

## On the Surface Chemistry of Molybdena–Alumina Catalysts Prepared from $\text{Mo}(\text{CO})_6$

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Catalysts were prepared by subliming  $\text{Mo}(\text{CO})_6$  onto partially dehydroxylated (PDA) and exhaustively dehydroxylated (DA) alumina made from the same parent preparation (American Cyanamid Aero 100PHF). The chemisorption of NO and CO on these materials was studied using volumetric, chromatographic, and spectroscopic techniques. ESCA data indicated that metallic Mo crystals formed on  $\text{Mo}(\text{CO})_6/\text{DA}$  whereas on PDA both  $\text{Mo}^{4+}$  and some lower valence state,  $\text{Mo}^{2+}$  or  $\text{Mo}^0$ , were present. NO chemisorbed on both preparations at 195 K without releasing either  $\text{N}_2\text{O}$  or  $\text{N}_2$ . The chemisorption on the PDA preparations was over tenfold higher than that on the DA-supported catalysts under these conditions, but on raising the temperature to 300 K the difference was reduced to a factor of 2. Moreover, redox chemistry occurred at this higher temperature as evidenced by the release of  $\text{N}_2\text{O}$  and  $\text{N}_2$ ; this was quantified. The amounts of NO actually chemisorbed under these conditions correlated well with the integrated IR band intensities. These data suggest that lower valence states are oxidized to  $\text{Mo}^{4+}$  at 300 K and that the observed IR bands stem from  $\text{Mo}^{4+}(\text{NO})_2$ , irrespective of the initial catalyst. Infrared spectra from residual CO remaining on decomposition of  $\text{Mo}(\text{CO})_6$  on DA and PDA at increasing temperatures up to 473 K showed bands which could be attributed to residual  $\text{Mo}(\text{CO})_6$  and/or to subcarbonyl species formed during decomposition. By 573 K, no residual bands could be observed. On adding-back CO at 300 K to the PDA preparation, bands at 1989 and 2170  $\text{cm}^{-1}$  appeared, suggesting the presence of  $\text{Mo}^{4+}$  and residual  $\text{Mo}^0$ . Spectra from similar experiments with the DA preparation demonstrated that chemisorbed  $\text{Mo}(\text{CO})_6$  was reforming and possibly some subcarbonyl species; there was scant evidence for any higher valence states. The results are discussed in terms of the current literature. © 1989 Academic Press, Inc.

### INTRODUCTION

Conventional molybdena–alumina catalysts are usually prepared by the incipient wetness technique (1–3). The equilibrium adsorption method (4–7) was developed to ensure more uniform coverage and control of site symmetry, factors essential for meaningful spectroscopic investigations. So far, however, there has been no evidence that these two kinds of preparation differ significantly in their catalytic properties after the reduction or sulfiding treatment used to convert them into their active forms. Indeed, recently it has been demonstrated (8) that in mechanical mixtures of

$\text{MoO}_3$  and alumina (in the usual proportions), the  $\text{MoO}_3$  will spread onto the alumina surface at elevated temperatures to produce essentially the same final catalyst. Similarly we have reported (5, 6) that the Raman spectrum obtained from a carbonyl prepared catalyst was indistinguishable after reduction–reoxidation from a conventional catalyst of similar loading made by the incipient wetness technique with the same alumina.

The molybdena bound to the surface of alumina with loadings of one monolayer or less is resistant to reduction. At 800 K average extents of reduction of  $e/\text{Mo} \sim 2$  (average number of electrons below  $\text{Mo}^{6+}$  by which the molybdena is reduced) are commonly reported, and indeed ESCA measurements (9) have shown that  $\text{Mo}^{4+}$  is the major species present. At somewhat higher

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temperatures, however, deeper reduction can be achieved (10), and at 1173 K and above metallic molybdena is formed (10–12, 20). After the standard sulfiding treatment, the average extent of reduction is also deeper [ $e/\text{Mo} \sim 3$ ] (13). With unsupported  $\text{MoS}_2$  further removal of S as  $\text{H}_2\text{S}$  in  $\text{H}_2$  is required to expose the active catalytic centers (CUS) required for cyclopropane isomerization (14).

Recently we completed a study (10) of the changes in surface chemistry which occur as a conventional (8% Mo) catalyst is reduced at higher temperatures (into the range  $2 < e/\text{Mo} < 6$ ). Confirming evidence (11, 12, 15) was obtained that metallic molybdenum begins to form at reduction temperatures of 1073 to 1173 K as  $e/\text{Mo} \rightarrow 5$  (average valence state of  $\text{Mo}^{1+}$ ). The oxygen chemisorption obtained at 195 K also increased, but then leveled off at  $\text{O}/\text{Mo} \sim 0.57$  for reduction temperatures above 973 K. Evidently the metallic molybdenum crystals are oxidized only on their surfaces under these conditions. NO chemisorption was complicated by two factors, viz., oxidation of lower valence states of molybdenum with the production of  $\text{N}_2\text{O}$  and  $\text{N}_2$  at room temperature (but not at dry ice temperature), and chemisorption on the alumina support (10, 16). This latter factor became increasingly important as the fraction of uncovered alumina surface increased (5, 14) with the extent of reduction. The data suggested in a general way that certain low-valence states were oxidized by NO to a final state which then chemisorbed NO as a dinitrosyl species as previously suggested (15, 22b). The present work was undertaken to better define the initial and final states of the redox system.

For the present investigation, catalysts were prepared by the reactions of  $\text{Mo}(\text{CO})_6$  on the surface of alumina. As shown by the extensive studies of Burwell and of Brenner and their co-workers (11, 17–21),  $\text{Mo}^0$  atoms which are released on decarbonylation may become oxidized by reducing the surface hydroxyl groups (17) when present, or

crystallize into metal in their absence (11, 17, 20, 21). These studies demonstrated how the degree of dehydroxylation of the alumina controls the course of this reaction. Partial dehydroxylation, using the usual pretreatment procedures (evacuation at 773 K), results in an alumina (partially dehydroxylated, PDA) which is about 20% covered with hydroxyl groups ( $\sim 3 \times 10^{14}/\text{cm}^2$  or  $\sim 1$  mmole/g). Alternatively, if the alumina is further dehydroxylated (DA) at successively higher temperatures up to 1173 K, it can be nearly completely dehydroxylated ( $\sim 99\%$  of residual OH are removed without substantial loss in surface area). Thus it was possible to draw comparisons with overlapping data (10, 11, 20, 21) for conventional catalysts reduced into the same range of average oxidation states ( $2 < e/\text{Mo} < 6$ ).

When  $\text{Mo}(\text{CO})_6$  was deposited on PDA at room temperature and then activated under vacuum (or in a stream of ultrapure He) at 373 K, very close to three CO/Mo were removed by what has been supposed to be ligand substitution of surface  $\text{O}^{2-}$  (or  $\text{OH}^-$ ) electron pairs for those of the CO lost. Further heating to 573 K effected removal of the remaining three CO and oxidation of the  $\text{Mo}^0$  by reduction of the alumina hydroxyl groups as evidenced by the evolution of  $\text{H}_2$ . At this stage the average oxidation number (deduced from the  $\text{H}_2$  evolved) was reportedly (17, 18, 22) close to 2 ( $e/\text{Mo} = 4$ ), and this result has been verified by ourselves. Thus, the catalytic system is well defined at this stage although whether it contained  $\text{Mo}^{2+}$  or a fortuitous mixture of lower and higher valence states has remained unsettled. To shed light on this point was an objective of the present work.

When  $\text{Mo}(\text{CO})_6$  was deposited on DA, no  $\text{H}_2$  was evolved and the Mo was forced to remain in its zero-valence state. It therefore became clustered (18, 21) into small (perhaps 30-Å) metallic particles and indeed may have formed a carbide or oxycarbide phase (11, 20, 21). Significantly, this catalyst was shown (11, 17, 19–21) to be ex-

tremely active for hydrogenolysis of propane and cyclopropane, and the isotopic exchange between  $D_2$  and cyclopentane, reactions which are characteristic of metals.

Howe and co-workers (22) have contributed much to the understanding of the  $Mo(CO)_6/PDA$  system. The decarbonylation process was studied and a number of subcarbonyl species were identified by their IR spectra (22a). Then, in their studies of NO adsorption (22b),  $N_2O$  formation was noted (but not quantified). They attributed this to oxidation of lower valence states to  $Mo^{4+}$ , on which additional NO was adsorbed, producing the same dinitrosyl species reported for reduced or sulfided conventional catalysts (5, 6, 14). Laniecki and Burwell (18) made a contemporary study of  $Mo/HA$ ,  $Mo/PDA$ , and  $Mo/DA$ . Adsorbed  $Mo(CO)_3$  was decomposed at 373 K and the IR spectra were recorded. Their experimental results were in general agreement with those of Kazusaki and Howe (22), but their interpretation of the low-frequency bands differed. In the present work, these studies are extended to higher temperatures and to the readsorption of CO after its complete elimination at 573 K.

Recently, Zecchina *et al.* (23) made a careful study and analysis of the spectra obtained from  $Mo(CO)_6$  adsorbed on DA-type preparations at room temperature only. The carbonyl was added in small successive doses and removed slowly by desorption. The analysis showed that the principal bands could be divided into sets of quartets stemming from the undissociated carbonyl molecules bonded through an oxygen of a ligand CO to an aluminum ion in either an octahedral or a tetrahedral surface site. On extended evacuation, a monomeric subcarbonyl similarly held was assigned to explain a third lower frequency quartet which replaced the others. These experiments were found most helpful in the integration of the present results into the literature.

In the present work attention was focused on which valence states may be present. ESCA and IR were used as tools

for this purpose, together with studies of the chemisorption of CO and NO, and of the redox properties of the latter.

#### EXPERIMENTAL

*Reagents and gas purification.* The  $\gamma$ -alumina was the same as that used by Burwell and co-workers (17-21). It was obtained from American Cyanamid (Aero 1000 PHF extrudate) and was reportedly 99.99% pure. Its BET surface area was 170  $m^2/g$ . The molybdenum hexacarbonyl was from Aldrich Chemical Co. It was evacuated several times at 78 K and briefly at room temperature to remove air and then stored in a vacuum-tight vessel. It was again evacuated at 78 K immediately before use in each experiment. Carbon monoxide (99.99%, Matheson) was passed through a molecular sieve trap at 423 K to remove possible traces of carbonyls. It was then distilled between liquid nitrogen traps before transfer to 5-liter storage bulbs attached to the BET system where it was stored at superatmospheric pressure. Nitric oxide (99.9%, Matheson) was purified by vacuum distillation between dry ice and liquid nitrogen traps using a pump-thaw-pump technique. No impurities could be observed by gas chromatography. Hydrogen (99.99%, Linde) was diffused through a (Pd-Ag alloy thimble) hydrogen purifier (Resource System, Inc.). The maximum level of  $O_2$  was  $<0.03$  ppm. High-purity helium (99.995%, Linde) was passed through a commercial He purifier (Hydrox, Matheson Model 8301 purifier) and through an activated oxy-absorbent (All-Tech Associates). This gas had  $<0.2$  ppm impurity (measured by gas chromatography). The oxygen used for pretreatment (99.9%, Linde) was passed through an anhydrous magnesium perchlorate trap to remove traces of water.

*Catalyst preparation.* The alumina was first calcined in flowing  $O_2$  at 773 K for 2 hr to remove possible carbon residuals and then in flowing pure He at the same temperature for 1 hr to yield a partially dehydrox-

ylated alumina (PDA). To increase the degree of dehydroxylation the temperature was raised from 773 to 1173 K in flowing He in four 100 K steps, each step being 30 min long. This alumina (DA) had no hydroxyl groups observable in its infrared spectrum. The  $\text{Mo}(\text{CO})_6$  was deposited on the pretreated alumina (PDA or DA) by the vacuum sublimation technique (17–21). The alumina was kept in contact with the hexacarbonyl vapor at room temperature overnight to assure saturation. The sample was then activated in flowing ultrapure He [ $\sim 60$  cc(STP)/min] from 300 K up to the final temperature at a rate of about 5 K/min.

The evolved gases resulting from the activation were flushed from the reaction chamber and collected in a series of two traps thermostated at 78 K. The CO was adsorbed quantitatively in a trap loaded with Davison Grade 62 silica gel; the  $\text{H}_2$  passed through this trap, but was collected downstream in a trap containing 5-Å molecular sieves. After the collection process was completed, the gases were released by warming the traps and quantitatively measured using standard GLC techniques (17). The amount of collected CO was used to estimate the molybdenum loading from the sample (by assuming that six CO molecules correspond to each Mo). These values were later compared with elemental analysis results provided by Galbreath Labs, Inc. The two values always agreed within a few percent.

*Spectroscopic techniques.* A sealable probe (24, 25) permitted the transfer of the treated catalyst without exposure to air from the vacuum system to the ESCA spectrometer. Alumina samples weighing  $\sim 100$  mg were mounted on the probe as platelets pressed at  $1800$  kg/cm<sup>2</sup> and given the required preparative procedures using high-vacuum techniques. Similar methods were used to prepare IR platelets.

The ESCA spectra were recorded using an AEI ES200A spectrometer equipped with an aluminum anode ( $\text{AlK}\alpha = 1486.6$  eV) operated at 12 kV and 22 mA (24–26).

The residual pressure inside the spectrometer was  $\sim 5 \times 10^{-8}$  Torr. The acquisition of the data was controlled by an Apple IIC microcomputer. The Al 2p line (74.5 eV) of the support was used as an internal standard for determination of binding energies (25). Overlapping peaks were resolved with a modified nonlinear least-squares fitting routine (GAMET) as described previously (26, 27).

*Infrared spectra* were recorded at room temperature on an IBM IR/30 Fourier transform spectrometer at a resolution of  $2$  cm<sup>-1</sup>. The infrared cell described previously (6, 14) had a built-in furnace which could be used to pretreat samples *in situ* at high temperatures. Samples were mounted in the cell as wafers having a thickness between 10 and 20 mg/cm<sup>2</sup>. After pretreatment, NO or alternatively CO chemisorption studies were made in the following way: 40 Torr of either pure gas was admitted into the cell at room temperature and the spectrum was recorded after 30 min. The sample was then evacuated for 40 min and the spectrum recorded again. Integrated intensities were obtained by the cut and weigh method and were normalized to unit wafer thickness (mg/cm<sup>2</sup>) and then corrected for differences in loading (Mo/mg).

*Oxidation and chemisorption studies* were made using bulk powder samples. About 300 mg of pretreated alumina (DA or PDA) was exposed to  $\text{Mo}(\text{CO})_6$ . After the deposition and activation of the  $\text{Mo}(\text{CO})_6$  on the support, the gray-black preparations were either reacted with a measured quantity of pure  $\text{O}_2$  at 773 K for 4 hr in the vacuum recirculation system or used in the NO chemisorption and reaction studies. On complete oxidation to  $\text{Mo}^{6+}$ , the preparations became white. The oxidation number (O.N.) before reoxidation could be calculated from the oxygen consumed. The experimental procedures and methods of calculation used to obtain the NO chemisorption data have been previously described (10). Briefly, the extent of reoxidation was calculated from the  $\text{N}_2\text{O}$  and  $\text{N}_2$

released when the catalysts were warmed to room temperature in NO from 195 K. [A known amount of NO (excess) was brought into contact with the pretreated catalyst at 195 K for 40 min. The gas phase was then swept out in a He stream into a silica gel trap at 78 K. The collected products were then flashed onto a GLC column and analyzed. No N<sub>2</sub>O or N<sub>2</sub> was released at 195 K. This process was repeated and then the catalyst was warmed to room temperature in NO at its initial pressure. After 40 min at 297 K, the contents of the catalyst vessel were swept onto traps as described above and measured separately.] The amount of strongly chemisorbed NO was obtained from a mass balance on the nitrogen, i.e.,

$$(\text{NO})_{\text{ch}} = (\text{NO})_0 - (\text{NO})_g - 2(\text{N}_2\text{O}) - 2(\text{N}_2), \quad (1)$$

where (NO)<sub>0</sub> is the initial number of micromoles of NO, (NO)<sub>g</sub> is the micromoles of NO remaining in the gas phase, (N<sub>2</sub>) is the micromoles of N<sub>2</sub>, and (N<sub>2</sub>O) is the micromoles of N<sub>2</sub>O formed in the redox process.

The final oxidation number, O.N., after the addition of NO was calculated as

$$(\text{O.N.})_{\text{final}} = (\text{O.N.})_{\text{initial}} + 2(\text{N}_2\text{O}/\text{Mo}) + 4(\text{N}_2/\text{Mo}). \quad (2)$$

(Note that the formations of N<sub>2</sub>O and N<sub>2</sub> are two- and four-electron processes, respectively.)

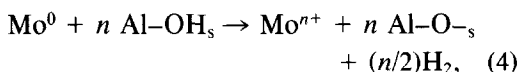
After the chemisorption and redox processes were completed at room temperature, the catalyst was heated under a stream of purified He to 800 K in the He stream and the desorbed products were collected in a silica gel trap thermostated at 78 K and subsequently analyzed by GLC. The total amount of "recoverable" NO could then be compared with that present on the catalyst before heating, i.e.,

$$(\text{NO})_{\text{ch}} \text{ vs } (\text{NO})_{\text{d}} + 2(\text{N}_2\text{O})_{\text{d}} + 2(\text{N}_2)_{\text{d}}, \quad (3)$$

where (NO)<sub>d</sub>, (N<sub>2</sub>O)<sub>d</sub>, and (N<sub>2</sub>)<sub>d</sub> were the micromoles of each product obtained in the desorption process to 800 K.

## RESULTS

*Stoichiometry.* Data on the activation of Mo(CO)<sub>6</sub> under He at temperatures 297 K < T < 573 K on the DA and PDA alumina supports are summarized in Table 1. The CO released to 573 K was nearly stoichiometric, the small (3%) discrepancy in CO/Mo possibly reflecting a small amount of C left on the surface of the activated catalyst after flushing at 573 K (17). An average oxidation number of 1.9 was calculated for the PDA catalyst from the hydrogen evolved (H<sub>2</sub>/Mo = 0.93), i.e.,



in agreement with the early literature (17-23). The key question then is whether an intermediate valence state, Mo<sup>2+</sup>, exists or if the data reflect a mixture of states, e.g., Mo<sup>4+</sup> and Mo<sup>0</sup>.

No measurable hydrogen evolution was detected from the DA catalyst; hence, its O.N. may be taken as zero. These data were confirmed by reoxidizing the preparations (Column 4); in each case the 4e/O<sub>2</sub> was, within the experimental error, adequate to oxidize all of the Mo present to Mo<sup>6+</sup>.

*Infrared studies.* Figure 1 shows infrared spectra of the carbonyl region for the Mo(CO)<sub>6</sub>/DA catalyst (20 mg/cm<sup>2</sup>) activated at different temperatures. A very intense band in the 1900-2000 cm<sup>-1</sup> region and weaker bands at 2120 and 1712 cm<sup>-1</sup> were the main features of the adsorbed carbonyl (Fig. 1a). These bands were replaced by others as the hexacarbonyl was decomposed at successively higher temperatures. After heating to 373 K about three CO/Mo remained and the band at 1592 cm<sup>-1</sup> appeared (Fig. 1b). These bands weakened on purging at 473 K (Fig. 1c). When the catalyst had been activated at 573 K no carbonyl bands were detectable (Fig. 1d).

No bands appeared in the OH region of the spectrum from parent alumina DA nor did significant bands appear during prepara-

TABLE I

Activation Data for Mo(CO)<sub>6</sub> Adsorbed on DA<sup>a</sup> and PDA<sup>b</sup> Aluminas at 573 K

Support	CO/Mo <sup>c</sup>	H <sub>2</sub> /Mo <sup>d</sup>	O <sub>2</sub> /Mo <sup>e</sup>	Oxidation number	
				I <sup>f</sup>	II <sup>g</sup>
DA	5.8	0.00	1.6	0.0	0.0
PDA	5.8	0.93	0.95	1.9	2.2

<sup>a</sup> Completely dehydroxylated alumina (DA) (~300 mg) was contacted overnight with Mo(CO)<sub>6</sub> and then treated in flowing He (60 ml/min) at 573 K. The loading was 13.0 μmole of Mo on 330 mg of Al<sub>2</sub>O<sub>3</sub>.

<sup>b</sup> Same as <sup>a</sup> but using partially dehydroxylated alumina (PDA). The loading was 10.1 μmole of Mo on 330 mg Al<sub>2</sub>O<sub>3</sub>.

<sup>c</sup> CO molecules evolved per Mo atom during the activation process in flowing He (60 ml/min) while temperature was raised (~4°C/min) from 297 to 573 K using Galbreath Mo analyses.

<sup>d</sup> H<sub>2</sub> molecules evolved per Mo atom during the same activation process.

<sup>e</sup> O<sub>2</sub> molecules consumed per Mo atom during reoxidation process at 773 K. Data were obtained in a static recirculation (BET) system as in Ref. (28).

<sup>f</sup> Oxidation number (O.N.) calculated in terms of the H<sub>2</sub> molecules evolved during the activation procedure under He from 297 to 573 K according to Eq. (4).

<sup>g</sup> Oxidation number (O.N.) calculated in terms of the O<sub>2</sub>/Mo consumed during reoxidation at 773 K assuming that Mo(VI) is the final state of the molybdenum.

tion and activation. By contrast, the spectra obtained from the PDA preparations (Fig. 2) clearly depict the interaction of the alumina hydroxyl groups with the adsorbed carbonyl. The parent alumina after dehydroxylation at 773 K had the typical OH spectrum (Fig. 2a) consisting of bands at 3771, 3730, 3686, and 3669 cm<sup>-1</sup>. On addition of Mo(CO)<sub>6</sub> at 297 K (Fig. 2b) the high-frequency bands (3371, 3730 cm<sup>-1</sup>) disappeared and a new broad feature appeared between 3500 and 3700 cm<sup>-1</sup>. At first sight this would appear to be hydrogen bonding, but this effect is unusual for alumina surfaces. Purging at 373 K had little effect (Fig. 2c); at higher temperatures (Figs. 2d and 2e) the bands at 3730 and in the 3669 to 3686 cm<sup>-1</sup> region were partially restored, but the 3771 cm<sup>-1</sup> absorption did not reappear. New bands at 3584 and 3523 cm<sup>-1</sup> did and these features were partially retained even after the Mo(CO)<sub>6</sub> was completely decarbonylated at 573 K (Fig. 2f).

The IR results for the Mo(CO)<sub>6</sub>/PDA (10

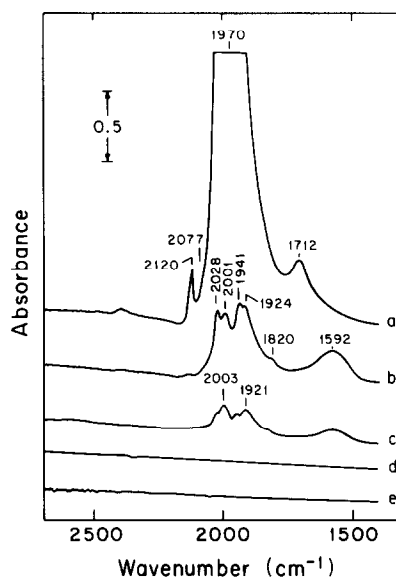


FIG. 1. Infrared spectra of the carbonyl region for alumina support DA and the Mo(CO)<sub>6</sub>/DA catalyst (wafer density, 10 mg/cm<sup>2</sup>): (a) after contact with Mo(CO)<sub>6</sub> overnight at room temperature; (b) following (a) and purging with He for 1.0 hr at 373 K; (c) after (b) and purging for 1.0 hr at 473 K; (d) after purging for 1.0 hr at 573 K; (e) alumina support.

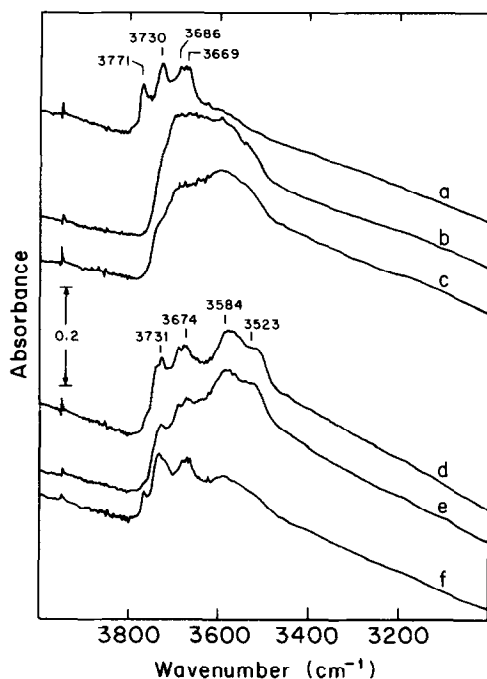


FIG. 2. Infrared spectra from the hydroxyl region for the PDA and Mo(CO)<sub>6</sub>/PDA preparations (wafer density, 10 mg/cm<sup>2</sup>): (a) PDA; (b) PDA after contact with Mo(CO)<sub>6</sub> at room temperature overnight; (c) after (b) following purging with He for 1.0 hr at 297 K; (d) after (c) following purging for 1.0 hr at 373 K; (e) after purging for 1.0 hr at 473 K; and (f) after purging for 1.0 hr at 573 K.

mg/cm<sup>2</sup>) are presented in Fig. 3. The general features of the spectrum (Fig. 3a) after overnight contact with the Mo(CO)<sub>6</sub> were similar to those found for DA (Fig. 1a). A very intense band in the 1900–2000 cm<sup>-1</sup> region, high-frequency bands at 2119 and 2077 cm<sup>-1</sup>, and a shoulder at 1787 cm<sup>-1</sup> were observed. Flushing with He at 297 K markedly reduced the intensity, but the resolution was improved (Fig. 3b); a strong pair developed at 1937 and 1990 cm<sup>-1</sup> and the shoulder at 1787 became resolved into bands at 1758 and 1804 cm<sup>-1</sup>. On flushing at 373 K further changes occurred (Fig. 3c). The overall intensity dropped, but the bands at about 2026, 1981, 1936, 1808, and 1756 cm<sup>-1</sup> remained. Bands at 2120 and 2078 were removed and a new band ap-

peared at 1557 cm<sup>-1</sup>. No carbonyl bands remained after activating the catalyst at 573 K (Fig. 3d). These spectroscopic observations on the Mo/PDA catalyst are in general agreement with earlier literature (15, 18, 20, 22, 23). The Mo/DA catalyst had not been previously characterized in quite this way.

CO has been extensively used as a tool for characterization of catalytic sites (3, 29, 30). The IR spectra from CO adsorbed on Mo/PDA and on Mo/DA catalysts are shown in Fig. 4. These catalysts, after activation at 573 K, showed no C=O stretch-

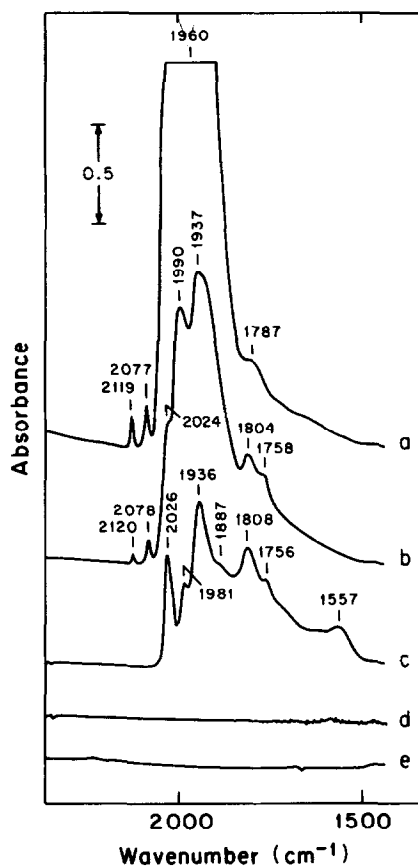


FIG. 3. Infrared spectra of the carbonyl region for the PDA and Mo(CO)<sub>6</sub>/PDA preparations (wafer density, 10 mg/cm<sup>2</sup>): (a) after contact with Mo(CO)<sub>6</sub> overnight at room temperature; (b) following (a) and purging with He for 1.0 hr at 297 K; (c) after (b) and purging with He for 1.0 hr at 373 K; (d) after (c) and purging with He for 1.0 hr at 573 K; and (e) partially dehydroxylated alumina (PDA).

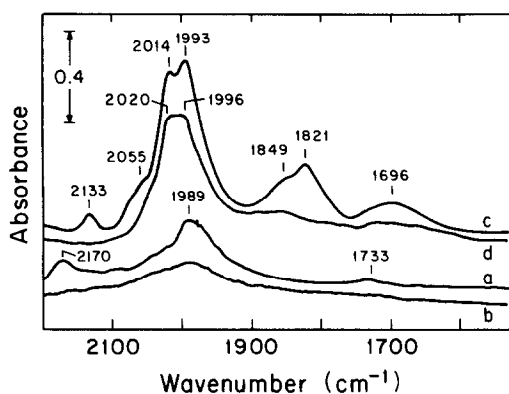


FIG. 4. Infrared spectra of CO adsorbed on  $\text{Mo}(\text{CO})_6/\text{Al}_2\text{O}_3$  activated in He flow at 573 K: (a) Mo/PDA in 40 Torr of CO at 297 K; (b) catalyst as in (a) after evacuation at 297 K for 30 min; (c) Mo/DA in 40 Torr of CO; and (d) catalyst as in (c) after evacuation at 297 K for 30 min.

ing bands (Figs. 1d and 3d). When 40 Torr of CO was added-back at 298 K (Fig. 4), broad weak bands centered at 1989 and 2170  $\text{cm}^{-1}$  appeared on the Mo/PDA (Fig. 4a); these were attenuated on evacuation (Fig. 4b). Significantly the bands formed on PDA, where the dispersion of Mo is much higher than on DA, were much less intense, suggesting that the adsorption is weak and only a fraction of the sites populated as reported by Knözinger and co-workers (3, 29) for adsorption on conventional catalysts. With the Mo/DA catalyst, the carbonyl bands in the 1990 and 2020  $\text{cm}^{-1}$  region were restored on addition of 40 Torr of CO at 298 K. Weaker bands appeared at 1696, 1821, 1849, 2055, and 2133  $\text{cm}^{-1}$ . Evacuation for 30 min at this temperature eliminated these and reduced the intensity of the 1993 and 2014  $\text{cm}^{-1}$  bands. A good correspondence of the principal parts of this spectrum was found with the data of Laniecki and Burwell (18), viz., 2133 vs 2131, 2055 vs 2080, 2014 vs 2014, 1993 vs 1992, and 1849 vs 1852  $\text{cm}^{-1}$ . These values are also in reasonable agreement with the data and its interpretation of Zecchina *et al.* (23). Consequently, they prove  $\text{Mo}(\text{CO})_6$  is being reformed from the  $\text{Mo}^0$  on this catalyst.

The infrared spectra for NO strongly chemisorbed on Mo/DA are presented in Fig. 5; the spectra (5a) and (5b) before and after, respectively, a high-temperature reduction in  $\text{H}_2$  were essentially identical. They may be compared with those for the PDA catalyst (Fig. 5c) and on an 8% molybdena-alumina catalyst (5, 6, 15, 22b, 31, 32) reduced at 943 K (Fig. 5d). The spectra were taken after contacting the corresponding activated catalysts with 40 Torr of NO at 298 K for 30 min and then evacuating the gas phase for 30 min at this temperature. All these spectra showed the same pair of bands: a low-frequency band (LFB) near 1700  $\text{cm}^{-1}$  and a high-frequency band (HFB) in the range 1806–1822  $\text{cm}^{-1}$ . The absolute intensities are reported in Table 2 together with their sum. The ratios of the LFB and HFB bands for these catalysts are also given along with the calculated bond

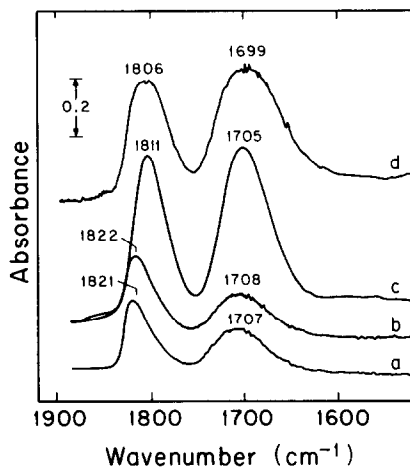


FIG. 5. Infrared spectra from strongly adsorbed NO on activated  $\text{Mo}/\text{Al}_2\text{O}_3$  catalysts. The wafers had a constant thickness of 20  $\text{mg}/\text{cm}^2$ . The loading of the Mo/PDA and Mo/DA catalysts was comparable (but the DA catalyst contained crystalline Mo—see text). In each case the catalyst was exposed to 40 Torr NO at room temperature for 30 min. The excess was removed by evacuation for 30 min at this temperature. (a) Mo/DA after treatment at 573 K in flowing He; (b) Mo/DA treated at 773 K in flowing He followed by  $\text{H}_2$  for an additional 1 hr at 943 K; (c) Mo/PDA treated at 573 K in flowing He; and (d) an 8% molybdena-alumina catalyst reduced with  $\text{H}_2$  at 943 K for 2 hr.



TABLE 2

IR Band Intensities and Bond Angles Corresponding to Dinitrosyl Spectra of Fig. 5<sup>a</sup>

Support	HFB <sup>c</sup>	LFB <sup>f</sup>	HFB + LFB	LFB/HFB	Θ <sup>g</sup>
DA <sup>b</sup>	185	195	380	1.1	92
DA <sup>c</sup>	178	192	370	1.1	92
PDA <sup>d</sup>	432	616	1048	1.4	100

<sup>a</sup> The integrated intensities were determined by the cut and weigh method. The intensities were normalized to the same loading of molybdenum, and to the same wafer thickness.

<sup>b</sup> Catalysts were activated as in Table 1. Loading was 1.5% Mo (corresponding to 52.4 μmole/330 mg); the wafer density was 20 mg/cm<sup>2</sup>.

<sup>c</sup> Catalyst activated as in Table 1 plus treatment in flowing He (60 ml/min) at 773 K for 1 hr and H<sub>2</sub> at 943 K for 1 hr. Loading was 1.4% Mo (μmole/330 mg); the wafer density was 20 mg/cm<sup>2</sup>.

<sup>d</sup> Catalyst activated as in Table 1. Loading 1.6% Mo; the wafer density was 20 mg/cm<sup>2</sup>.

<sup>e</sup> High-frequency (symmetric stretching) band, arbitrary units.

<sup>f</sup> Low-frequency (asymmetric stretching) band, arbitrary units.

<sup>g</sup> The angle Θ in degrees between the two NO oscillators; Θ was calculated from  $I_{\text{HFB}}/I_{\text{LFB}} = \cot^2(\Theta/2)$  according to Ref. (33).

angle between the two NO molecules (33). The band intensities obtained from the Mo/PDA catalyst were significantly higher than those from the Mo/DA system (just the re-

verse was found with CO, vide ultra). The ratio of the total intensities for these two catalysts was 2.8.

*The chemisorption and reduction of NO* by these catalysts (after activation at 573 K) were determined at 195 and 297 K and the data are presented in Tables 3, 4, and 5. The chemisorption values for NO were corrected for chemisorption on the support (10, 16). This amounted to 33 and 12 μmole/300 mg of support at 195 and 297 K, respectively, for the γ-Al<sub>2</sub>O<sub>3</sub> pretreated at 1173 K. For the γ-Al<sub>2</sub>O<sub>3</sub> pretreated at 773 K the corresponding values were 15 and 4.6 μmole/300 mg of support.

At 195 K oxidation of the molybdenum (reduction of the NO) was not detected (neither N<sub>2</sub>O nor N<sub>2</sub> was released from either the Mo/DA or the Mo/PDA catalysts). In the former case the corrected NO uptake at 195 K (Table 3) was zero within experimental error. The value 0.06 NO/Mo resulting from the calculation suggests that NO is not chemisorbed on Mo<sup>0</sup> or else the metal surface area is very small. For the Mo/PDA, the value was close to 2 NO/Mo.

On raising the temperature to 297 K, re-

TABLE 3

NO Chemisorption on Mo/(DA)<sup>a</sup> and Mo/(PDA)<sup>b</sup> (Preparations Had Been Activated at 573 K under Flowing He)

Support	Total ads. at 195 K <sup>c</sup>	Corrected ads. at 195 K as NO/Mo <sup>d</sup>	Ads. at 297 K (μmole NO (ads.)) <sup>e</sup>	Corrected ads. at 297 K as NO/Mo <sup>f</sup>
DA	33	0.06	22	0.91
PDA	34	1.9	25	2.1

<sup>a</sup> Same activation as in Table 1. The loading was 10.3 μmole of Mo/300 mg.

<sup>b</sup> Same activation as in Table 1. The loading was 9.8 μmole of Mo/300 mg.

<sup>c</sup> Total uptake of NO (μmole NO/300 mg) at 195 K. The estimated accuracy is ±2 μmole NO/300 mg.

<sup>d</sup> Corrected uptake of NO (NO/Mo) at 195 K. The support contributions to the NO chemisorption at 195 K were 33 and 15 μmole/300 mg of support for the DA and PDA, respectively. The possible error in the value for (DA) was larger than the value derived; for (PDA) it was estimated as ±0.3.

<sup>e</sup> Same as <sup>c</sup> but at 297 K where the blanks for the support were 12 and 4.6 μmole/300 mg; the data have been corrected for NO consumed in oxidizing the catalyst (Eq. (1)). The estimated accuracy of the results is ±2 μmole NO/300 mg.

<sup>f</sup> Same as <sup>d</sup> but at 297 K. The support contributions to the NO chemisorption at this temperature were 12 and 4.6 μmole NO/300 mg support for the DA and PDA, respectively. The possible error in the data is estimated to be no more than 15%. The value shown for Mo/DA suggests that only about one-half the total Mo is available for chemisorption of the dinitrosyl species shown in Fig. 5.

TABLE 4  
Reduction Products Formed by Oxidation of  
Catalysts Mo/(DA)<sup>a</sup> and Mo/(PDA)<sup>b</sup> with  
NO at 297 K

Support	Molecular ratio		Initial oxidation No. <sup>c</sup>	Final oxidation No. <sup>f</sup>
	(N <sub>2</sub> O/Mo) <sup>e</sup>	(N <sub>2</sub> /Mo) <sup>d</sup>		
DA	0.81	0.13	0.0	2.1
PDA	1.0	0.020	2.1	4.1

<sup>a</sup> Same activation procedure and loading as in Table 3.

<sup>b</sup> Same activation procedure and loading as in Table 3.

<sup>c</sup> Micromoles of N<sub>2</sub>O produced at 297 K per micromole of Mo.

<sup>d</sup> Micromoles of N<sub>2</sub> formed at 297 K per micromole of Mo.

<sup>e</sup> For the Mo/PDA the initial O.N. was taken as the average between the two values given in Table 1.

<sup>f</sup> The final oxidation number was calculated on the basis of a two-electron process associated per one N<sub>2</sub>O molecule formed and a four-electron process per N<sub>2</sub>. This value is an average assuming all the Mo is accessible for oxidation. If small metal particles were present initially with a surface-to-volume ratio of 0.5, the final O.N. would be 4.2. Something like this seems likely, in view of the results shown in Tables 3 and 5; see text. Burwell (21) reported a percentage exposed of ~30% for a similar preparation.

duction of the NO was detected (Table 4) for both catalysts. In the case of the Mo/DA catalyst the final average oxidation number was 2.1 while for the Mo/PDA system the corresponding value was 4.1; i.e., in each case the change in oxidation state was approximately 2.0. The corrected uptake of NO at 297 K (Table 3) for the Mo/DA catalyst increased from zero (at 195 K) to 0.91 NO/Mo while for the Mo/PDA system the value remained close to 2. It is evident in this latter case that the molybdenum centers must be completely dispersed and each must hold 2 NO as dinitrosyls (or dimers) regardless of the oxidation state (O.N. ~ 2 before oxidation and ~4 afterward). The low values for Mo/DA may result from formation of crystalline metal, only part of which may be oxidized by NO at 297 K.

The mass balance experiments (Table 5) showed that with the Mo/PDA system it was possible to recover 92% (23 μmole out of the 25 μmole) of the NO which was chemisorbed at 297 K by heating the catalyst sample under He at successively higher temperatures up to 803 K, albeit that more

than one-half of this was recovered as decomposition products. With the Mo/DA catalyst only 16 μmole or 72% of the chemisorbed NO could be recovered from the 22 μmole originally chemisorbed at 297 K; i.e., a significant fraction (28%) of the nitrogen remained on or in the preparation at 803 K. This is in good agreement with our earlier observation (10) made with a conventional 8% Mo catalyst reduced to Mo<sup>0</sup> at 1173 K.

ESCA spectra were determined for the Mo/DA and Mo/PDA activated at 573 K and for the former reoxidized in 1 atm of O<sub>2</sub> at 523 K. These data are presented in Figs. 6, 7, and 8, respectively. The experimental parameters derived by curve-fitting of these spectra (26, 27) are summarized in Table 6. Where Mo<sup>0</sup> is reported (first row), the percentage peak area due to this species is a lower limit because metal particles much larger than the escape depth for electrons may be present.

The Mo/DA catalyst (Fig. 6) was activated in helium at 773 K followed by H<sub>2</sub> for 1 hr at 943 K to free the surface of any retained carbon (19). Three sets of doublets [Mo 3d(5/2), 3d(3/2)] were required to fit the experimental points; these are identified as I, II, and III in Fig. 6 and Table 6. Tentative assignments of these doublets to valence

TABLE 5  
Comparison of the Recovered Products with  
the NO Chemisorbed at 297 K<sup>a</sup>

Support	Total ads. of NO at 297 K (μmole/300 mg) <sup>b</sup>	Products desorbed to 803 K (μmole of NO/300 mg) <sup>c</sup>			
		NO	N <sub>2</sub>	N <sub>2</sub> O	Total
DA <sup>d</sup>	22	7.8	4.3	3.6	16
PDA <sup>e</sup>	25	10	8.4	4.2	23

<sup>a</sup> After flushing with He at 297 K and determination of residual chemisorption, the He flow was continued to 803 K and all products were collected and analyzed by GLC.

<sup>b</sup> NO chemisorbed at 297 K after purging with He.

<sup>c</sup> Micromoles of products calculated as NO desorbed under He at 803 K/300 mg of support.

<sup>d</sup> Same catalyst (preparation and activation) as in Table 3.

<sup>e</sup> Same catalyst (preparation and activation) as in Table 3.

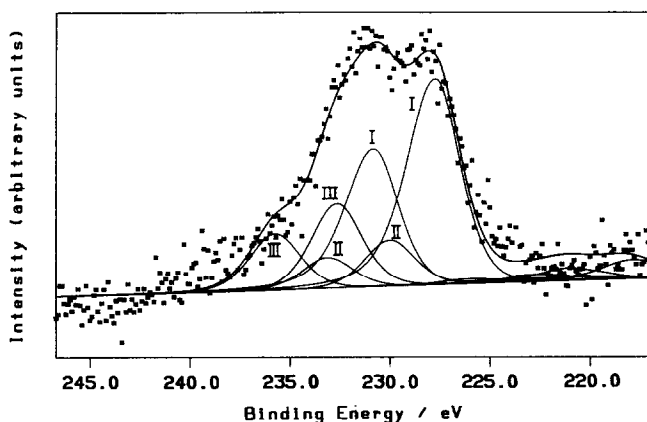


FIG. 6. ESCA Mo 3d spectrum for the Mo(CO)<sub>6</sub>/DA activated for 1 hr at 773 K under flowing He followed by treatment with H<sub>2</sub> at 943 K for 1 hr. The peak parameters are listed in Table 6.

states are shown in Column 5. Doublet I contains about 65% of the total molybdenum envelope (lower limit, last column); Doublet II has about 12% while Doublet III has the remaining 23% (upper limits). The experimental  $I_{\text{Mo}}/I_{\text{Al}}$  intensity ratio obtained for this catalyst which contained 1.5% Mo was 0.12.

For the Mo/PDA catalyst activated in helium at 573 K, only two sets of doublets (A and B in Fig. 7 and Table 6) were necessary to fit the experimental data. Doublet A contained about 34% of the total molybdenum envelope area while Doublet B had the re-

maining 66%. The assignment of Doublet B to Mo<sup>4+</sup> is unequivocal; the assignment of Doublet A to Mo<sup>2+</sup> is uncertain. Conceivably, it could stem from highly dispersed Mo<sup>0</sup> since in this case the binding energies would be shifted to higher values than those of the crystalline metal. The experimental  $I_{\text{Mo}}/I_{\text{Al}}$  intensity ratio for this catalyst which contained 1.4% Mo was 0.20, demonstrating the higher dispersion.

The Mo/DA preparation was treated in O<sub>2</sub> for 4 hr at 523 K and the resulting ESCA spectrum is shown in Fig. 8. Two sets of doublets (1 and 2) were required to fit the

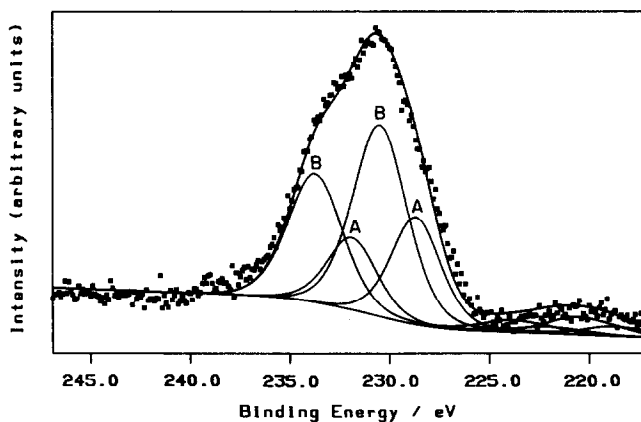


FIG. 7. ESCA Mo 3d spectrum for the Mo(CO)<sub>6</sub>/PDA activated at 573 K under flowing He. The peak parameters are listed in Table 6.

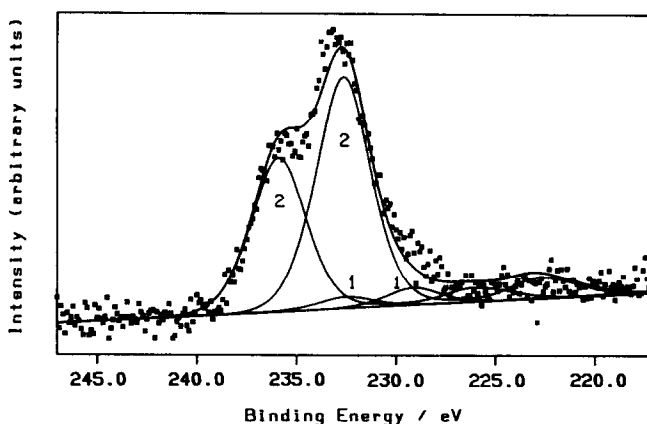


FIG. 8. ESCA Mo  $3d$  spectrum for a reoxidized catalyst.  $\text{Mo}(\text{CO})_6/\text{DA}$  was activated as described in Fig. 6. It was then treated in  $\text{O}_2$  at 523 K before recording the spectrum. The peak parameters deduced are given in Table 6.

experimental points, but Doublet 2 ( $\text{Mo}^{6+}$ ) contained 96% of the total molybdena envelope. The experimental  $I_{\text{Mo}}/I_{\text{Al}}$  intensity ratio for this catalyst was 0.13.

#### DISCUSSION

In agreement with earlier work (11, 17, 19, 21, 22), the Mo/DA and Mo/PDA catalysts after decarbonylation at 573 K had average oxidation numbers (Table 1) of about

0 and 2, respectively. Bowman and Burwell (19) reported a value of  $1.9 \pm 0.1$  for their PDA after activation in He at 573 K, i.e., very close to our value of 2.1. Our results for the Mo/DA preparation (from both the  $\text{H}_2$  evolved during activation and the  $\text{O}_2$  consumed during total reoxidation) indicated that essentially all the molybdenum was initially in the zero-valence state. A value of O.N. = 0.36 has been reported (11)

TABLE 6

ESCA Parameters<sup>a</sup> Deduced Using Curve-Fitting Techniques of Ref. (26)

Doublet	Support	Binding energy (eV) <sup>c</sup>			FWHM (eV) <sup>f</sup>		% of Total Mo peak area <sup>g</sup>
		Mo $3d(3/2)$	Mo $3d(5/2)$	Assignment	Mo $3d(3/2)$	Mo $3d(5/2)$	
I	DA <sup>b</sup>	230.7	227.6	$\text{Mo}^0$	2.85	2.85	65
II	DA	233.1	230.0	$\text{Mo}^{4+}$	2.95	2.95	12
III	DA	235.7	232.6	$\text{Mo}^{6+}$	2.95	2.95	23
A	PDA <sup>c</sup>	231.7	228.5	$\text{Mo}^{2+}$ (?)	2.95	2.95	34
B	PDA	233.4	230.2	$\text{Mo}^{4+}$	3.15	3.15	66
1	DA <sup>d</sup>	232.0	228.9	$\text{Mo}^{2+}$ (?)	3.15	3.15	4
2	DA	235.9	232.8	$\text{Mo}^{6+}$	3.05	3.05	96

<sup>a</sup> Derived from Figs. 6, 7, and 8.

<sup>b</sup> Catalyst was prepared as in Table 1; the loading was 1.5% Mo or about  $1 \times 10^{20}$  Mo/g.

<sup>c</sup> Catalyst was prepared as in Table 1; the loading was 1.4% Mo or about  $1 \times 10^{20}$  Mo/g.

<sup>d</sup> Catalyst was prepared as in <sup>b</sup> followed by treatment in  $\text{O}_2$  at 523 K for 4 hr.

<sup>e</sup> The Al  $2p$  peak of the support (74.5 eV) served as the reference line for catalyst samples. This value was referenced to vapor-deposited gold.

<sup>f</sup> Full width at half-maximum (eV).

<sup>g</sup> Percentage of the total Mo envelope area occupied by each doublet.

for a similar preparation after activation under He at 773 K; this fell to 0 after subsequent reduction in H<sub>2</sub>. It should be emphasized, however, that all intermediate oxidation numbers (between 0 and 6) are *average* values and do not necessarily reflect the presence of one or another single oxidation state. Some objectives of the present research were to identify these oxidation states of the decomposed carbonyls (at 573 K), to look for an intermediate oxidation state of Mo<sup>2+</sup> or Mo<sup>3+</sup> in the PDA preparation, and to identify the initial and final states when the catalysts were reoxidized with NO at room temperature. This appeared to be straightforward using ESCA on the one hand and the IR spectra of chemisorbed CO on the other, but in practice several complicating factors appeared which imposed uncertainties in interpretation of the results as outlined below.

In the ESCA experiments, a single doublet was anticipated for the Mo/DA preparation. The data (Fig. 6, Table 6) indicated that 65% of the total molybdenum was present as metallic Mo<sup>0</sup>, with the remaining 35% being present as Mo<sup>4+</sup> and Mo<sup>6+</sup>. These figures may be misleading, however, because the crystallite size of the metal will make the former a lower and the latter figure an upper limit. It can therefore be concluded that this preparation approximated our expectation, but contains small amounts of higher oxidation states due to imperfections in our techniques of preparation or handling. The binding energies found for Doublet I were 227.6 eV (3d(5/2)) and 230.7 eV (3d(3/2)). These values are within the expected range for metallic molybdenum; i.e., values of 3d(5/2) of 227.4 (9), 228.0 (34, 35), and 228.3 (36) have been reported. Cimino and De Angelis (37) reported a value of 226.8, but they used a C 1s reference state value of 283.8, which is lower than the currently accepted value of 284.6 to 285.0. When correction for this is made, a value of 227.8 is obtained. Thus, the ESCA data, as well as the oxidation number derived for this preparation, lead to

the conclusion that Mo/DA is comprised mainly of metallic crystallites of Mo supported on the surface of dehydroxylated alumina, confirming much earlier work (11, 20, 21). This is consistent with the data contained in Tables 3, 4, and 5 which may be interpreted by assuming that roughly one-half the zero-valent Mo is available at the surface for reoxidation ( $\Delta O.N. \sim 2$  to achieve Mo<sup>4+</sup>) while the other half is in the bulk where it may form nitride on decomposition of NO (73% recovery of N). Chemisorption of NO on the Mo<sup>4+</sup> thus formed then occurs (Fig. 5) leading to an average NO/Mo = 0.91.

In order to calibrate the high end of the binding energy scale for the molybdenum species, the Mo/DA catalyst was reoxidized with O<sub>2</sub> at 523 K. The resulting ESCA spectra (Fig. 8) consisted mainly (96% of the spectral area) of one doublet at 232.8 and 235.9 eV; these values are in good agreement with Mo(VI) species from the existing literature (9, 34). The remaining 4% of the area is obviously due to a lower valent species, but the accuracy of these data was too low to make an assignment with much confidence.

In the case of the Mo/PDA catalyst, the situation was still more complicated; this catalyst presumably had an *average* oxidation number of 2.1 (Table 1). A priori, one might expect either a pair of doublets corresponding to roughly equal amounts of Mo<sup>0</sup> and Mo<sup>4+</sup> or a single doublet stemming from Mo<sup>2+</sup>. Two doublets (A and B) were obtained (Fig. 7) with binding energies of 228.5 and 231.7 eV, and at 230.2 and 233.4 eV (Table 6). The larger Doublet B which contained about 66% of the total molybdenum area is assignable to Mo<sup>4+</sup>. The second, Doublet A, should therefore correspond to Mo<sup>0</sup> (the value of 34% being a lower limit), but the binding energy of 228.5 eV (3d(5/2)) appears high for Mo<sup>0</sup>. Indeed it is close to that expected for Mo<sup>2+</sup> (Mo 3d(5/2) = 228.9 eV) based on a linear interpolation between the values for Mo<sup>4+</sup> and Mo<sup>0</sup>. However, this assignment cannot be

made with confidence, either, because relaxation phenomena or final state effects (38) observed in the case of films or very small metal particles could lead to a shift to higher binding energies for Mo metal. It could be that the Mo<sup>0</sup>, if present in this preparation, is very highly dispersed, thus raising its B.E. from that of the metallic phase. In this case the situation could also be described by the Mo<sup>δ+</sup> sites envisioned by Peri (15).

An equipment breakdown prevented us from pursuing these experiments further. Moreover, since we were unable to determine the average oxidation number on the same sample used in the ESCA experiment, we are left to conclude that we have observed Mo<sup>4+</sup> and some lower valence state which we are unable to assign with confidence. However, some further facts may be taken into account. These are summarized in subsequent paragraphs.

Zhdan *et al.* (39) reported three doublets from a related preparation which they assigned to Mo<sup>6+</sup>, Mo<sup>4+</sup>, and Mo<sup>2+</sup>. However, their binding energies for these species did not agree well with those obtained in the present work. They made no attempt at signal deconvolution, so it is possible that the same species were observed as in the present work, but with binding energies shifted by charging effects or misassigned reference states.

Roxlo *et al.* (40) recently reported an XPS study of a lithographically textured MoS<sub>2</sub> crystal. Two components were observed, one band at 229.0 eV (dominant) which they assigned to Mo<sup>4+</sup> and a shoulder at about 228.2 eV. The binding energy shift (from Mo<sup>4+</sup>) was suggested to correspond to reduction of Mo<sup>4+</sup> to Mo<sup>3+</sup> at the CUS of MoS<sub>2</sub>. Thus, it is possible that we have observed Mo<sup>2+</sup>, but that during preparation it was oxidized further than the sample of Table 1. (A pressed wafer weighing ~100 mg mounted on the sealable ESCA probe was used.)

When a plot of the Mo 3d(5/2) binding energies vs oxidation number was made us-

ing our assignments for Mo<sup>0</sup>, Mo<sup>4+</sup>, and Mo<sup>6+</sup> from Table 6, the smooth curve shown in Fig. 9 was obtained. When the binding energy value (228.5 eV) was fit onto the curve (circled point), the corresponding oxidation number was exactly that for Mo<sup>2+</sup>. These data are shown as a matter of interest for whatever they may be worth. Since an accepted standard for valence state Mo<sup>2+</sup> is not available, the apparent fit may be fortuitous. The data do show, however, that the assignment of the 228.5 peak to Mo<sup>2+</sup> is not unreasonable. Mo<sup>2+</sup> has been repeatedly suggested to exist under certain conditions (3, 13, 29, 32, 39, 44). Taken collectively the existing ESCA data are inconclusive, but it is evident that this problem can be solved with further work.

The infrared experiments of Fig. 4 were made to assist in the identification of the valence states present. Zaki *et al.* (29) have reviewed the literature on the assignments of CO stretching frequencies to chemisorption on various molybdenum valence states. Frequencies of 2204, 2170 to 2195, and 2100 to 2128 cm<sup>-1</sup> have been related to Mo<sup>5+</sup>, Mo<sup>4+</sup>, and Mo<sup>2+</sup>, respectively. Frequencies below 2100 have been associated (30) with Mo<sup>0</sup> and with molybdenum car-

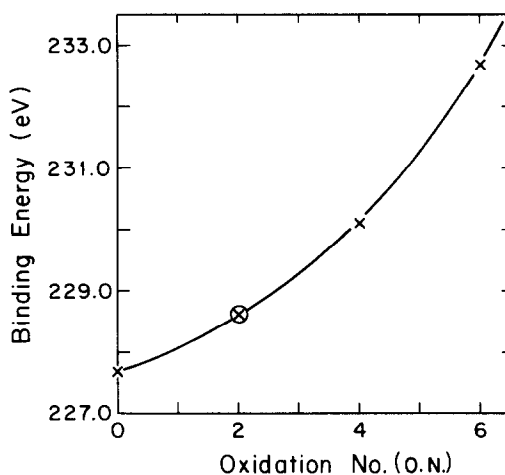


FIG. 9. Mo 3d(5/2) binding energies taken from present work. The assignments for all but the circled point are certain. The latter was placed on the curve drawn through the other three.

bonyl and subcarbonyl species (18, 22, 23). Zecchina *et al.* (23) made a very detailed study of Mo/DA at room temperature during adsorption and desorption into vacuum and were able to assign all except the lowest frequency bands at 1670 and 1520  $\text{cm}^{-1}$  to three sets of quartets predicted by group theory. Two of these sets corresponded to  $(\text{CO})_5\text{Mo}-\text{CO}\rightarrow\text{Al}$ , where the carbonyl is bonded by Lewis acid-base interaction via a carbonyl oxygen to an exposed Al site residing in either an Oh or a Td site. The third was formed at the expense of the other two and was suggested to stem from a monomeric subcarbonyl, perhaps  $(\text{CO})_4\text{Mo}-\text{CO}\rightarrow\text{Al}$ . An additional weak band at 1670  $\text{cm}^{-1}$  (presumably because of its small population) was assigned to the  $\text{Mo}(\text{CO})_6$  held similarly on extra-strong "defective" Lewis sites; this converted into the corresponding subcarbonyl species absorbing at 1520  $\text{cm}^{-1}$  on extended evacuation. Their data agree well with those of Laniecki and Burwell (18) as well as with five of the principal bands shown in Fig. 4c. This spectrum was generated after adding-back CO following decomposition of the carbonyl at 573 K (Fig. 1d). As noted earlier, these observations demonstrate conclusively that  $\text{Mo}(\text{CO})_6$  is reformed by reaction of CO at 298 K with the metallic molybdenum of Mo/DA. This spectrum provides no evidence, however, for the presence of the small amount of ionic molybdenum observed by ESCA. Nevertheless, it could be concluded that the two measurements are in agreement within the experimental uncertainties.

The results obtained from Mo/PDA (Fig. 4a) are unfortunately not so conclusive. This spectrum was much weaker than that for Mo/DA (Fig. 1c) in spite of the fact that the loading was comparable. Room temperature spectra for CO adsorbed on conventional catalysts (29) are weak; they show only "the tips on the icebergs." This is because site coverage with CO on ionic molybdenum is sparse. Unfortunately we did not have equipment to do the low-tempera-

ture experiments where something more might have been learned. Spectrum (4a) (taken after (3d) on adding-back CO to the system) does show two unmistakable things:  $\text{Mo}^0$  is present and so is  $\text{Mo}^{4+}$ . This evidence supports the view that Mo/PDA contains a mixture of valence states. Although no evidence of  $\text{Mo}^{2+}$  was obtained, this result is not conclusive so this matter must be left for further work.

Work on these systems is incomplete. Zecchina *et al.* (23) studied  $\text{Cr}(\text{CO})_6$ ,  $\text{Mo}(\text{CO})_6$ , and  $\text{W}(\text{CO})_6$  adsorbed on DA alumina, but only at room temperature; Kazusaka and Howe (22) studied the decomposition of  $\text{Mo}(\text{CO})_6$  on PDA only, while similar experiments were carried out by Laniecki and Burwell (18) on HA, PDA, and DA aluminas. In none of these cases was the re-adsorption of CO studied by IR after complete decomposition of the carbonyl at 573 K as was attempted in the present work. Note the complete disappearance of all bands after treatment in flowing He at 573 K (Figs. 1d and 3d). Where comparison can be made all these data are in fair agreement although several differences in interpretation exist. Other uncertainties remain. Under some conditions CO may dissociate in the presence of metallic molybdenum, forming an oxycarbide. Although we have no evidence for this in our studies, the dissociation of NO and the disappearance of nitrogen and oxygen were observed (Table 5). Comparison with other literature reveals a variety of inconsistent observations and opinions concerning band assignments. Guglielminotti and Giannello (41) used photoreduction of conventional  $\text{MoO}_3/\text{SiO}_2$  catalysts with CO and observed intense IR bands at 2128 and 2030  $\text{cm}^{-1}$  and a lower intensity band at 2043; from the constant intensity ratio and isotopic experiments the authors concluded that the first two bands are due to a dicarbonyl species on  $\text{Mo}^{2+}$  (we did not observe these bands on Mo/PDA where  $\text{Mo}^{2+}$  may be present in substantial quantities). These authors (41) suggested that the 2043  $\text{cm}^{-1}$  was due to a monocar-

bonyl  $\text{Mo}^{2+}$  species. Kazansky *et al.* (45) have argued that the same bands are associated with  $\text{Mo}^{4+}$  centers produced at oxygen vacancies. Thermally reduced  $\text{MoO}_3/\text{SiO}_2$  ( $\text{H}_2$ , 723 K) did not show these bands; when the catalysts were contacted with CO, bands at 2203 and  $2181\text{ cm}^{-1}$  were assigned to CO adsorbed on  $\text{Mo}^{5+}$  and  $\text{Mo}^{4+}$  ions, respectively. On sulfided molybdena–alumina catalysts, Knözinger and co-workers (3) reported a band at  $2110\text{ cm}^{-1}$  which was assigned to a  $\text{Mo}^{2+}$ –CO complex. When the same catalyst was reduced in  $\text{H}_2$  (773 K) only IR bands higher than  $2160\text{ cm}^{-1}$  were developed. These were assigned to a  $\text{Mo}^{4+}$ –CO complex. Other workers (15, 42–45) have offered other suggestions. With some additional work, surely order can be brought to this chaotic situation.

The NO adsorption experiments proved to be very interesting. In agreement with previous results (10), redox reactions were not observed at 195 K, but became evident at room temperature and above. With the Mo/PDA system (average O.N. = 2) the chemisorption at 195 K was 1.9 NO/Mo (Table 3), i.e., about 2 NO on each Mo regardless of valence state. On raising the temperature to 297 K, 1  $\text{N}_2\text{O}/\text{Mo}$  was released (Table 4) indicating 1 O left on the catalyst and oxidation of 2 e/Mo. Now 2.1 NO/Mo were adsorbed on sites of O.N. = 4 (Table 3). It is reasonable, therefore, to deduce that all the lower states were oxidized to  $\text{Mo}^{4+}$  and that this is the valence state corresponding to most of the reported IR spectra (as in Fig. 5). It is well documented (3, 5, 13, 15, 23, 32, 43) that when NO is chemisorbed on a variety of reduced molybdena catalysts, two bands appear in the infrared spectra (around 1810 and  $1710\text{ cm}^{-1}$ ), which are assignable to a dinitrosyl or dimeric NO species. The present data show that 2 NO are attached to every Mo in this preparation, thus demonstrating the complete dispersion of the Mo ions on Mo/PDA. Clearly the much less strongly held CO is populating only a fraction of these sites at room temperature.

The situation was not so straightforward with Mo/DA (average O.N. = 0). On this catalyst (Table 3) the amount of strongly chemisorbed NO was negligible (zero within experimental error) at 195 K after correction for adsorption on the support. However, a weak adsorption on fairly large Mo crystallites would have yielded the same result. Interestingly, oxidation of the metallic Mo occurred, followed by chemisorption of NO when the temperature was raised to 297 K in the ambient NO atmosphere. As with Mo/PDA, the overall oxidation number increased by 2 e/Mo (Table 4), but since only  $\text{Mo}^0$  was present initially (Table 1), the final average O.N. = 2.1 was derived. Note, however, that if the percentage of exposed Mo was 50%, a final O.N. = 4.2 would be calculated in agreement with the Mo/PDA catalyst. Moreover, the corrected adsorption at 297 K (Table 3) for this situation would be 1.8 NO/ $\text{Mo}^{4+}$ , again in reasonable agreement with the Mo/PDA catalyst as well as with the fact that the NO is chemisorbed on the Mo sites in pairs (Fig. 5). Whereas this analysis must be considered tentative for the present, it seems the best overall rationalization of all of the facts. The IR spectra of Fig. 5 are in accord with this picture. Note the band intensities from the Mo/DA preparations (Figs. 5a and 5b) are much less intense than those from Mo/PDA (Fig. 5c).

Burwell and co-workers (11, 19, 21) studied the chemisorption of several molecules ( $\text{CO}$ ,  $\text{H}_2$ ,  $\text{O}_2$ ) on Mo/DA and made TEM measurements. Although there was some uncertainty, the percentage exposed was taken as 30%, corresponding to about 30-Å crystals. This value is in reasonable agreement with our estimate of ~50% exposed. In view of these data it seems unlikely that the negligible NO adsorption at 195 K on our Mo/DA catalyst could be due to a particle size effect.

The ratio of the integrated IR intensities from NO chemisorbed on DA and PDA catalysts taken from Table 2 is  $(375/1048) = 0.36$ , a value falling between our estimate of



roughly 50% and Burwell's of 30% exposed sites on metallic crystallites. The data suggest that it is necessary to oxidize lower valence states to  $\text{Mo}^{4+}$ , before chemisorption as dinitrosyl can occur in agreement with earlier suggestions (15, 22b).

The present work was undertaken to further clarify the surface chemistry of  $\text{Mo}(\text{CO})_6$ /alumina catalysts and the relationships of these to the more conventional ones made by solution impregnation techniques. A second objective was to define and quantify the reoxidation chemistry which occurs during chemisorption of NO on these surfaces (to define the initial and final valence states present), and a final objective was to determine the valence states present in the Mo/PDA system. Progress was made toward each of these, but more work will be required before unequivocal answers to all these questions are in hand. The needed experiments are now evident.

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