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The Surface Chemistry of Molybdena–Alumina Catalysts Reduced in H_2 at Elevated Temperatures

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The changes in surface chemistry which occurred as a molybdena–alumina catalyst (8% Mo) was reduced to increasing extents in H_2 at temperatures between 500 and 900°C were characterized by measuring the chemisorptions of NO (at −78 and 24°C) and of O_2 (at −78°C) and these data were supplemented by studies of the hydrogenation of benzene. Interesting changes occurred as the catalyst was reduced under more severe conditions than those ordinarily used. The average extent of reduction, e/Mo, increased monotonically from 1.7 (mainly Mo^{4+}) at 500°C to 5.0 (Mo^0 present) at 900°C, while the surface area decreased by less than 25%. The oxygen chemisorption increased concomitantly from nearly zero at $e/\mathrm{Mo} = 0.08$ to $\mathrm{O/Mo} = 0.5$ at $e/\mathrm{Mo} \approx 3.0$; it reached a maximum of $\mathrm{O/Mo} = 0.55$ at $e/\mathrm{Mo} \approx 4$ and then decreased slightly at the highest reduction temperature. The NO chemisorption behaved similarly but dropped more precipitously at the highest temperature. The ratio of the two chemisorptions changed from 2NO/O ($4NO/O_2$) at 500°C (standard preparation) to $2NO/O_2$ above $e/\mathrm{Mo} = 3$ (700°C reduction temperature). NO chemisorbed at −78°C without evident decomposition, but at room temperature and above, N_2O and N_2 were evolved in amounts corresponding to oxidation of 20 to 45% of the total Mo by $2e$, the amount increasing with the extent of reduction. Moreover, as the extent of reduction increased, it was found that chemisorption of NO on the support became an important fraction of the total. Hydrogenation of benzene did not occur at atmospheric pressure at temperatures up to 250°C until $e/\mathrm{Mo} \approx 5$ where metallic molybdenum evidently was present. Thus, the sites responsible for hydrogenation of simple olefins were ineffective for benzene and this reaction provides a simple diagnostic tool for the detection of Mo^0. © 1988 Academic Press, Inc.

INTRODUCTION

Early folklore held that molybdena–alumina hydrodesulfurization (HDS) catalysts are not reduced below Mo^{4+} and that this is the active state of the catalyst. Similarly it has been assumed that sulfided catalysts are essentially supported MoS_2. Massoth's studies (*1*) of the reduction of these materials nicely contrasted this behavior of molybdena–alumina with that of molybdena–silica which behaved like mechanical mixtures of MoO_3 and silica, i.e., underwent reduction to Mo^0. Most of these studies were made at temperatures below 600°C. Tungsta–alumina catalysts were found to be even more difficult to reduce (*2*). More recent and detailed studies (*3, 4*) suggested that minor amounts of lower valence states can be introduced into conventional molybdena–alumina (8% Mo) catalysts at reduction temperatures up to 600°C. However, under only slightly more severe conditions, average valence states below Mo^{4+} ($e/\mathrm{Mo} > 2$) began to appear (*4*) and studies of sulfided catalysts (*5*) revealed average valence states closer to Mo^{3+} than to Mo^{4+}, a fact which has been recently confirmed (*6*). Meanwhile, Burwell and coworkers (*7, 8*) were studying the decomposition of $Mo(CO)_6$ on alumina surfaces. In the course of this work, they prepared probably the first alumina-supported *metallic* molybdenum catalyst (*8*) by decom-

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posing the carbonyl on a (nearly) completely dehydroxylated alumina (DA) followed by reduction with H_2. In the same work they showed that essentially the same result could be obtained by reducing MoO_3/alumina preparations with H_2 at 950°C. Almost simultaneously Yao (*9*) independently published TPD data which demonstrated that a conventional catalyst became completely reduced as the temperature approached 900°C. This collective work suggested the possibility that small amounts of lower valence states (even Mo^0) might exist in most of the preparations studied in the past and indicated the need to sort out the nature of the sites responsible for various catalyst functions. Thus, the present paper examines the changes in valence state and in the chemisorptions of O_2 and NO as the severity of the reduction was increased into the range $500°C < T < 900°C$, as well as in the catalytic activity for the hydrogenation of benzene.

Weller and co-workers (*10*) devised a technique to measure the "equivalent molybdena surface" using the chemisorption of O_2. Millman and Hall (*11*) showed that this chemisorption was site selective and Tauster *et al.* (*12*) reached a similar conclusion for MoS_2 preparations. The data suggested that the chemisorption was occurring on the coordinatively unsaturated sites (CUS) which effect catalysis. Linear correlations were demonstrated between oxygen chemisorption and the rates of propylene hydrogenation (*11*) or the HDS of dibenzothiophene (*12*). This technique has been widely used (*12–16*) for estimation of site concentrations.

NO was first found to be a selective poison for propylene metathesis (*17*) and then for hydrogenation (*18*) over reduced molybdena–alumina catalysts; site concentrations could be estimated from the lethal dose required just to eliminate the catalytic activity. Further investigation (*11, 19*) demonstrated that NO and oxygen chemisorbed on the same sites in a ratio of about 4 : 1. IR spectra (*20, 21*) from catalysts having the lethal dose or less showed that each site held two NO molecules (dinitrosyl or dimeric species). Thus, it was deduced that the catalytic sites had high coordinative unsaturation and therefore lower than normal valence states. Shuxian *et al.* (*22*) showed that oxygen chemisorbed in a molecular form on MoS_2 at 188 K, but became dissociated below room temperature. Thus, the approximate 4 : 1 ratio evidently reflected the equivalence of one oxygen atom to the NO pair. This has been discussed in more detail elsewhere (*23–25*).

In addition to the chemisorption properties outlined above, evidence of partial oxidation of the chemisorption sites by these gases has been noted from time to time (*18, 22, 26–28*). Although no quantitative data exist, the indications are that the fraction of the chemisorption sites which become oxidized is a function of the average oxidation state of the molybdenum as well as the temperature, time, loading, preparation, and pretreatment procedures. This suggested to us that certain low valence sites might become oxidized whereas those having higher valence might not, e.g., Mo^{2+} vs Mo^{4+}. If so, the production of N_2O and/or N_2 might provide a method of site analysis. Consequently this question has been further examined herein.

The high activity of transition metals and their alloys with II-B metals for the hydrogenation of benzene to cyclohexane is well known (*29–50*). Usually the intermediate cyclohexene and cyclohexadiene are not observed, suggesting that the ring may become saturated in one residence on the surface. Either these catalysts are poisoned or their behavior is strongly modified by sulfur compounds, especially H_2S. Most of this work has been carried out at $P_{H_2} \approx 1$ atm and at mild temperatures (65–250°C) above which the reaction becomes thermodynamically limited.

Sulfur-tolerant catalysts are needed for coal hydrogenation. Sulfided nickel–tungsta catalysts (*51–53*) have been studied and are reportedly (*54*) more active than the usual molybdena catalysts (*55*). However, conventional molybdena–alumina catalysts are extremely active for the hydrogenation of simple olefins (*24*), as well as for HDS. As shown herein, however, they are *not* active for benzene hydrogenation at $P_{H_2} \approx 1$ atm (although the reaction proceeds smoothly at elevated pressures).

Chappen and Brenner (*56*) have reported benzene hydrogenation rates at 100°C and atmospheric pressure for molybdena catalysts prepared by decomposition of $Mo(CO)_6$ onto dehydroxylated and partially dehydroxylated aluminas. Catalysts derived from salts of Mo, W, Fe, Os, and Co gave substantially higher activities after reduction at 1000°C than at 600°C. The authors stated that this was consistent with other work showing that complete reduction to the metal greatly enhances the ability to hydrogenate benzene. Similarly Burwell and co-workers have reported on the hydrogenolysis of cyclopropane and propane to methane and ethane over carbonyl-derived catalysts (*8, 57, 58*). It was clear that the lower the "oxidation number," the more active these catalysts became for these reactions. Hydrogenolysis is typically a metal-catalyzed reaction. When tested over a conventional reduced molybdena–alumina catalyst (*18*) hydrogenolysis did not occur below 500°C. As shown herein, while nearly inactive after activation at lower temperatures, after reduction at 900°C molybdenum catalysts became as active for benzene hydrogenation as any catalyst previously reported. These observations suggested to us that benzene hydrogenation at atmospheric pressure might be used as a diagnostic tool to indicate the presence or absence of metallic molybdenum. Hence, a study of this reaction is a central part of this work. The underlying reasons for the onset of hydrogenation activity at higher pressures for catalysts reduced or sulfided in the conventional fashion will be taken up in a later paper.

The work of Burwell and co-workers outlined above has shown rather nicely that quite similar supported Mo–metal catalysts can be prepared either by the carbonyl route or from the supported oxides, provided the catalysts are properly reduced at 950°C. Moreover, the percentage of the supported metal exposed has been estimated (*58*) from CO chemisorption at 25°C to be in the vicinity of 30%. Furthermore, although no evidence was presented, it was stated (*59*) that "EXAFS examination indicates that (these catalysts) contained metallic molybdenum" and "Dr. M. J. Jacaman kindly examined reduced MoO_3/DA by dark field electron microscopy. It contained particles of metallic molybdenum with a rather wide distribution of sizes, the average diameter of which was 30 Å." These catalysts should compare fairly with ours after a 900°C reduction.

EXPERIMENTAL

Catalysts and pretreatment. The (8% Mo) catalyst was the same preparation studied previously (*5, 11, 20, 23, 24*). It was made by the incipient wetness technique using $(NH_4)_6Mo_7O_{24}$ and Ketjen CK-300 alumina. It had a surface area of 185 m^2/g. In the *standard procedure*, an aliquot (usually ~200 mg) was calcined overnight at 500°C in flowing dry oxygen and then evacuated for 30 min at the same temperature. The catalyst was then reduced for 2 hr in ultrapure hydrogen flowing at ~70 cm^3/min at 500°C. Following evacuation for 1 hr at 500°C, it was cooled *in vacuo* to room temperature where the experiments were initiated. The catalysts were reactivated between experiments by employing the same *standard procedure* which resulted in an average extent of reduction of about $e/Mo = 1.7$ (the average number of electrons per Mo that the catalyst has been reduced to below Mo^{6+}). Reproducibility was very good.

In the present work higher reduction temperatures were employed in some experiments to increase the extent of reduction. Following the standard procedure, the temperature was ramped linearly upward at

2°C/min to the final temperature where the treatment was continued for 2 hr. The extent of reduction (*e*/Mo) was determined by measuring the O_2 consumption required for complete reoxidation using volumetric techniques (*3*, *4*). This provided a calibration curve from which duplicate preparations could be made for hydrogenation and chemisorption experiments. Blank experiments were also made with the alumina support. The pretreatment consisted of calcination overnight at 500°C in flowing dry O_2, evacuation at 500°C for 1 hr, and subsequent heating (5°C/min) to the final temperature under vacuum. The evacuation was extended for 2 hr at the final temperature.

Sulfided molybdena–alumina was prepared by the conventional method (*5*, *24*). Following pretreatment the catalyst was sulfided in a flowing stream (77 ml/min) of 10% H_2S in H_2 at 350°C for 4 hr.

Gases and reactants. The benzene was Aldrich 99+% spectrophotometric grade reagent dried over sodium; it was outgassed before use by a repeated freeze–pump–thaw technique.

Cylinder oxygen (99.6%) obtained from Linde was dried by passing through columns filled with $CaCl_2$ and anhydrous $MgClO_4$. That used for the quantitative reoxidation experiments and for chemisorption measurements was condensed, pumped, and then distilled between two liquid nitrogen traps, and finally the center cut was distilled into a 5-liter storage bulb where it was stored at superatmospheric pressure.

The helium gas (Linde, nominal purity 99.995) was passed in sequence over $CaCl_2$, anhydrous $MgClO_4$, and activated charcoal at −195°C. When used as a carrier gas in chemisorption experiments, it was further purified using a Matheson Hydrox purifier. The maximum impurity (O_2) content at this stage was tested by Burwell's methods (*7*, *8*) and estimated to be ≤ 1 ppm.

Ultrapure H_2 and D_2 were made by diffusion through Pd–Ag thimbles. The 10% H_2S–H_2 mixture (Matheson Gas Products) had a nominal purity of 99.5% and was used as received. Most of the remaining 0.5% was N_2.

NO (Matheson, nominal purity 99.99%) was distilled between dry ice and liquid nitrogen traps to eliminate NO_2 and N_2O. The purified gas was stored at superatmospheric pressure in 5-liter bulbs in the BET system used for these investigations. No impurities could be detected by chromatographic methods. The CO_2 was Matheson research grade (purity 99.995); it was frozen, outgassed, and stored before use.

Procedures. Most of the catalytic experiments were made at 100°C in a static stirred reactor with a total volume of about 1100 cm^3, but a few exceptions are noted in the text. About 40 cc (NTP) of benzene vapor was distilled into the reactor by freezing it onto the wall above the catalyst at the temperature of liquid N_2. Then H_2 was introduced to provide a H_2/C_6H_6 molar ratio of about 10. Circulation was started and the reaction was initiated by replacing the liquid nitrogen trap with a furnace at the preset temperature. For each experiment ~200 mg of a freshly reduced or sulfided molybdena–alumina was used.

Analyses of products in these experiments were obtained using a quadrupole mass spectrometer (ULTEK QUAD 250A) which was connected to the reactor system via a leak valve. Thus, the changing product distribution could be monitored continuously. The time lag was ~1 min, and less than 2% of the total gas volume was removed during the entire experiment (2 hr). A low ionization voltage (~12 eV) was used to avoid fragmentation.

Static adsorption measurements. These were made with a standard BET system. The oxygen chemisorption measurements were carried out at −78°C employing the double isotherm method of Weller *et al.* (*10*). The CO_2 chemisorption was determined as follows: ~100 mg of the pretreated support or catalyst was exposed to a measured volume of this gas for 15 min at room temperature. The excess CO_2 was then removed into a −196°C trap inside the burette system from which it was regenerated and measured. The amount of chemisorbed CO_2 was then obtained by difference. The adsorbent temperature was then raised to 500°C aand the desorbed CO_2 was recovered and measured in a similar fashion. The two values served as a check on each other. It has been shown (*24*) that CO_2 adsorbs selectively on the free alumina surface (and not on the molybdena surface). Thus, the fraction, *f*, of free alumina surface was calculated from

$$f = V_{\text{cat}}/0.88V_{\text{supp}}, \qquad (1),$$

where V_{cat} and V_{supp} are the micromoles of CO_2 chemisorbed per gram on the catalyst and on the alumina support pretreated in the same way, respectively, and the factor 0.88 is the weight fraction of support in the catalyst.

The irreversible NO chemisorption was determined at −78 and 24°C. To observe small amounts of N_2 and N_2O formed (due to oxidation of the catalysts) the following procedure was used. A known amount of NO (excess) was admitted to the reactor which contained ~100 mg of the pretreated catalyst at −78°C. After 40 min, the gas phase was flushed with ultrapure helium onto a silica gel trap thermostated at −196°C. Flushing was continued for 15 min before the collected sample was released onto a gas chromatographic column where it was separated and measured using a conventional thermal conductivity detector. Three columns in series were required to separate the NO from its reduction products (N_2 and N_2O). A $\frac{1}{8}$ in. × 10 ft stainless-steel column packed with 30/60 mesh 5-Å molecular sieve was followed by a $\frac{1}{8}$ in. × 8 ft column packed with 80/100 mesh Porapak R joined to a $\frac{1}{8}$ in. × 10 ft column packed with Porapak R coated with 10% polyethyleneimine. All three columns were needed to separate N_2 from NO. For the determination of the N_2O the molecular sieve column was bypassed and only the Porapak columns were used. The column temperature was 40°C.

After this analysis was completed, a second inlet of NO (to approximate the original amount) was admitted at −78°C and the whole procedure repeated. Very little more NO was chemisorbed in this step (≤5%). Now a third inlet of NO was made at −78°C; then the catalyst vessel was isolated and the temperature was raised to 24°C (water bath). After a reaction time of 1 hr, the gaseous products were flushed onto the columns and the analytical procedure was repeated. Finally, a fourth inlet of NO was made, this time at 24°C, and the cycle repeated. Very little further reaction or chemisorption was observed in this step, but the increments were taken into account. Finally, the sample was flushed with He as the temperature was slowly raised to 530°C (about 1 hr) and held at this temperature for an additional hour while the desorbed gases were collected in the traps and analyzed as before. Mass balances on the nitrogen were then determined.

The data from the NO experiments were treated as follows: the amount of each recovered product (NO, N_2O, and N_2) was determined separately by GLC. Then, the mass balance equation was used to determine the chemisorption, i.e.,

$$(NO)_0 = 2(N_2O) + 2(N_2) + (NO)_g + (NO)_{ch}, \qquad (2)$$

where $(NO)_0$ is the number of micromoles of NO initially in contact with the catalyst, $(NO)_g$ the number of micromoles of NO left in the gas phase after the chemisorption process, (N_2O) the micromoles of N_2O, and (N_2) the number of micromoles of N_2 produced by oxidation of molybdenum. The last three quantities were calculated from the chromatogram. Given these quantities, the amount chemisorbed $(NO)_{ch}$ could be calculated. It should be noted that the number of O atoms deposited on the catalyst by reoxidation of the Mo is equal to (N_2O) plus $2(N_2)$ and that these were zero for experiments at −78°C.

When the catalyst sample was ramped in He up to 530°C while the desorbed products were collected and subsequently analyzed chromatographically, the amount of NO "recoverable" by heating could be determined and compared with $(NO)_{ch}$, i.e.,

$$(NO)_{ch} \text{ vs } (NO)_d + 2(N_2O)_d + 2(N_2)_d, \quad (3)$$

where $(NO)_{ch}$ was the cumulative chemisorption determined at the end of the experiments at 24°C and $(NO)_d$, $(N_2O)_d$, and $(N_2)_d$ are the micromoles of each gas desorbed in the process described above.

Chemisorption of NO on the support (*60, 61*) was not negligible, especially for the higher reduction temperatures. Hence, blanks were determined for the support pretreated in the same way as the catalyst. Correction was then made by taking into account the fraction of exposed alumina surface derived from Eq. (1),

$$(NO)_{Mo} = (NO)_{ch} - 0.88f(NO)_{Al} \quad (4)$$

where $(NO)_{Al}$ is the number of micromoles of NO held by the alumina surface per gram after identical pretreatment procedures, f is the fraction of free alumina surface as determined by Eq. (1), and $(NO)_{ch}$ is the micromoles of strongly chemisorbed NO determined from Eq. (2). Given these data, the NO strongly chemisorbed on the molybdena sites $(NO)_{Mo}$ could then be calculated; i.e., $(NO)_{ch}$ could be corrected for the NO adsorbed on the exposed alumina surface.

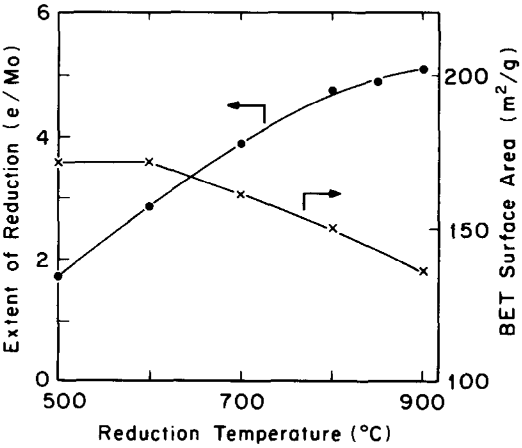

FIG. 1. Variation of the extent of reduction, e/Mo, ●, and the BET surface area, ×, with the temperature of reduction.

RESULTS

Hydrogenation of benzene. The hydrogenation of benzene to cyclohexane is favored thermodynamically at all temperatures below about 280°C. Most of the present studies were made at 100°C. Previous work (*62*) had shown that the benzene could not be hydrogenated in this temperature range at $P_{H_2} \approx 1$ atm over reduced or sulfided catalysts prepared in the usual ways. On the other hand reports exist (*56*) showing that benzene can be hydrogenated under comparable conditions over catalysts prepared by decomposition of $Mo(CO)_6$ onto alumina supports. Therefore the effect of raising the reduction temperature with our catalyst was investigated with Yao's work (*9*) in mind. The variations in the extent of reduction and BET surface area with reduction temperature are shown in Fig. 1. Evidently considerable Mo^0 must be present at 800°C and above. The surface area loss was more modest, i.e., ~20%.

The experimental data for benzene hydrogenation obtained from catalysts reduced at successively higher temperatures are summarized in Table 1. These results show that catalysts reduced at temperatures up to 700°C do not hydrogenate benzene at $P_{H_2} = 0.36$ atm. Significant conversions first appeared when the catalyst was reduced at 800°C and these increased steeply between 800° and 900°C.

Oxygen chemisorption. Oxygen chemisorption data for these preparations are presented in Fig. 2 where comparison is made with more limited data taken from the literature. At $e/Mo \geq 3$, the chemisorption corresponded to about $O/Mo = 0.5$. It must be borne in mind, however, that at these high extents of reduction more than one O may be adsorbed per Mo site. The sulfided catalyst had a relatively low oxygen che-

TABLE 1

Hydrogenation of Benzene over Reduced Molybdena–Alumina Catalysts (200 mg) as a Function of Extent of Reduction (*e*/Mo)[a]

Reduction temp. (°C)	*e*/Mo	Conversion of benzene			O_2 chemisorption (atoms $g^{-1} \times 10^{-20}$)
		(%)	Molec. sec^{-1} $g^{-1} \times 10^{-16}$	TOF[b] (sec^{-1} $Mo^{-1} \times 10^{3}$)	
500	1.7	0	0	0	1.00
600	2.8	0	0	0	2.50
700	3.9	0	0	0	2.85
800	4.7	1.2	1.8	0.03	2.83
850	4.9	3.3	4.3	0.08	2.85
900	5.1	36	56	1.1	2.50

[a] Conversion of benzene was measured at 100°C after 1 hr in a stirred static reactor; molar ratio $C_6H_6 : H_2$ was 1 : 10; *e*/Mo is the average number of electrons the Mo has been reduced below Mo^{6+}.

[b] Turnover frequencies based on total Mo in reactor. For comparison values of 6.5×10^{-3} and 5.3×10^{-2} molec./sec/ Mo(atom) were reported in Ref. (*70*) for catalysts prepared from $Mo(CO)_6$/dehydroxylated Al_2O_3 (1000°C) reduced at 600 and 1000°C, respectively.

misorption (■) until excess S was removed by H_2 treatment; then (■) it approached the curve defined by the remaining data. These data adequately define a common curve with the previously published data (*10, 11, 19*), all of which were obtained with lower values of *e*/Mo. The data of Weller *et al.* (*10*) were converted into O/Mo and *e*/Mo before plotting. Several other papers (*12–16*) have dealt with the oxygen chemisorption, but these results could not be included in Fig. 2, because *e*/Mo values were not available.

The data of Fig. 2 show a maximum (O/Mo = 0.57) in the range 3.9 < *e*/Mo < 5.0 or at reduction temperatures between 700 and 850°C, but the ratio decreased again when the catalyst was reduced at 900°C. When *e*/Mo ≥ 3 it seems reasonable to suppose that a portion of the molybdenum has become metallic and that sintering of the metal surface area was responsible for the leveling and decrease in activity at higher extents of reduction. These data (also listed in Table 1) showed no relationship with the benzene hydrogenation data, in contrast with the earlier results for hydrogenation of simple olefins (*4, 11, 23, 24*) and for HDS (*12*). Clearly an additional requirement exists for benzene hydrogenation and the data suggest that this is the presence of metallic Mo.

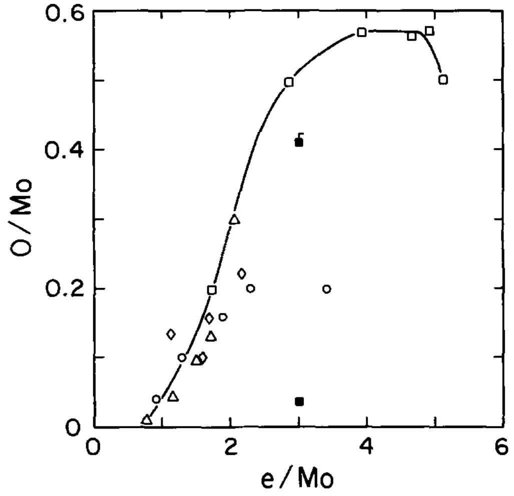

FIG. 2. Relationship between oxygen chemisorption (O/Mo) and the extent of reduction (*e*/Mo). In the present work, □, the chemisorption, was measured at −78°C by the method of Weller *et al.* (*10*). These data are compared with literature data; △, at −196°C, Weller technique (*11*); ○, at −78°C, pulse technique (*19*); ■, sulfided catalyst which received standard pretreatment and, ■, sulfided Mo/Al_2O_3 (above) after treatment with flowing hydrogen at 500°C after the sulfiding; ◇, reduced catalyst, taken from (*8*).

TABLE 2

CO_2 and NO Chemisorptions on the Alumina Support[a]

Pretreat. temp. (°C)	Amount adsorbed (μmol/g of alumina)			
	CO_2 at 24°C[b]	CO_2 at 24°C[c]	NO at −78°C[d]	NO at 24°C[e]
500	168	168	294	176
600	203	203	273	214
700	158	159	327	257
800	102	103	372	260
900	60.7	60.6	301	247

[a] The Al_2O_3 used was ~100 mg Ketjen CK-300. The pretreatment consisted in calcination under dry O_2 for 12 hr at 500°C followed by evacuation at each of the higher temperatures for 120 min.

[b] Total micromoles of CO_2 adsorbed per gram of alumina measured volumetrically by the method of Ref. (*63*).

[c] Total micromoles of CO_2 adsorbed per gram of alumina measured by heating the sample at 500°C for 20 min after the adsorption process, collecting the CO_2 evolved in a trap at −196°C, and measuring it in the burette system (*63*).

[d] Total micromoles of NO chemisorbed per gram of alumina at −78°C. (Reference blank for correction of catalyst data.)

[e] Total micromoles of NO chemisorbed per gram of alumina at 24°C. (Reference blank for correction of catalyst data.)

Chemisorption of CO_2. This was used to estimate the fraction of uncovered support surface area (*23, 24*). Data collected at room temperature from the alumina support and the 8% molybdena–alumina catalyst are summarized in Tables 2 and 3, respectively. For the alumina (Table 2) the CO_2 chemisorption, in agreement with previous work (*60*), first increased modestly and then decreased sharply as the pretreatment temperature passed through 600°C. For the molybdena–alumina catalyst (Table 3) the uptake of CO_2 behaved similarly, but with a continuous increase in the fraction of free alumina surface with reduction temperature.

TABLE 3

Determination of the Fraction of Free Alumina Surface on the 8% Molybdena–Alumina Catalyst by CO_2 Chemisorption[a]

Reduct. temp. (°C)	CO_2 chemisorption[b] (μmol/g)	Fraction[c] free alumina surface area of the support
500	89.6	0.61
600	140	0.78
700	121	0.87
800	79.5	0.88
900	50.7	0.94

[a] After final reduction at listed temperatures.

[b] Micromoles of CO_2 adsorbed per gram of catalyst measured volumetrically according to Ref. (*63*).

[c] Calculated as $f = V_{cat}/0.88V_{supp}$ where V_{cat} is $\mu mol/g_{cat}$, and V_{supp} is $\mu mol/g_{Al_2O_3}$ (Table 2).

Chemisorption of NO. This was determined for the alumina support and the molybdena catalyst at −78 and 24°C. These data are summarized in Tables 2 and 4, respectively. For the support, the NO uptake at −78°C was erratic, but fairly constant. Like the molybdena–alumina catalyst, however, the total adsorptions tended to pass through a maximum at intermediate reduction temperatures. The corrected values (for NO adsorbed only on the molybdena) showed similar trends. Interestingly, approximately 25% of the total molybdenum ions of the catalyst reduced to $e/Mo \approx 2$ at 500°C [from Table 4—398/(2 × 833)] were holding $(NO)_2$ pairs (*20, 21*), i.e., an order of magnitude higher than reported for catalysts reduced much less extensively (*18*). This fraction was further increased by a few percent by reduction at higher tem-

TABLE 4

NO Chemisorption on the 8% Molybdena–Alumina Catalyst as a Function of the Reduction Temperature[a]

Reduction temp. (°C)	NO adsorption (μmol/g catalyst)				
	Total ads. (−78°C)[b]	Corrected for ads. on support (−78°C)[c]	Total ads. at (24°)[d]	Corrected for ads. at 24°C on support[e]	O atoms[f] deposited (24°C) (μmol/g)
500	556	398	414	320	166
600	660	473	512	366	294
700	741	488	422	225	348
800	728	440	418	217	370
900	500	251	312	108	270

[a] For details on the reduction procedure, see text. The 8% Mo catalyst contains 833 μmol of Mo/g_{cat}.

[b] Total micromoles per gram of NO chemisorbed on the catalyst at −78°C.

[c] Corrected for adsorption on the support using Eq. (4), i.e., micromoles per gram of NO chemisorbed on the molybdena phase at −78°C.

[d] Total micromoles of NO per gram chemisorbed per gram of catalyst at 24°C.

[e] Corrected for adsorption on support using Eq. (4), i.e., micromoles of NO chemisorbed on the molybdena phase at 24°C.

[f] Obtained from $N_2O + 2N_2$ formed at 24°C.

peratures, but fell precipitously (to ≈15%) when the temperature was increased to 900°C.

The chemisorption values deduced (after correction for the support and for gas consumed in oxidizing the Mo ions) were much lower at 24°C than at −78°C. Evidently, the total number of chemisorption sites is reduced by oxidation of the molybdenum, but not on a 1 : 1 basis. The simple model (*28*) (oxidation of lower valent molybdenum to Mo^{4+} followed by chemisorption of NO as dinitrosyl on these same centers) does not appear to hold.

The results of the experiments in which the NO chemisorbed at 24°C is desorbed or decomposed by heating to 530°C in a stream of He are summarized in Table 5. Except for the catalyst reduced at 900°C, the total amounts (last column, Table 5) of NO recovered (as NO, N_2O, and N_2), although systematically lower, agreed within 10% with the strongly chemisorbed NO values at 24°C (second column). The results for the catalyst reduced at 900°C were very different since only 55% of the NO chemisorbed at 24°C could be accounted for after heating the sample at 530°C. The results for this catalyst invariably were out of line with the remainder of the data, strongly suggesting that it differed in some important way from the rest of the preparations.

Reduction of NO. Table 6 lists the products recovered after heating systems from −78 to 24°C. NO is reduced as the catalyst is reoxidized. This redox process was not observed for the chemisorption of NO at

TABLE 5

Comparison of the Recovered NO Products with that Chemisorbed[a]

Reduct. temp. (°C)	Total ads. at 24°C (μmol NO/g)	Products desorbed to 530°C as micromoles of NO per gram of catalyst			
		NO	N_2	N_2O	Total
500	414	162	140	76	378
600	512	—	—	—	—
700	422	175	136	69	380
800	418	182	136	59	377
900	312	91	61	20	172

[a] Micromoles of NO per gram of catalyst desorbed as NO, N_2, and N_2O while heating the catalyst after NO adsorption up to 530°C in a He stream (60 cm^3/min) at about 4°C/min.

[b] Taken from column 4 of Table 4.

TABLE 6

Products Obtained from the Reduction of NO at 24°C on the 8% Molybdena–Alumina Catalyst Reduced to Varying Extents at Varying Temperatures[a]

Reduct. temp. (°C)	μmol N_2O/g[b]	μmol N_2/g[c]	Initial[d] oxidation No.	δ(e/Mo)[e]	Final[f] oxidation No.
500	110	28	4.2	0.4	4.6
600	166	64	3.1	0.7	3.8
700	180	84	2.1	0.8	2.9
800	170	100	1.2	0.9	2.1
900	99	36	0.9	0.4	1.3

[a] See Fig. 1 for corresponding *e*/Mo values. Products were collected from a flowing He stream on a silica gel trap at −78°C, then flashed, and measured.

[b] Micromoles of N_2O formed per gram of catalyst at 24°C measured chromatographically.

[c] Micromoles of N_2 formed per gram of catalyst at 24°C measured chromatographically.

[d] The average oxidation number is defined as 6-*e*/Mo. The initial *e*/Mo were measured by complete reoxidation of duplicate preparations (Fig. 1).

[e] δ(*e*/Mo) were determined from amounts of N_2O and N_2 recovered and used to calculate the final oxidation number. See Eqs. (5 and 6).

[f] Sum of columns 4 and 5.

−78°C. Formation of both products (N_2O and N_2) increased with the reduction temperature up to 800°C, but fell precipitously for the catalyst reduced at 900°C. The extents of reoxidation, δ(*e*/Mo), were calculated from the oxygen atoms deposited on molybdenum (last column of Table 4). The final oxidation numbers are given in the last column of Table 6. The initial values of extents of reduction $(e/\mathrm{Mo})_i$ were obtained from the amounts of oxygen required to completely reoxidize the catalysts (Fig. 1), and the final values by correcting for reoxidation by NO. Clearly, the changes in ON brought about by these reoxidation processes, while significant, were much smaller than the changes already obtained in the initial reductions in H_2. On the other hand, presumably the catalytic sites were oxidized selectively.

The dependencies of the (NO)/Mo (−78°C) and (NO)/O_2 chemisorption ratios on *e*/Mo (or oxidation number) are shown in Fig. 3. The previously reported value (*19*) of about 4 for the NO/O_2 ratio for preparations made in the usual way was confirmed, but note the step decreased to about 2.0 as the *e*/Mo increased (or as the oxidation number was decreased) with more severe reduction. Scrutiny of the data shows that this was due to increasing uptake of O_2 as the NO chemisorption was relatively constant (compare Figs. 2 and 3).

DISCUSSION

Catalysts reduced below 600°C, as is the customary procedure, have *e*/Mo ≈ 2; they

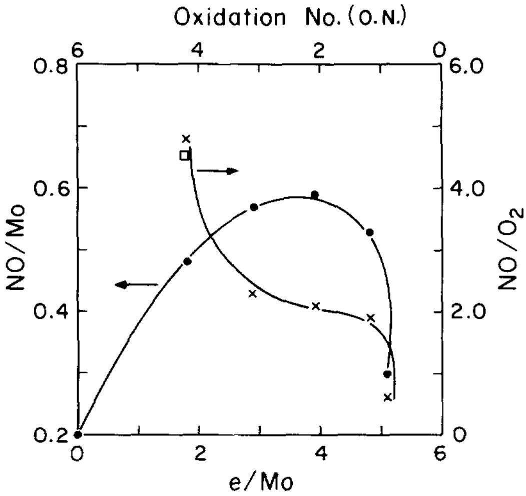

FIG. 3. Ratios of the corrected NO chemisorption at −78°C to total Mo (●) and to the O_2 chemisorption (×) plotted as a function fo the extent of reduction, *e*/Mo. □, Datum taken from Ref. (*17*).

contain mainly Mo^{4+} together with smaller amounts of Mo^{5+} balanced by some lower valence state, but no evidence of Mo(0) or metallic molybdenum has been expected or reported. Indeed the finding of Brenner and Burwell and their co-workers (*7, 56*) that the Mo(0) produced by decarbonylation of $Mo(CO)_6$ is spontaneously oxidized by reducing alumina hydroxyl groups makes it highly unlikely that Mo(0) could exist until or unless the preparation is heated into the range where complete dehydroxylation of the alumina is closely approached, i.e., to temperatures in excess of 800°C in accord with earlier findings (*7, 8*). It is entirely reasonable, therefore, to attribute the onset of the hydrogenation of benzene and the hydrogenolysis of propane and cyclopropane (*57–59*) to the presence of metallic molybdenum. Hence, the former reaction carried out with $P_{H_2} \approx 1$ atm may be used as a sensitive diagnostic test for this metal.

The catalyst reduced at 900°C (e/Mo = 5.1) showed a behavior which was distinct in several respects. Its ability to chemisorb NO was greatly diminished compared with catalysts reduced at lower temperatures (Fig. 3). The oxygen chemisorption (Fig. 2), on the other hand, decreased by only 15% compared with the catalyst reduced at 800°C and was still more than double the amount chemisorbed by the same catalyst reduced at 500°C. These two chemisorptions are thought to measure the same CUS centers. How, then, can this apparent discrepancy be rationalized? The departure in the behavior of these two probes occurred when the molybdena catalyst was reduced into the range (e/Mo $\approx$ 5) where the metallic molybdenum was being produced, and this strongly increased the oxygen uptakes. This was reflected not only in the onset of benzene hydrogenation but also in paraffin hydrogenolysis (*57–59*).

Holl *et al.* (*64*) reported extensive paraffin hydrogenolysis over "clean" evaporated Mo films whereas paradoxically over "reduced powders" paraffin isomerization occurred. The effect of reduction temperature on the behavior of molybdena–alumina catalyst was also studied. According to their analysis, up to and including 750°C, the reaction mechanisms were essentially acidic. On reduction at 950°C, however, the mechanism changed and resembled that recorded for molybdenum powder. Something appears wrong with this analysis. Reduced molybdena-alumina catalysts do not have acidic properties; they do form the metallacyclobutane intermediates (*23*) required for the observed (*64*) paraffin isomerization. Hydrogenolysis is characteristic of clean metal surfaces; metallacyclobutane chemistry occurs on ionic molybdenum. Evidently the "reduced powders" were not clean.

Films of molybdenum metal are known to chemisorb oxygen in substantial quantities, viz., O/Mo = 1.27 (*65*), and 1.5 on the (100) plane of molybdenum (*66*). Brennan and Graham (*67*) obtained a value of $p = 2.3$ at −195°C and $p = 3.0$ at 0°C ($p = N(O)/N(Kr)$, where N(Kr) is the number of krypton atoms present in the physical monolayer and N(O) is the number of oxygen atoms adsorbed by the metallic surface).

Knowledge concerning the chemisorption of NO on metallic molybdenum is incomplete. It is known (*68, 69*) that the adsorption is dissociative at room temperature on clean Mo surfaces, but that its nature is modified by preadsorption of oxygen. This work was done on a wire and on a FEM tip; related work with supported Mo metal, or even with single-crystal Mo surfaces, does not appear to exist. We may suppose, therefore, that a strong molecular chemisorption of NO on metallic Mo cannot occur without first oxidizing the surface. Results soon to be published from this laboratory (*70*) support this view. When a catalyst was prepared by decarbonylation of $Mo(CO)_6$ on completely dehydroxylated alumina (a supported Mo^0 catalyst) a dramatic decrease in the chemisorption (NO/Mo) was observed at −78°C over that on a similar preparation where $Mo(CO)_6$ was reacted with a partially dehydroxylated alumina. Thus, NO may be a very useful probe for assaying the CUS on *ionic* molybdenum (produced at low and intermediate reduction temperatures), but when the metallic state is formed, its value as a diagnostic tool is lost.

As shown in Table 5 the "recoverable" NO (after heating at 530°C) was always about 10% less than that known to be on the catalyst before heating, except for the 900°C reduced catalyst. In this case, only 55% of the chemisorbed NO could be recovered. A possible explanation for this loss of NO from the mass balance is the formation of a molybdenum nitride or oxynitride (*71*). Mo_2N is usually prepared from the reaction of molybdenum metal (or MoO_3) with NH_3 at temperatures above 520°C. In our case, only once the metallic state has been formed (and only after this stage) would the formation of these compounds be possible.

The onset of catalytic activity for the hydrogenation of benzene (Table 1) did not follow the chemisorption data, indicating that the basic reason for the increase in activity for the catalysts reduced at high temperature (900°C) is not the number, but the nature of the sites. This result points to the creation of a new kind of site responsible for this reaction, one which is not required for hydrogenation of simple olefins. The extensive literature (*29–50*) regarding high activity of transition metals for the hydrogenation of benzene affords a ready explanation.

In order to estimate the amount of molybdenum in an "oxidizable form" (low oxidation state molybdenum) the following assumptions were made: (a) the final oxidation state of the oxidized molybdenum species is Mo^{4+} (*21, 28, 72*), and (b) the initial oxidation state was either Mo^0 or Mo^{2+}. From the total oxygen atoms deposited on the catalyst ($[N_2O] + 2[N_2]$), the number of electrons transferred during the redox process can be calculated. With the assumptions made, the percentage of the total molybdenum which is oxidizable can then be estimated; the results are listed in Table 7 for each assumption. Rough agreement with the data of Fig. 2 was obtained on the basis that the initial state was Mo^{2+}. The data suggest a definite increase in the percentage of oxidizable Mo as the temperature of reduction is increased up to 800°C. Thus, the problem of titrating only the catalytic sites becomes complicated by reoxidation when it occurs. This probably cannot be avoided with either O_2 or NO. The corrected amount of chemisorbed NO at −78°C (Table 4) showed a similar trend.

TABLE 7

Estimation of the Fraction of Low Valent Molybdenum after Reduction at Varying Temperatures[a]

Reduct. temp. (°C)	*e*/Mo	Oxygen supplied[b] (μmol/g) ($\{N_2O\} + 2\{N_2\}$)	Oxidizable Mo (%)[c]	Oxidizable Mo (%)[d]
500	1.7	166	10.0	20.0
600	2.8	294	17.6	35.2
700	3.9	348	20.9	41.8
800	4.7	370	22.2	44.4
900	5.1	270	16.2	32.4

[a] Calculated from oxygen deposited on catalyst by reduction of NO based on total Mo.

[b] Oxygen atoms ($\mu mol/g_{cat}$) deposited on the catalyst by reoxidation of the molybdenum by reaction with NO at 24°C. (See Table 4.)

[c] Percentage of oxidizable Mo assuming an initial oxidation state of zero and a final state of four.

[d] Percentage of oxidizable Mo assuming an initial oxidation state of two and a final state of four.

These results suggest that at this temperature the NO chemisorption may be a fair measure of the total coordinatively unsaturated sites (molybdenum ions with oxidation states of 4+, or lower). When the temperature is raised to 24°C (Table 7) a fraction of these becomes oxidized, presumably the lower states. Thus, some NO is consumed by reduction and some is used by additional chemisorption on the oxidized sites, but as noted earlier this cannot be a simple stoichiometric process. It should be emphasized that molybdena–alumina catalysts after milder reductive pretreatments would be less affected by this complication and thus yield more meaningful results (*19, 20, 23, 24, 74*). For the catalyst reduced at 900°C an unexpected decrease in the amount of oxidizable molybdenum was observed. Possibly this can be attributed to the formation of metal crystallites.

Finally a word of caution is needed regarding the method used in this work to obtain the NO data in making comparisons with data obtained using other procedures. The redox reaction is surely a rate process affected by the external variables. In earlier work (*19, 24, 73, 74*) carried out under conditions less favorable for oxidation, no NO reduction products were detected for catalysts reduced at temperatures up to 600°C. In the present work, a static system was used (long contact time) and provisions were made to analyze the total sample, not an aliquot; therefore very small amounts of N_2O and N_2 could be detected. Others (*10, 15, 16, 19*) have noted that variable results can be obtained for both NO and O_2 chemisorption depending upon the experimental technique employed, e.g., passing small pulses vs static experiments or dry ice vs room temperature. Indeed, the XPS data of Shuxian *et al.* (*22*) indicated dissociation of NO on MoS_2 at $T > 130$ K. The present work points out an additional complication, viz., the effects of forming substantial quantities of molybdenum in valence states lower than Mo^{4+}. It should be emphasized also that the new insight provided by the present work does not alter some of the major conclusions reached earlier, e.g., that NO adsorbs on CUS capable of holding two molecules and which activate H_2 and catalyze hydrogenation and cyclopropane isomerization. It is the quantitative aspects which are affected and for conventional catalysts reduced or sulfided at 500°C or below, the error may be no more than 20%.

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