Site Selective Chemisorptions on Molybdena–Alumina Catalysts

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NO was found to adsorb selectively on the molybdena portion of reduced molybdena–alumina catalysts and CO_2 on the uncovered alumina portion of the surface. These two chemisorptions had little effect on each other. The chemisorption of NO was correlatable with coordinative unsaturation developed during reduction (by the removal of oxygen as H_2O or CO_2); NO molecules were chemisorbed as pairs on sites which also dissociatively adsorbed H_2 and catalyzed hydrogenation. The chemisorption amounted to NO/□ = 0.43 or to less than 1 NO pair for every 10 Mo (depending upon the extent of reduction). Alumina hydroxyl groups were regenerated as the catalyst was reduced and the CO_2 chemisorption increased concomitantly. At 500°C these quantities reached maximum values of about 50% recovery of the hydroxyls lost from the alumina when the catalyst was prepared and to a CO_2 chemisorption of about 80 μmol/g. The intensities of the CO_2 bands of the ir spectra were lower for reduced molybdena–alumina catalysts than for the parent alumina, but were otherwise identical. These bands remained unchanged when NO was added to the system and the NO bands remained unchanged when the previous spectrum for the CO_2 was subtracted. Within the experimental error the reverse experiment, where CO_2 was added to a catalyst on which NO had been previously chemisorbed, gave the same results. Interestingly, a bicarbonate band about 3610 cm^{-1} appeared on CO_2 adsorption, while the highest frequency band from the alumina OH (at 3792 cm^{-1}) was strongly diminished. An attempt was made to use these tools to determine the parts of the surface on which pyridine adsorption occurs. When CO_2 was adsorbed first, it was eluted by pyridine and Lewis bound pyridine (LPy) was formed on the alumina surface. When NO was chemisorbed first its concentration was not greatly affected by the chemisorption of pyridine, but the two NO bands shifted to lower frequency by about 50 cm^{-1} and their relative intensity was altered. When pyridine was adsorbed first, the NO bands still formed but with lower intensity; the same shift to lower frequency was observed.

INTRODUCTION

Recently we reported (*1*) that all detectable Brønsted acidity disappeared from molybdena–alumina catalysts on reduction, whereas their activity for cyclopropane isomerization was increased (*2*). Moreover, the ir bands corresponding to Lewis bound pyridine (LPy) were indistinguishable (except for intensity) from those formed on the surface of the parent alumina used for the molybdena–alumina preparation. Hence, the question arose as to whether or not pyridine adsorbed on the molybdena portion of the surface contributed to the spec-

tra, or only that on the alumina. This question was investigated in the present work.

Similarly, NO was reported to selectively chemisorb on coordinatively unsaturated sites (CUS) of the reduced molybdena surface in pairs (*3*); the corresponding ir spectra were interpreted as stemming from dinitrosyl species although other interpretations are possible (*4, 5*). It was then found that NO acted as a selective poison for the hydrogenation of olefins (*6*) and that the hydrogenation rates were correlatable with the extent of the chemisorption when measured in separate experiments (*3*).

In related experiments, O_2 was found to function in much the same way (*7*), although no ir spectra were expected no observed. These chemisorptions also corre-

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lated with the hydrogenation activity and CUS concentration (7, 8). The chemisorbed amounts of O_2, however, were only about half those of NO under comparable circumstances. In both cases the chemisorptions were small, corresponding to only a few percent of the Mo present at extents of reduction where the catalytic rates could be readily measured (e/Mo ≈ 1.5). The chemisorption of O_2 has become a laboratory index for catalytic activity for hydrodesulfurization (8). Thus, this chemisorption can be applied to sulfided as well as reduced Molybdena–alumina catalysts, although debate continues concerning the nature of the chemisorption (9–11).

The strong irreversible chemisorption of H_2 has been studied on these catalysts (12). It, too, was found to correlate with catalytic activity for propene hydrogenation and provided a measure of the site density somewhat smaller than that provided by O_2. This chemisorption was investigated by NMR (13); these data suggested that H_2 became dissociatively adsorbed on sites which chemisorbed O_2 or NO. Since these chemisorptions appear to be specific for the catalytically active sites, the more we can learn about them the better we can understand the nature of these sites. Interestingly, spectroscopic studies of strong selective poison molecules such as NO provide a means of observing directly adsorption on sites where undetectable catalytic intermediates may be presumed to form.

The chemisorption of CO_2 on alumina is well known. Characteristic infrared spectra have been reported (14–16). Moreover, CO_2 has been found to be a selective poison for isotopic exchange reactions (17, 18) and for the *ortho–para* H_2 separation (19). Indeed, it has been suggested (20) that a bidentate species, formed on alumina, effectively eliminated exchange between D_2 and benzene. We have now found that CO_2 is adsorbed selectively on the alumina portion of molybdena–alumina catalysts, while NO is adsorbed independently on the CUS of the molybdena portion of the surface.

Moreover, the data reveal some interesting features concerning the changes which occur as the microscopic bound molybdena clusters (21) are reduced.

EXPERIMENTAL

The catalyst. The catalyst investigated was the same molybdena–alumina preparation (8% Mo) used in most of our earlier work (2, 3, 6, 7, 12, 13, 22, 23, 28). It was made by the incipient wetness method and contained about 5×10^{20} Mo/g. This loading was selected as the amount required to just about cover the support with an epitaxial monolayer. The alumina support was Ketjen CK-300. The surface area of the catalyst was 185 m^2/g and that of the alumina was 192 m^2/g.

Infrared measurements. For the spectroscopic work, calcined aliquots of the catalysts were pressed into platelets having a thickness of about 10 mg/cm^2. These were mounted on a Pyrex rack which positioned them between the KBr windows (13 mm path length) of a vacuum-tight spectroscopic cell.

The catalyst rack assembly could be moved magnetically upward about 20 cm into a self-contained furnace built around the vacuum tight cell. The temperature was maintained using a commercial controller (Omega Model-49). Temperatures were measured using a thermocouple positioned close to the catalyst platelet. Temperatures up to 550°C were easily achieved.

Gases could be passed over the catalyst and evacuated at selected temperatures. The vacuum-tight cell was attached to a conventional system which routinely reached 10^{-6} Torr. Oxidation and reduction treatments of the catalyst were made using flowing streams of purified O_2 and H_2, respectively.

After pretreatment (usually at 500°C), the catalyst was evacuated at 500°C for 30 min after oxidation, or for 1 hr after reduction, and cooled to room temperature before adsorption of the gas to be studied. Finally, the catalyst and its rack assembly were

moved back between the KBr windows for spectroscopic investigation.

A Nicolet Model-MX-1 Fourier transform spectrometer was used in the absorbance mode. The resolution of the spectrometer was maintained automatically at 2 cm^{-1} over the region studied. The number of scans required to produce the spectra shown were 64 for NO, CO_2, and pyridine and 640 for the surface hydroxyl region. Integrated intensities were derived by the cutting and weighing method.

Gravimetric measurements. Gravimetric measurements were made with a Cahn (Model 2000) electrobalance to determine the degree of coordinative unsaturation ($\square$/Mo), or the extent of a chemisorption of NO.

The balance was attached to a conventional BET type vacuum system which routinely reached 10^{-5} Torr. Before each experiment the catalyst was calcined in flowing O_2 overnight at 500°C before evacuation for 40 min at this temperature. It was then reduced with flowing H_2. When the desired extent of reduction was reached, the catalyst was evacuated for 1 hr and cooled in He. The data were calculated (6, 22) as the average degree of coordinative unsaturation ($\square$/Mo) measured by the weight difference between the oxidized and the reduced states of the catalyst. After a brief evacuation (5 mins) to remove the He, NO or CO_2 was admitted at 20°C and at the desired pressure. The extent and rate of chemisorption were determined from the weight changes.

Gases and reagents. The tank O_2 was passed through a Linde 13X molecular sieve purification column before use. The H_2 was ultrapure; it had been passed through the Pd–Ag thimble of a RSI commercial purifier. Matheson NO (nominal purity 99.9%) was further purified by a freeze-pump–thaw-freeze technique, the cycle being repeated several times with vacuum transfer between two traps. Finally, the gas was passed through an isopentane slush (-155°C) and into a storage vessel. The final frozen NO was crystal clear. The Airco CO_2 (nominal purity 99.99%) was also frozen and pumped repeatedly before it was stored. The pyridine was dried over 5A molecular sieves; it was distilled and the center cut was collected and redistilled. The final distillate was collected over anhydrous KOH and stored over activated 5A molecular sieves in a tube which could be attached to the vacuum system. It was frozen, pumped, and surrounded by a controlled temperature bath to fix the vapor pressure (usually at 4 Torr).

RESULTS

Photographically reproduced spectra from CO_2 and NO adsorbed singly or successively are shown in Fig. 1. Care was taken to ensure that these spectra were identically scaled. The spectrum from CO_2 adsorbed on the parent γ-alumina after pretreatment at 500°C (Fig. 1A) may be compared with that for CO_2 chemisorbed on a reduced molybdena–alumina catalyst (Fig. 1B). Note that the same bands are present, but are much weaker in the latter case.

Figure 1C shows the spectrum obtained when NO was adsorbed following the experiment of Fig. 1B. Note that the CO_2 bands remained at the same positions while the bands expected for the NO pair appeared 1817 and 1714 cm^{-1}, respectively. Although the CO_2 bands appeared to be weakened, this could be attributed to a change in the background level, because when spectrum B was subtracted from C to obtain D the CO_2 bands were virtually eliminated without creating negative peaks. This subtraction process was made possible by the self-contained computer of the Nicolet spectrometer, in which the baseline match is made at frequencies in the 1900 and 2000 cm^{-1} region. Results from reverse experiments are given in the remaining spectra. When NO was chemisorbed on the reduced catalyst after evacuation the resulting spectrum (Fig. 1E) was almost identical to Fig. 1D. When CO_2 was then added, Fig. 1F was obtained. The difference spec-
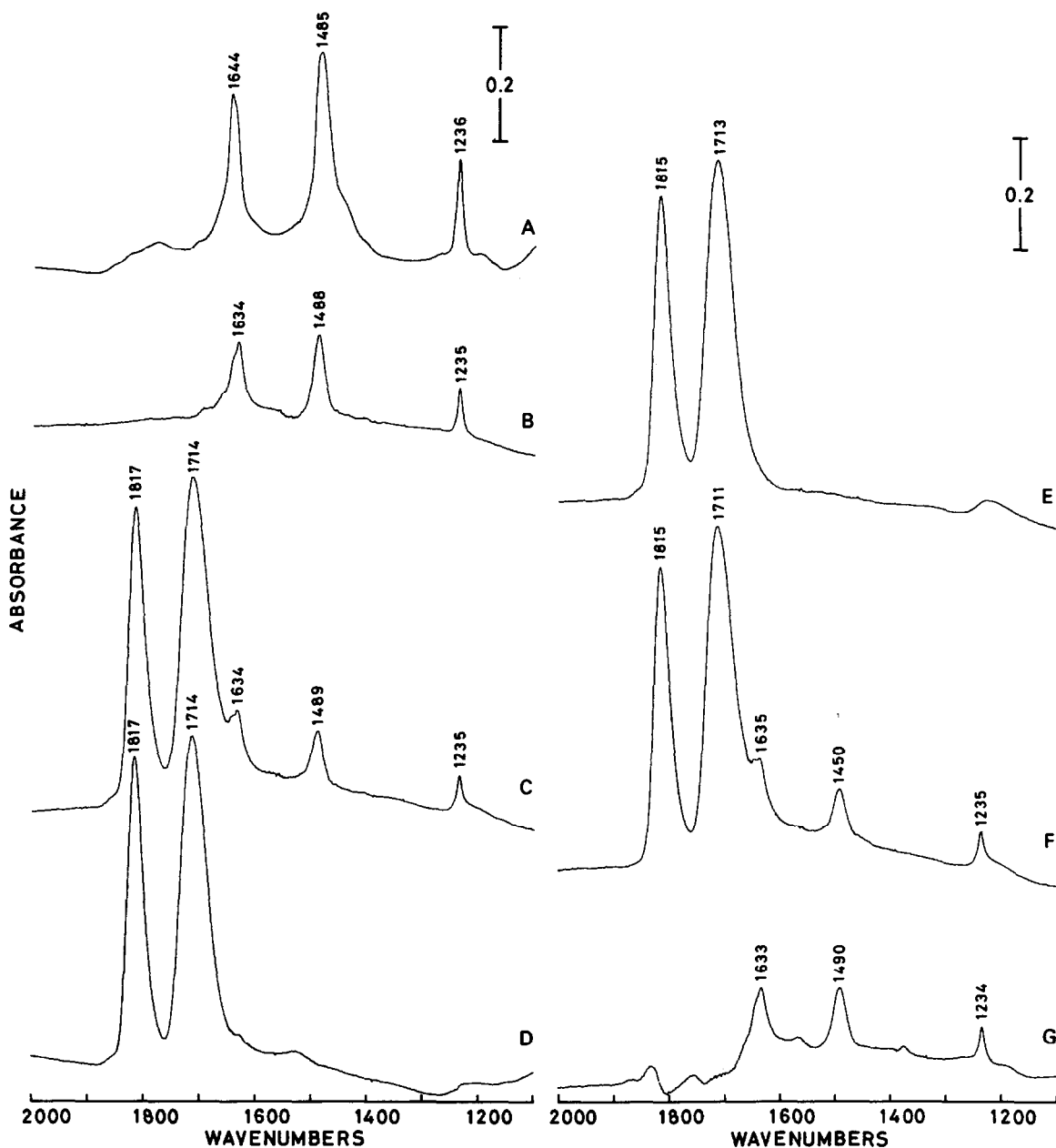
FIG. 1. Infrared spectra of CO_2 and NO adsorption on alumina and molybdena–alumina catalysts: (A) alumina exposed to 50 Torr of CO_2 for 30 min and evacuated for 30 min, both at room temperature; (B) reduced molybdena–alumina ($\square$/Mo = 0.5) exposed to 50 Torr of CO_2 for 30 min and evacuated for 30 min both at room temperature; (C) after recording Spectrum B, the sample was exposed to 5 Torr of NO for 30 min and evacuated for 30 min both at room temperature; (D) computer subtraction of Spectrum B from Spectrum C; (E) reduced molybdena–alumina ($\square$/Mo = 0.5), exposed to 5 Torr of NO for 30 min and evacuated for 30 min, both at room temperature; (F) after recording Spectrum E, platelet was exposed to 50 Torr of CO_2 for 30 min and evacuated for 30 min, both at room temperature; (G) computer subtraction of Spectrum E from Spectrum F. M Spectrum F, above the band at 1450 cm^{-1} is mislabeled; it should read 1490.

trum (Fig. 1G) shows the CO_2 bands remaining leaving only vestiges of the strongly chemisorbed NO. The data suggest that NO and CO_2 chemisorb on two different parts of the surface and that the latter is chemisorbed on the uncovered alumina portion.

Separate microbalance experiments were made to determine quantitatively the extent of oxygen removal as H_2O and the extent of chemisorption of NO versus time. The former we report as the anion vacancy concentration, $\square$/Mo (atom/atom) or the CUS concentration. Results of a typical experiment are shown in Fig. 2, where the characteristics of the NO chemisorption are depicted. Following the initial rapid uptake during the first 10 mins, a slow zero-order process set in which continued for many hours. Whatever the nature of this process, the NO spectrum became invariant after the first 30 mins. Consequently, the extent of the chemisorption producing Fig. 1E was estimated by extrapolation back to $t = 0$ as indicated. The results obtained in this way were plotted versus the CUS concentration in Fig. 3. These data confirm and extend the earlier work of Lombardo et al. (6) which is shown as the dotted line. Significantly, virtually no NO was chemisorbed before the
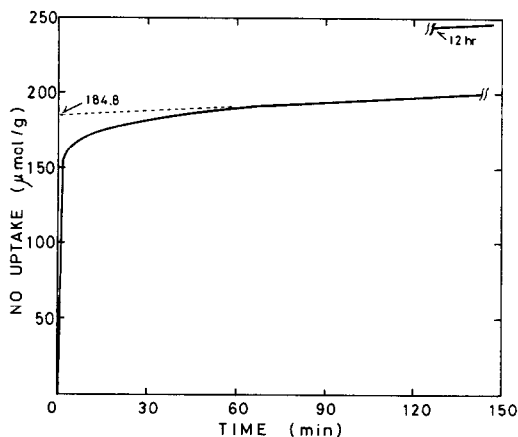

FIG. 3. NO uptake intercepts derived as in Fig. 2 on reduced molybdena–alumina as a function of CUS concentration. Dotted line taken from earlier work (6).

CUS concentration reached about 0.08, possibly because the nature of the NO pairs requires multiply coordinative unsaturation for chemisorption. The slope obtained from the new data corresponded to NO/$\square$ = 0.43, while the corresponding value from the previous data (6) was NO/$\square$ = 0.37.

Spectra for the hydroxyl region for the parent alumina (A), the oxidized molybdena of alumina catalyst (B), and the same catalyst after reduction in H_2 to increasing extents (C–F) are presented in Fig. 4. Spectrum D is similar to, but better resolved (because of the higher resolution of Nicolet spectrometer), than the one which we published earlier (23). These spectra confirm that the alumina hydroxyl groups are eliminated as they are replaced by a molybdate species when the raw catalyst is formed, but that some of these are regenerated as the catalyst is reduced with H_2. In the present experiments, a maximum recovery of alumina surface was obtained (Fig. 5) above which the alumina OH remained constant or decreased somewhat. This was to be expected from the reduction studies of Hall and LoJacono (22), where the recovery was measured as H_1. This quantity reached a maximum near e/MO = 1.0 ($\square$/Mo = 0.5). As shown in Fig. 5, only about

FIG. 2. Time dependence of the NO chemisorption ($p = 20$ Torr) at 20°C on reduced molybdena–alumina ($\square$/Mo = 0.5). Strong chemisorption corresponding to spectra was taken as the intercept on the ordinant extrapolated from slow linear process as indicated.
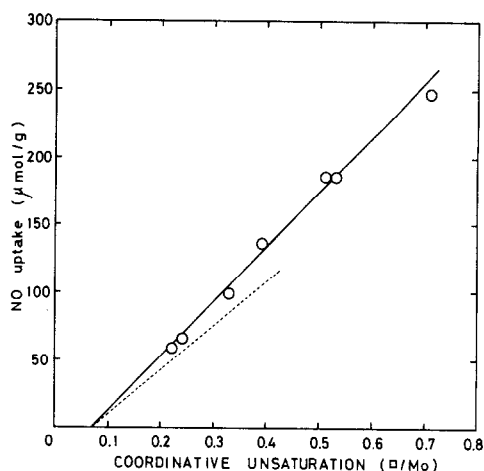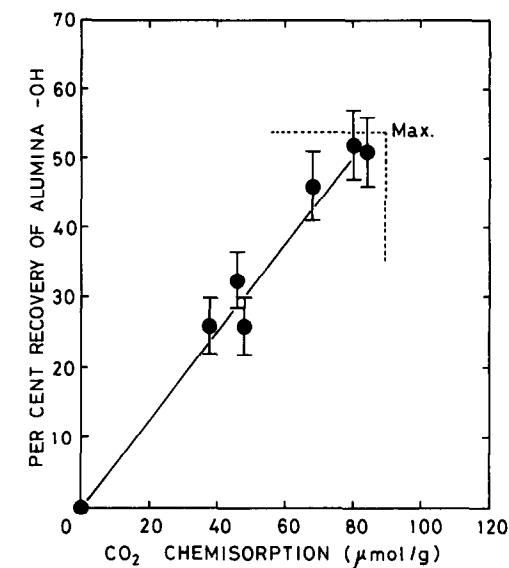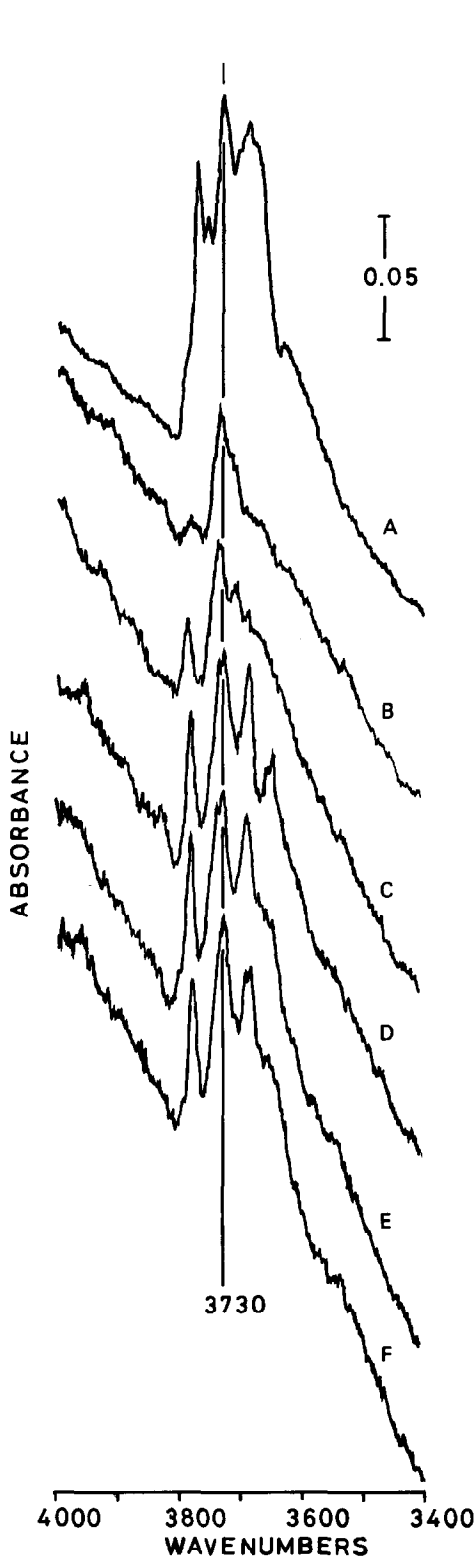
FIG. 5. Correlation between the percentage recovery of alumina OH on reduction and the CO_2 chemisorption. The latter data were determined by gravimetric measurements with a microbalance in separate experiments. Preparation was exposed to 50 Torr of CO_2 at 20°C for 2 hr and evacuated for 30 min at 20°C. Recovery of OH was calculated from integrated intensities of the adsorption spectra.

50% of the original alumina OH groups could be recovered upon reduction. Interestingly, however, the CO_2 chemisorption also reached a maximum at about the same point, suggesting that a part of the alumina surface remained bound to the reduced molybdena. This idea was supported by the fact that the CO_2 chemisorption was a linear function of the alumina surface recovered, but reached a maximum with e/Mo. Another interesting feature of the CO_2 chemisorption is revealed in Fig. 6. The relatively strong high frequency band of alumina at about 3774 cm^{-1} (shown in Fig. 4A) was nearly completely eliminated (Fig. 6) and a new band at 3610 cm^{-1} was formed

FIG. 4. Infrared spectra of the hydroxyl region for alumina and molybdena–alumina after evacuation at 500°C for 2 hr: (A) alumina; (B) unreduced molybdena–alumina; (C) B reduced until □/Mo = 0.39; (D) reduced until □/Mo = 0.51; (E) reduced until □/Mo = 0.71; (F) reduced until □/Mo = 0.82.
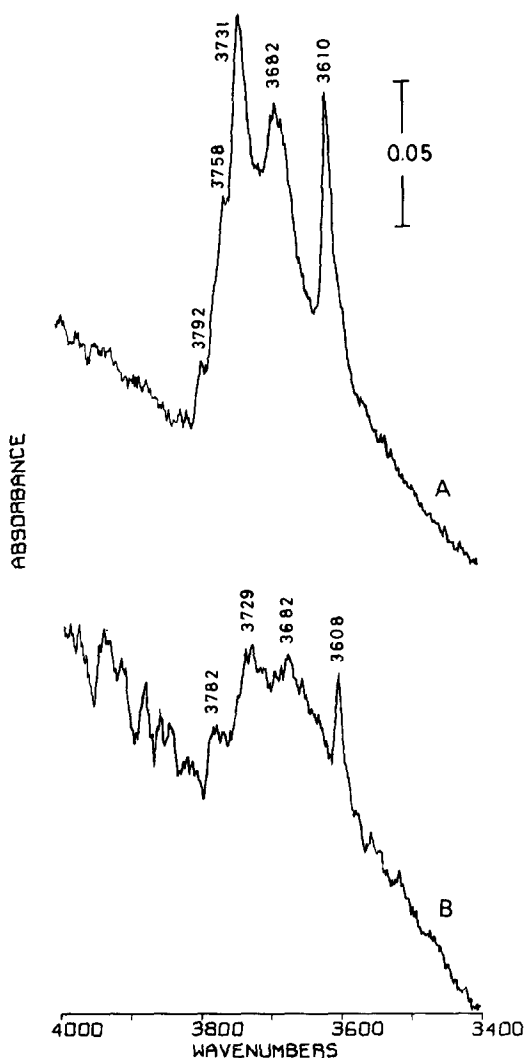
FIG. 6. Spectra of hydroxyl region after addition of CO_2 to alumina and reduced molybdena–alumina (preparations had been evacuated at 500°C before exposure): (A) 50 Torr of CO_2 exposed to alumina for 30 min and evacuated for 30 min both at room temperature; (B) reduced molybdena–alumina ($\square$/Mo = 0.5) exposed to 50 Torr of CO_2 for 30 min and evacuated for 30 min both at room temperature.

when CO_2 was chemisorbed. The new band has been attributed to the formation of a bidentate species (14, 20). The spectrum in the OH region following chemisorption of CO_2 on the reduced molybdena–alumina catalyst ($\square$/Mo = 0.5) is shown in Fig. 6B. Comparison with Fig. 4D shows that the

result is again the same as with the γ-alumina.

These tools discriminate between the uncovered alumina surface and the molybdena–alumina portion. It was, therefore, of interest to use them to examine the chemisorption of pyridine to determine on which portion of the surface it is chemisorbed (or whether it resides on both). The ir spectrum from pyridine adsorbed on the reduced catalyst in the same manner as used previously (1) is shown in Fig. 7E; it corresponds to that of LPy. This spectrum was virtually unaltered when NO was exposed to the sample (Fig. 7F), except for the appearance of the expected NO bands. Note, however, that these bands appear broader and weaker than usual and that they are shifted by 30 to 50 cm^{-1} to lower frequencies, e.g., compare Fig. 7F with 7A. The data suggest that at least some pyridine is chemisorbed on sites which would otherwise hold NO. Interestingly, however, when pyridine was added to the preparation used in Fig. 7A, the NO portion of the spectrum was altered in an unexpected way. The changes which occurred upon adding three successive doses (0.09 μmol/g each) are shown in Figs. 7B, C, and D. The LPy bands increased in intensity, as expected, while the NO bands broadened and shifted in frequency. The absolute integrated intensities of the NO bands did not change much, however, when pyridine was adsorbed as the second step, although the relative intensities of the bands did. These data are shown on Fig. 8 where a comparison can be made with the reverse experiment (flagged points) in which pyridine was adsorbed first. These confirm that pyridine is not a selective poison; it will adsorb on both parts of the surface if chemisorption on the molybdena portion is not already blocked by the very strong chemisorption of NO. This is in agreement with our earlier finding (6) that whereas NO is a selective poison for hydrogenation, pyridine and NH_3 are unselective poisons.
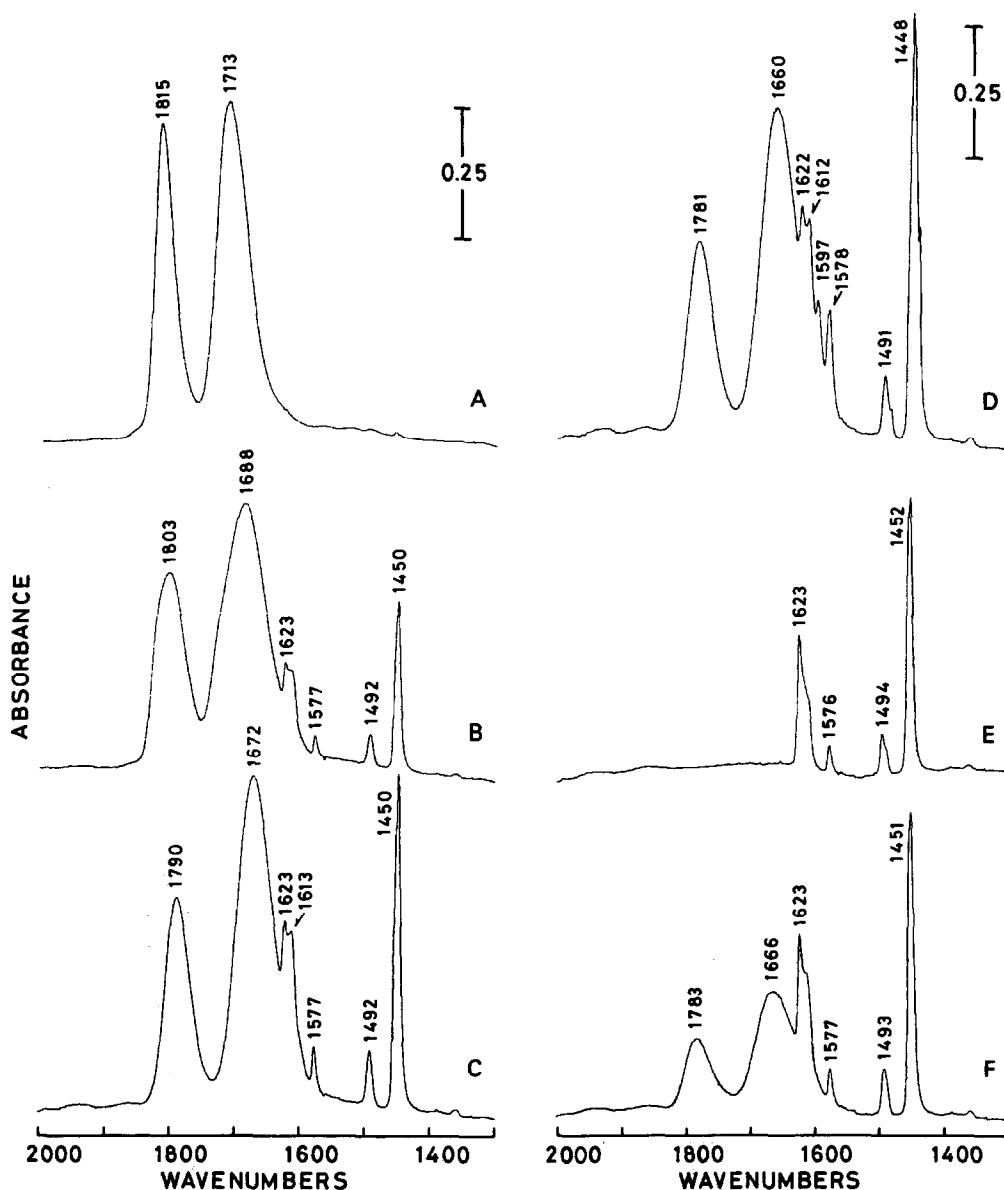
When similar experiments were at-

FIG. 7. The interaction of pyridine with NO on a reduced molybdena–alumina catalyst ($\Box$/Mo = 0.5): (A) spectrum taken after exposure to 5 Torr of NO at room temperature and evacuated for 30 min; (B) 0.09 mmol/g of pyridine was admitted after recording Spectrum A; (C) an additional dose of pyridine was added (0.18 mmol/g total); (D) another dose of pyridine was added (0.27 mmol/g total); (E) spectrum from reduced molybdena–alumina which had been exposed to 4 Torr of pyridine for 1 hr before evacuation for 2 hr, both at 200°C; (F) spectrum taken after exposure to NO after recording E (5 Torr of NO at room temperature followed by evacuation, both for 30 min at room temperature).

tempted with CO_2 it was found that no chemisorption of CO_2 occurred when pyridine was adsorbed first and that CO_2 was eluted by pyridine in the reverse experiment, i.e., the ir bands from chemisorbed CO_2 disap-

peared and those of LPy appeared when pyridine was admitted.

Some data of interest are collected in Fig. 9 where the integrated intensities of the LPy band at about 1450 cm^{-1} are plotted for
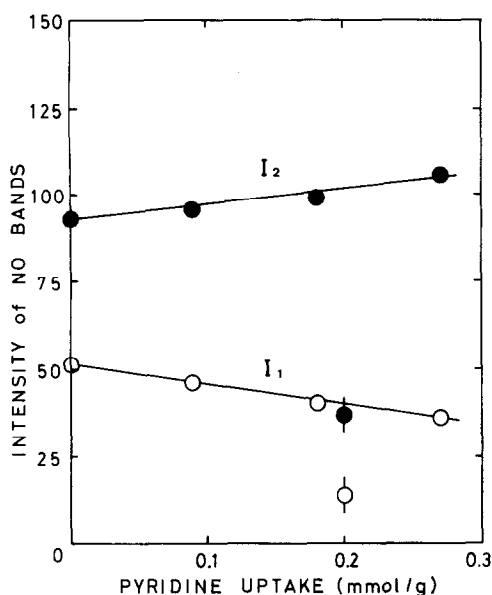
FIG. 8. The change of integrated intensities of NO doublet after addition of doses of pyridine; data taken from Spectra of Fig. 7; I_1 and I_2 are integrated intensities of higher and lower frequency NO bands, respectively; ◐,● are data for the reverse experiment (data from Fig. 7E).

an experiment where 90 μmol doses of pyridine were admitted successively to preparations of the freshly reduced catalyst and to one on which Co$_2$ had been previously chemisorbed. Both sets of data fell on the same curve. Moreover, the curve passed through the point (flagged) obtained by the somewhat different procedure used earlier (*1*). Interestingly, a quite different result was obtained when NO was adsorbed prior to dosing with pyridine. Figure 9 can be regarded as a plot of Beer's law. The curve of higher slope for the LPy intensity data suggests that the adsorption coefficient is higher when coadsorbed NO is present than when it is not. The effects of the adsorption of pyridine on the alumina portion of the surface are evidently felt by NO chemisorbed on the molybdena.

DISCUSSION

The present work contributes to the growing understanding of the surface chemistry of molybdena–alumina catalysts. Pre-

viously we concluded (*13*) that the epitaxial monolayer model would require modification, although certain basic elements of this earlier picture were confirmed, e.g., (a) molybdate is indeed bound to the alumina surface by replacement of the surface hydroxyl groups of the support (*23*) and (b) between one and two OH groups disappear per Mo added. Moreover the results of several studies, including Raman spectra of the raw catalysts (*21, 24–28*) as well as our NMR data (*13*), suggested the presence of molybdate clusters (Mo–O–Mo bonds). This leads to the recently published work of Wang and Hall (*21*) where convincing evidence is presented showing that the polyanions from solution are adsorbed intact on the alumina surface and become bound in a way analogous to that suggested earlier for the monomeric anion. Indeed, it was shown
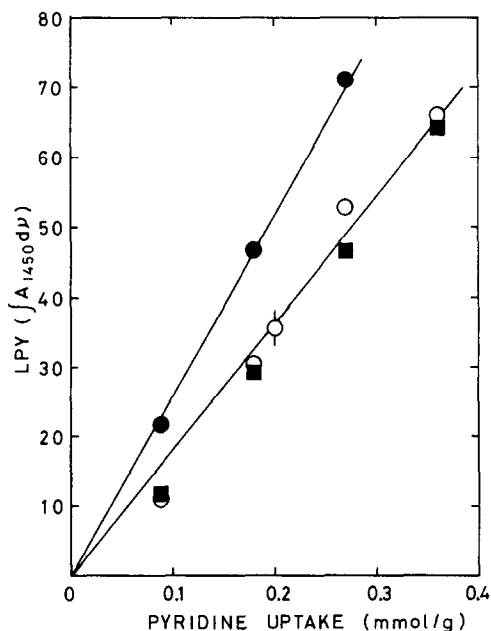

FIG. 9. Beer's Law plots for (LPy) on the reduced catalyst with or without preadsorbed CO$_2$ or NO; ○, represents pyridine adsorption on reduced molybdena–alumina (□/Mo = 0.5) at room temperature; ◐ represents the sample exposed to 4 Torr of pyridine at 200°C for 1 hr followed by evacuation for 2 hr at 200°C; ■, CO$_2$ was adsorbed (68.0 μmol/g) before addition of pyridine to reduced catalyst; ●, NO was adsorbed (184.9 μmol/g) before addition of pyridine to reduced molybdena–alumina.

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that if the pH of the solution were adjusted to the point where the MoO_4^{-2} is the dominant species in solution, the monomeric species is produced on the support surface, but at loadings much lower than usually used. The present paper bears on the changes which occur during reduction. The data of Figs. 4 and 5 show how the alumina surface becomes uncovered during this process. About half of the missing hydroxyl groups could be recovered and the chemisorption of CO_2 increased concomitantly. The latter was shown (Fig. 1) to be specific for the alumina surface. It did not interfere with the chemisorption of NO, which was found to adsorb on CUS produced as the catalyst was reduced (Fig. 3). Note also that neither of these molecules was chemisorbed on the unreduced catalyst and that NO did not chemisorb until $\square$/Mo ≈ 0.1. The latter chemisorption was correlatable with the catalytic activity (6, 12); the chemisorption occurs with pairs of NO molecules and it is therefore thought to occur at sites having multiple coordinative unsaturation. If three-dimensional structures exist, such sites could readily occur on edges or corners of microcrystalline material. Others have expressed similar views concerning the O_2 chemisorption (8–10).

The data of Figs. 7 and 8 show two interesting features, viz., the ratio of the integrated intensities of the asymmetric (1713 cm^{-1}) and symmetric (1815 cm^{-1}) stretching modes of the dinitrosyl (or dimer) bands increased with pyridine coverage while both bands shifted to lower frequencies. The latter effect suggests that the adsorption of pyridine (largely on the uncovered alumina surface) increased the electron back-donation into the NO adsorbed on the molybdena CUS, thus decreasing its bond order. The change in the intensity ratio is similar to that observed by Fateley et al. (30) with NO in a frozen argon or CO_2 matrix. These workers reported that the ratio increased as the dimer concentration was diluted in the matrix. The results in Fig. 7 agree with this observation provided the coadsorbed pyri-

dine can in some way reduce the dimer–dimer interactions, e.g., by decrease in bond angle.

Studies of the preparation and genesis of molybdena–alumina and related catalyst systems (21, 28) have suggested that the raw catalyst can be pictured as the alumina surface randomly populated with polymolybdate anions. These small clusters of seven or so Mo with their associated oxygen become bound to the surface on calcining. Upon reduction, some of these surface bonds are broken as missing alumina hydroxyl groups are reformed. During this process the bilayer clusters must also reorganize into MoO_2 structures not much bigger than the polyanions from which they were formed. These still are bound to the surface of the support as evidenced by the effect of the chemisorption by pyridine on the frequencies and adsorption coefficients of previously chemisorbed NO. It has long been recognized (22) that these reduced catalysts can be readily reoxidized and that such redox cycles can be carried out repeatedly without noticeable change.

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