Site Selective Chemisorption on Sulfided Molybdena–Alumina Catalysts

Recently Segawa and Hall (*1*) reported that NO chemisorbed selectively on the catalytically active sites for hydrogenation of reduced molybdena–alumina catalysts; CO_2, on the other hand, chemisorbed only on the alumina portion of the surface, while pyridine adsorbed nonselectively on both. Sulfided catalysts were not investigated nor was the chemisorption of NH_3. The presently reported data were collected to fill in these deficiencies.

Interestingly, NO, NH_3, and pyridine (Py) were all found (*2*) to function as poisons for the hydrogenation of the propylene, whereas CO_2 did not. NO chemisorbed selectively in pairs on the coordinatively unsaturated sites of both reduced and sulfided catalysts and it was suggested (*3*) that these were Mo^{+2} centers and were the same sites on which O_2 chemisorbs as atoms. The basic molecules, Py and NH_3, have been found to also poison hydrodesulfurization, cyclopropane isomerization, propene polymerization, and metathesis (*2, 4*). On this basis these reactions have been called acid catalyzed (*6–13*). Sulfided catalysts have been said to have stronger acidity than their oxidic precursors or the parent alumina (*5–7*), and sulfiding has been suggested to enhance the Brønsted acidity (*8, 9*). More recent work (*1*) has brought these ideas into serious question. This problem is further explored in the present work.

The catalyst used for the present studies was prepared by the equilibrium adsorption method of Wang and Hall (*14*); it contained 5×10^{20} Mo/g on Ketjen-CK 300 γ-alumina. The molybdena is thought to be present in oxidic clusters of seven or so Mo (or as a sulfide) in both the raw and active states (*14, 15*).

In general, the gases used and the spectroscopic techniques employed were identical with those used in our earlier paper (*1*). The H_2 was purified by passage through an Ag–Pd thimble and the He through successive large traps of freshly activated 5-Å zeolite and charcoal, both at 78 K. The O_2 was dried by anhydrous $CaCl_2$ followed by $Mg(ClO_4)_2$. The NH_3 (Matheson anhydrous 99.9%) and NO (Linde, 98.5%) were further purified by distilling the gases from one trap to another using a repeated freeze-pump-thaw-freeze technique. The Py was multiply distilled, dried, and stored over 5-Å molecular sieves as before. For sulfiding, H_2S (Airco, 99.5%) was blended with purified H_2 and used without further purification.

The spectra were recorded using a Nicolet MX-1 FT spectrometer after 160 scans. The wafer thickness was ~10 mg/cm². All samples were calcined overnight in flowing O_2 and evacuated, both at 500°C. As required the catalysts were reduced in flowing H_2 at 500°C or sulfided in a stream of 10% H_2S/H_2 at 350°C. In either case the flow rate was 70 cm³ (NTP)/min and the treatment times were 1 and 4 h, respectively. In both cases the catalysts were then purged with He for 1 h at 500°C. (In one set of experiments, the final He purge step was carried out at room temperature over a freshly sulfided catalyst. Thus, the possibility that residual adsorbed H_2S might generate Brønsted acidity was investigated.) The spectra obtained from pyridine adsorbed on the oxidized, reduced, and sulfided forms of the catalyst are compared with that from
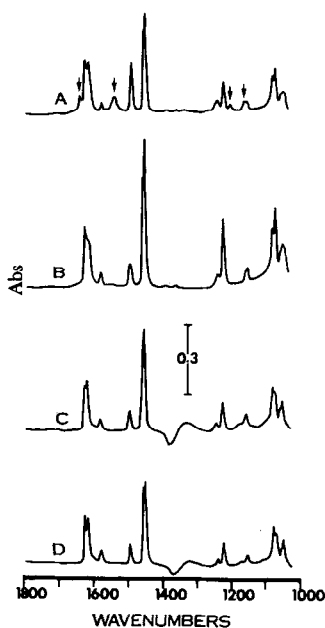
FIG. 1. Spectra from pyridine on a molybdena–alumina catalyst (5×10^{20} Mo/g) cat, prepared by the equilibrium adsorption method). All samples were precalcined at 500°C overnight. Spectrum A is for the freshly oxidized catalyst after 15 min evacuation at 500°C. Spectrum B is for the reduced catalyst. Reduction was carried out at 500°C in flowing H_2, ~70 cm^3 (NTP)/min, for 1 h ($\square$/Mo = 0.5, e/Mo = 1.3) and the catalyst was evacuated at 500°C for 1 h. Spectrum C is for the sulfided catalyst. Sulfiding was carried out at 350°C in 10% H_2S/H_2 mixture flowing at a rate ~70 cm^3 (NTP)/min for 4 h, then the catalyst was pumped with He at 500°C for 1 h. Spectrum D is for alumina, Ketjen CK-300, after evacuation at 500°C for 1 h. Pyridine was adsorbed at room temperature at 4 Torr for 30 min followed by 30 min evacuation at 100 and 200°C. The background spectrum has been subtracted. Arrows indicate the bands assigned to BPy.

the parent alumina in Fig. 1. The band positions are listed in Table 1 where those corresponding to pyridinium ion are in boldface for easy reference. These bands were detected only when the catalyst was in its completely oxidized form. The remaining bands were all present in nearly the same intensities even when the adsorbent was the alumina base. In all cases the Py was adsorbed at room temperature by exposing the wafer to its vapor at ~4 Torr. The exposure time was 30 min. The spectra were re-

corded at room temperature following a 30-min evacuation at 100°C and again after a similar treatment at 200°C.

Corresponding spectra of the bending vibrations of chemisorbed NH_3 are shown in Fig. 2; the band positions are listed in Table 1 with those attributable to NH_4^+ in boldface (17, 18). Knozinger (17) has summarized the frequencies associated with the various forms of chemisorbed NH_3. The NH_3 was adsorbed at room temperature at a pressure of 50 Torr for 30 min and evacuated at the same temperature for 30 min before recording the spectra. Higher evacuation temperatures were not feasible because of decomposition with concomitant reduction. The spectra were all qualitatively similar. All of the significant bands appeared on all three catalyst preparations and on the alumina base. Interestingly, bands corresponding to NH_4^+ appeared in all cases, but were much stronger on the oxidized form of the catalyst than in any of the other cases. As noted above, Brønsted acidity was not detectable with Py after reduction or sulfidation. The sulfided and re-

TABLE 1

Observed Spectra of Chemisorbed Pyridine and NH_3 on Molybdena–Alumina Catalysts

Sample	Observed frequencies, cm^{-1}	
	Adsorbed pyridine	Adsorbed ammonia
Oxidized Mo/γ-Al$_2$O$_3$	1071, 1081, 1156, **1163** **1203**, 1222, 1242 1451, 1490, **1540** 1576, 1614, 1625, **1639**	1255, —, **1449** 1613, **1675**
Reduced Mo/γ-Al$_2$O$_3$	1070, 1078, 1153, — —, 1223, 1240 1451, 1493, — 1578, 1611, 1623, —	1250, **1407, 1475** 1612, **1680**
Sulfided Mo/γ-Al$_2$O$_3$	1074, 1079, 1156, — —, 1223, 1243 1450, 1493, — 1576, 1616, 1624, —	1267, **1398, 1471** 1612, **1683**
γ-Al$_2$O$_3$	1071, 1079, 1154, —, —, 1224, 1241, 1450, 1494, —, 1577, 1614, 1624, —	1183, 1212, **1391,** **1476,** (1508), (1554), 1618, **1690**

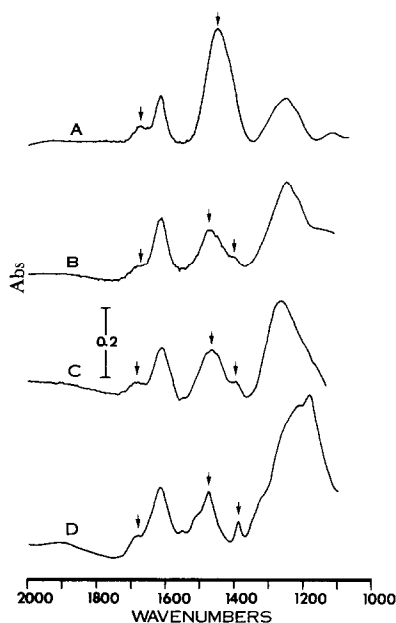Note. Frequencies in boldface were attributed to protonated species.

FIG. 2. Spectra from ammonia adsorbed on molybdena–alumina catalysts, prepared by the equilibrium adsorption method. All samples were precalcined at 500°C overnight. Spectra A, B, C, and D were recorded after identical pretreatments described in Fig. 1. Ammonia was adsorbed at room temperature at 50 Torr for 30 min followed by 30 min evacuation at room temperature. The background spectrum has been subtracted in each case.

duced preparations gave closely similar spectra (Figs. 2B and C) just as they did with Py (Figs. 1B and C).

The origin of the NH_4^+ bands is not without ambiguity. The same bands appeared on the alumina base together with weak bands at 1508 and 1554 cm^{-1} which are attributable (18) to NH_2^-. It is therefore possible that disproportionation occurred on either the acid–base pair sites or by some other mechanism not currently understood.

The sulfided catalyst was investigated using NO and CO_2 to define the location of the chemisorbed Py and NH_3. With the former, the results were in all respects strictly comparable with those reported earlier by Segawa and Hall (1) for reduced catalysts. The NO was found to adsorb selectively on the molybdena portion and the CO_2 on the uncovered alumina portion of the surface.

These chemisorptions had little effect on each other. The NO chemisorbed in pairs on sites which chemisorb O_2 as atoms (3). The intensities of the CO_2 bands were lower for the sulfided molybdena–aluimina 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 CO_2 was subtracted. When CO_2 was added to a catalyst on which NO had been previously chemisorbed essentially the same results were obtained. When Py was added to a system having presorbed CO_2, the CO_2 was eluted as evidenced by the disappearance of the CO_2 bands from the spectrum. When NO was chemisorbed first the dinitrosyl bands remained undiminished in intensity when Py was added, but were shifted to lower frequency by about 50 cm^{-1}. Finally, when pyridine was adsorbed first, the NO bands still formed but with much lower intensity and the same shift to lower frequency was observed. It is therefore evident that a large portion of the Py adsorption occurs on the alumina surface although it does chemisorb and poison the active catalytic sites of the molybdena. Reference should be made to Fig. 1 of Ref. (1) to appreciate these results. Evidently the chemisorption of Py cannot be used to measure the concentration of these catalytically active sites.

NH_3, like Py, was found to chemisorb unselectively on both the alumina and the molybdena portions of the surface. It effected the complete desorption of preadsorbed CO_2 showing that much of the adsorption is on the alumina portion of the surface. The data obtained are summarized in Fig. 3. The spectra from NO adsorbed on the reduced and sulfided catalysts are shown as the solid and dashed curves, respectively, in Fig. 3A. In each case the catalyst was contacted with 8 Torr of NO for 1 h and evacuated for 30 min, both at room temperature, before these spectra were taken. The same treatment was used before NH_3 was
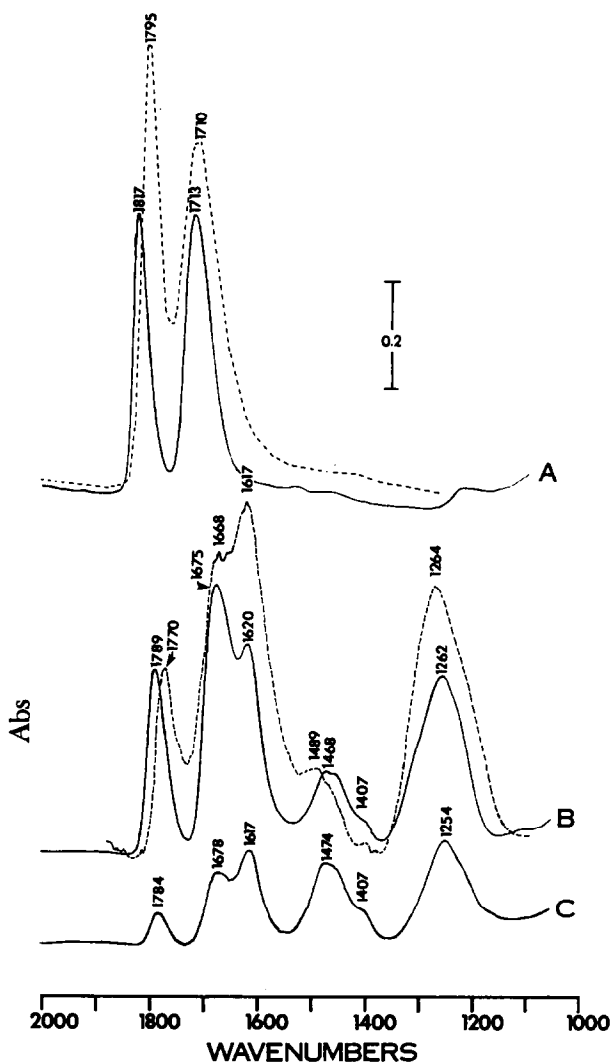
FIG. 3. Interaction of NH$_3$ and NO on reduced or sulfided molybdena–alumina catalysts (5 × 10^{20} Mo/g prepared by the equilibrium adsorption method). Reduction and sulfiding (when required) were carried out as described for Fig. 1. Ammonia was adsorbed at 50 Torr for 30 min at room temperature followed by 30 min evacuation at room temperature. NO was adsorbed at 8 Torr for 1 h at room temperature, followed by 30 min evacuation at room temperature. Spectrum A is from adsorbed NO. Spectrum B is from adsorbed NO and subsequent adsorption of NH$_3$. Spectrum C is from adsorbed NH$_3$ and the subsequent adsorption of NO. The solid curves are for the reduced catalysts and dashed curves are for the sulfided one. Interestingly, unlike the reduced catalyst (Spectrum C), when sulfided the identical spectrum was produced when first exposed to NH$_3$ followed by NO as when the order was reversed (dashed curve, B). The background spectrum has been subtracted in each case.

added to the preadsorbed NO (Fig. 3B). In this case the expected NH$_3$ bands appeared (probably mainly from the alumina portion of the surface) and the NO bands were noticeably shifted to lower frequencies, broadened and changed in relative intensi- ties as reported earlier for pyridine (1). Both the reduced and the sulfided catalyst responded similarly in these experiments. The NO was not desorbed, but appeared to experience an electronic interaction. Finally, when NH$_3$ was chemisorbed first and
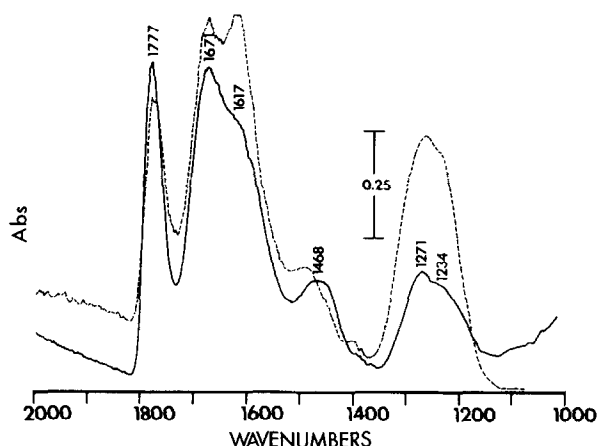
FIG. 4. The coadsorptions of NO and NH₃ on sulfided molybdena–alumina. The spectrum shown as the solid line was taken from the preparation which had been allowed to cool to room temperature from 350°C in the 10% H₂S/H₂ sulfiding mixture before evacuation. The procedure for the introduction of NO and NH₃ was identical to that described for Fig. 3B. For comparison, a similar spectrum (dashed line) is shown taken from a sample which had been purged in He for 1 h at 500°C following the sulfiding treatment.

then NO was added, the NO bands from the reduced catalyst were strongly suppressed in intensity, thus demonstrating again that the NH₃ is also strongly chemisorbed on molybdena sites (Fig. 3C). Unexpectedly the sulfided catalyst responded somewhat differently in these experiments than did the reduced one. The preadsorption of NH₃ did not repress the chemisorption of NO. Virtually identical spectra were obtained regardless of the order of exposure to NO and NH₃, both are depicted by the dashed curve B. After the prechemisorption of CO_2 on either catalyst, the spectra after adding NH₃ became indistinguishable from those of the chemisorbed NH₃ shown in Figs. 2B and C. In these experiments 50 Torr of NH₃ was equilibrated with the catalyst wafer for 30 min before evacuation for an equal interval at room temperature.

The spectrum from chemisorbed NO and NH₃ on sulfided molybdena–alumina which had been allowed to cool to room temperature in the 10% H₂S/H₂ stream is compared in Fig. 4 with the one from a sample purged at 500°C in He after sulfiding. Again, the resulting spectra were not dependent upon the order in which the sulfided sample was

exposed to these gases. The band intensities from the dinitrosyl species and from the NH₄⁺ (1468–1489 cm⁻¹) were not significantly affected by cooling in the H₂S/H₂ sulfiding mixture, but those from the Lewis bound form were noticeably weakened. (Compare also the bands centered on ~1620 and ~1260 cm⁻¹ in Fig. 4 with those of dashed curve B in Fig. 3B.)

The NO bands from our sulfided catalysts were shifted to lower wavenumbers, as were Okamoto's (19), although the shifts observed here were smaller. Peri (20) reported no shift. It is likely that the shift (or lack of it) is due to slight differences in the pretreatment and post-treatment used. By contrast, the CO_2 bands were in all cases at the same position: 1231, 1332, 1447, 1482, 1572, and 1641 cm⁻¹. These bands have all been assigned to the several species formed on the partially dehydroxylated surface of alumina (16, 21, 22). Since there is no direct interaction between these species and the supported molybdena species this invariance (except for changes in intensity) was as expected and as observed previously (1).

It was possible with the present spec-

trometer to obtain good quality spectra below 1050 cm^{-1}. Thus Figs. 1 and 2 and Table 1 contained data for lower frequencies than have been previously reported. Interestingly, with pyridine it was possible to associate two of these bands (at 1163 and 1203 cm^{-1}) with pyridinium ion.

The question as to whether reduced and/or sulfided molybdena–aluimina catalysts have Brønsted acidity strong enough to catalyze carbonium ion reactions remains to be addressed. No evidence of such acidity was found using pyridine except for the catalyst in its oxidized form. With NH_3 the presence of NH_4^+ was characterized unambiguously in all preparations. The bands were, however, much less intense with the reduced and/or sulfided preparations than with the catalyst in its completely oxidized state. NH_3 is a much stronger base than Py and it could be argued that the weaker acidity is being detected to which Py does not respond. Moreover, it could be further suggested that if NH_4^+ can form so may carbonium ions by an analogous mechanism whatever it may be. The data show, however, that the NH_4^+ bands characterized for the alumina support are approximately as intense as those for the reduced or sulfided catalysts and that the strongest bands were obtained from the oxidized form of the catalyst as previously reported for pyridine (1). Moreover, since a large fraction of the base is held by the alumina, the data suggest that Brønsted acidity, if any, should be associated with the alumina hydroxyl groups. These apparently can be made to function (reluctantly) for cyclopropane isomerization above 200°C (24) and for cumene dealkylation (25) (inefficiently) above 450°C. Interestingly, Massoth (9) has noted that a sulfided catalyst did not catalyze cumene dealkylation up to 400°C. It may also be argued that a cocatalyst such as H_2S or even H_2 may function to produce Brønsted acidity by heterolytic dissociative adsorption under dynamic reaction (HDS) conditions at say 350°C. If so, supporting evidence should be sought.

The term acidity is used loosely in the literature. Usually the evidence is circumstantial, e.g., reaction products typically found for a Brønsted acid catalyst appear (among others) or nitrogen bases are strongly adsorbed and TPD yields several peaks. Whereas we do not deny the possibility of Brønsted acid catalysis under dynamic HDS conditions, we think that alternative explanations should be sought which are consistent with known organometallic and inorganic chemistry and with results obtained under milder reaction conditions.

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