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NOTES

Investigation of NO Adsorption on Reduced Molybdena–Alumina Catalysts

The chemisorption of small molecules has proven to be a useful probe for characterizing active sites on supported catalysts. In the case of molybdena catalysts, particularly useful molecules include O_2 (*1–5*), H_2 (*6*), NO (*7–10*), and CO_2 (*12*). These types of studies have revealed several interesting features about this catalyst. Oxygen studies have shown that a catalyst which contains ≈8 wt% Mo on a 190 m^2/g alumina support has about 50% of the alumina surface covered by molybdena (*1*). Additionally, the amount of oxygen chemisorbed has been shown to correlate with hydrogenation activity (*2*), dibenzothiophene hydrodesulfurization activity (*5*), and the activity for hydrodenitrogenation of gas oil (*16*). Also, hydrogen adsorption studies have revealed the existence of strong electric fields at the surface which are presumably associated with the active centers (*13*) and are capable of activating the H_2 at 77 K (*6*). Nitric oxide and CO_2 chemisorption have shown that NO adsorbs on the molybdena portion of the surface while CO_2 adsorbs on the alumina support (*11, 12*). Additionally, as the extent of reduction was increased, both the CO_2 chemisorption and the integrated intensity of the alumina hydroxyl groups (infrared, IR), were directly proportional to the extent of reduction (*20*). This result, together with other studies (*14*), strongly suggested that the exposed alumina surface area increases with reduction or sulfidation. Because of the utility of NO as a titrant for the molybdenum portion of the surface along with its large infrared extinction coefficient, NO chemisorption provides a useful probe for the way in which the properties of reduced molybdena vary with hydrogen reduction and how this relates to the development of its catalytic activity.

Previous studies of NO adsorption on molybdena–alumina catalysts were concerned with the nature of the chemisorption sites. Millman and Hall (*7*) proposed that a dinitrosyl complex was formed and concluded the active molybdenum sites contained two coordinately unsaturated centers. Earlier, Peri (*8, 9*) and Yao (*10*) suggested that the molybdenum–NO species could be a NO dimer complexed to molybdenum. This moiety was assigned on the basis of the observation that adsorbed NO (which has localized C_{2v} symmetry) exchanged in pairs when exposed to ^{15}NO as observed in the IR by the decrease in the two bands due to $^{14}NO{-}^{14}NO$ species and the increase in the two bands due to the $^{15}NO{-}^{15}NO$ species without any intervening mixed isotopic species being observed. A recent study, however, has shown that $[Mo(NO)_2(CH_3CN)_4](BF_4)_2$ adsorbed on alumina behaves almost identically to the traditional catalyst (*17*). However, irrespective of the detailed nature of the bonding of NO to Mo, NO titration does provide a selective probe for the molybdenum portion of the surface (*12*).

Thus, we have carried out a study to ascertain how sensitive the IR spectra of NO adsorbed on alumina-supported molybdena catalysts are to changes in the Mo surface brought about by reduction, initial coordination environment, and Mo loading at various NO coverages and exposures. From these studies we anticipate gaining some insight into changes occurring on the Mo and how the sites develop and interact. Additionally, because NO itself acts as a poison

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for catalytic reactions (*18*) there are strong implications that the adsorption sites and the catalytically active sites are identical.

CATALYSTS

The catalysts used in this study were prepared either by the incipient wetness method or by an equilibrium adsorption method which has been described elsewhere (*15*). The support material for all catalysts was Ketjen CK-300 γ-Al_2O_3 which has a surface area of 192 m^2/g.

The infrared spectra were obtained by using pressed platelets, which had a thickness of 10 mg/cm^2, mounted in a cell described previously (*17*). The spectra were recorded on a Nicolet Model MX-1 Fourier transform spectrometer operated in the absorbance mode. A spectral resolution of 2 cm^{-1} was maintained. Sixty-four scans were required to obtain the spectra shown here. Integrated intensities were derived by cutting out the appropriate bands and weighing the chart paper.

The procedures used for purifing gases have been described elsewhere (*11, 12*).

PHYSISORBED SPECIES

The IR spectra shown in Fig. 1 are typical of NO adsorbed on molybdena–alumina catalysts which have been reduced in H_2 for 1 h at 500°C. These spectra illustrate the presence of an NO species which can be partially removed by evacuation at ambient temperature. Figure 1a shows the spectrum after evacuation for 2 min and Fig. 1b after evacuation for 30 min (corresponding to the removal of weakly bound NO). The IR spectrum of the weakly held species (Fig. 1c) was obtained by subtracting the spectrum show in Fig. 1b from that shown in Fig. 1a. A small part of the NO desorbed by evacuation was similar to the spectrum of gas-phase NO. The peaks in Fig. 1c with frequencies at 1895 and 1854 cm^{-1} are likely mononitrosyl species because the similarity of this spectrum to the gas-phase NO frequencies is good (1901 and 1852 cm^{-1} for the P and R branches). Similar spectra have been reported by Peri (*9*), although no definite assignments were made concerning the nature of the weakly held species, the agreement in band positions and relative intensities is remarkable.

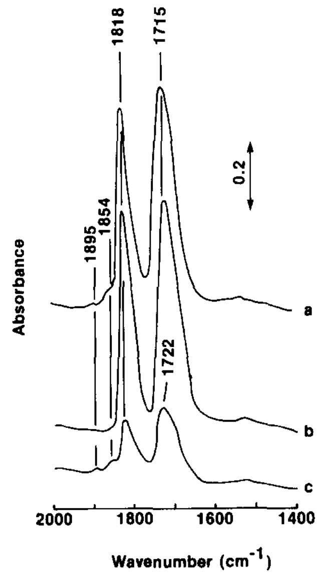

FIG. 1. Spectra of NO adsorbed on 8% Mo/γ-Al_2O_3 reduced 1 h in 60 cm^3/min of flowing H_2, evacuated, and exposed to 10 Torr NO for 30 min at room temperature. (a) Evacuated for 2 min, (b) 30 min evacuation after obtaining spectrum a, (c) difference between spectrum a and spectrum b.

RELATIVE BAND INTENSITIES

Hall (*19*) has shown that the coordination environment of Mo can be varied from nearly all tetrahedral sites to almost completely octahedral sites merely by altering the preparation conditions. The IR spectra of NO adsorbed on the same samples as reported in that study are shown in Fig. 2. The spectra were recorded following a 1-h reduction in H_2 and 1 h evacuation (both at 500°C) with a subsequent 30-min exposure to 20 Torr NO at 25°C followed by 30 min evacuation at 25°C. In all cases these spectra exhibit identical frequencies for the NO bands (within experimental error). The relative intensities of the two bands, however, differ significantly. Yao (*10*) has reported similar differences in relative intensity of the two bands with varying cov-

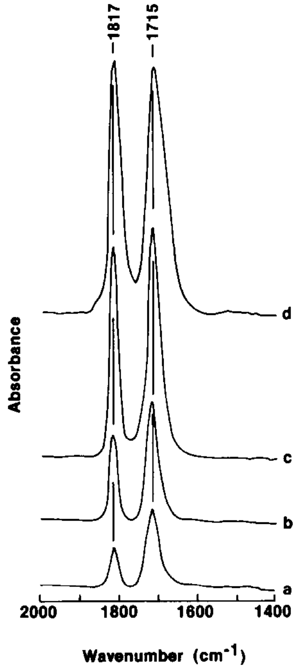

FIG. 2. The effect of Mo loading on the spectra of NO at constant reduction time, temperature, and H_2 flow rates. The preparation of the catalysts has been described in Ref. (*15*). The Mo loadings, expressed as atoms of Mo × 10^{20}/g, are: (a) 1.1, (b) 2.8, (c) 4.6, and (d) 7.3.

erage. The relative intensity differences may therefore be ascribed to differences in coverage resulting from variations in extents of reduction. Wang (*15*) has shown that the catalyst with the highest loading was more extensively reduced (e/Mo = 2.2) than the catalyst with the lowest loading (e/Mo = 0.9); intermediate loadings having extents of reduction between these extrema.

To evaluate whether the change in relative intensity of the bands varied with extent of reduction, a standard 8% Mo catalyst (prepared by impregnation) was reduced to differing extents by varying the temperature of the 1-h H_2 reduction (60 cm^3/min) from 325°C (for the lowest reduction) up to 500°C. The final evacuation temperature was 500°C for 1 h for all reduction temperatures. An identical procedure to that reported above was used for the NO adsorption. The absolute intensities, the sum of the intensities, and the ratio of the intensities of the 1715- and 1817-cm^{-1} bands are reported in Table 1 for five different extents of reduction, ranging from 0.5 e/Mo to 2.0 e/Mo. The data show that the integrated intensities of both bands increase with increasing reduction, but not at the same rate. With minimal reduction (0.5 e/Mo) the low-frequency band (1715 cm^{-1}) is about 2.4 times the intensity of the high-frequency band. As the extent of reduction increased, this ratio falls to about 1.6 at reductions of 1.6 e/Mo and greater. Whether this ratio represents a lower limit cannot be determined from these data. This will be discussed in greater detail below. However, the sum of the intensities of the two bands do correlate well with the extent of reduction, having a correlation factor of 0.986.

Following the experiments described above, the samples were subjected to thermal desorption at increasingly higher temperatures. Spectra were recorded after annealing at each temperature (1 h) prior to recording the spectra. The data in Fig. 3 shows a plot of the variation in the intensities of the two bands as a function of both extent of reduction and desorption temper-

TABLE 1

NO Band Intensities as a Function of the Extent of Reduction

e/Mo[b]	Integrated intensities[a] (cm^{-1})			
	1817	1715	Summation 1817 + 1715	$\frac{1715}{1817}$
0.55	75	180	255	2.40
0.81	160	320	480	2.00
1.22	310	570	880	1.84
1.60	480	780	1260	1.62
2.05	560	910	1470	1.62

[a] Integrated intensities were determined by the cut and weigh method.

[b] The reduction temperatures were 325, 350, 400, 450, and 500°C, respectively. Subsequent evacuation was carried out at 500°C in all cases.

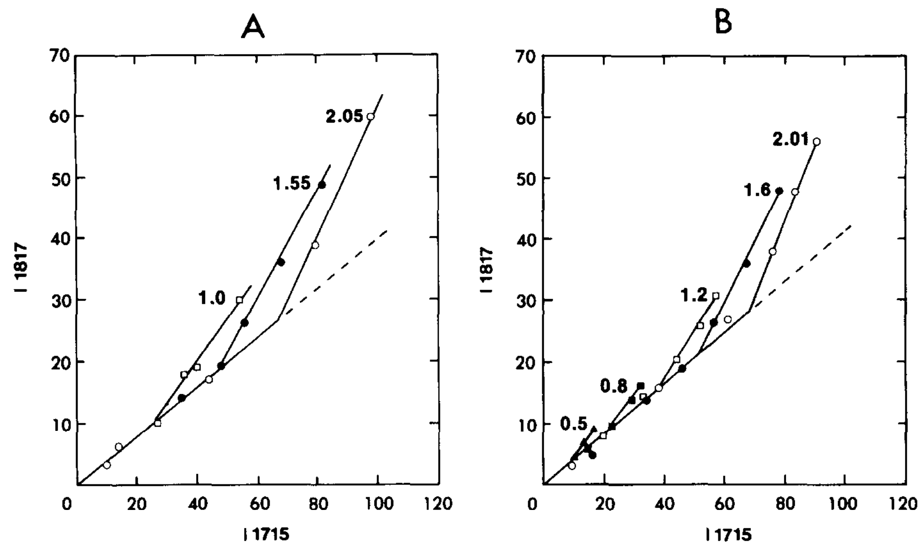

FIG. 3. The variation in the integrated intensities of the 1817- and 1715-cm^{-1} band as a function of coverage for the 8% Mo catalyst reduced to different extents expressed as e/Mo. The catalysts were reduced in 60 cm^3/min flowing H_2 for 1 h. They were evacuated for 1 h at the reduction temperature and to NO as described in Fig. 1. The extents of reduction are indicated. In (A) the coverage was varied by evacuation for 1 h at successively higher temperatures, up to 350°C. In (B) the coverage was varied by successive exposure to small doses of NO (1.8 × 10^{18} molecules/dose).

ature. It is evident from these data that the two bands do not lose intensity at the same rate for any of the extents of reduction, and that as the extent of reduction increases the high-frequency band grows more rapidly than the low-frequency band, although both bands do increase in intensity with increasing extent of reduction. Plots of the intensity of the two bands versus desorption temperature shows that both bands disappear at the same temperatures. This is in contrast to the data of Yao and Rothschild (*10*), who found that the high-frequency band disappeared completely while a small band at lower frequency remained.

BOND ANGLE VERSUS COVERAGE

The data for the intensities of the symmetric (1817 cm^{-1}) and antisymmetric (1715 cm^{-1}) stretching bands, shown in Fig. 3, have been converted into bond angles, using the formula of Yao (*10*), and plotted versus coverage, θ, in Fig. 4. The definition of θ used here is the relative coverage (i.e., the quantity of NO adsorbed divided by the maximum NO adsorption for that particular extent of reduction). This allows data for all extents of reduction to be plotted using the same ordinate. As seen in the figure, the data for all extents of reduction are well represented by one curve with two

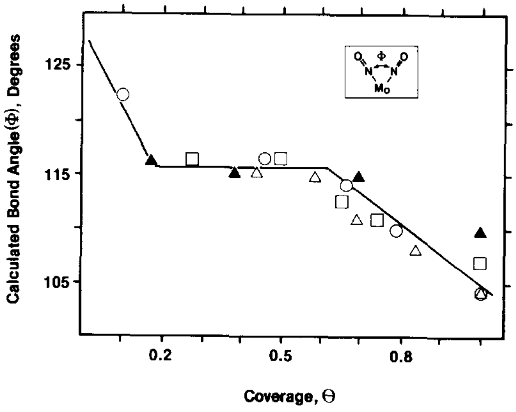

FIG. 4. The variation of the calculated bond angle between the NO molecules as a function of the coverage. The data used to calculate the bond angle was from Figs. 3A and B. The calculation method used to obtain the bond angle has been described in Ref. (*10*).

apparent break points at $\theta \approx 0.2$ and 0.8. At low coverage the bond angle between the two NO molecules is relatively large and falls rapidly with increasing coverage. At intermediate coverages, the bond angle is invariant to coverage, while at higher coverage the bond angle decreases still further. There is some indication that at the higher coverages there may be some dependence of the decreasing slope on extent of reduction (note the ordering of the points at $\theta = 1.0$). Further support for this can be found in the spectra reported by both Peri (*9*) and Yao (*10*) for a 900°C reduction. At this high reduction temperature our calculated bond angle, from their data, is about 82–88°C.

SLOW ADSORPTION KINETICS

Recently it has been shown that the rate of NO adsorption can be divided into two regions; a fast initial adsorption followed by a slow adsorption process (*3*). The spectra shown in Fig. 1 represent surface species resulting from the fast portion of the adsorption while those shown in Fig. 5 show spectra arising from slow adsorption kinetics. These spectra were obtained by first recording a spectrum as shown in Fig. 1a and then continuing the NO adsorption. The spectra were recorded as a function of time. Difference spectra for each interval are shown in Fig. 5. It is apparent that there is very little difference between the spectra in Fig. 5 (which show the NO species associated with the slow adsorption), and those of the species with the fast adsorption shown in Figs. 1 and 2.

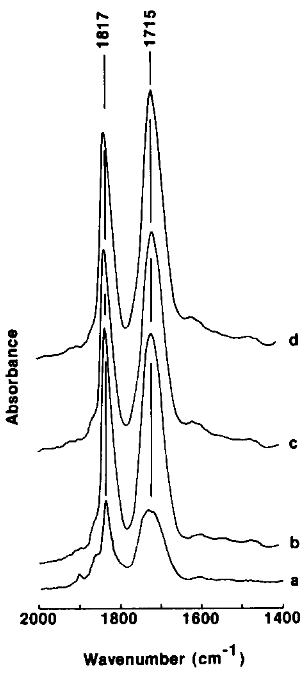

FIG. 5. Spectra of the slow adsorption of NO. After obtaining the spectrum as in Fig. 1b the catalysts was reexposed to NO and spectra recorded at the times indicated. The spectra shown are the result of subtracting the initial spectrum from those obtained at the indicated times.

This strongly suggests that the species arising from the slow adsorption process are identical to those which arise from fast adsorption. Hardee and Hightower (*18*) have assigned the spectrum of NO on reduced Co–Mo/γ-Al_2O_3 to three mononitrosyls. Based on the stability of the three bands, they assigned one to NO on Co and the other two to NO on two different Mo species. Their data show that the low-frequency band for NO on Mo is the most thermally stable, in agreement with others (*8–10*). Based on typical heats of adsorption as a function of coverage it is expected from their arguments that the low-frequency band (1715 cm^{-1}) would be due largely to the fast adsorption and the 1817-cm^{-1} band the slow adsorption. Our data shows that this clearly is not the case, so that it appears the same species is responsible for both the slow and fast adsorption. The slow adsorption may be due to a slow surface rearrangement following the rapid adsorption, as proposed by Valyon and Hall (*3*) to account for the adsorption of NO (and its associated spectrum) following surface saturation with oxygen. The similarity between the complexes derived from the slow and fast adsorption, however, are indicative of different types of Mo which are capable of forming the same or very nearly the same dinitrosyl complex, but at different rates.

In summary, the use of NO as a probe for the Mo portion of an alumina-supported Mo catalyst does produce changes in the spectrum of the adsorbed NO. The relationship between the spectral changes (differences in relative intensity of the two bands) and the catalytically active sites, however, is not entirely clear. That the spectral changes with coverage for catalysts reduced to different extents are nearly identical, except at saturation coverage, indicates that the NO is not particularly sensitive to the development of the catalytic sites. The sharp decrease in bond angle as saturation coverage is approached could be indicative of site crowding, since it is known that the Mo agglomerates when reduced (*20*). The above conclusions do in fact suggest that the similarity of the spectral properties of NO adsorbed on what should be different Mo surfaces might be due to NO forcing the surface atoms into a configuration which permits the formation of the dinitrosyl species, in a manner similar to the rearrangement proposed by Valyon and Hall (*3*).

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