

Polynuclear Metal Complexes as Model Mixed Oxide Catalysts: Selective Chemisorption of Ammonia and Nitric Oxide

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Model mixed oxide catalysts were prepared by supporting polynuclear metal (M^{3+} and Cu^{2+}) complexes of the form $M[(\mu-OH)Cu(\mu-OCH_2CH_2NR_2)]_6^{3+}$ ($M = Al, Cr, \text{ and } Fe$) on Cab-O-Sil (28 wt% loading). The supported complexes exhibited both Brønsted (bridging OH groups) and Lewis (Cu^{2+} ions) acidities. While the coordinatively saturated central M^{3+} ion was not an available Lewis site, changing M^{3+} influenced catalyst acidity through an apparent ligand effect. Reported are acidity characterizations by ammonia adsorption, first with Cu^{2+} ions open to estimate overall acidity, and second with Cu^{2+} ions blocked to evaluate the Brønsted acidity. Selective sorption of nitric oxide was an effective Lewis site poison at temperatures to 80°C. Ammonia sorption to unpoisoned supported complexes revealed increasing overall acidity for the series Al to Cr to Fe (with NH_3 adsorption heats of 4.6, 8.1, and 8.2 kcal/mol, respectively). Ammonia sorption to NO-poisoned supported complexes indicated increasing Brønsted acidity with NH_3 adsorption heats of 2.6, 8.5, and 8.2 kcal/mol, respectively. © 1988 Academic Press, Inc.

INTRODUCTION

In an effort to describe mixed oxide acid catalysis, we previously reported the preparation and preliminary characterization of polynuclear metal (M^{3+} and Cu^{2+}) complexes of the form $M[(\mu-OH)Cu(\mu-OCH_2CH_2NR_2)]_6(ClO_4)_3$ ($M = Al, Cr, \text{ and } Fe$) supported on Cab-O-Sil (1, 2). These could be supported as a monolayer of intact complexes at loadings to 28 wt% (1). Moreover, the complexes showed Brønsted and Lewis acidity for which the total acidity depended on the coordinatively saturated central metal ion (cmi) of the complex, M^{3+} (2). It appeared prudent to characterize how the individual site acidities responded to changes in the cmi.

The M^{3+} ion is fully coordinated with octahedral symmetry, and the six cupric ions are connected to the cmi through six OH bridges. Each Cu^{2+} exhibits square planar symmetry with four ligands (OH bridge, two alkoxide bridges, and $-NR_2$). Another OH bridge (linking an adjacent Cu^{2+} to the cmi) occupies the Jahn–Teller

position of the Cu^{2+} ion as a “distant” fifth ligand. Thus, each cupric ion shows one coordinately unsaturated site (CUS) and the disklike complex as an entity has three CUS per face since the M^{3+} is coordinatively saturated. See references (1) and (2) for a detailed description of the structure of the complex.

Our earlier work (2) showed that the cupric ion is the sole center of Lewis acidity; the bridging hydroxide groups between the Cu^{2+} and M^{3+} ions were identified as Brønsted acid sites. While the fully coordinated cmi was not available for direct interaction with adsorbing species, it was observed that overall acidity (Cu^{2+} Lewis sites plus OH Brønsted sites) changed by varying M^{3+} . Recently, we have attempted to characterize by ammonia adsorption the acidities of the specific Brønsted and Lewis sites as a function of the ligand effect for changing cmi. In the present work, we report the ammonia sorption properties of the supported complexes, first with cupric ions open to estimate total acidity, and second with cupric ions blocked to probe

acidities of the individual Brønsted and Lewis sites.

Our initial attempt to block the cupric ion involved synthesis of complexes with large aminoalkyl groups (i.e., R = *n*-butyl) (2). Both scale model studies and IR spectra of ammonia chemisorption suggested that the *n*-butyl groups sterically hindered sorption to the Lewis sites (2). However, subsequent work (1) revealed that the complexes bind to the support via an ion exchange mechanism by releasing H⁺ and perchlorate counterion for each net ionic interaction. Complexes with smaller aminoalkyl groups (R = ethyl) could exchange ions completely with the support, allowing for removal of all ClO₄⁻, whereas, *n*-butyl complexes showed a steric hindrance to total ion exchange and retained some ClO₄⁻. We studied the fully ion-exchanged system (R = ethyl with no ClO₄⁻ present) so as to eliminate the unknown influences of the counterion on ammonia sorption to the supported complexes.

Studies of the fully exchanged system (1) suggested the majority of the disk-shaped complexes must be oriented flat against the support surface to allow three ion-exchanging interactions. Thus, we expect three OH groups (Brønsted sites) and three Cu²⁺ ions (Lewis sites) to be available for sorption, and the coordinatively saturated M³⁺ cmi is inaccessible. We report here our efforts to selectively block the cupric ions from ammonia sorption by poisoning with nitric oxide.

EXPERIMENTAL

We described previously the procedures for preparing the supported catalysts having loadings to 28 wt% (1, 2). The loading of complex on Cab-O-Sil (M-5, 200 m²/g, Cabot) in the present study was 28 wt%, which corresponds to a monolayer covering of complex on the support (1). Infrared spectra were collected by means of the equipment and procedures described previously (2). NO-poisoned samples were

prepared in the IR cell by exposing the catalyst wafers to NO at 5 Torr for 1 h at 40°C. Prior to the IR analysis these wafers were evacuated at 40°C for 1 h to remove the weakly sorbed NO. Reported are single-scan absorbance-mode spectra.

The ammonia isotherms were developed with the equipment described in Ref. (2) and the following procedure. We measured NH₃ pick-up by subtracting the weight of the sample (after 1 h exposure) at the desired temperature and pressure from the weight of the same sample when subsequently exposed to pure nitrogen for 1 h at the same temperature and total volumetric flow rate. This procedure desorbed the weakly bound ammonia from the sample. We repeated the procedure for increasing ammonia partial pressures from 0.5 to 30 Torr (1 Torr = 133.3 Pa) at temperatures of 40, 80, and 125°C. The nitric oxide pick-up was determined in a similar manner at temperatures of 40 and 80°C for NO partial pressures of 0.2 to 5 Torr. The samples were flushed with nitrogen subsequent to the NO exposure to drive off any weakly sorbed NO. The NO-poisoned samples were prepared in the thermal gravimetric apparatus by exposing a fresh sample to NO (5 Torr for 1 h) at the desired temperature of the isotherm. These poisoned samples were titrated for ammonia pick-up in the manner described for the fresh catalysts.

Gases for gravimetric studies, including 5.04% NH₃ (balance N₂, Matheson), 5.14% NO (balance N₂, Matheson), and N₂ (HoloX) were dried through beds of activated molecular sieves on delivery. Gases for IR studies, including anhydrous NH₃ (99.99%, Matheson) and NO (99.0%, Matheson), were pretreated in a similar manner.

RESULTS

NO Chemisorption

We confirmed the chemisorption of NO by IR spectroscopy of thin, self-supporting wafers of the Cab-O-Sil-supported catalysts

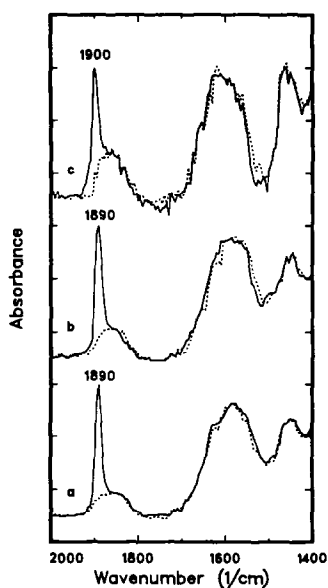


FIG. 1. IR spectra of chemisorbed NO on supported polynuclear metal complexes. Dotted lines, background spectra; solid lines, spectra after NO exposure. (a) Fe complex; (b) Cr complex; (c) Al complex.

exposed to NO at 5 Torr for 1 h and evacuated to 1×10^{-6} Torr for 1 h at 40°C (Fig. 1). The background spectra before NO exposure, are indicated by dotted lines, and the spectra after NO exposure are the solid lines. The background spectra show peaks at 1880, 1600, and 1460 cm^{-1} . Exposure to NO produced one additional strong absorbance near 1900 cm^{-1} . Apparently, the vibrational frequency of the NO changes with cmi of the complex. NO sorbed to the supported Fe and Cr complexes showed the lower frequency (1890 cm^{-1} , Figs. 1a and 1b), whereas the Al complex showed the higher frequency (1900 cm^{-1} , Fig. 1c).

NO adsorption isotherms, determined in the thermal gravimetric apparatus, were "flat" at temperatures of 40 and 80°C and NO partial pressures between 0.2 to 5 Torr for all supported catalysts (see Fig. 2). The pick-up of NO is reported as moles of NO per mole of polynuclear metal complex in

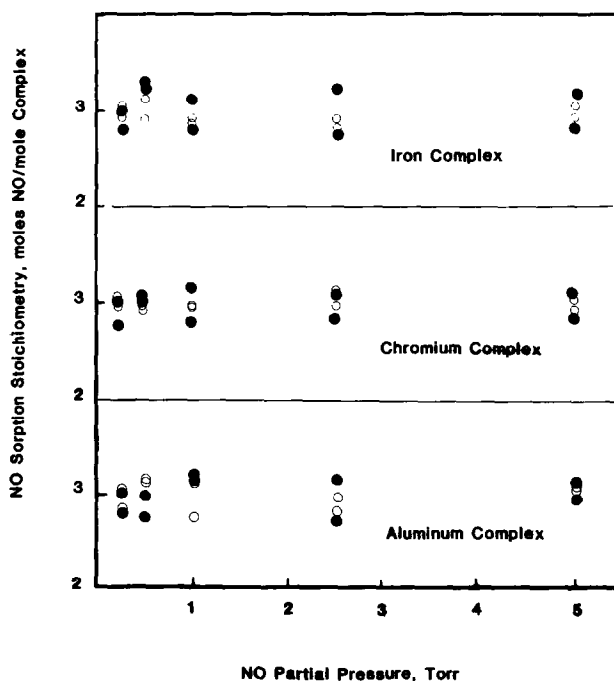


FIG. 2. NO sorption stoichiometry of supported polynuclear metal complexes. \circ , $T = 40^\circ\text{C}$; \bullet , $T = 80^\circ\text{C}$.

TABLE 1

Nitric Oxide Chemisorption to Supported Complexes

T (°C)	NO stoichiometry (mol NO/mol complex)		
	Aluminum	Chromium	Iron
40	3.01 ± 0.45	3.03 ± 0.33	2.99 ± 0.47
80	3.04 ± 0.38	3.05 ± 0.20	2.94 ± 0.25

Note. Uncertainties are reported at the 95% confidence level.

the supported sample. We define this mole ratio as the NO sorption stoichiometry. Even at the lowest pressures, the pick-up of NO at both temperatures is close to a stoichiometry of 3. The mean NO stoichiometries of NO are given in Table 1 with 95% confidence level uncertainties.

Ammonia Chemisorption to Unpoisoned Catalysts

The gravimetric data of ammonia retained after the nitrogen purge are reported as moles of ammonia per mole of polynuclear metal complex in the sample; we define this mole ratio as the ammonia sorption stoichiometry. These ammonia sorption data at 40, 80 and 125°C were fit to Langmuir isotherms (Figs. 3–5) for the supported Al, Cr, and Fe complexes. The Langmuir model for single-site, associative sorption was used at each of the three temperatures to extract the following parameters: ammonia sorption stoichiometries at saturation (Table 2), equilibrium adsorption coefficients (Table 3), and heats of adsorption (Table 4). For all three tem-

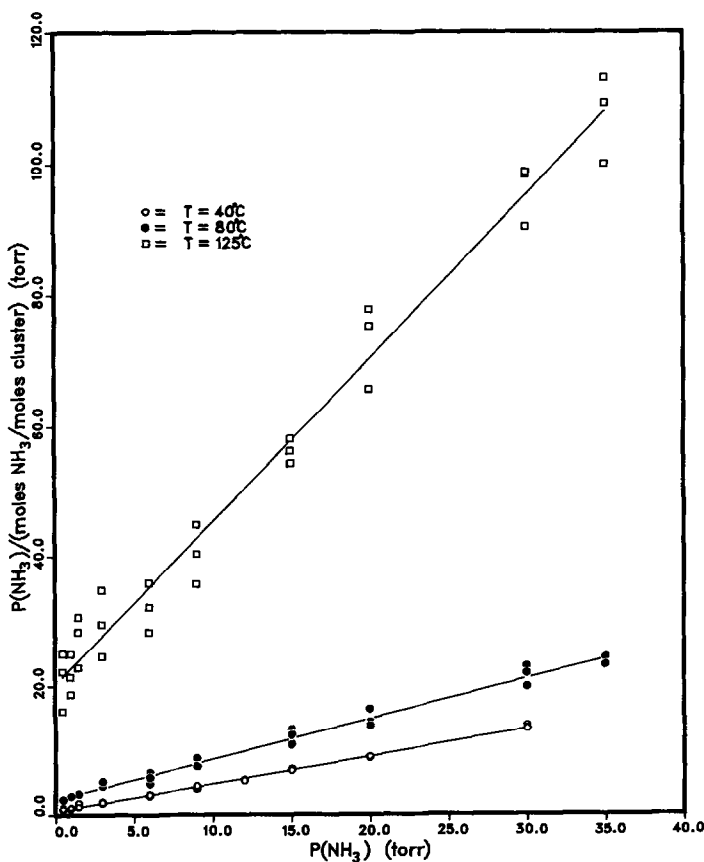


FIG. 3. Langmuir isotherms of ammonia chemisorption to supported polynuclear Al complex.

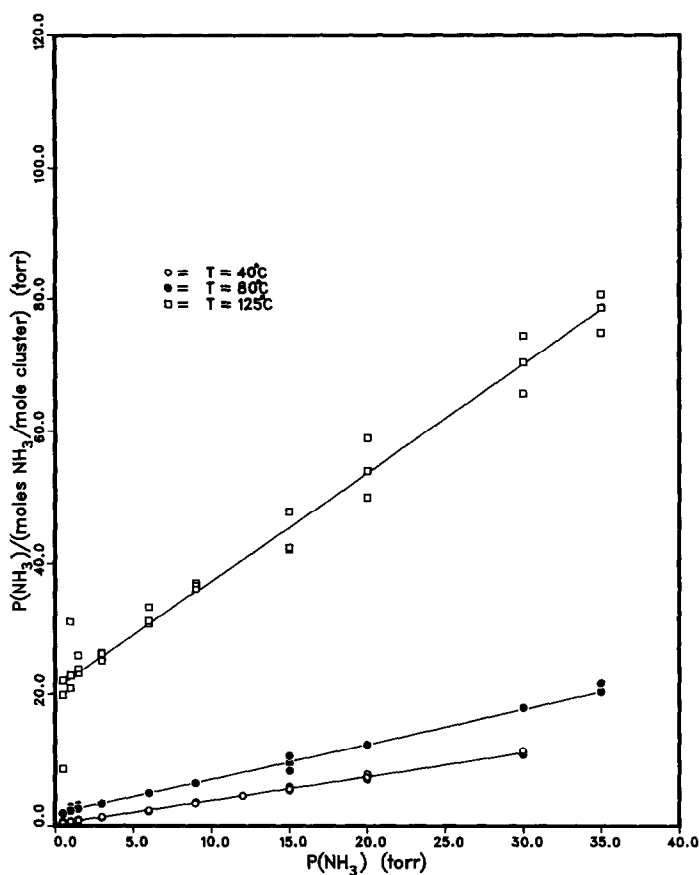


Fig. 4. Langmuir isotherms of ammonia chemisorption to supported polynuclear Cr complex.

peratures (40, 80, and 125°C), the saturation stoichiometry was greatest for the Fe complex (3.12, 2.20, and 0.75), least for the Al complex (2.39, 1.61, and 0.40), and inter-

mediate for the Cr complex (2.76, 1.90, and 0.61). The equilibrium adsorption coefficients at each temperature followed the same trend with M^{3+} , except for 125°C,

TABLE 2
Ammonia Langmuir Constants, Saturation Stoichiometries

Complex	NO-poisoned?	Ammonia saturation stoichiometry (mol NH ₃ /mol complex)		
		40°C	80°C	125°C
Aluminum	—	2.39 ± 0.05	1.61 ± 0.07	0.40 ± 0.02
Aluminum	Yes	0.89 ± 0.03	0.40 ± 0.02	—
Chromium	—	2.76 ± 0.06	1.90 ± 0.06	0.61 ± 0.04
Chromium	Yes	1.85 ± 0.04	1.20 ± 0.03	—
Iron	—	3.12 ± 0.04	2.20 ± 0.04	0.75 ± 0.04
Iron	Yes	2.10 ± 0.04	1.47 ± 0.03	—

Note. Uncertainties are reported at the 95% confidence level.

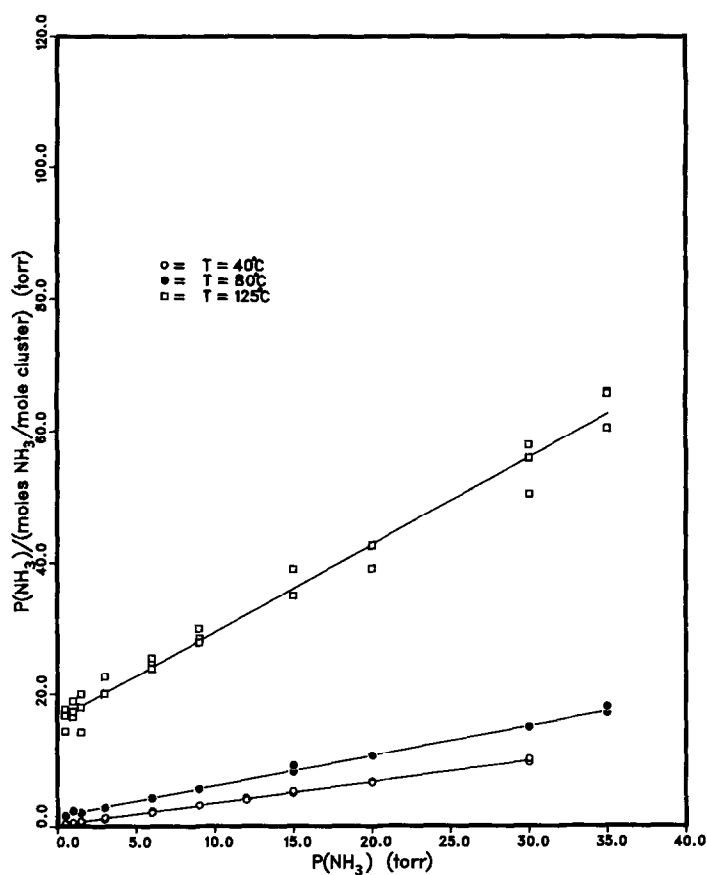


FIG. 5. Langmuir isotherms of ammonia chemisorption to supported polynuclear Fe complex.

where the Al complex showed the greatest value of K . The heats of adsorption were nearly the same for the Cr and Fe complexes (8.15–8.20 kcal/mol), and the Al

complex showed the smallest heat (4.56 kcal/mol).

In IR experiments, thin wafers of the supported complexes were exposed to low

TABLE 3

Ammonia Langmuir Constants: Equilibrium K Values

Complex	NO-Poisoned?	Equilibrium K values (Torr ⁻¹)		
		40°C	80°C	125°C
Aluminum	—	0.58 ± 0.09	0.25 ± 0.04	0.12 ± 0.01
Aluminum	Yes	0.27 ± 0.03	0.16 ± 0.008	—
Chromium	—	1.26 ± 0.43	0.28 ± 0.04	0.079 ± 0.01
Chromium	Yes	1.32 ± 0.35	0.28 ± 0.02	—
Iron	—	1.35 ± 0.34	0.31 ± 0.03	0.082 ± 0.01
Iron	Yes	1.38 ± 0.35	0.31 ± 0.02	—

Note. Uncertainties are reported at the 95% confidence level.

TABLE 4
Heats of Adsorption for Ammonia

Sites available	Heats of adsorption (kcal/mol)		
	Aluminum	Chromium	Iron
Both	4.56 ± 1.28	8.20 ± 2.06	8.15 ± 1.45
Brønsted	2.87 ± 0.59	8.46 ± 1.53	8.22 ± 1.22

Note. Uncertainties are reported at the 95% confidence level.

partial pressures of ammonia at 40°C. The ammonia partial pressures were adjusted for each supported complex so that the ammonia stoichiometry was near 1. These ammonia pressures were determined from the correlated sorption stoichiometry data at 40°C. The blank IR absorbance spectra (Fig. 6, curve a, and dotted lines of curves b and c) of the catalysts before admission of the ammonia show only two broad peaks at 1600 and 1460 cm^{-1} . With the sorption of ammonia, peaks developed near 1600 cm^{-1}

for all three catalysts; however, the intensities of these peaks are different (curve c for all three complexes). This peak is more intense for the aluminum complex than for the chromium and iron complexes. The iron and chromium complexes also show sharp absorbances near 1450 cm^{-1} whereas the aluminium complex shows a very small peak at this frequency (curve c). The spectra denoted by curve b are for NO-poisoned catalysts, described in the next section.

Ammonia Chemisorption to NO-Poisoned Catalysts

Thin wafers of the supported polynuclear metal complexes ($M = \text{Al}, \text{Cr}, \text{and Fe}$) were exposed to NO at 5 Torr for 1 h at 40°C and evacuated to 1 μT for 1 h at 40°C to produce NO-poisoned catalysts. These samples were examined by IR spectroscopy in the ammonia deformation region (Fig. 6, curve b). The NO exposure produced no absorbance between 1400 and 1700 cm^{-1} (Fig. 6, curve a, and dotted lines in curve b); however, a single large peak

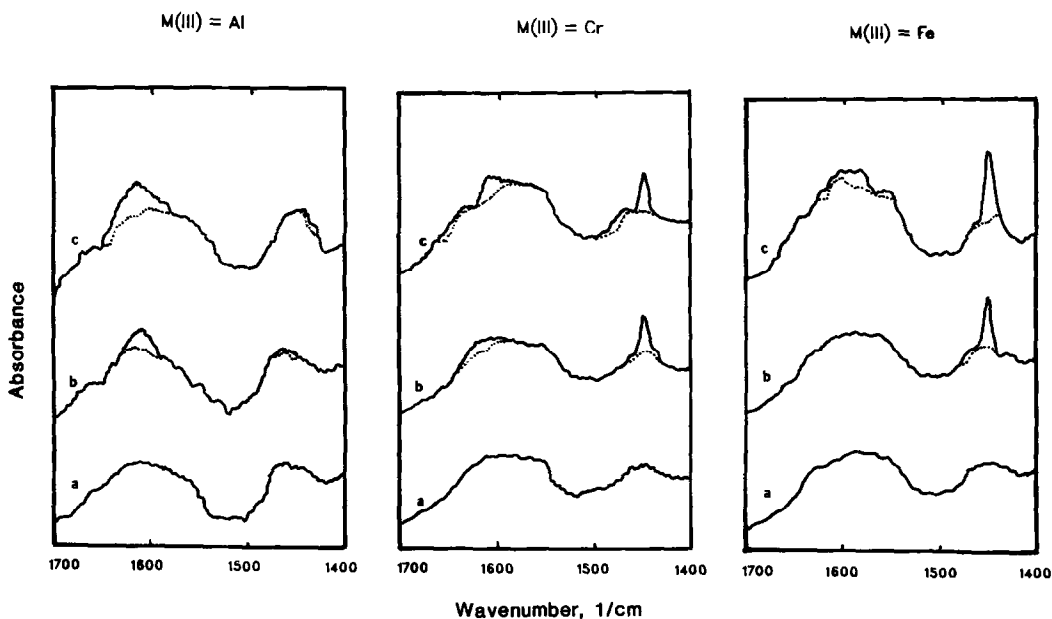


FIG. 6. IR spectra of ammonia on poisoned and unpoisoned catalysts. (a) Background spectra; (b) ammonia on NO-poisoned catalysts; (c) ammonia on unpoisoned catalysts.

developed in the NO-stretch region (Fig. 1). These samples were subsequently exposed to ammonia at partial pressures necessary to produce an ammonia stoichiometry near 1 (except for Al, maximum stoichiometry 0.71). Once again, correlated ammonia adsorption data determined for the NO-poisoned samples (see next paragraph for a discussion of these data) were used to prescribe the proper ammonia pressures at 40°C. IR spectra of these samples were recorded after evacuation (Fig. 6b, solid curves). The NO-poisoned iron complex showed only one sharp, intense absorbance at 1450 cm^{-1} . The chromium sample showed a sharp, intense peak near 1450 cm^{-1} and a weak, broad relaxation near 1610 cm^{-1} . The aluminum complex showed one peak near 1610 cm^{-1} and a weak, poorly defined peak near 1450 cm^{-1} . The peaks at 1600–1610 cm^{-1} in the IR spectra of the poisoned and unpoisoned catalysts

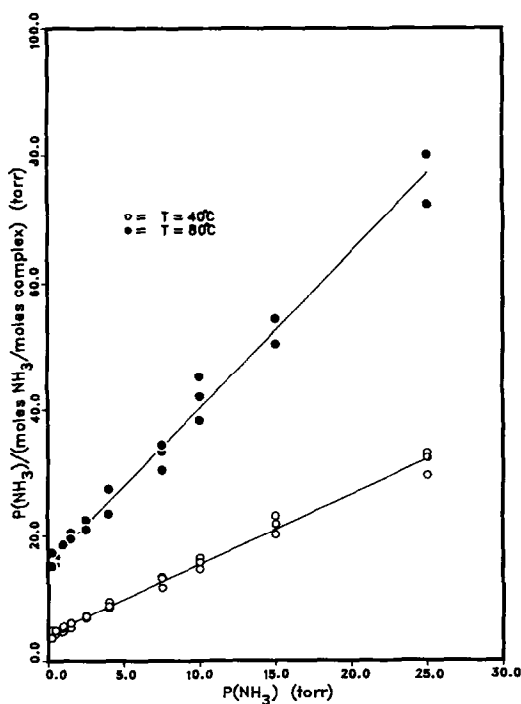


FIG. 7. Langmuir isotherms of ammonia chemisorption to supported polynuclear aluminum complexes poisoned by NO.

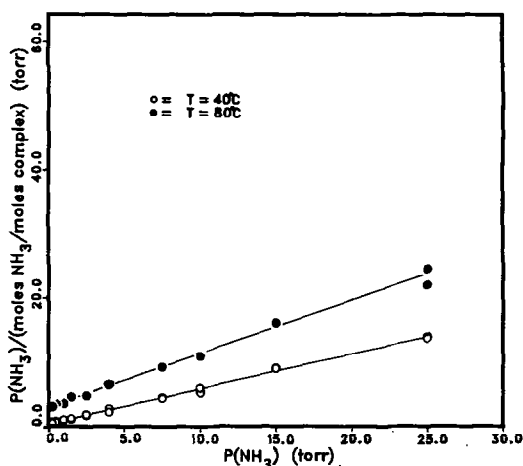


FIG. 8. Langmuir isotherms of ammonia chemisorption to supported polynuclear chromium complexes poisoned by NO.

(Fig. 6, curves b and c) were smaller in the NO-poisoned samples than in the unpoisoned samples. The peaks at 1450 cm^{-1} were only slightly different in the NO-poisoned samples. The vibrational frequency of the NO was unaffected by the sorption of ammonia (1890–1900 cm^{-1} for NO).

Ammonia sorption data, linearized to Langmuir isotherms at temperatures of 40 and 80°C, are shown in Figs. 7–9 for the supported Al, Cr, and Fe complexes, which were poisoned with NO prior to the ammonia sorption. Langmuir isotherm fits of the data yielded the saturation stoichiometries (Table 2), adsorption equilibrium constants (Table 3), and the heats of adsorption (Table 4) for these NO-poisoned samples. The saturation ammonia pick-up changed with cmi: Fe = 2.10, 1.47; Cr = 1.85, 1.20; Al = 0.89, 0.40 mol NH_3 /mole complex at 40 and 80°C, respectively. The NH_3 adsorption coefficients of the supported Cr and Fe complexes poisoned by NO were the same within experimental error but the K values for the supported Al complex were much smaller (Figs. 10–12). As with the unpoisoned complexes, the heats of adsorption for the chromium and iron complexes were the same, within

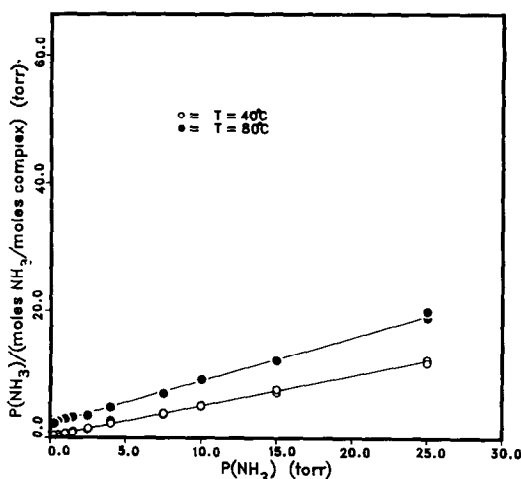


FIG. 9. Langmuir isotherms of ammonia chemisorption to supported polynuclear iron complexes poisoned by NO.

experimental error (8.46 and 8.22 kcal/mol), but the heat of adsorption for the aluminum complex was much lower, 2.87 kcal/mol.

Poisoning the Al complex by NO decreased the saturation pick-up from 2.39 to 0.89 mol NH_3 /mole complex at 40°C. Decreases in ammonia uptake on poisoning by NO were observed for the Cr and Fe complexes. The ammonia equilibrium constants at 40 and 80°C decreased significantly in the Al complexes when the cupric sites were blocked by NO; however, no significant differences were observed in the K values between the NO-poisoned and unpoisoned complexes of Cr and Fe. The ammonia heats of adsorption for the Cr and Fe complexes changed little upon poisoning by NO; however, the heat of adsorption for the Al complex decreased from 4.59 to 2.87 kcal/mol on poisoning by NO.

DISCUSSION

The selective poisoning of the Cu^{2+} sites is confirmed by the IR spectra and the NO stoichiometry of the samples exposed to NO. The NO stoichiometry data suggest the cupric ions are the sorption sites since the isotherms show a stoichiometry of three NO molecules per complex, mirroring the

number of cupric ions per complex available for chemisorption when the complexes are supported on Cab-O-Sil.

Next, consider the IR data for NO sorption to the supported complexes. Others have correlated the IR spectrum of chemisorbed NO with spectra of molecular NO and model complexes to identify the metal site of NO bonding (3, 4, 6). In the present case, the observed relaxation at 1890–1900 cm^{-1} compares favorably to the NO peak observed at 1890 cm^{-1} on CuO/SiO_2 (4). In the latter study, vibrations from 1510 to 1605 cm^{-1} were attributed to NO interaction at oxygen sites or adsorption of NO_2 impurities, not to NO sorption to a cupric site (4).

The single vibration near 1900 cm^{-1} of NO chemisorbed to the supported complexes suggests that only one type of Lewis site is present. Others have reported multiple IR relaxations for NO chemisorbed to transition metal ions such as Cr^{3+} and Fe^{3+} (see Ref. (6) for review). In this study, however, the absence of multiple IR peaks confirms that the coordinatively saturated M^{3+} ion [$\text{M} = \text{Al}, \text{Cr}, \text{Fe}$] is not a site for NO sorption. From these IR data and the

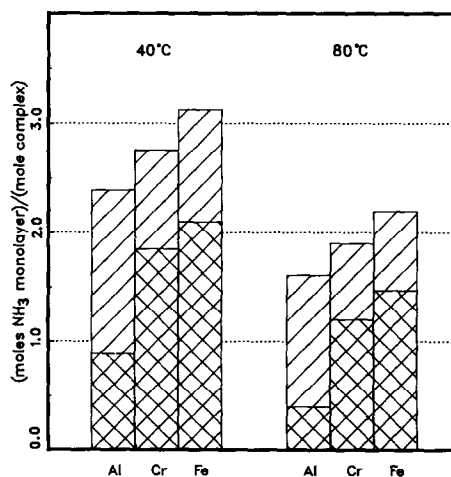


FIG. 10. Ammonia sorption stoichiometry to supported polynuclear metal complexes. X , NO-poisoned, Z , total minus NO-poisoned.

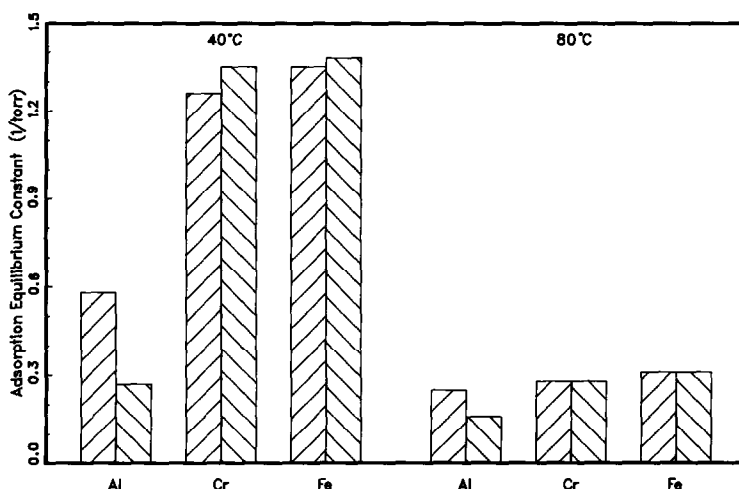


FIG. 11. Ammonia equilibrium adsorption constants for supported polynuclear metal complexes. \square , Unpoisoned; \boxtimes , NO-poisoned.

NO stoichiometry, we conclude that NO binds exclusively to the CUS on Cu^{2+} .

The observed NO stretching frequencies are 14–24 cm^{-1} higher than the value reported (1876 cm^{-1}) for gaseous NO (5). It has been proposed that all NO vibrations above 1850 cm^{-1} indicate a linear MNO orientation (3); thus, we speculate that the NO is bound to the Cu^{2+} site in the linear form.

Furthermore, our earlier results showed that CO does not chemisorb to the intact supported complexes (2). Since CO requires back donation of metal electron density, it appears that the complex is not capable of back-bonding to NO either. Finally, NO does not chemisorb to Cab-O-Sil or Brønsted acid sites (4).

Ammonia is bound to the complex either by donating an electron pair to an acceptor, hydrogen bonding between the nitrogen of ammonia and the hydrogen on the OH bridge, or by accepting a proton from the OH bridge. In the case of the first two, the ammonia symmetry is trigonal pyramidal (C_{3v}), whereas in the last case, the ammonium ion has tetrahedral symmetry (T_d) (7). The deformation relaxation is near 1600 cm^{-1} for trigonal pyramidal symmetry, and it is near 1450 cm^{-1} for tetrahedral symmetry (7). Thus, ammonia shows nearly the same IR relaxations when bound to either a Lewis acid (cupric ions) or for hydrogen bonding to OH bridges. Since the M^{3+} is coordinatively saturated, we do not believe that NH_3 binds to it.

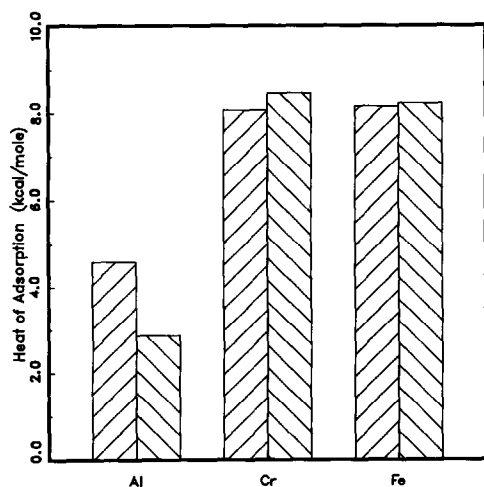


FIG. 12. Ammonia heats of adsorption for supported polynuclear metal complexes. \square , Unpoisoned; \boxtimes , NO-poisoned.

The IR spectra of the unpoisoned complexes show ammonia deformation relaxations characteristic of both symmetries.

The IR data for these complexes show that the Brønsted acidity of the supported Cr and Fe catalysts is greater than that of the supported Al catalysts. However, we cannot tell how the Lewis acidity changes with c_{mi} in the unpoisoned complexes because Lewis and hydrogen-bonded ammonia give the same relaxation near 1600 cm^{-1} . We must block all the Lewis sites with NO and then chemisorb ammonia to these poisoned complexes.

The IR spectra of the NO-poisoned aluminum complexes subsequently exposed to ammonia (Fig. 6, curve b) show vibrations characteristic of ammonia bound only to the OH bridges. The vibration near 1600 cm^{-1} indicates hydrogen-bonded ammonia, whereas the very small peak at 1450 cm^{-1} indicates protonated ammonia. From the relative intensities of these two relaxations, we infer that the majority of the ammonia is hydrogen bonded to the aluminum complex. The IR spectra of ammonia exposed to NO-poisoned iron complexes show the other extreme in bonding to the OH bridges. Only one peak is observed at 1450 cm^{-1} in the spectrum of ammonia bonded to the OH bridges of the iron complex. We may conclude that the Brønsted acidity of the OH bridges in this complex is sufficiently strong to bind all the ammonia as ammonium ions. The IR spectra of ammonia bound to NO-poisoned chromium complexes is similar to that for the iron complex; however, there is a small amount of hydrogen bonding of the ammonia to the OH bridges. These IR data show the chromium and iron complexes are stronger Brønsted acids than the aluminum complex. The effect of changing the c_{mi} is to increase drastically the ability of the complex to protonate ammonia.

The ammonia sorptions confirm the relative differences in the total acidity of the unpoisoned complexes as a function of the c_{mi} . At all three temperatures, the saturation stoichiometry is greatest for the Fe complex, least for the Al complex, and intermediate for the Cr complex. Whereas

the earlier data (2) were restricted to one temperature (54°C), the present study at three temperatures allows for heats of chemisorption to be developed from the change in K values with temperature. The methodical change in the heats from 4.6 to 8.2 kcal/mol confirms the differences in the total acidity arising from the ligand effect of the c_{mi} . These heats of adsorption data characterize the ammonia affinity for both Brønsted and Lewis sites present in the complex. It is of interest to determine how the Brønsted sites are affected by the c_{mi} .

The ammonia pick-ups of the NO-poisoned complexes measure the sorption to the Brønsted sites alone since all the Lewis sites are poisoned irreversibly by NO. We show the saturation stoichiometries in Fig. 10 for the three complexes at two temperatures (40 and 80°C) as stacked-bar graphs. The unpoisoned, ammonia site density at saturation is the total bar height; the Brønsted site density is the NO-poisoned pick-up. The Lewis site density is the difference between the two bars (total minus NO-poisoned). These data show interesting trends if we may associate site preference to the corresponding ammonia pick-up. The Brønsted and total site densities increase through the Al, Cr, and Fe series of complexes, whereas the Lewis site density decreases through this series. The relative site populations also change through the series of complexes. The Lewis site density is greater than the Brønsted site density for the aluminum complex and the reverse is true for the chromium and iron complexes. These data clearly show a ligand effect of the c_{mi} on the sorption of ammonia to the Brønsted sites. Moreover, it is clear that all complexes bind ammonia at the hydroxide bridges, but the strength of the sorption is weaker in the aluminum complex (hydrogen bonding) than it is in the chromium and iron complexes (protonation). The IR data in Fig. 6 confirm these conclusions.

We may gain additional insight on the nature of ammonia interaction to the spe-

cific sites by examining the K values and the heats of adsorption. The equilibrium K values for the three complexes at two temperatures are given in Fig. 11. The heights of the bars indicate the magnitude of the K value. Through the series of complexes (Al, Cr, and Fe), the K values increase drastically for the Brønsted sites at 40°C but less dramatically for the total sorption. The heats of adsorption corroborate these trends (Fig. 12 and Table 4). Notice that the heat of adsorption to the Al complex is much larger when both sites (4.6 kcal/mol) are present than when only Brønsted sites (2.9 kcal/mol) are present. This indicates that the Brønsted sites are the weaker of the two sites in the Al complex. Within the uncertainty of the data, the heats of adsorption to the chromium and iron complexes are the same when both sites are present or when only the Brønsted sites are present in the complex.

These data may be explained by a model showing a cmi ligand effect that is different for the copper ions (Lewis sites) and the hydroxide protons (Brønsted sites). Changing the cmi from aluminum to either chromium or iron has a drastic effect on the ability of the complex to protonate ammonia (Brønsted acidity). The difference in binding strengths is indicated by the large *difference* in Brønsted-site heats of adsorption (5.6 kcal/mol) between the aluminum and chromium complexes. Iron and chromium bind the protonated ammonia to the OH bridges with equal strengths since the heats of adsorption to the Brønsted sites are similar (8.2 vs 8.5 kcal/mol, respectively). This difference in binding strengths with changing cmi is reflected in the ammonia stoichiometries to the complexes. The decrease in ammonia bound to Lewis sites with changing cmi is more than offset by the increase in ammonia bound to Brønsted sites. Apparently, the ligand effect on the sorption stoichiometry to the OH bridges (Brønsted

sites) is stronger than for the sorption stoichiometry to the cupric ions (Lewis sites). This result is expected since the Lewis sites are more remote from the cmi than the Brønsted sites.

CONCLUSIONS

The data on ammonia chemisorption to polynuclear metal complexes supported on Cab-O-Sil (28 wt%) showed a ligand effect on acidity for changes in the central metal ion from Al to Cr to Fe. The neighboring Brønsted sites are affected more by the ligand effect than the next nearest neighbors, the Lewis sites. The magnitude of the ligand effect on the chemisorption properties can be quite large (c.a., increasing the ammonia pick-up by as much as 50%). We expect the ligand effect may be operative for some commercial, mixed oxide catalysts. In the case of acid-type catalysts, the present study illustrates how the ligand effect is used to effect changes in both Brønsted and Lewis acidity. The results of this study may suggest a means to synthesize commercial catalysts with controlled acidity.

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