO_3) of the samples before reduction. The curve is again concave upward, as in Fig. 2. However, if correlation is sought not with gross composition but with MoO_2 content after reduction, it is more sensible to examine activity vs O_2 chemisorption, taken as a measure of MoO_2 content (see Fig. 3). Figure 5 is the plot of activity vs O_2 chemisorption for the entire series of samples. Now the curve is convex upward; the correlation, though quite good, is not linear.

Russell and Stokes (*1*) published some of the first research on the relation of catalytic activity to specific surface area of a supported catalyst. Studying the dehydrocycli-

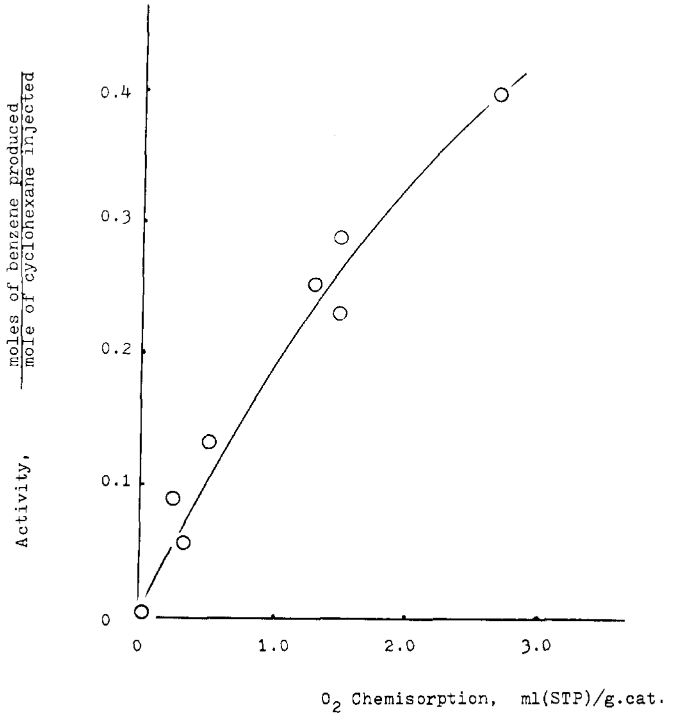

FIG. 5. Activity and oxygen chemisorption of reduced MoO_3–Al_2O_3.

zation of *n*-heptane over MoO_3–Al_2O_3 prereduced at 500°C, Russell and Stokes found that activity increased linearly with MoO_3 concentration, provided that the MoO_3 loading did not exceed the capacity for monolayer coverage. This quantitative result has to be viewed with two reservations:

1. Conversion of *n*-heptane was measured in a continuous-flow system in which deactivation was severe. Since the yield of toluene plus olefins changed rapidly with time on stream, activity was arbitrarily measured at a time when the coke deposited on a standard (reference) catalyst was 4 g/100 ml of catalyst.
2. Rather large particles (4 to 8 mesh) were used, and there was evidence that the molybdena distribution was not uniform (*10*).

Very recently Millman and Hall (*14*) have applied low-temperature O_2 chemisorption for the assay of a MoO_3–Al_2O_3 catalyst of fixed MoO_3 loading but reduced to varying extents. Smooth correlations were found between amount of O_2 chemisorbed and extent of reduction, anion vacancy concentration, and catalytic activity for propylene hydrogenation. Their plot of hydrogenation rate vs O_2 chemisorption was, like Fig. 5, not quite linear; the range of O_2 chemisorption shown in their Fig. 3 corresponded to extents of reduction from 0 to about 1.5 e/Mo ($2e/\text{Mo} \approx MoO_2$). It is not yet clear what relation the results of Millman and Hall bear to those in this paper. Since catalysts with different MoO_3 loading exhibit different reducibility (cf. Table 2), samples with a single loading but reduced to different extents are not necessarily comparable, even for like values of O_2 chemisorption.

Consideration of Figs. 3 and 5 suggests that activity for cyclohexane dehydrogenation, for the samples studied here, may be associated with the amount of reduced molybdena (or equivalent MoO_2), the surface area of which can be estimated by O_2 chemisorption at low temperature. It is tempting to identify the catalytically active sites with Mo^{4+} species in the surface. The usual caution is in order, however: correlation does not necessarily imply causality. Activity, extent of reduction, and O_2 chemisorption may change in a parallel way, but surface Mo^{4+} ions are not necessarily the sites responsible for dehydrogenation activity.

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