

The Chemisorption of O₂ and NO on Reduced and Sulfided Molybdena–Alumina Catalysts

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The chemisorptions of O₂ and NO were investigated at –78°C and at room temperature using pulse-flow and volumetric techniques. The oxygen chemisorption was fast and irreversible while the NO chemisorption, after a fast initial process, increased slowly with time. This latter portion could be removed by evacuation and readsorbed or replaced with O₂. The strong NO chemisorption was approximately four times larger than that of O₂. Infrared spectra showed that the strongly chemisorbed NO was present in pairs, suggesting that the oxygen chemisorption was as atoms. The interference of one chemisorption by the other was studied. The introduction of O₂ did not affect the strongly chemisorbed NO whereas approximately one NO molecule was chemisorbed per oxygen atom on the oxygen saturated surface. This process was also observable in the infrared spectra. A characteristic pair of bands at 1817 and 1713 cm⁻¹ which appeared on chemisorption of NO on the reduced catalyst (and at 1795 and 1704 cm⁻¹ on the sulfided catalyst) have been assigned to a dinitrosyl species or NO dimer. These bands were unaffected when O₂ was admitted to the system. On the other hand, when the NO was admitted to an oxygen-covered surface the same bands appeared but with much lower intensities. As previously reported, both chemisorptions were correlatable with the anion vacancy concentration. The results could be rationalized by assuming that these chemisorptions took place on Mo²⁺ centers (two anion vacancies on the same Mo). Sulfided catalysts produced nearly identical results.

INTRODUCTION

Interest in the selective chemisorption of O₂ (1–28) and of NO (26–35) on promoted and unpromoted molybdena–alumina catalysts (reduced or sulfided) as well as on MoS₂ has quickened in recent years. This interest has been stimulated by several factors. First, correlations have been established between the extent of chemisorption and catalytic activity for hydrogenation (17, 21, 26), dehydrogenation (6), and for HDS (9–20, 28); similar correlations have been made (7, 21, 26, 31) with the degree of coordinative unsaturation of the molybdenum ions (CUS). That they are selective to the catalytically active sites has been established by poisoning experiments (26, 27)

and is supported by the relatively small fraction of the total molybdenum ions which are involved. Additional evidence has been furnished by studies of the effect of these chemisorptions on the subsequent adsorption of H₂ (22, 27, 36). Finally, they yield spectroscopically observable species: NO by ir (29–33, 35, 37) and O₂ by EPR (23–25).

Catalytic intermediates can seldom be studied directly because of their facile nature, low concentration, and because of interfering bands from other adsorbed materials. The study of strongly chemisorbed poison molecules held selectively on the catalytic centers affords the possibility of gaining insight into their chemical and physical nature. Both O₂ and NO fulfill this role, but difficulties in interpretation remain. For example, the chemisorption of NO is several times larger than for O₂ (27) yet both correlate with catalytic activity

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and act as poisons for reactions at low temperature (where the poison is stable in H₂). The possible interaction of one chemisorption with the other has so far not been tested. It is the subject of this report.

Parekh and Weller (1) considered a reduced molybdena-alumina catalyst as a supported microcrystalline MoO₂ (1-6). They adopted a technique devised by Brunauer and Emmett (38, 39) to measure the "equivalent molybdena surface" by the selective chemisorption of O₂. This model was at variance with current ideas concerning the formation of an epitaxial monolayer of molybdena on alumina by replacement of the alumina hydroxyl groups. Based on this model our studies of the reduction process (50, 51) with its concomitant development of coordinative unsaturation of the transition metal ions led us to suggest that the chemisorptions were site selective (21). Correlations were demonstrated between oxygen chemisorption and the extent of reduction and with the anion vacancy concentration, \square , as measured by the oxygen atoms removed as H₂O on reduction. The latter was linear, but had an intercept on the abscissa which suggested that the first 20% of the O removed did not produce sites for chemisorption. Finally, a linear correlation was demonstrated between the rate of propylene hydrogenation at room temperature and the oxygen chemisorption (26). A similar correlation between the catalytic activity for HDS and oxygen chemisorption was first reported by Tauster *et al.* (10); significantly, their data did not correlate with the surface areas of their MoS₂ preparations.

More recent attempts to correlate O₂ chemisorption with catalytic activity have met with diverse results. It has been reported (9), for example, that on one series of catalysts a linear correlation was obtained for olefin hydrogenation, but not for HDS where nevertheless a monotonic increase was obtained. Another study (20) revealed no correlation at all for a variety of supported molybdena catalysts of varying

composition, promoter concentration, preparation procedures, and supports. It is evident, for example, that cobalt molybdena-alumina catalysts and unpromoted molybdena-alumina have similar oxygen chemisorptions (7, 9) whereas they differ by nearly an order of magnitude in catalytic activity for HDS. It is suspected, therefore, that the chemisorption may measure a number of sites but not the specific activity per site.

Millman and Hall (29) and Peri (37) independently reported that NO adsorbed on reduced molybdena-alumina catalysts in pairs, i.e., as a dinitrosyl species or an NO dimer. A similar earlier discovery was made for chromia-alumina catalysts by Kugler *et al.* (40, 41) who attributed their results to a somewhat different dimeric species than envisioned by Peri. Whatever the exact nature of the species Millman and Hall (21) concluded that oxygen and NO chemisorbed on the same sites, viz., multiply coordinatively unsaturated Mo ions of low valence state. Interestingly, the chemisorption of NO and CO both correlated linearly with the anion vacancy concentration and both yielded the same intercept on the abscissa in the chemisorption of O₂ (26). Moreover, all three gases acted as poisons for olefin hydrogenation at room temperature. The chemisorptions were small but selective; they involved only a few percent of the total Mo present. It was established (31) that the NO adsorbed on the molybdena portion of the surface, but not on the alumina.

The chemisorption of either NO or oxygen on reduced molybdena-alumina catalysts in amounts equivalent to the lethal dose for low temperature hydrogenation were found to have profound effects (22, 27) on the adsorption of H₂ at a temperature of liquid nitrogen. The "chemisorbed" amount was greatly reduced. The effect on the NMR signal was even more dramatic (27). Its properties were changed from those corresponding to hydrogen adsorbed on the reduced catalyst to those of the unre-

duced catalyst by an amount of oxygen equivalent to only a trivial change in the extent of reduction. Further evidence (22) suggested that the dissociative chemisorption of H_2 was eliminated by the poison.

Studies involving unsupported MoS_2 have provided new perspectives. This material crystallizes in the chalcogenide structure consisting of broad basal planes of sulfur atoms with layers of Mo atoms in between. Coordinatively unsaturated centers can occur naturally at the edges. By variation of the ratio of the edge area to the basal plane area, Tanaka and Okuhara (42) related olefin isomerization and hydrogen exchange to the edge sites and acidic properties to sites on the basal planes. Stevens and Edmonds (13) reported that the hydrodesulfurization of thiophene did not correlate with a high density of edge planes although hydrogenation did. Moreover, their ESCA data, when correlated with measurements of the chemisorption of butanol, indicated that O_2 probably was chemisorbed at the edge planes. Chianelli and Tauster (12) expressed reservations concerning the validity of the former conclusion and rebuttal was offered by Stevens and Edmonds (14). Chadwick and Breysse (11) presented a compromise picture in which it was supposed that H_2 is dissociated at edge sites, but that this is followed by spillover of H atoms onto the basal planes where hydrogenation of thiophene takes place. Interestingly all parties agree that both O_2 and H_2 are chemisorbed (presumably dissociatively) at the edge sites where olefins may be hydrogenated at low temperatures.

Given the chalcogenide structure it is important to understand how the edge sites may be terminated. Tanaka and Okuhara (42) have advanced the picture that multiple coordinative unsaturation is present at the edges in different degrees depending upon pretreatment, etc. Evidently local electrical neutrality is maintained by producing molybdenum ions of valence state lower than Mo^{4+} . Thus, Mo^{3+} or Mo^{2+} would correspond to sites having one, two,

or three coordinatively unsaturated centers, *vide infra*. Similar mixed low valence states have been considered as catalytic centers for supported chromia catalysts (43-46).

EXPERIMENTAL

Catalysts and pretreatment. The same catalyst (8% Mo on Ketjen CK-300 γ -alumina) was used as in much of our previous work. To minimize ambiguity in the spectroscopic measurements, however, model catalysts made by our equilibrium adsorption method (48, 49) were also employed. Before reduction or sulfiding, the catalysts were treated in flowing oxygen overnight at the selected temperature (400 to 700°C). The catalysts were then reduced with H_2 at a flow rate of about 70 cm^3 (NTP)/min for from 0.5 to 2.0 h at this temperature. These variations allowed the extent of reduction to be controlled over the desired range. The latter was not determined exactly; instead the anion vacancy concentration, \square/Mo , was determined from the amount of H_2O produced in the reduction. This parameter increased monotonically with the extent of reduction, e/Mo , but differed from it by the hydroxyl groups produced and retained by the catalyst on reduction with H_2 . Hall and Lo Jacono (50) reported that when $e/Mo = 1$, $\square/Mo = 0.25$, but when $e/Mo = 2$, $\square/Mo \approx 1$. On the basis of the epitaxial monolayer model (50, 51) \square/Mo was readily interpretable as the oxygens missing from the capping layer of the surface bound molybdena. For reasons summarized in a recent review (52), this model has been found to provide an unacceptable description of the surface chemistry. It is now thought that the raw catalyst consists of small patches of the surface-bound polymolybdate ions which on reduction reorganize into submicroscopic crystallites of surface-bound MoO_2 (or MoS_2) containing seven or so Mo ions. Because of the structural rearrangement which must take place, the interpretation of \square/Mo is nebulous. We use it here as a rough measure of the CUS around

the molybdenum ions because it is easily measurable and because many earlier correlations have been made with this parameter.

Catalysts which had already been reduced as described above were sulfided in a mixture of 10% H₂S in H₂ at 350°C for 4 h. The catalyst was then purged in helium at 500°C for an additional hour. A description of the changes occurring during this process and the method of calculation of □/Mo for these catalysts will be given elsewhere (53).

Static adsorption measurements. Studies were made at room or dry-ice temperature using a standard BET system. The two isotherm method of Weller was adopted for measurements of O₂ chemisorption. For NO, equilibrium isotherms could not be obtained; after a fast initial uptake a slow, zero-order process was observed; the amount adsorbed thus increased very slowly for at least several days (31). The initial chemisorption at room temperature was derived by the method of Segawa and Hall (31), *vide infra*.

Because of the possibility of a slow oxidation process at higher temperatures, the oxygen chemisorption values were obtained at -78°C. Several indications of this reaction exist in the EPR (24) and chemisorption (1) literature. Sulfided catalysts afford additional opportunities for oxidation (8, 9, 17-20). At -78°C, after a fast initial uptake, the amount adsorbed did not increase further with time.

Gases. The O₂ and NO were research grade gases obtained from Linde; the specified purities were 99.5 and 98.5%, respectively. The chief impurities in the O₂ and in the NO were N₂ and CO₂. They were further purified by repeated freeze-pump-thaw evaporation cycles at 78 K. Flowing O₂, when required, was passed through a series of columns filled with activated 13X molecular sieves, CaCl₂, Mg(ClO₄)₂, and ascarite. The H₂ and He were passed through commercial diffusers; the impurity of these was estimated to be about 1 ppb.

The 10% H₂S/H₂ mixture was a Matheson premixed gas.

Pulse adsorption experiments. Repeated pulses containing about 10 μmol of O₂ or NO were introduced from a 0.25-cm³ sample loop into a purified He stream flowing at ~60 cm³/min over ~1 g of catalyst at -78°C. The unadsorbed effluent gas was collected in a silica-gel trap downstream at -195°C. Pulses were repeated at about 2-min intervals and after every 2 or 3 pulses the amount collected was determined by flashing through a thermal conductivity detector. The adsorbed amount was calculated as the difference between gas input and that recovered. After several pulses the peak areas became constant, but nevertheless indicated that a small fraction of each pulse was being adsorbed. This process may be regarded as similar to the slow isothermal uptake of NO, but was much smaller and less important, *vide infra*.

In pulse experiments no O₂ desorption was detectable in 30 min in contrast with the NO adsorption.

Infrared measurements. Spectra were recorded at room temperature using a Nicolet MX-1, FT-IR spectrometer. Data were collected for 5 min at 32 scans/min before recording. The cell assembly has been described previously (31); *in situ* treatments of the catalyst wafers were made in various gases, or in vacuum, at elevated temperatures before moving the wafer into the optical cell. For the present experiments, a minor modification made possible adsorption of gases and evacuation at -78°C before recording the spectra. The wafers had a "thickness" of about 10 mg/cm² (face); a catalyst made by our equilibrium adsorption method (48, 49) and having about the same loading (8% Mo) as that used in the adsorption experiments was employed for the spectroscopic studies. Measurements were made in the absorbance mode and the spectrum taken before NO adsorption was recorded and subtracted from that after chemisorption using the spectrometer's self-contained computer. For these experi-

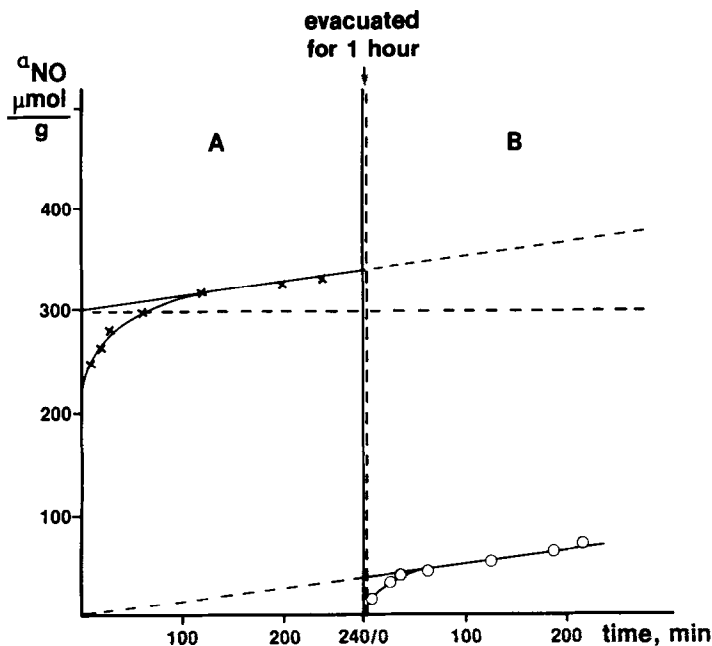


FIG. 1. Adsorption of NO in 100 Torr and 25°C on a sulfided catalyst in a BET system. Reduction was carried out with flowing H_2 at 500°C for 1 h followed by 1-h purging with He at 500°C. ($\square/\text{Mo} \approx 0.5$). This reduction was followed by sulfiding for 4 h at 350°C and for purging 1 h with He at 500°C. (A) Adsorption as a function of time. (B) Adsorption after 1 h evacuation of the NO adsorbed in Experiment A.

ments the catalysts were exposed to about 8 Torr NO for 2 h before a 1-h evacuation to 10^{-6} Torr.

RESULTS

Adsorption Experiments

The typical time dependence of the NO chemisorption at constant pressure over reduced and/or sulfided catalysts is depicted in Fig. 1. Similar results were obtained at room temperature and at -78°C . After the rapid initial uptake, a slow linear zero-order process set in which continued for days (31). Initially it was thought that this process might correspond to a slow reoxidation of the catalyst, but in the present experiments no oxidation products (N_2 or N_2O) were detected in the residual gas after 4 h. Moreover, when at this point the system was evacuated for 1 h and the adsorption repeated with a new sample of gas the data in Fig. 1B were obtained. As shown by the dotted lines, the amount of gas pumped

off matched exactly the amount adsorbed in the second slow process. Thus, the extrapolated intercepts on the ordinate were used to measure the NO chemisorptions. Values obtained in this way are plotted as Curve 1 in Fig. 2 for the catalyst reduced to different extents.

Curve 2 of Fig. 2 was derived from pulse experiments at -78°C , i.e., the irreversible adsorption. The dashed Curve 3 is replotted data (31) taken at 20 Torr in a flow microbalance. In all three cases a linear increase in the NO chemisorption was observed up to about $\square/\text{Mo} = 0.5$ ($e/\text{Mo} \sim 1.3$). At higher extents of reduction these curves leveled indicating a maximum adsorption of about 0.45 NO/Mo. The oxygen chemisorption (Curve 4) behaved in a similar fashion; it showed a maximum chemisorption of about 0.1 O_2/Mo . The ratio of these maxima is 4.5. The O_2 chemisorption shown as the dashed Curve 5 was determined by the pulse technique and is replotted from Ref.

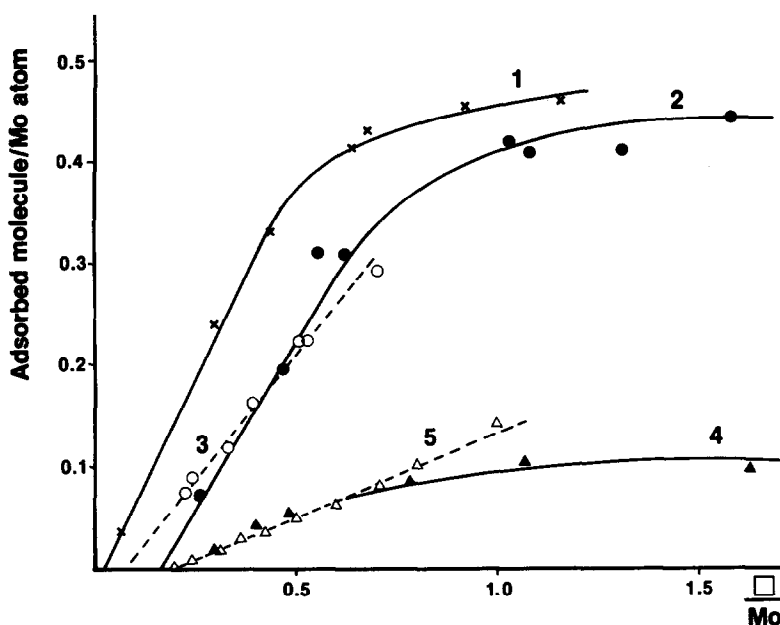


FIG. 2. NO and O₂ adsorption on the reduced catalysts as a function of the vacancy number (\square/Mo). Note that $300 \mu\text{mol/g} \approx 0.4 \text{ molecules/Mo}$. (1) NO = \times , 25°C, 100 Torr, volumetric measurement. (2) NO = \bullet , -78°C, pulse technique. (3) NO = \circ , 25°C, gravimetric measurement at 20 Torr from Ref. (31). (4) O₂ = \blacktriangle , -78°C, pulse technique. \triangle , -78°C, pulse technique from Ref. (21).

(21). The initial slopes of Curves 1, 2, 3 are 0.71, 0.64, and 0.5 NO/ \square , respectively. The initial slope of Curve 4 was 0.16 O₂/ \square . Thus the ratio NO/O₂ as derived from the initial slopes was again around 4, suggesting that an adsorbed dinitrosyl species was approximately equivalent to an adsorbed oxygen atom. For sulfided catalysts the NO/O₂ ratio was also about 4 as with the reduced catalysts. Consistent results were obtained at -78°C (last two entries of Column 5 of Table 1).

Note the intercepts on the abscissa on Fig. 2 which nearly disappeared at high NO pressures. It was first thought that this intercept should be attributed to the absence of sufficient coordinative unsaturation for the formation of dinitrosyl species. However, in the view of the possibility of additional sites being made available by oxygen diffusion (Scheme 1), the smaller intercepts at higher pressures may simply reflect an enhancement of the ease of trapping of CUS, *vide infra*.

Results obtained from pulse experiments over reduced molybdena-alumina catalysts are summarized in Fig. 3, where the residual, irreversible adsorption is plotted against the total adsorbate passed in the series of pulses. In all cases the curves could be divided into two portions: an initial portion of unit slope where all of the gas contained in the pulse was irreversibly chemisorbed and a second portion where part of the pulse desorbed extremely slowly during the time between pulses. The intercept obtained by extrapolation of these two portions shown in Fig. 3A is plotted as a point on Curve 2 of Fig. 2, together with related data for catalysts reduced to varying extents. As is shown in Curves B and C of Fig. 3, similar unit slopes were obtained for O₂ chemisorption, albeit in much smaller amounts. Where comparison could be made, the intercept values were in good agreement with data obtained by the difference between two isotherms at -78°C.

Curves B and C of Fig. 3 record results of

TABLE 1

Volumetric Adsorption Measurements on Reduced and Sulfided Molybdena- γ -Alumina (8% Mo) Catalysts

Adsorbate ^a	Adsorption Temperature (°C)	\square/Mo^b	NO/Mo ^c	NO/Mo ^d
NO	25	0	0.07	0.27
NO	25	0.35	0.26	0.32
NO	25	0.51	0.37	0.39
NO	25	0.87	0.45	0.35
NO	-78	0	—	0.44
O ₂	-78	0	—	0.10

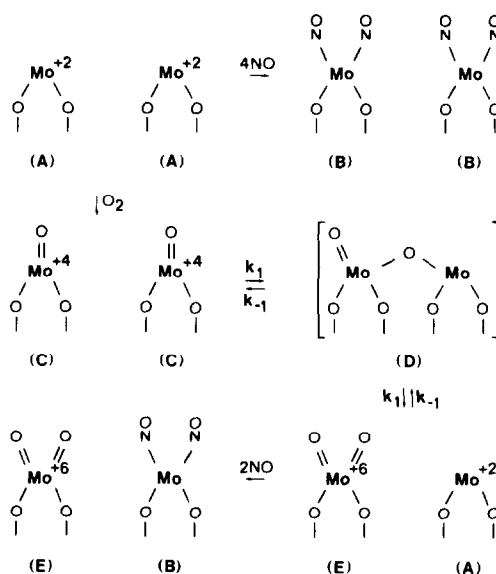
^a The NO adsorption was time dependent and made at 100 Torr. The adsorbed amount was obtained by extrapolation of the linear region to zero time (see Fig. 1). The O₂ adsorption was determined by the double isotherm method (Ref. (6)).

^b The anion vacancy concentration was determined before sulfiding. It corresponds to the H₂O produced during reduction.

^c This ratio was determined before sulfiding from the measurements described in footnote *a*; see Fig. 2, Curve 1.

^d NO adsorbed on the sulfided catalysts. Line 6, Column 5 gives O₂/Mo ratio.

experiments where following oxygen chemisorption, pulses of NO were passed over the catalyst. No O₂ was desorbed. The NO chemisorption on the oxygen-saturated surface resembled closely that on the fresh surface: it had a portion where pulses were totally adsorbed followed by a semi-reversible portion, but a significant new relationship became apparent. The ratio of the new NO adsorption to the saturation O₂ chemisorption, *c/b*, was 2.1 in both of the cases. Other determinations gave similar results regardless of variations in \square/Mo . Restated, it has been found that an *additional two molecules* of NO per adsorbed oxygen molecule can be chemisorbed on a surface already presaturated by oxygen chemisorption. In the reverse experiment much smaller amounts of O₂ could be chemisorbed on a surface saturated with NO. However, this could be understood in



SCHEME 1. The species depicted above are not intended to imply a function for the alumina-bound monomeric tetrahedral species frequently used in epitaxyl monolayer models (50, 52). Rather, they are intended to represent pairs of exposed Mo ions at the edges of small clusters of partially reduced, surface-bound, molybdena.

terms of the reversible nature of a portion of the latter as shown in Fig. 1.

Chemisorption data for sulfided catalysts are given in Table 1. In the first four experiments the catalyst was prereduced to varying extents, as indicated in Column 3, before sulfiding. Values corresponding to the NO/Mo values for the reduced catalysts were picked off Fig. 2 and are listed in Column 4 where they may be compared with the experimental values obtained after sulfiding (Column 5). It is apparent that the latter were reasonably constant and did not depend significantly upon whether the catalyst was prereduced before sulfiding or not.

Infrared Spectroscopic Measurements

The spectrum obtained from a wafer reduced for 1 h in flowing H₂ at 500°C is recorded in Fig. 4A. The two bands which have been attributed to either dinitrosyl species (29) or an NO dimer (37) appeared

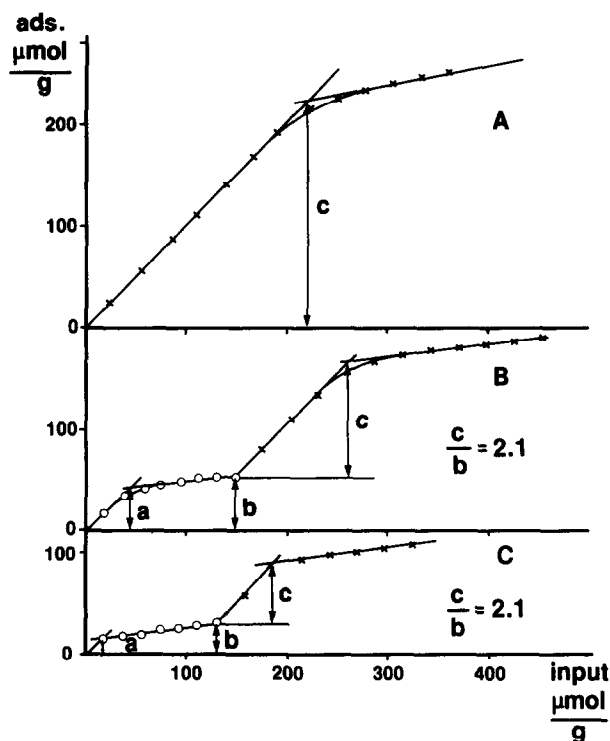


FIG. 3. Adsorbed amount ($\mu\text{mol/g}$) as a function of the amount of adsorbate pulsed through the reduced catalysts ($\mu\text{mol/g}$) at -78°C . (A) NO adsorption on reduced catalyst, $\square/\text{Mo} = 0.62$ (\times). (B) O_2 adsorption on reduced catalyst, $\square/\text{Mo} = 0.50$ (\circ), followed by NO adsorption (\times). (C) O_2 adsorption on reduced catalyst, $\square/\text{Mo} = 0.29$, followed by NO adsorption.

TABLE 2

Infrared Data for NO Adsorption on Reduced and/or Sulfided $\text{Mo}/\text{Al}_2\text{O}_3$ Catalysts^a

Expt. No.	\square/Mo^b	ω_{sym} (cm^{-1})	ω_{antisym} (cm^{-1})	$\frac{I_{\text{sym}}^c}{I_{\text{anti}}}$	θ^d	NO/Mo ^e
1	0.3	1815	1710	0.608	104	0.26
2	0.5	1817	1713	0.626	103	0.37
3	0.9	1820	1715	0.700	100	0.45
4	0	1796	1704	0.539	107	0.27
5	0.3	1795	1704	0.552	106	0.32
6	0.5	1795	1704	0.639	107	0.39
7	0.9	1798	1710	0.611	104	0.35

^a Catalyst loading was 5×10^{20} Mo/g. It was prepared by the equilibrium adsorption method (48, 49, 52). The first three experiments were made with reduced catalysts and the remainder with sulfided preparations.

^b The catalysts were treated as follows. In Experiments 1, 2, and 3, the platelets were reduced in flowing H_2 at 450, 500, and 600°C for 30 min to 1 h and then purged with He for 1 h at the reduction temperature. The catalyst used in Experiment 4 was sulfided without prereduction and purged with He for 1 h at 500°C . Those of 5, 6, and 7 were reduced as in 1, 2, and 3, respectively, before sulfiding at 350°C for 4 h, followed by a 1-h purging at the reduction temperature with He. The approximate vacancy number of the wafer after reduction (or prereduction) was determined in separate experiments as the water produced in reduction under similar conditions.

^c The ratio of the intensities of the symmetric and antisymmetric NO stretching vibrations.

^d The angle, θ , was calculated from $I_{\text{sym}}/I_{\text{antisym}} = \cot^2(\theta/2)$, where θ is the angle between the two NO oscillators.

^e Volumetrically determined NO adsorption in separate experiments after reduction (1, 2, 3) or prereduction and sulfiding (5, 6, 7) [from Table 1].

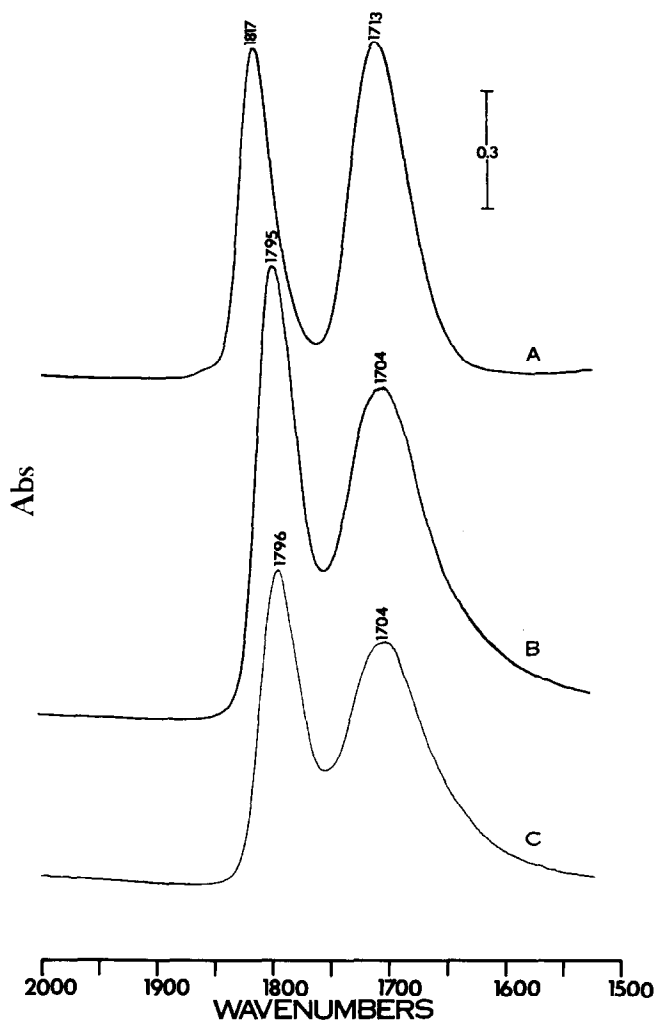


FIG. 4. Spectra of adsorbed NO after 1 h contact followed by 1 h evacuation at room temperature. (A) Catalyst reduced in flowing H_2 at $500^\circ C$ for 1 h followed by 1 h purging with He at $500^\circ C$. (B) Reduced and sulfided catalyst. Reduction as in (A); sulfidation at $350^\circ C$ for 4 h in 10% H_2S/H_2 mixture, followed by a 1-h purge with He at $500^\circ C$. (C) Sulfided as (B) without prereduction.

at 1713 and 1817 cm^{-1} , respectively. Similar spectra were obtained from catalysts sulfided at $350^\circ C$ after reduction (Fig. 4B) or without prereduction (Fig. 4C), but with lower band frequencies, viz., 1704 and 1795 cm^{-1} , respectively. Parameters derived from the ir spectroscopic data are summarized in Table 2.

The interaction between chemisorbed O_2 and NO (and vice versa) was tested. Figure 5A (solid line) is a spectrum from NO adsorbed on a reduced catalyst. Oxygen was

then added and Fig. 5A (dotted line) was recorded. These two spectra when superimposed were found almost identical. The reverse experiment, however, was quite different. When O_2 was chemisorbed before NO was added to the system (Fig. 5B) the spectrum was only about half as intense as without the presorbed O_2 . This result is in nearly perfect agreement with the adsorption data of Fig. 3. Significantly, the NO molecules still adsorbed in pairs or not at all.

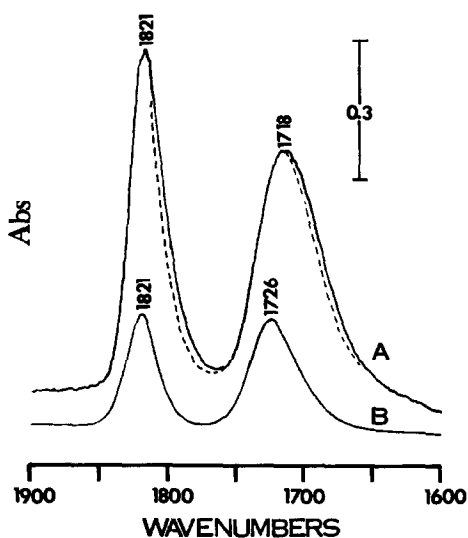


FIG. 5. Spectra from NO adsorbed on reduced catalysts. Reduction was carried out with flowing H₂ for 1 h at 500°C, followed by purging with He for 1 h at 500°C. (A) Adsorption of NO (10 Torr, 30 min, room temperature, 30 min evacuation). The spectrum indicated by the dotted line was recorded after O₂ was introduced in the cell (20 Torr for 2 min, followed by 30 min evacuation). (B) Adsorption of NO (10 Torr for 30 min at room temperature followed by a 30-min evacuation) after preadsorption of O₂ (20 Torr, 2 min, 30 min evacuation; the same results were obtained when the exposure time was increased to 30 min.).

DISCUSSION

A salient feature of the NO chemisorption was that the molecules adsorbed in pairs or not at all. Moreover, the chemisorbed amount was dependent on the extent of reduction and on the presence or absence of prechemisorbed oxygen. Adsorption and spectroscopic properties were almost identical on sulfided and on unsulfided but reduced catalysts. The literature is in overall agreement on all of these points although a few discrepancies are found which may be attributed to differences in catalysts, treatment procedures, etc. The two bands reported in this work at 1715 and 1820 cm⁻¹ have been attributed to the anti-symmetric and symmetric stretching vibrations of an adsorbed dinitrosyl complex (29) or to a NO dimer (37). For the reduced

catalysts both the intensities and relative intensities varied with extent of reduction, but these frequencies hardly changed. On sulfiding a significant shift to lower frequencies was observed (to 1700 and 1795 cm⁻¹) but otherwise the behavior was in all ways similar to that of the reduced catalysts. Interestingly, still lower frequencies (1680 and 1780 cm⁻¹) have been reported (33) for another catalyst sulfided at 400°C. The lower wavenumbers on sulfiding were suggested to result from an effect of sulfur producing more negatively charged dinitrosyls. Peri (46) reported that a sulfided catalyst after evacuation did not chemisorb NO. In this case, reduction of the sulfided catalyst at temperatures between 500 and 600°C were required before the dinitrosyl bands appeared. This is at variance with the present work.

The chief new findings reported herein could be explained by two (or more) different kinds of sites; practically anything can be explained in this way. In the present instance, however, the relative amounts of such sites would need to remain constant with varying extents of reduction and it would be further necessary to assume that one kind could adsorb O₂ while both kinds adsorbed NO. The low probability that all these constraints could be satisfied simultaneously led us to seek another explanation.

The possible and likely valence state of the Mo centers on which the chemisorbed species are bound should be first considered. It must be lower than Mo⁶⁺ because the chemisorption is first observed only after a specific minimum amount of reduction (Fig. 2). Moreover, the coordinative unsaturation must be sufficient to permit the formation of dinitrosyl species. The evidence that the chemisorption takes place along the edges of the chalcogenide wafers of MoS₂ (42) suggests that the chemisorption is likely to occur where two adjacent anions are missing. Finally, all inorganic dinitrosyl compounds contain an even number of *d*-electrons and the only known Mo-dinitrosyl complex is Mo(II)(NO)₂ (54). In the

past, it has been generally supposed that the active catalytic center measured by these chemisorptions is Mo^{4+} , which is the majority species. We have noted (21), however, that the relatively small portion of the total molybdenum present at the active centers, together with the high extent of coordinative unsaturation required to form the dinitrosyl species, suggested a lower valence state, "possibly Mo^{3+} ." We now suggest that it may be Mo^{2+} (Scheme 1).

A similar situation has existed for the past 25 years concerning the valence states of active chromia-silica or chromia-alumina catalysts (43, 44). Though direct evidence has long existed that the major surface species produced on reduction is Cr^{2+} (47), nearly every valence state between Cr^{2+} and Cr^{6+} has been proposed as the active centers for polymerization. Such proposals were based on correlations between characterization parameters and catalytic activity (43). Recently, Merryfield *et al.* (44) clearly demonstrated that in commercial catalysts Cr^{2+} is the active site or is its precursor for ethylene polymerization.

The NO adsorption on reduced chromia-silica and chromia-alumina catalysts has been found more complex than on molybdena-alumina (30, 45, 46). The spectra have been interpreted in terms of dinitrosyl or dimeric species formed on Cr^{2+} or on Cr^{3+} ions and monomeric NO may exist. Dimeric species have also been reported to be formed on reduced chromia (40, 41).

In some quarters lower valence states of Mo have been regarded as unlikely for NO adsorption sites because the spectra appear when the average valence state is still close to Mo^{6+} . Interestingly, Peri (46) presented evidence for Cr^{2+} formation after high temperature (500–600°C) evacuation of chromia-alumina preparations whereas only Cr^{3+} was detected after reduction in hydrogen. These observations offer an explanation for the fact that the adsorbed NO species gives the same spectrum on molybdena-alumina regardless of the degree of reduction, i.e., the same low va-

lence state adsorption centers may form in small amounts at special locations on these complex catalysts under fairly mild conditions. Chromia-alumina and molybdena-alumina differ in one other aspect. The former in its reduced state is completely poisoned for NO chemisorption by preadsorption of O_2 whereas the latter is not.

The findings of the present work are consistent with the chemistry outlined in Scheme 1 where it is suggested that pairs of Mo^{2+} are present along the crystallite edges, each necessarily having two missing anions. As shown, such a pair of adjacent Mo^{2+} (A) could form two dinitrosyl species (B). Alternatively, the same pair could adsorb one O_2 molecule as two atoms (C). The latter might be expected to disproportionate to the fully coordinated Mo^{6+} (E) and an Mo^{2+} (A) by a self-diffusion of the oxygen (sulfur) anion via the bridged transition state (D). This equilibrium could then be shifted by the chemisorption of further NO, as observed, and the ratio, $\text{NO}/\text{O}_2 = 2$ (rather than 4) would then be expected. Not only does this model explain all of the observations, it affords a simple explanation for the fact that the chemisorption of NO occurs only in pairs, or not at all.

Scheme 1 must be regarded with some skepticism at present, although ancillary data tend to add some support. First of all, when the *average valence state* is known to be less than Mo^{4+} , one or more lower valence states must be present. This situation has been documented several times (34, 50, 52, 53). Certainly then Mo^{2+} is a possibility. Interestingly, if Mo^{2+} is the active site for H_2 dissociation, one of the chief objections to a homolytic oxidative adsorption of H_2 on transition metal ion centers will have been relaxed. As pointed out by Burwell and Stec (55), known oxidative adsorptions of H_2 in inorganic chemistry invariably involve ions in low valence states. It has been argued that Mo^{4+} (d^2) is unsuitable for this purpose, but Mo^{2+} could fulfill this role.

O_2^- has been observed in EPR studies

(24) of chemisorption of O₂ at -180°C. As the temperature was raised to room temperature, however, O⁻ appeared together with O₂⁻. On evacuating the gas phase oxygen and slowly raising the temperature to 150°C the O₂⁻ signal disappeared and the O⁻ was alone observable. When ¹⁷O₂ was used in hopes of learning more about the paramagnetic species, all of the tracer was lost by exchange with the ordinary oxygen of the solid. Although the spin-density of the paramagnetic species was an order of magnitude lower than the oxygen chemisorptions reported here, the data nevertheless demonstrate the rapid mixing of the oxygen atoms present on the surface. Interestingly, the EPR signal from Mo⁵⁺ was not changed by the low temperature chemisorption of either O₂ or NO demonstrating a lack of interaction with this species.

To the best of our knowledge no physical evidence has been advanced suggesting the presence of Mo²⁺ in either reduced or sulfided catalysts. By nature, the catalytic centers are a minority species never exceeding about 20% of the total molybdenum. It seems possible, therefore, that these special edge sites have escaped detection by ESCA or other spectroscopic means. Whether Scheme 1 is ultimately found to be correct or not, the authors hope that the present evidence will stimulate further research.

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