Studies of the Hydrogen Held by Solids

XXII. The Surface Chemistry of Reduced Molybdena–Alumina Catalysts

W. S. Millman, M. Crespin, A. C. Cirillo, Jr., S. Abdo,
and W. Keith Hall*

*Laboratory for Surface Studies, Department of Chemistry, University of Wisconsin,
Milwaukee, Wisconsin 53201*

The surface hydroxyl concentrations of a fresh molybdena–alumina catalyst (8% Mo) and of the alumina from which it was made have been determined as a function of the temperature of pretreatment. Similar data were obtained for catalysts reduced with H_2 or with CO. In all cases, the hydroxyl concentrations decreased with increasing pretreatment temperatures. The difference between the curves for the parent alumina and the molybdena–alumina preparation made from it provided a measure of the number of hydroxyl groups eliminated as the epitaxial monolayer of molybdena was grown onto the surface. The values obtained (1.7 ± 0.6 OH/Mo) showed that the surface hydroxyl groups of alumina are replaced by molybdate anions. When the catalyst was reduced with CO to about $e/Mo = 1.5$ (average valence, $Mo^{+4.5}$), the curve obtained was almost identical with that for the unreduced catalyst, but when the catalyst was reduced with H_2, values for the retained hydrogen were higher than for the oxidized catalyst and approached those of the parent alumina as its evacuation temperature was increased to 550°C. This increase in hydroxyl concentration was in agreement with earlier deductions.

The hydroxyl region of the infrared spectra of similar preparations was recorded. Four distinct bands could be characterized for the parent alumina at 3780, 3740, 3705, and 3650 cm^{-1} and a shoulder at 3795 cm^{-1}. The same bands were present on the oxidized catalyst, but with lower intensities and with altered intensity ratios; i.e., some bands were affected more than others as hydroxyl groups were replaced by molybdena species. Spectra from catalysts reduced with CO were indistinguishable in the OH region from those for the unreduced catalyst. No new bands appeared when the catalysts were reduced with H_2, but the intensities of bands attributable to alumina OH increased with the 3795 cm^{-1} band strengthening noticeably more than the others. Thus, the new hydroxyl groups introduced on reduction are probably alumina OH rather than MoOH as previously supposed. A form of hydrogen which is chemisorbed but which can be removed from the catalyst as H_2 on evacuation at the reduction temperature also appeared in the OH region, mainly as a continuous contribution to the low frequency edge. From absorption coefficients derived from the present data, it was deduced that about twice as many hydrogen atoms were present in the H_2 formed than were supplied by these OH groups; i.e., the chemisorption appears heterolytic with half the atoms unseen by ir. A search was made for a band attributable to Mo–H, but without success. A brief study was made of this adsorption process, which was found to be slow but reversible, and to have a positive pressure dependence. When the catalyst was reduced with CO, rather than with H_2, a portion of the CO remained irreversibly chemisorbed in electronically comparable amounts. Infrared spectra of such samples contained a band at about 1585 cm^{-1} attributable to a carbonate species. Data for the two reducing gases differed in that no reversibly chemisorbed CO was observed. At room temperature, CO was also chemisorbed as a linear species with the stretching frequency (2190 cm^{-1}) higher than that of the gaseous molecule (2143 cm^{-1}).

* To whom all correspondence concerning this article should be addressed.

INTRODUCTION

A model describing surface chemistry and how it changes with pretreatment or reduction has often proved useful in catalytic studies. An objective of our research (1–3) has been to construct and test such models for the molybdena–alumina catalyst system. The approach has been to understand as well as possible the state of the parent catalyst and then to characterize the changes which occur as the catalyst surface is altered. Hopefully, from this information the surface chemistry of the reduced or pretreated catalyst may be deduced. Previous workers (4–6) have provided us with a description of the parent catalyst in which it was postulated that MoO_4^{-2} groups are grown onto the surface of alumina, forming an epitaxial monolayer by replacing the OH groups which are normally required to terminate the lattice. Accordingly, two OH groups would be eliminated for each Mo introduced. This postulate has been confirmed in a general way in the present work.

Earlier ir studies of the hydroxyl region of alumina (7, 8a) and molybdena–alumina catalysts (8b, 9) have been reported. The individual bands for the molybdena–alumina catalysts, however, were not resolved. This has been accomplished in the present work resulting in additional insight into how and where the molybdena moieties have added to the surface and into the changes which occur on reduction. Nearly half the hydrogen consumed in the reduction process during its early stages is retained on the surface (10). According to the model which we advanced to explain these data (1), this hydrogen (H_I) should be held as MoOH groups. The present results show that the bands corresponding to AlOH groups strengthen as the catalyst is reduced; new bands which might be attributed to MoOH groups were not observed. This has led us to reconsider the

model and this chemistry is rewritten herein.

CO was substituted for H_2 as the reducing agent with a view to clarifying the role of H_I. A related amount of irreversibly chemisorbed CO_I was observed and its ir spectrum recorded. The results confirm the role of H_I in maintaining the charge balance on the lattice.

In our previous work (1, 10), a reversibly held form of adsorbed hydrogen (H_R) was observed and its magnitude was shown to correlate with the vacancy concentration developed on reduction. It was natural to suspect that this form of hydrogen might be active in various hydrogenation reactions. The manner in which hydrogen chemisorbs is of central importance in considering reaction mechanisms. If H_2 dissociates heterolytically as happens over ZnO, a related mechanism (11) would be expected to follow. If, however, H_2 dissociates homolytically on a single multiply coordinatively unsaturated Mo^{+n} ($n \leq 4$), the mechanism may be similar to those written for homogeneous mononuclear catalyzed reactions (12, 13). Since H_R is present in relatively large amounts (one H_2 for about three vacancies) it was possible to determine its contribution to the ir spectra. These results and their implications are recorded herein.

EXPERIMENTAL

Technique and Apparatus

All experiments were carried out in an all glass BET system with an attached circulating loop which has been described previously (14). Measurements of the hydrogen contents by isotope dilution (D_2 exchange) were made as described previously (15, 16), but with appropriate modification which allowed for the fact that water was sometimes produced by reduction during exchange. In these cases it was necessary to bring all three phases (the hydrogens, the water, and the cata-

lyst hydroxyls) into isotopic equilibrium. Volumetric carbon monoxide reduction experiments were made as described previously for the reductions with H_2 (1, 10).

The catalyst studied was a molybdena–γ-alumina catalyst containing 8% Mo. The base alumina (Ketjen CK-300) had a BET surface area of 192 m^2/g and the catalyst 185 m^2/g; enough molybdena was present to just about cover one epitaxial layer on a [100] surface of this area of roughly half the BET surface.

In all experiments described here, the catalysts were pretreated overnight in flowing O_2 at 500°C. When reduction was required, the techniques and definitions used in Ref. (1) were employed. The extent of reduction was calculated from the amount of H_2 or CO consumed after correcting for reversible adsorption. In a few cases the extent of reduction was *estimated* from the H_2O or CO_2 produced using appropriate corrections for bound gas, e.g., OH which contributes to the state of reduction, derived from the earlier work (1). The error in this last method was estimated as about ±0.2 e/Mo. For the experiments described herein, the term *reduced catalyst* may be taken to mean about 1.5 e/Mo for the D_2 exchange experiments and 1.3 ± 0.2 e/Mo for the ir experiments. This extent of reduction corresponds to that region in which the irreversibly held hydrogen (H_I) did not vary much with the extent of reduction (1, 10).

Infrared

Infrared spectra were recorded on a Beckman ir-12 spectrometer. Two cells were used which had different transparency ranges. The first was constructed of quartz with Infrasil windows (Optical Cell Co., Beltsville, Maryland) and was transparent in the region 4000 to 2200 cm^{-1}. The second cell was a standard design containing a quartz section into which the pellet could be raised for heating and then lowered into a section containing Irtran-2 windows

(Eastman Kodak Co., Rochester, New York). This cell was transparent in the region 700–4000 cm^{-1}. All spectra of the OH and OD region were recorded in the Infrasil cell while the Irtran-2 cell was used for looking at regions below 2300 cm^{-1}. Self-supporting pellets were obtained by pressing ~200 mg of sample at 25,000 psi for γ-Al_2O_3 or 30,000 psi for molybdena-alumina. One point BET determinations showed that not more than 5% of the surface area was lost during pressing. Integrated intensities were derived by cutting out the appropriate bands and weighing the silica paper. The resolution was ±7 cm^{-1} with the slitwidths used.

Reversible Hydrogen

The amount of H_R could be calculated from the data obtained in reduction-oxidation cycles or it could be determined directly by cooling the catalyst to room temperature in H_2 following reduction, evacuating, and then reheating to the reduction temperature before töplering with a Sprengle pump, which returned the gas desorbed into the gas burette where it was measured. Alternatively, with small samples (e.g., the ir platelets) the H_R was determined by a similar procedure (17) in which the gas released at 485°C was swept with a He carrying gas stream into a 5 Å molecular sieve trap thermostated at 78°K. The H_R could then be flashed and determined as in GLC.

RESULTS

Infrared Spectroscopy

Infrared spectra of Ketjen CK-300 γ-alumina and the reduced and unreduced molybdena–alumina catalysts were all similar in the hydroxyl region. These spectra are compared in Fig. 1 for different dehydration temperatures. The platelets were equilibrated with 20 Torr H_2O vapor overnight and then evacuated for 2 hr at 25, 100, 200, ..., 700°C, with spectra re-
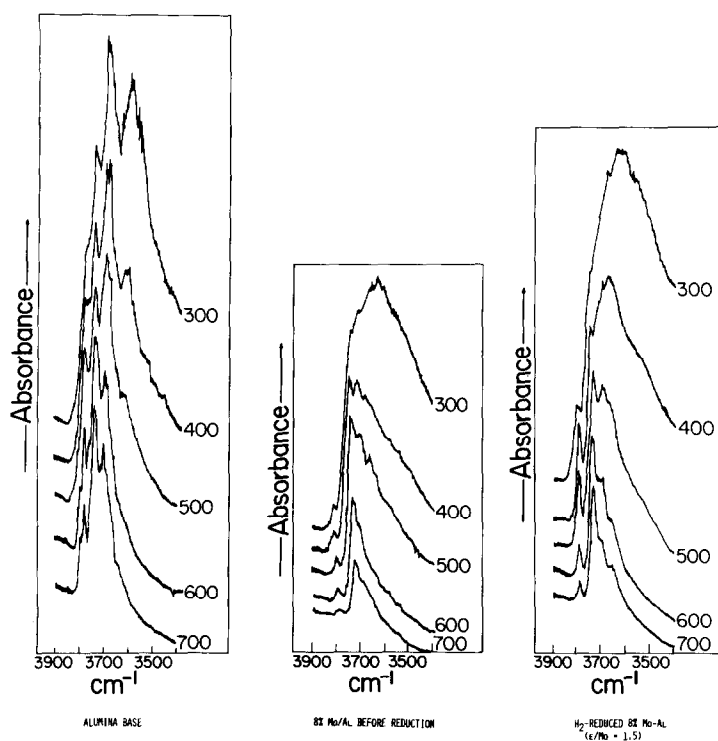
FIG. 1. Infrared spectra of the OH region for the three catalysts: (a) Ketjen CK-300 γ-Al₂O₃; (b) MoO₃ on Ketjen CK-300 γ-Al₂O₃ in the oxidized state; (c) MoO₃ on Ketjen CK-300 γ-Al₂O₃ reduced by 1.3 ± 0.2 e/Mo. The numbers to the right of the spectra indicate the evacuation temperature. Band maxima are listed in Table 1; those for each spectrum matched these numbers to ±5 cm⁻¹. Some translation was permitted in preparing the figures to avoid overlapping spectra. Hence, in some cases, the maxima appear to be shifted.

corded after each treatment. Several features are evident: the OH bands decreased in intensity when molybdena was added to alumina; band intensities grew as molybdena was reduced and the individual bands became better resolved, particularly at the higher extents of dehydroxylation; the band frequencies present with alumina alone remained when molybdena was added and no new frequencies appeared; no new bands were observed after reduction that were not present on both the alumina and unreduced molybdena–alumina.

The frequency of the OH bands are listed in Table 1. It is evident that no significant differences appeared in the spectra of these preparations. This differs somewhat from the results of Fransen *et al.* (*9*), who reported a new band. This

difference might be due to the loading and/or the method of preparation of the respective catalysts.

Quantitative results concerning the amounts of hydrogen held by these preparations under several circumstances are reported in Fig. 2 where they are expressed as OH/cm² and as a function of pretreatment temperature. To establish that correct values were derived for the molybdena catalysts, where water was produced during exchange with D₂, known amounts of H₂O were added to the systems prior to the exchange (or after with reequilibration). The hydrogen contents obtained accounted for both the initial catalyst hydrogen content (previous result) and the added water to 0.01 cm³ (STP).

The data in Fig. 2 are the "lined-out"

surface hydroxyl concentrations (per cm²) of catalysts. This was confirmed by treating the alumina in a Cahn microbalance with flowing dry N_2 at the same dehydroxylation temperatures used for the D_2 exchange experiments. When no further weight change occurred, the residual hydrogen contents duplicated those from D_2 exchange. The shape of the present alumina curve differs from that reported by Hall and van Cauwelaert (18) because the latter data were not always for lined-out preparations. Note that: (a) hydroxyls are removed from alumina when molybdena is added, and (b) hydroxyls are replaced as the molybdena is reduced with H_2.

It was desirable to be able to correlate the exchange data (Fig. 2) with the in-

TABLE 1

Frequencies of OH Bands for Catalysts[a]

γ–Al_2O_3	OH (cm⁻¹) Catalyst	
	Unreduced molybdena– alumina	Reduced molybdena– alumina
3795[b]	3795	3795
3780	—	—
3740	3730	3735
3705	3700	3700
3650[c]	3680[c]	3680[c]
~3550[d]	~3600[d]	~3650[d]

[a] The error in position of the band center increases with band width and decreasing frequency. The errors in the individual bands are 3795, ±4 cm⁻¹; 3780, ±4 cm⁻¹; 3740–3730, ±5–6 cm⁻¹; 3700, ±7 cm⁻¹; 3680, ±10 cm⁻¹; 3600 and 3550 (both) ±~15 cm⁻¹. The lowest frequency band also varies in position with different preparations and this is the principal cause of the bands below 3700 cm⁻¹ deviating more than ±7 cm⁻¹, the error due to changing slit widths.

[b] The presence of this shoulder is evident only after dehydrogenation at or above 600°C.

[c] Band is a broad shoulder and the frequency listed represents the approximate center.

[d] These bands are very broad, presumably due to extensive hydrogen bonding; the frequency listed represents the center of the band after dehydroxylation at 300°C. At lower dehydroxylation temperatures the band center shifted to lower frequencies.
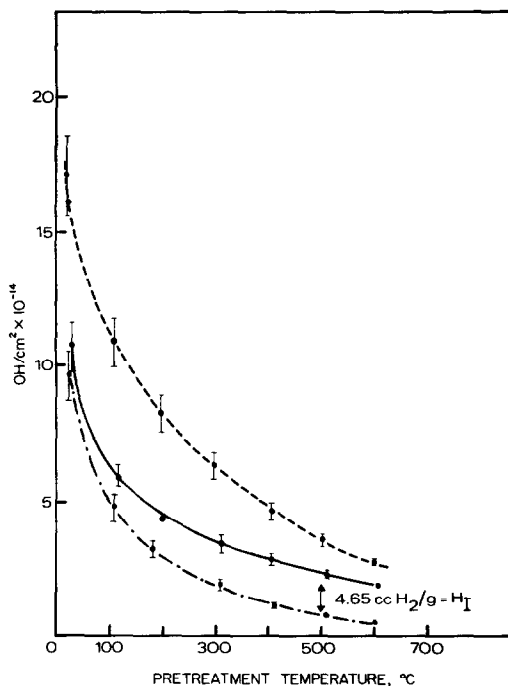

FIG. 2. The number of hydroxyl groups per unit area for the catalysts. Results were obtained by isotope dilution. (– – – –) Ketjen CK-300 γ-Al_2O_3; (———) 8% Mo/γ-Al_2O_3 (1.5 e/Mo); (–·–) 8% Mo/ γ-Al_2O_3 (oxidized) and CO reduced (1.5 e/Mo).

frared spectra for the catalysts (Fig. 1). The method used in determining the area under the infrared spectra of the OH region is shown in Fig. 3. The background was determined by dehydroxylating the sample at 700°C followed by extensive deuterium exchange. The OH and OD spectra could be combined to produce a background. As is evident from Fig. 3 the primary contribution to the OH region is due to water-like hydrogen bonded species.

The correlation between the integrated intensities (cut and weigh method) and the known hydrogen contents (Fig. 2) is shown in Fig. 4 for an oxidized molybdena–alumina sample. The correlation coefficient for these data was 0.994. The major deviation lies at very low OH coverage. Similar curves were constructed for the other catalysts and as seen in the example given in Fig. 4 a linear relationship exists. An estimate of errors due to
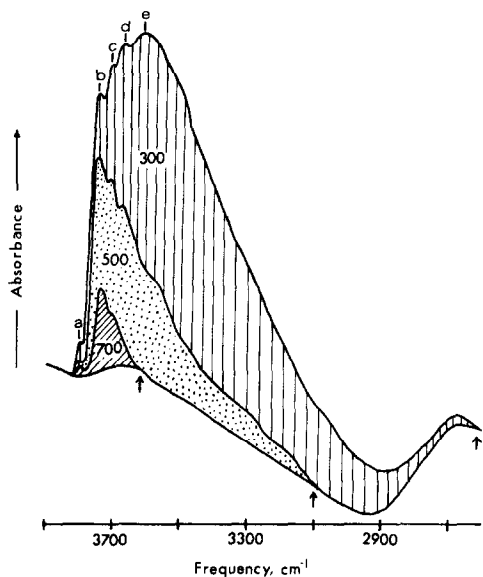
FIG. 3. Spectra of the OH region on oxidized molybdena–alumina as a function of pretreatment temperature. The entire OH envelope was used to determine the integrated areas used in Fig. 4. Peak positions are indicated at (a) 3795; (b) 3730; (c) 3700; (d) 3680; and (e) ~3600 cm⁻¹.

sample positioning in the infrared beam and fitting of the baseline leads to the upper limit of 20% error. The data of Fig. 4 indicate that only at low coverages (700 and 600 degree dehydroxylation) is this limit approached. The transmission was about 6% fo the catalysts studied.

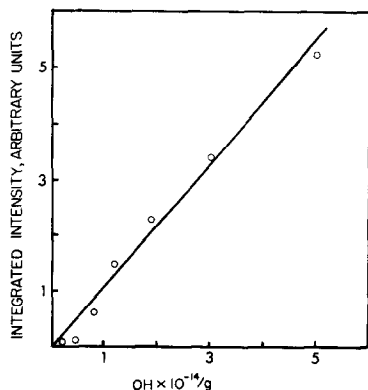Figure 5 is a plot of the number of OH groups lost per Mo added as the monolayer

TABLE 2

Volumetric Measurements of Hydrogen
Reversibly Chemisorbed at 508°C

e/Mo	P (final), Torr	H_R (measured)[a] (cm³(STP) H_2/g)	H_R (calc.)[b] (cm³(STP) H_2/g)
1.3	3.4	1.82	1.88
1.3	27	2.79	2.53
1.3	95	3.59	3.20
1.5	160	4.66	4.45
1.5[c]	1000	7.53	—

[a] H_R (measured) = H_2 collected by 16 hr. evacuation with Sprengle pump.

[b] H_R (calc.) = $[H_2] - 2[O_2]$, where $[H_2]$ and $[O_2]$ are the amounts of H_2 and O_2 which have been removed from the gas phase at the moments these experiments were terminated. See Ref. (1).

[c] Spectroscopic platelet of Figure 8.

was grown onto the alumina surface, derived from the data of Fig. 2. Calculations were made as a function of the pretreatment temperature although the most significant value should be that at room temperature. The curve indicates that about 1.7 ± 0.6 OH's were lost from the alumina for every Mo bound to the surface. This is in rough agreement with previously developed ideas (4–6), i.e., about 2 OH/Mo.

FIG. 4. Beer's Law plot for oxidized molybdena–alumina. The ordinates were taken from the data of Fig. 3 and the abscissa from Fig. 2.
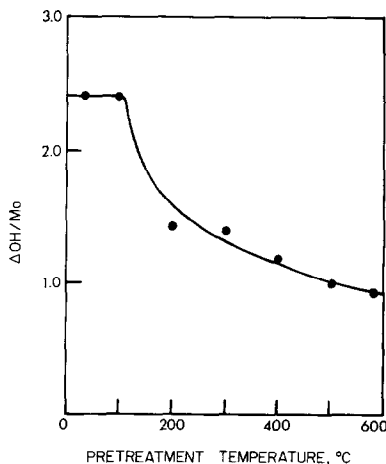

FIG. 5. Hydroxyl loss from alumina concomitant with formation of molybdena monolayer.
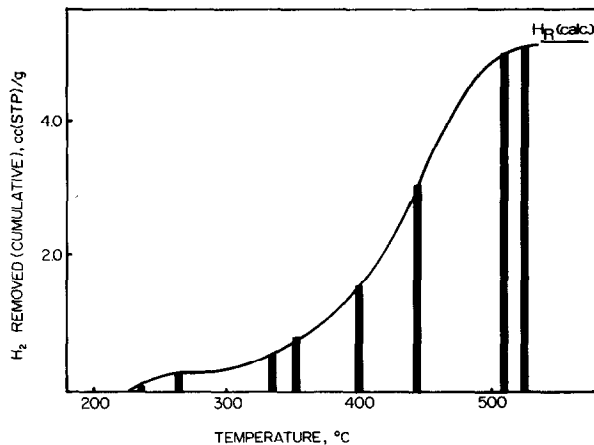
Fig. 6. The temperature dependence for desorption of hydrogen reversibly held following reduction, (H_R), from a catalyst reduced by 1.4 e/Mo at 500°C. The catalyst was evacuated for periods of 16 hr at successively higher temperatures starting at room temperature.

H_R-Volumetric Measurements

The data in Table 2 demonstrate the reversibility and pressure dependence of the chemisorbed hydrogen (H_R). Good agreement was obtained for the measured and calculated values. The desorption of this gas was activated; Fig. 6 shows the amounts it was possible to remove at several temperatures with a Sprengle pump. Fig. 7 shows the pressure dependence for readsorption of H_R (after removal as above) along with the sluggishness of the readsorption. That H_R is indeed H_2 was shown chromatographically on the system patterned from Burwell and Stec (17).

H_R-Infrared

Spectra of the OH region of reduced molybdena–alumina with H_R present or absent are presented in Fig. 8. The H_R was measured (17) as 7.53 cm³ (STP)/g while the water liberated was 0.40 cm³ (STP)/g. These values correspond to H_R = 2.2 × 10¹⁴ H/cm² and water = 0.1 × 10¹⁴ H/cm². From the extinction coefficient for the platelet, the ir OH region lost 1.1 × 10¹⁴ OH/cm². Thus, correcting for
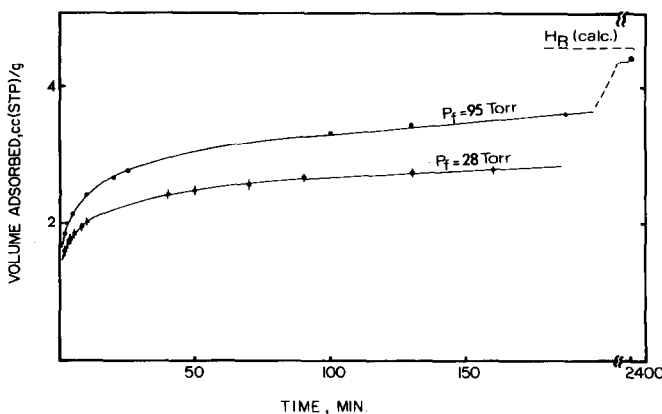

Fig. 7. Rates of readsorption of H_R at 500°C. The catalyst had been reduced by 1.3 e/Mo at 500°C and degassed for 1.5 hr. at this temperature to <10⁻⁵ torr. Final pressures are shown.
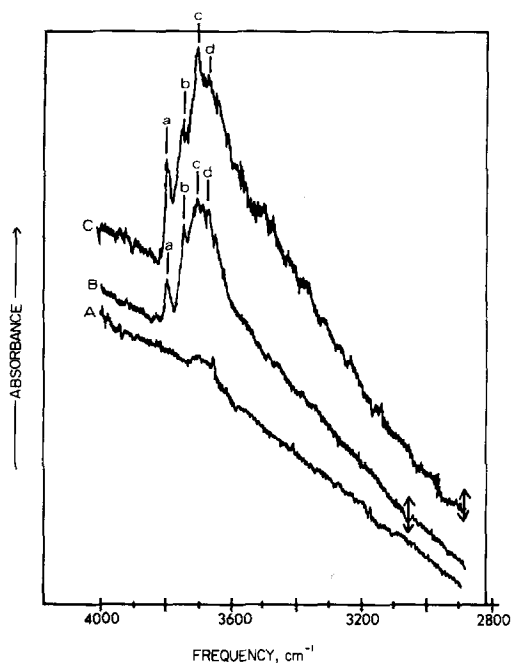
FIG. 8. Spectra showing the effect of reversibly adsorbed hydrogen on the hydroxyl region. A = background; B = H_R removed; C = H_R [~7 cm³ (STP)/g] present; ↕ = the point of intersection with the background. Peak positions are indicated at (a) 3795, (b) 3735, (c) 3700, and (d) 3660 cm⁻¹.

H_2O, the $\Delta OH/H_R \times 100 = 45\%$, suggesting that for every H_2 formed, there was a loss of one OH group from the surface. The source of the other (invisible) hydrogen remains unknown. All bands and the low frequency tail decreased in intensity as H_R was removed.

CO Reduction

The stoichiometry of the molybdena–alumina reduction with hydrogen has been reported previously (1, 10). In Table 3 such data are compared with results for reduction with CO. The reproducibility of the data for H_2 reduction has been previously demonstrated (1); for reduction with CO this point is established in the last three lines of Table 3 where the experiment was repeated three times under the same conditions. The principal dif-

ference between the two reducing agents is that little or no reversibly held CO was found corresponding to the substantial quantities of H_R.

Although generally a little smaller, values of CO_I were similar to those for H_I (Table 3). Perhaps one CO molecule satisfies the same valence requirements as one H_2 (two H atoms). The irreversibly held CO was a linear function of the extent of reduction. This was not true for H_2 (1, 2), where H_I reached a maximum at about 1 e/Mo. Nevertheless, the same type of species was present, i.e., H_I,
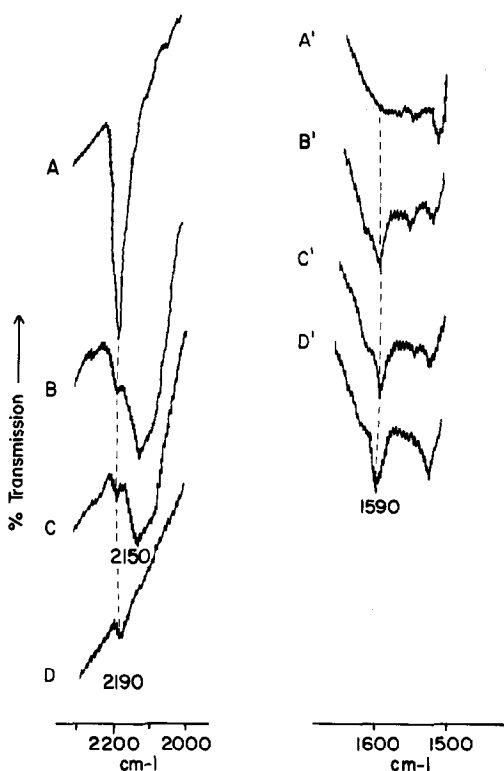
FIG. 9. Spectra of preparations treated with CO for the carbonate and molecular C–O stretching regions. Curves A are for the catalyst reduced with H_2 and evacuated at 500°C before exposing to 60 Torr of CO at 25°C and then evacuating for 5 min; Curves B are for the catalyst reduced with CO at 500°C and cooled to 25°C in an ambient pressure of 60 Torr; Curves C were obtained after Curves B after evacuating 45 min at 25°C. Curves D follows Curves C after evacuation at 500°C for 100 min.

TABLE 3

Comparison of Reduction–Oxidation Cycles for CO and H_2
over 8% Molybdena–Alumina Catalyst

Gas	Temp. (°C)	Gas Consumed or Produced, cm^3 (STP)/g						
		[H_2] or [CO][a]	W_R or W'_R[b]	H_I or CO_I[c]	H_R or CO_R[c]	2 [O_2][d]	W_0[e]	e/Mo[f]
H_2	500	17.21	9.24	4.83	3.14	14.07	4.19	1.52
H_2	500	17.36	—	—	—	—	—	—
CO	400	16.75	12.84	3.72	0.19	16.56	3.51	1.78
CO	500	16.48	13.50	2.84	0.14	16.34	2.30	1.76
H_2	500	11.66	4.99	4.20	2.45	9.19	2.63	0.99
CO	500	11.22	9.52	1.51	0.19	11.03	1.32	1.19
CO	500	11.61	10.37	1.22	0.02	11.59	0.99	1.25
CO	500	12.47	10.65	1.41	0.41	12.06	1.39	1.30

[a] Total reactant consumed (measured by disappearance from the gas phase) during circulation over the catalyst and through a liquid nitrogen trap (to remove H_2O or CO_2).

[b] The H_2O or CO_2 formed was measured volumetrically following the reduction.

[c] These were determined by loss from the mass balance as described in Refs. (1 and 10) by the equations: $H_I = 2 [O_2] - W_R$ and $H_R = [H_2]_c - 2 [O_2]$.

[d] The consumption of oxygen atoms in the reoxidation step.

[e] The H_2O or CO_2 produced by reoxidation. Ideally these figures should equal the H_I or CO_I of column 5.

[f] Calculated from oxygen consumed for reoxidation (column 7).

H_R and CO_I, CO_R, although with quantitative differences.

Infrared of CO-Reduced Catalyst

The hydroxyl regions of the spectra were identical before and after reduction with CO (unlike H_2-reduced catalysts). New bands were present after reduction, however, at 1590 cm^{-1} and at frequencies higher than that for CO itself (Fig. 9). Evacuation of the catalyst removed the latter, but not the sharp band at 1590 cm^{-1} which had been observed previously (8b) and assigned to a carbonate species. The high frequency band (at 2190 cm^{-1}) was completely removed by evacuation. It may therefore correspond to H_R, while the carbonate band may be comparable with H_I, i.e., CO_I.

DISCUSSION

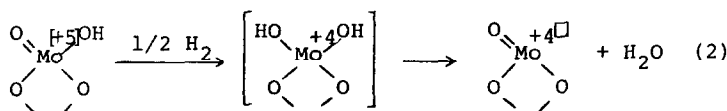Direct evidence has been presented (Figs. 1, 2, 5) demonstrating that terminal hydroxyl groups of the alumina support are eliminated when the molybdena–alumina catalyst is formed. This provides strong support for the model (4–6) which assumes that an epitaxial molybdena monolayer grows on the support. The data suggest that about two surface hydroxyls are eliminated for each Mo^{+6} added to the surface, but they are not sufficiently precise to rule out the possibility that the number is smaller, e.g., more nearly 1 OH/Mo^{+6}. This is important. The catalyst was produced by reacting the alumina surface with a solution of $(NH_4)_6Mo_7O_{24}$ (the incipient wetness technique). It has been supposed that the paramolybdate ions break up during the calcination step and distribute themselves on the several surface lattice planes of the alumina in registry with the crystal structure below. If instead the paramolybdate ions maintain their integrity so that clusters of Mo^{+6} become bound to the surface, the ratio would approach unity rather than 2. This is no longer an unlikely possibility. EPR studies (3) have suggested

that on reduction much of the Mo^{+5} which is formed is antiferromagnetically coupled. The short Mo–Mo distance in paramolybdate clusters should make this possible. Moreover, both Knözinger (*19*) and Brown *et al.* (*20*) have recently assigned a band in the Raman spectra of similar preparations to vibrations of edge-shared molybdena octahedra such as those of the paramolybdate ion. Whatever the real situation, the important point is that the molybdena species are chemically bound to the alumina surface where they substitute for the hydroxyls they replace.

Knözinger and Ratnasamy (*8*) have suggested assignments for the various hydroxyl frequencies from the alumina surface (Table 1). They supposed that different kinds of hydroxyl groups are
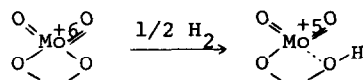
necessary to terminate the major low-index crystal planes of alumina and that the several frequencies depend on local environments specified by the underlying lattice. It is tempting but perilous to attempt to deduce the relative amounts of different molybdena configurations which might be formed from changes in the relative intensities of the bands before and after formation of the molybdena monolayer. For what it is worth, the most unambiguous change was the complete disappearance of the 3780 cm^{-1} band which is supposed to stem from an OH capping a tetrahedral site.

Earlier (*1*), in the absence of infrared data, we pictured the reduction process as follows:

$$
\begin{array}{c}
\text{O} \diagdown \overset{+5}{Mo} \diagup \text{O} \\
\text{O} \diagup \quad \diagdown \text{O} \\
\diagdown \diagup
\end{array}
\xrightarrow{1/2 \ H_2}
\begin{array}{c}
\text{O} \diagdown \overset{+5}{Mo} \diagup \text{OH} \\
\text{O} \diagup \quad \diagdown \text{O} \\
\diagdown \diagup
\end{array}
\qquad (1)
$$

$$
\begin{array}{c}
\text{O} \diagdown \overset{+5}{Mo} \diagup \text{OH} \\
\text{O} \diagup \quad \diagdown \text{O} \\
\diagdown \diagup
\end{array}
\xrightarrow{1/2 \ H_2}
\left[
\begin{array}{c}
\text{HO} \diagdown \overset{+4}{Mo} \diagup \text{OH} \\
\text{O} \diagup \quad \diagdown \text{O} \\
\diagdown \diagup
\end{array}
\right]
\longrightarrow
\begin{array}{c}
\text{O} \diagdown \overset{+4}{Mo} \diagup \square \\
\text{O} \diagup \quad \diagdown \text{O} \\
\diagdown \diagup
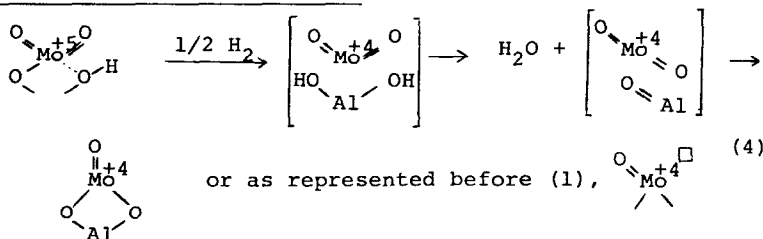\end{array}
+ H_2O \qquad (2)
$$
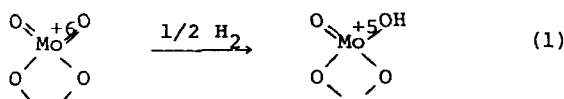
The oxygens shown above the Mo represent those in the capping layer while those below belong to the support and in turn are bonded to the aluminum cations. In the present work, no new OH bands were detected in the infrared spectra from catalysts reduced with H_2 which were not also found in the spectra from the alumina support. On the other hand, five alumina bands present in the oxidized catalyst all strengthened as the catalyst was reduced. These findings strongly suggest that on

reduction it is not the oxygens of the capping layer which are attacked, as depicted in Eqs. (1) and (2), but the bond between Mo and the surface oxygen (Eq. (3)).

$$
\begin{array}{c}
\text{O} \diagdown \overset{+5}{Mo} \diagup \text{O} \\
\text{O} \diagup \quad \diagdown \text{O} \\
\diagdown \diagup
\end{array}
\xrightarrow{1/2 \ H_2}
\begin{array}{c}
\text{O} \diagdown \overset{+5}{Mo} \diagup \text{O} \\
\text{O} \diagup \quad \diagdown \text{O}^{-H} \\
\diagdown \diagup
\end{array}
$$

Thus, as the reduction proceeds to Mo^{+4}, H_2O is removed from the sublayer, but the resulting molybdena species remain bound to the alumina as indicated by

$$
\begin{array}{c}
\text{O} \diagdown \overset{+5}{Mo} \diagup \text{O} \\
\text{O} \diagup \quad \diagdown \text{O}^{-H}
\end{array}
\xrightarrow{1/2 \ H_2}
\left[
\begin{array}{c}
\text{O} \diagdown \overset{+4}{Mo} \diagup \text{O} \\
\text{HO} \diagdown \ \overset{}{Al} \diagup \text{OH}
\end{array}
\right]
\longrightarrow
H_2O +
\left[
\begin{array}{c}
\text{O} \diagdown \overset{+4}{Mo} \diagdown \text{O} \\
\text{O} \diagdown \ \overset{}{Al}
\end{array}
\right]
\longrightarrow
$$

$$
\begin{array}{c}
\text{O} \\
\parallel \\
\overset{+4}{Mo} \\
\text{O} \diagup \ \diagdown \text{O} \\
\diagdown Al \diagup
\end{array}
\qquad \text{or as represented before (1),} \qquad
\begin{array}{c}
\text{O} \diagdown \overset{+4}{Mo} \diagup \square \\
\diagup \quad \diagdown
\end{array}
\qquad (4)
$$

This interaction is an essential feature; the difficulty in reducing the molybdenum ions below Mo^{+4} when supported on alumina is well known and quite different from that for MoO_3 or molybdena on silica catalysts.

During the early stages of the reduction up to half the hydrogen consumed remained on the catalyst as new hydroxyl groups. This earlier observation (1, 10) was confirmed in the present studies both by the deuterium exchange data and by infrared spectroscopy. Each such hydroxyl represented a one-electron reduction while each oxygen removed from the surface as H_2O corresponded to a two-electron process. The latter may be visualized to result from the instability of two hydroxyls associated with a single Mo ion (Eq. (2) or (4)). Thus, in our earlier analysis (1), the Mo^{+5} concentration was equated to the new irreversibly held hydrogen (H_I) and the Mo^{+4} concentration to the amount of H_2O produced. A self-consistent picture was developed from these ideas, which was supported by the general trends of the data and the manner in which the curves could be extrapolated to their intercepts at $e/Mo = 2$. It was reported, however, that the Mo^{+5} concentrations measured by EPR were very much lower than those predicted (1). Nevertheless, recent ESCA measurements (21, 22) have supported the higher values and indeed have indicated that the Mo^{+5} concentration may exceed half of the total Mo during the early stages of the reduction. Moreover, reasons have been advanced (3) for thinking that much of the Mo^{+5} cannot be detected by EPR. Thus, although we believe that the earlier model may now require revision, it appears that the estimates of ion concentrations calculated from the reduction data based on Eqs. (1) and (2) were at least semiquantitatively correct. Fortunately, all of the reasoning used in support of the earlier model can also be applied to support the new interpretation presented in Eqs. (3) and (4).

When CO was substituted for H_2 as the reducing agent, the data obtained were quite analogous to those for H_2 (Table 3). Irreversibly held CO was found bound to oxygen as a carbonate species just as the H_I was held as hydroxyls. Although the CO_I tended to be somewhat smaller than H_I, the amounts were nonetheless comparable. Both reducing agents also produced a reversibly held species although that from CO was more weakly bound than that from H_2 (H_R). The complimentary chemistry found for the two reducing agents emphasizes the necessity to satisfy the valence requirements of the surface during the reduction process.

Reduction with CO rather than H_2 did not alter materially the activity nor the selectivity of the catalyst. Reactions investigated included hydrogenation of ethylene (14) and propylene (23), metathesis and polymerization of propylene, and the isomerization of cyclopropane to propylene (23, 24). A strong Brønsted acid is required to open the cyclopropane ring. It is now clear that this does not depend on protons introduced during the reduction; those remaining associated with the alumina surface when the catalyst is prepared appeared to be activated as the molybdena was reduced. This is discussed in more detail elsewhere (24).

Previously (1, 10), the quantity H_R was deduced from the difference between the amount of hydrogen consumed in the reduction and the amount of O_2 consumed to restore the catalyst to its initial state; i.e., it was reasoned that the missing hydrogen was removed during the evacuation at elevated temperature (so that O_2 could be introduced). This was confirmed in the present work by the direct measurement and identification of the H_R and by the finding that once removed it could be substantially readsorbed. The surprising feature, however, was the sluggishness of

these processes. Consequently, H_R cannot be identified with the chemisorption required to hydrogenate ethylene at or about room temperature. It may, on the other hand, function in processes such as hydrodesulfurization which occur under much more stringent conditions. The present data indicate that H_R is a form of chemisorption where H_2 has been heterolytically dissociated to produce a hydroxyl group and another species which cannot be detected by ir. It should be emphasized that the amount of missing hydrogen is quite large, as much as 0.5 mmol/g in some cases. This provides an intriguing mystery because any consideration of hydrogenation catalysis must start with an assumption of the way hydrogen is dissociated and held by the surface. Thus, for example, quite different schemes have been deduced for the hydrogenation of simple olefins over ZnO (11) and for MoS_2 (13). With the former the dissociation of hydrogen has been shown to be heterolytic; with the latter it has been suggested to be homolytic and mononuclear as in catalysis by transition metal complexes (12). We (14) have presented our reasons for thinking that olefin hydrogenation over molybdena–alumina catalysts is effected by heterolytically dissociated H_2. Thus, one wonders whether the species used at low temperature for hydrogenation is a portion of H_R having a very low activation energy and heat, or whether H_R represents a separate phenomenon. Another interesting question is whether the H_R is an intermediate in the reduction process. If one assumes that the missing hydrogen is some kind of a molybdenum hydride species, the adsorption would be heterolytic and nonreductive. To act as a reducing agent another step for which we have no direct evidence would be required. Nevertheless it is interesting to conjecture that it would then seem necessary to write

$$Mo^{+n}-H + O^{-2}(s) \rightarrow OH^-(s) + Mo^{+n-2},$$
$$(5)$$
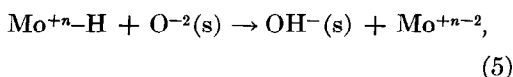
where $O^{-2}(s)$ and $OH^-(s)$ may be taken to represent those species depicted in Eqs. (3) and (4).

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