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Polynuclear Metal Complexes as Model Mixed Oxide Catalysts

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Selective chemisorptions of CO and NH_3 were used to describe the sorption properties of polynuclear metal complexes of Cu^{2+} and M^{3+} (M = Al, Cr, and Fe) supported on silicon dioxide (Cab-O-Sil). On those samples heated to less than 180°C no IR spectrum of CO could be detected; thus, indicating all the Cu ions were cupric and the ferric, chromic ions were coordinately saturated. IR spectra of chemisorbed NH_3 showed relaxations at frequencies characteristic of Lewis-bound (3350–3280 cm^{-1}) and protonic-bound (3210–3175 cm^{-1}) NH_3 for all clusters having open cupric sites. The Lewis-bound NH_3 IR peaks disappeared when the Cu^{2+} sites were sterically blocked whereas the relaxations of NH_3 bound to other sites (3210–3175 cm^{-1}) did not. The 54°C isotherm of the strongly bound NH_3 showed an average site density that increased from 2.2 to 3.0 sites/cluster with M = Al, Cr, and Fe. For an Fe complex with all the Cu^{2+} sites sterically blocked the NH_3 site density was 1.8 sites/cluster. The activation energy for desorbing NH_3 from the 32 wt% samples changed with M^{3+}: 11.9, 14.8, 16.0 kcal/mol for Al, Cr, and Fe, respectively. Desorption of NH_3 from the 10 wt% samples corrected for NH_3 bound to the exposed Cab-O-Sil showed E_d = 11.9, 19.8, and 21.8 kcal/mole. The E_d for the Lewis-bound NH_3 to the Cu^{2+} was only 32 kcal/mole and that for the NH_3 bound to other sites was 17.6 kcal/mole for the Fe–Cu/Cab-O-Sil (10 wt%).

INTRODUCTION

One problem of current interest to oxide catalysis is the development of theories to explain the unusual catalytic properties of multimetal oxide catalysts. An example is the strong Lewis and Brønsted acidity developed on silica–alumina as compared to the neutral acidity of pure silica and the weak Lewis acidity of some pure, dehydrated aluminas (*1*).

The theories to describe mixed oxide catalysis suffer an "immature" state of development relative to the multimetallic theories (*2*) due in part to the difficulty of characterizing the oxide catalysts. Model catalysts together with model reactions are often useful in refining theories. In this work, the sorption properties of a model acid catalyst are examined to be related to changes in the microstructure.

Beckler (*3*) described a family of polynuclear metal complexes (hereafter referred to as clusters) which simulated some of the features described by Peri (*4*). These complexes were fabricated to have both exposed and saturated metal ions, O, OH bridges, and two different types of metal ions. Well-characterized single crystals of the seven-metal ion clusters (Fig. 1) were supported without destruction on SiO_2. Subsequent studies demonstrated the OH vibrational frequencies and extinction coefficients of the clusters in solution changed as the central metal ion (cmi) was changed from Fe^{3+}, Cr^{3+}, to Al^{3+}. The OH bond strength decreased as the cmi was changed to Al, Cr, and Fe. It was pertinent to question what types of sorption sites were developed on the cluster and how the sorption properties of the cluster were influenced by changes in the central metal ion.

Owing to the high degree of characterization and to the stability of the microenvironment during the impregnation, these clusters appeared to be excellent model catalysts to test theories on the catalysis by mixed metal oxides. In the present case, the ligand effect between metal ions was examined.

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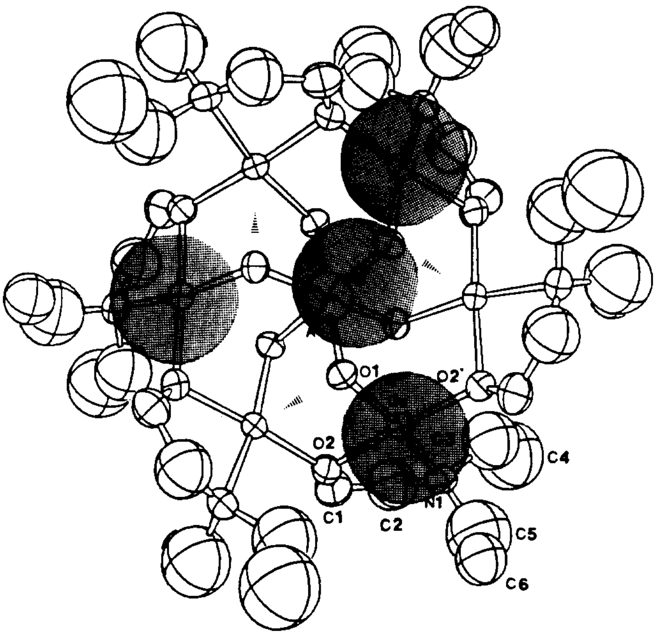

FIG. 1. Representation of polynuclear metal oxide complex cation-supported on flat surface, Al, aluminum central metal ion; Cu, cupric ion; C1–C6, hydrocarbon groups; N1, tertiary amine ligand to cupric ion; O1,O1′, bridging hydroxide; O2,O2′, bridging oxygens.

Sorption properties were investigated using two gases:

(a) CO to probe for the presence of Cu^{1+}, Fe^{3+}, and Cr^{3+} upon thermal decomposition of cluster.

(b) Ammonia to distinguish between Lewis/Brønsted acid sites, to titrate acid site density, and to characterize strength of acid sites.

THEORY

Chemisorption to the clusters. A representation of the cluster cation resting on a flat surface is given in Fig. 1. Each cluster showed six cupric ions having a coordinatively unsaturated site (CUS) and six OH bridges of which only three of each were accessible from the gas-phase side of the supported complex. Babb (*5*) discussed the effective blocking of the remaining three Cu^{2+} by the bridging OH (O1; see arrows in Fig. 1). In this representation O1′ were pointing toward the surface (away from viewer) and O1 were pointing toward the gas phase. The cmi was coordinately saturated. The tertiary amine nitrogen (N1), the ethyl, *n*-butyl, and alkoxide hydrocarbon groups (C1–C6) do not support sorption. Therefore, the maximum number of adsorption sites for each supported cluster was six: three each of cupric ions and hydroxide bridges.

Scale models of the cluster and NH_3 were constructed to describe base adsorption to the sites. The assumed mechanism for ammonia sorption to the cupric ion was donation of the N lone pair to form a coordination bond (*6–8*). However, base adsorption to the hydroxide bridges was assumed to be accompanied by a partial charge transfer from the OH hydrogen through the N of the ammonia (*6, 7, 9*).

Single, ammonia molecules had free access to each of the three cupric ions and hydroxide bridges when ethyl groups were present in the cluster. Thus, the first NH_3 molecule may be sorbed to any of the six sites. Sorption of the second NH_3 molecule was restricted according to placement of the first molecule. Figure 1 also depicts the

NH_3 sorption sites as shaded areas; the dark arrows point to the sorption sites. A molecule chemisorbed to the cupric ion partially hindered sorption to the adjacent OH bridge (01) and conversely. Sorption on one OH bridge however showed slight steric hindrance to sorption on either of the other two OH bridges. With *n*-butyl groups replacing the ethyl groups on the cluster, only two OH bridges were accessible.

Carbon monoxide should not chemisorb to the cluster which is intact. The ground state electronic configuration of the cupric ion does not provide for the strong back donation into the π antibonding orbitals required for *strong* CO sorption (*7*). Since the cmi was saturated, no strong CO sorption to it was expected. Partial destruction of the cluster which reduced the cupric ions to cuprous and/or exposed a CO-chemisorbing cmi should create the proper conditions for strong CO sorption. Thus, exposure to CO and evacuation at room temperature constituted a test for supported cluster integrity.

Temperature-programmed desorption. The design of the TGA did not allow high flow rate of gas through the bed; thus, an alternative procedure was devised for the temperature-programmed desorption. The partial pressure, p, of the active gas over the sample was constant throughout the heating/cooling cycle. With the customary assumptions for first-order associative sorption of the ammonia (*10*), the net rate of adsorption was

$$r = v_m d\theta/dt = k_1 p(1 - \theta) - k_2\theta. \quad (1)$$

The calculus may be invoked at the maximum desorption rate to give

$$k_2 T_m^2/\beta = \frac{v_m}{R}\left[\frac{K^* p E_a(1 - \theta^*) - \theta^* E_d}{K^* p(1 - \theta^*) - \theta^*}\right] \frac{1}{K^* p + 1}, \quad (2)$$

where the asterisk indicates the variable was evaluated at the temperature of the maximum desorption rate, T_m.

For strong chemisorption $E_d \gg E_a$

$$2 \ln T_m - \ln \beta = \frac{E_d}{RT_m} + \ln \frac{v_m E_d}{R k_2^0} \frac{1}{(Kp + 1)}. \quad (3)$$

For the case of equal energies for adsorption/desorption then Eq. (2) reduces to

$$2 \ln T_m - \ln \beta = \frac{E_d}{RT_m} + \ln\left[\frac{v_m E_d}{k_2^0 R(1 + K^0 p)}\right], \quad (4)$$

where $K^0 = k_1^0/k_2^0$.

Equations (3) and (4) suggested the data of T_m and β may be used to extract E_d.

EXPERIMENTAL

Preparation of the single crystal complexes having the central metal ion (cmi) as Fe^{3+}, Cr^{3+}, or Al^{3+} and the technique for supporting the clusters on SiO_2 were described by Babb (*5*).

Infrared spectra were collected using a Perkin–Elmer 281-B spectrometer operated in the absorbance mode described earlier (*3*). A conventional gas cell in combination with a Pyrex glass vacuum system used in the gaseous chemisorption studies was described elsewhere (*5*). Fumed, amorphous silica of high surface area (200 m^2/g) obtained from the Cabot Corporation (M-5 Cab-O-Sil) was the support. This high-purity silica was formed into the self-supporting wafers of about 50 mg weight as was the impregnated Cab-O-Sil.

A Perkin–Elmer TGS-II together with the System IV microprocessor was used for the thermogravimetric analysis. The gases were mixed in a stainless-steel gas handling manifold equipped with Fisher–Porter flowmeters. The total gas flow rate to the apparatus, 784 (STP) cm^3/min (10^6 cm^3/m^3), ensured that mass transport to the sample did not taint the results.

Reagent grade acetonitrile was used in all the solutions. Reagent grade ammonia, CO, and He (Matheson) were used in all chemisorption studies. Stock methanol and re-

TABLE 1

Catalysts of Supported Clusters

Cluster	Support	Loading (wt%)	TGA	IR	Catalyst
Al–Cu (ethyl)	Cab-O-Sil	10	X	X	AE/C.10
		32, saturated	X	X	AE/C.32
Cr–Cu (ethyl)	Cab-O-Sil	10	X	X	CE/C.10
	Cab-O-Sil	30.9, saturated	X	X	CE/C.31
Fe–Cu (ethyl)	Cab-O-Sil	10	X	X	FE/C.10
	Cab-O-Sil	32, saturated	X	X	FE/C.32
Fe–Cu (*n*-butyl)	Cab-O-Sil	12.5	X	X	FN/C.13

agent grade chemicals were used in the preparation of the clusters.

Gas chemisorption IR study. The gas cell was used to degas the supported clusters and to contact the same with a chemisorbing gas. Overnight evacuation (18 h at 0.7 Pa) was sufficient to degas the thin, partially transparent samples. The samples may be heated to temperatures less than 250°C in one end of the cell removed from the IR beams under the vacuum conditions. Typically a "baseline" spectrum was run after such overnight evacuation and prior to introducing the chemisorbing gases at partial pressures to 30 Torr. The exposure time was 30 min followed by evacuation at room temperature for 30 min after which spectra were recorded immediately.

TGA chemisorptions of NH_3. Samples of cluster/Cab-O-Sil were treated to an 18-h heating in dry N_2 (50 cm^3/min) at 154°C to be weighed in stagnant N_2 at 54°C. These samples were subsequently exposed for 30 min at 54.0 ± 0.1°C to N_2/NH_3 having ammonia partial pressures between 1.5 and 28 Torr (200 Pa to 3.33 kPa). The gas stream was stopped and the weight of the sample was recorded at each increasing partial pressure. The "reversible" weight changes were measured upon repeating this process to the same sample such that the weight changes attending weak NH_3 sorption plus density changes may be subtracted from the sample weight changes upon the first sorption.

Temperature-programmed desorption. An NH_3 partial pressure of 5.18 Torr (690 Pa) was established over the 15- to 20-mg samples with 53–54°C as the initial temperature and 153–154°C as the final temperature. The heating/cooling cycle logged into the System IV microprocessor was of fixed length of 114.4 min for all values of the heating/cooling rate, β(2.5–20 K/min). This cycle length ensured *reproducible* total sample weights at the beginning of each cycle.

Catalysts preparation. The preparation of the clusters and the procedure for supporting the clusters on Cab-O-Sil was described elsewhere (*3*). The catalysts prepared for this study are listed in Table 1 with the methods of analysis. The Cab-O-Sil supported samples designated as saturated were prepared by repeated impregnations of a previously air-dried sample (383 K, 18 h) with a cluster/acetonitrile solution (3×10^{-3} g/ml) until the sample would not adsorb cluster (31–32 wt%).

Postcollection data processing. Repetitive scanning of the data (four to five IR and two TPD scans) enhanced the signal/noise ratio. Subsequent processing of the IR data included "background" subtraction of the catalyst IR spectrum prior to exposure to yield the chemisorbed spectra, difference spectra to show the effects of various pretreatments and/or to illustrate the effects of site blocking and smoothing. The density effects were subtracted from each TPD spectrum using spectra of N_2 gas at the same conditions.

RESULTS

Thermal Decomposition of Clusters

Repeated attempts to sorb CO gas at pressures to 30 Torr and room temperature onto the Cab-O-Sil-supported clusters (10 and 32 wt%) failed to produce large peaks in the spectrum (4000–600 cm^{-1}) when the clusters were heated to temperatures of 180°C and less; whereas heating the cluster to 185 and 200°C under a vacuum caused the 2130-cm^{-1} peak in the CO spectrum to increase (Figs. 2A, B, C). Similar results were observed for the Cab-O-Sil-supported Fe cluster (not shown).

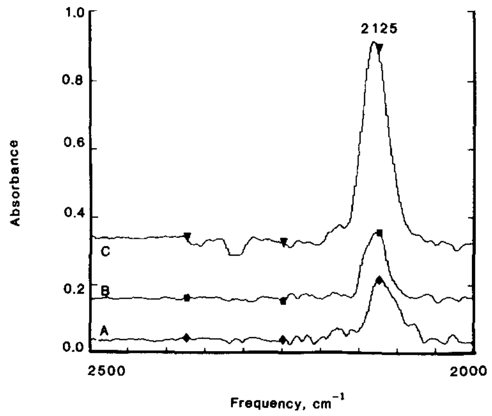

FIG. 2. IR spectra of CO on Cab-O-Sil-supported cluster of Cr (31 wt%). (A) ♦, Sample heated to 150°C. (B) ■, Sample heated to 185°C. (C) ▼, Sample heated to 200°C.

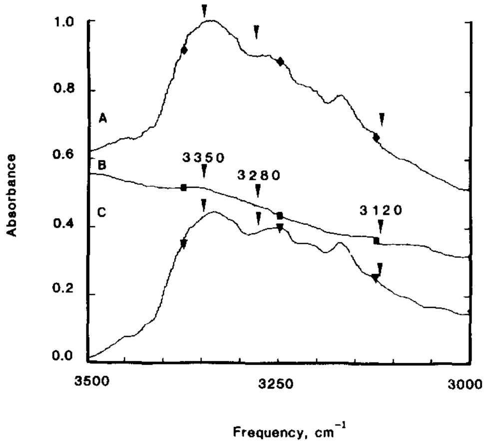

FIG. 4. IR spectra of NH_3 sorbed to Cr–Cu/Cab-O-Sil (30.9 wt%) at 327 K and 24.8 Torr NH_3. (A) ♦, Catalyst after NH_3 exposure. (B) ■, Catalyst before NH_3 exposure. (C) ▼, Spectra A − B; difference spectra.

Sorption of NH_3 to the Clusters

The identity and acidity of the chemisorption sites were characterized by NH_3 sorption.

Identification of sorption site. The infrared spectra of the chemisorbed NH_3 (p_{NH_3} = 1.5 Torr, room temperature) on Cab-O-Sil-supported samples (50 mg) of the *n*-butyl and ethyl Fe–Cu complexes at the same number density of clusters/g of catalyst (12.5 and 10 wt% loading, respectively) are shown in Fig. 3. Both catalysts showed peaks near 3350 and 3280 cm^{-1}; however, the intensities were less for *n*-butyl Fe–Cu (Fig. 3B) than for the ethyl Fe–Cu (Fig. 3A). The difference spectra (A − B = C) showed the vibrational spectra of NH_3 sorbed to the Cu^{2+} sites. Similar results were obtained for an NH_3 partial pressure of 23.4 Torr (not shown).

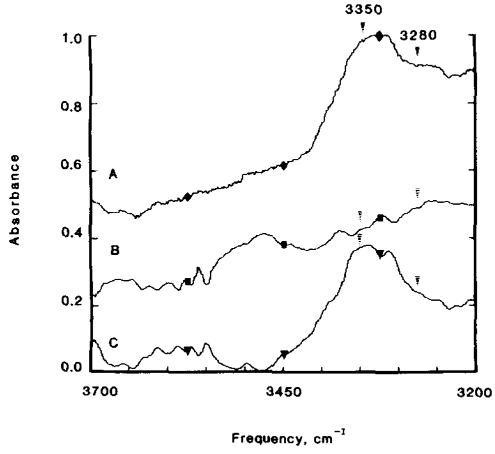

FIG. 3. IR spectra of NH_3 chemisorbed at 327 K and 1.5 Torr on ethyl- and *n*-Butyl Cu–Fe/Cab-O-Sil. (A) ♦, Ethyl Fe–Cu/Cab-O-Sil (10 wt%). (B) ■, *n*-Butyl Fe–Cu/Cab-O-Sil (12.5 wt%). (C) ▼, Spectra A − B.

The broad peak near 3200 cm^{-1} prompted further study of the region 3500–3000 cm^{-1} (Fig. 4) for a Cr–Cu/Cab-O-Sil (30.9 wt%) sample (50 mg) exposed to NH_3 at 24.8 Torr. Spectrum A is the catalyst after exposure to NH_3 and spectrum B is just prior to exposure. Spectrum C is the difference: A − B. The chemisorbed NH_3 spectrum (Fig. 4C) showed relaxations at 3338, 3250, 3210, and 3175 cm^{-1}. The chemisorbed NH_3 spectrum of Fig. 4C is characteristic of the other two supported clusters.

NH_3 sorption isotherms. The strong sorption of NH_3 at 54°C as a function of ammonia partial pressure for the Cab-O-Sil-supported clusters (AE/C.32, CE/C.31, FE/C.32, FE/C.10, FN/C.13) are shown in Fig. 5. These data were reported as the ratio of moles NH_3 sorbed per mole of cluster on the support. Other data for AE/C.10,

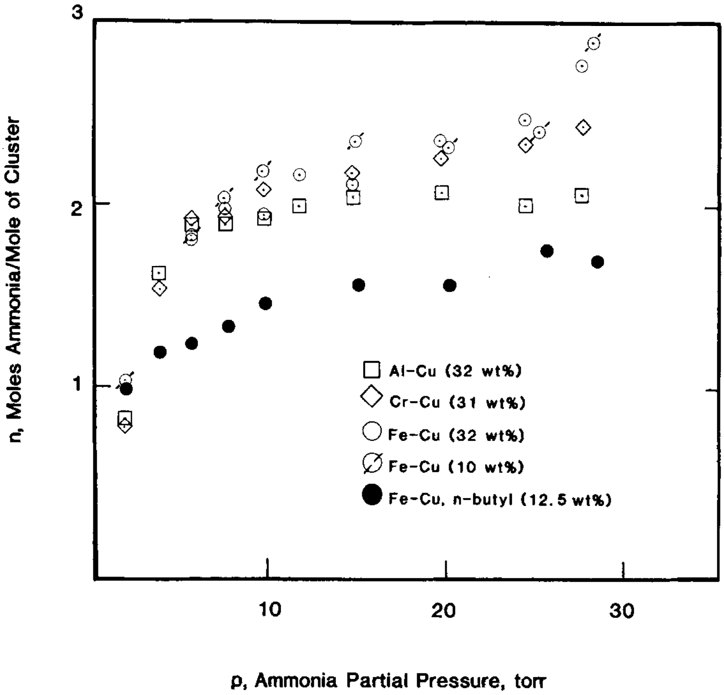

FIG. 5. Ammonia isotherms of Cab-O-Sil-supported clusters at 327 K.

CE/C.10, and Cab-O-Sil are reported in Table 2.

The strong pickups of the ethyl Fe–Cu at 10 and 32 wt% were nearly the same; whereas, the strong pickup of the *n*-butyl Fe–Cu (12.5 wt%) was consistently lower than the ethyl Fe–Cu (10 wt%) samples. Cr–Cu at two loadings (10 and 31 wt%) showed nearly equal amounts of strong NH_3 sorption at each pressure and the same was true for the two Al–Cu samples (10 and 32 wt%). For the sake of clarity, the Al and Cr 10 wt% data were not reported in Fig. 5.

A closer examination of the isotherms developed at 54°C showed a clear trend in the sorption of NH_3. At 31–32 wt% loading ethyl Fe–Cu showed the highest NH_3/cluster ratio (2.8 at 28 Torr) followed by ethyl Cr–Cu (2.4 at 28 Torr), and the lowest was the ethyl Al–Cu (2.1 at 28 Torr). The *n*-butyl Fe–Cu sample (12.5 wt%) showed a much lower ammonia pickup of 1.8 moles NH_3/mole cluster at $p_{NH_3} = 28.0$ Torr.

The sorption data were fit to a simple Langmuir equation describing associative chemisorption, single site stoichiometry. Figure 6 reports these linearized fits as p/n vs p where the slope is the reciprocal of the "saturation coverage" (n). Data for the 10 wt% Al–Cu and Cr–Cu on Cab-O-Sil were not reported in Fig. 6. The smallest value of n (moles NH_3/mole cluster), Table 2, was for the *n*-butyl Fe–Cu at 12.5 wt% (1.75 ± 0.32) followed by ethyl Al–Cu (2.23 ±

TABLE 2

Langmuir Constants of NH_3 Sorbed to Cab-O-Sil-Supported Clusters at 327 K

Catalysts	Strong sorption, n^a
AE/C.32	2.23 ± 0.13
AE/C.10	1.95 ± 0.50
CE/C.31	2.62 ± 0.16
CE/C.10	2.75 ± 0.30
FE/C.32	3.00 ± 0.40
FE/C.10	2.87 ± 0.49
FN/C.13	1.75 ± 0.32
Cab-O-Sil	0

[a] Moles NH_3/mole cluster.

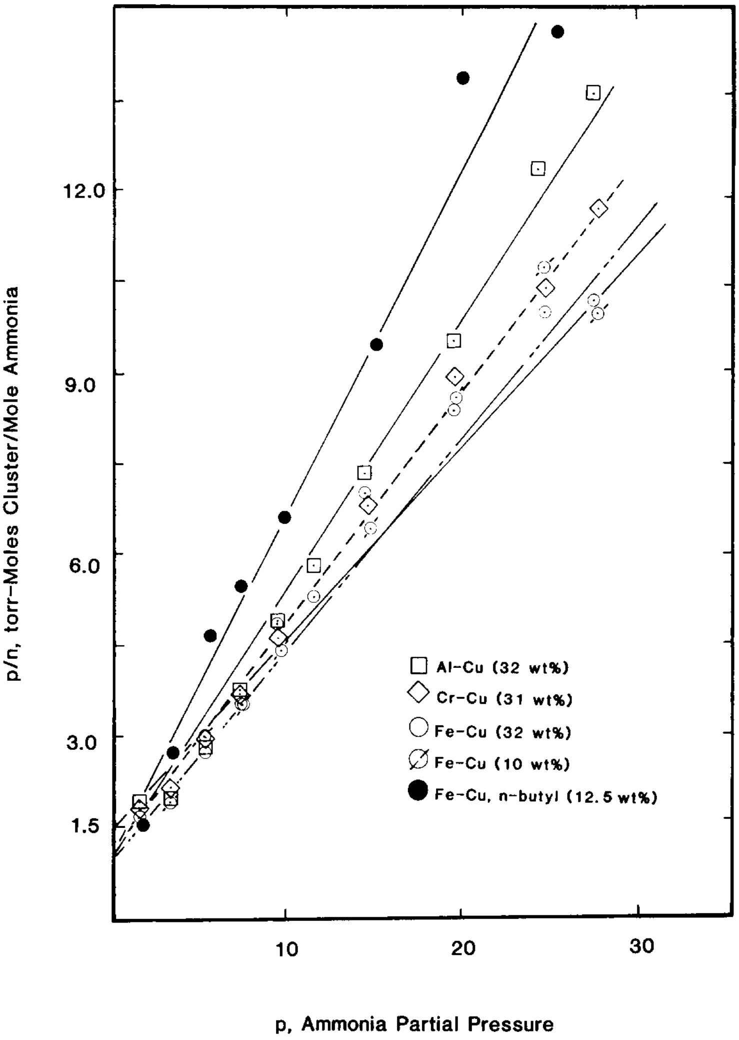

FIG. 6. Langmuir isotherms of NH_3 on Cab-O-Sil-supported clusters at 327 K.

0.13), ethyl Cr–Cu (2.62 ± 0.16), ethyl Fe–Cu (3.00 ± 0.4), all at 31–32 wt%, and ethyl Fe–Cu at 10.0 wt% (2.87 ± 0.49). The remaining two 10 wt% samples showed n equal to 1.95 ± 0.5 and 2.75 ± 0.3 for Al–Cu and Cr–Cu, respectively. The Cab-O-Sil showed no strong pickup. The uncertainty in the saturation pickup, n, includes statistically 95% of all the data.

Temperature-programmed desorption. Since much of the strong chemisorption occured at NH_3 pressures of 5.18 Torr (690 Pa) this pressure was chosen for the temperature-programmed desorptions. The locations of the desorption rate maxima, T_m, were established by finding the average zero of smoothed first temperature derivative spectra at each β. These T_m data for each β yielded an activation energy plot (Fig. 7).

For the 31–32 wt% samples the desorption activation energies (Table 3) were as follows: AE/C.32—11.9 ± 1.7, CE/C.31—14.8 ± 1.3, and FE/C.32—16.0 ± 1.6 kcal/mole. The E_d for the 10 wt% and 12.5 wt% Fe–Cu/Cab-O-Sil (ethyl and n-butyl, respectively) were 13.5 ± 1.2 and 12.3 ± 1.5 kcal/mol. For the other 10 wt% samples,

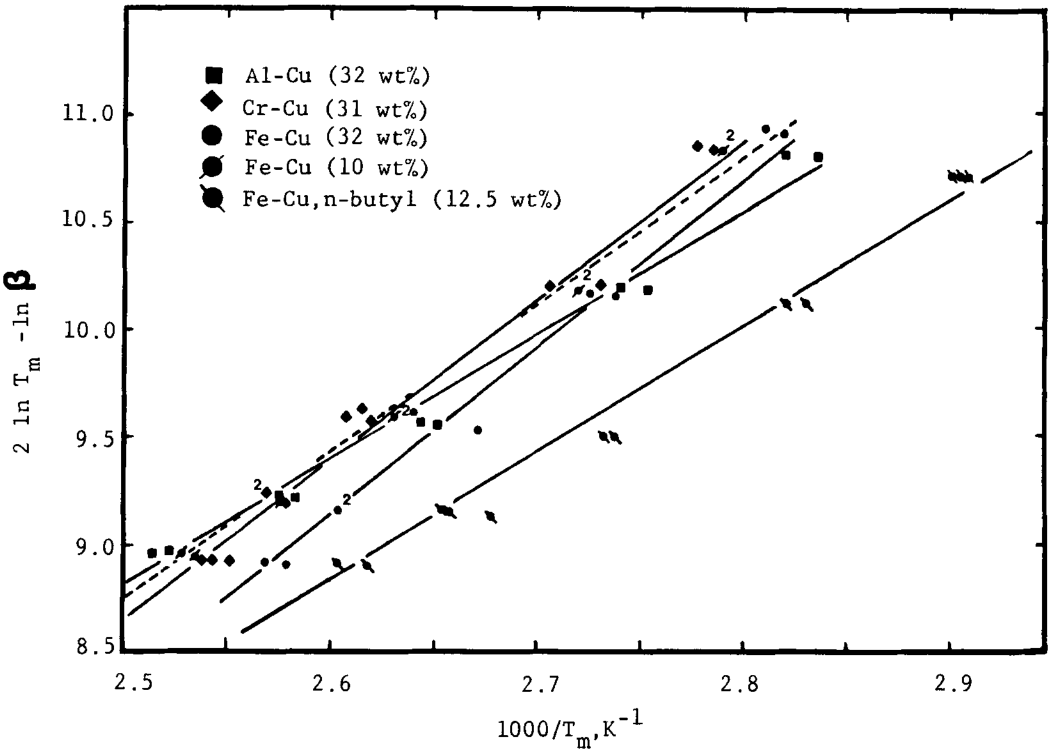

FIG. 7. Desorption activation energy plot for NH_3 on supported clusters.

the E_d were as follows: AE/C.10—11.8 ± 2.6; CE/C.10—11.1 ± 1.3; and that for Cab-O-Sil was 12.1 ± 1.1 kcal/mole.

These results showed the influence of both strong and weak sorptions to the cluster and to the exposed Cab-O-Sil surface. The spectrum of a pure Cab-O-Sil sample, multiplied by the appropriate weighting factor equal to the Cab-O-Sil surface area (67%) exposed by the 10 wt% sample, was subtracted from the spectra of the 10 wt% supported cluster samples to give the NH_3 TPD sorbed to the cluster only. This procedure, gave E_d of 21.8 ± 3.1 for FE/C.10; 19.8 ± 4.5 for CE/C.10, and 11.9 ± 1.8 kcal/mol for AE/C.10.

The temperature-programmed desorption at 5 K/min from the Cab-O-Sil-supported Fe–Cu clusters (10 and 12.5 wt%) having the free and sterically hindered Cu^{2+} sites and nearly the same exposed Cab-O-Sil surface area is shown in Fig. 8. The unhindered Cu^{2+} sample (Fig. 8A) showed a

TABLE 3

Summary of NH_3 TPD from Cab-O-Sil-Supported Clusters

Catalysts	E_d (kcal/mole)
AE/C.32	11.9 ± 1.7
AE/C.10	11.8 ± 2.6
CE/C.31	14.8 ± 1.3
CE/C.10	11.1 ± 1.3
FE/C.32	16.0 ± 1.6
FE/C.10	13.5 ± 1.2
FN/C.13	12.3 ± 1.5
Cab-O-Sil	12.1 ± 1.1
Difference spectra	
AE/C.10-Cab-O-Sil	11.9 ± 1.8
CE/C.10-Cab-O-Sil	19.8 ± 4.5
FE/C.10-Cab-O-Sil	21.8 ± 3.1
FE/C.10-Fn/C.13	
Low-temperature site	17.6 ± 0.3
High-temperature site	32.0 ± 3.0

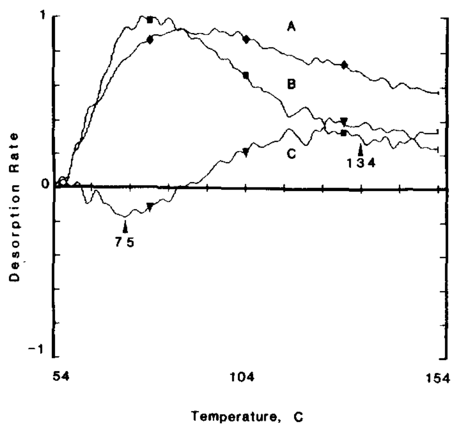

FIG. 8. TPD spectra of FE/C.10 and FN/C.13, $\beta = 5$ K/min. (A) ◆, FE/C.10 TPD spectrum. (B) ■, FN/C.13 TPD spectrum. (C) ▼, TPD spectrum generated by A − B.

maximum rate at a temperature higher than the sample with blocked Cu^{2+} ions (Fig. 8B). The spectrum of the sterically hindered Cu^{2+} was subtracted from that of the unhindered sample to develop the NH_3 desorption spectrum shown in Fig. 8C. Two peaks are apparent which shift with β; one negative peak at "low" temperatures and a positive peak at "high" temperatures. The temperatures of the peak extrema at $\beta =$ 2.5, 5, 10, and 20 K/min were used to develop E_d of 32 ± 3 kcal/mole for the positive peak and 17.6 ± 0.3 kcal/mole for the negative peak (Fig. 9).

DISCUSSION

Identification of sorption sites. The most convincing evidence to confirm the cupric ion as *one* NH_3 sorption site comes from the ethyl and *n*-butyl Fe–Cu experiments supported on Cab-O-Sil. The IR spectra (Fig. 3A) showed two peaks near 3350–3320 and 3280–3265 cm^{-1} which identified these sites as Lewis acids (*6*, *7*). Moreover, these peaks disappeared when the butyl groups blocked the cupric ions (Fig. 3B). The cupric ion will accomodate the NH_3 lone pair as a ligand (*5*). Thus, we conclude the cupric ions are the seat of Lewis acidity in clusters.

Other vibrational states of chemisorbed NH_3 showing frequencies near 3200 cm^{-1} were present on the clusters. Cab-O-Sil will not retain NH_3 at the conditions of this analysis (Table 2 and Ref. (*7*)); thus, we attribute the peaks at 3210 and 3175 cm^{-1} to NH_3 bound to site(s) on the cluster other than Cu^{2+}. The bridging hydroxides may provide sorption sites through the OH protons to the NH_3 nitrogen. This sorption may be weak such that complete activation of the hydroxide proton does not occur. Instead, an asymmetric NH_4 complex is presumed to develop showing only a partial charge. Thus, the familiar symmetric ammonium ion spectrum showing a peak at 3120 cm^{-1} was not observed (*7*).

Temperature-induced decomposition. Babb (*5*) showed the CH vibrational spectra of the clusters changed significantly as the Cab-O-Sil-supported samples were heated above 180°C. CO chemisorption apparently was another diagnostic for thermal decomposition of the clusters. CO should not give rise to a chemisorption peak when the cluster was intact since the cupric ions do not chemisorb CO (*5*). Figure 2 showed only a small CO peak centered at 2125 cm^{-1} for the Cr–Cu sample which had been heated to temperatures of 150 and 180°C (Figs. 2A, B). Apparently, only some of the clusters were decomposed in this sample which had experienced long periods of heating at 180°C. This peak grew signifi-

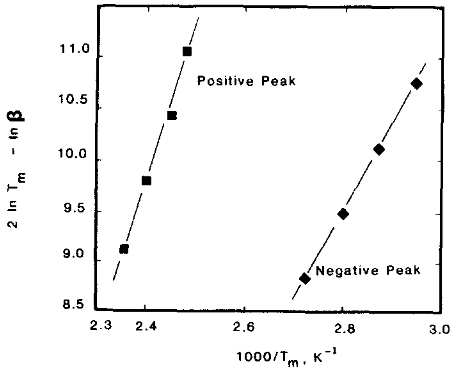

FIG. 9. Activation energy plot for difference spectra: ethyl- and *n*-butyl Fe–Cu/Cab-O-Sil.

cantly with subsequent CO exposures after the temperature was increased to 200°C for 1 h under vacuum indicating decomposition of the clusters. As the complex decomposed we speculate the organic ligands were removed from the Cu^{2+} ions which were reduced to Cu^{1+} readily by the hydrocarbon fragments. Further, we speculate the cmi was exposed by rupture of the cmi-OH bonds. Chromic, cuprous, and ferric ions are known to strongly sorb CO with IR relaxations at 2200–2100 cm^{-1} (*7*). Exposure of the samples to temperatures lower than 180°C does not cause significant decomposition of the clusters.

NH_3 isotherms. Since the exposed Cab-O-Sil surface did not chemisorb NH_3, the strong sorption of NH_3 was used to characterize the cluster site density. The largest NH_3 pickup (moles NH_3 chemisorbed/mole of cluster) was 3.0 +/− 0.4 for FE/C.32. Since the IR ammonia site study showed sites other than Cu^{2+} were present (Fig. 3) and the strong sorption for the sample with all the Cu^{2+} blocked (*n*-butyl Fe–Cu) was 1.8 moles NH_3/mole cluster, an explanation was sought to describe the results. Two explanations included the following:

(a) The actual site density was 6 per cluster; however, the complex populated the surface as a distribution of monomers, dimers, trimers, *x*-mers, etc.

(b) Some chemisorption sites were sterically hindered by sorption to adjacent sites (see Theory).

The formation of *x*-mers could explain an observed strong sorption stoichiometry less then 6. A distribution of *x*-mers having a number-averaged value of *x* equal to 2 could explain the observed result of 3 moles NH_3/mole cluster. However, this explanation does not explain the constant ammonia/cluster stoichiometry with increasing loading of cluster/Cab-O-Sil.

One could imagine the distribution of monomers, dimers, trimers, etc., *x*-mers would change to larger values of *x* as the saturation loading of cluster was accomplished. This shift in distribution to larger values of *x* should depress the observed NH_3 sorption stoichiometry. This was not observed. These results suggested the majority of the clusters were supported as single entities, and the observed NH_3 strong sorption mirrors the site stoichiometry/cluster. The calculated saturation loading for the clusters as monomers, each occupying 1.13 nm^2, on Cab-O-Sil (SA = 200 ± 25 m^2/g) was 29 ± 2 wt% which compared favorably to the observed value of 31–32 wt% (*11*).

A better explanation of the NH_3 sorption data was sterically hindered chemisorption described in the Theory Section. This model suggested the NH_3 stoichiometry was 3 molecules NH_3/cluster when the cupric sites were available. A fourth NH_3 could be added but with steric strain. The placement of the first 3 NH_3 molecules need not be limited to Cu^{2+} sites only. When the cupric sites were blocked, two of the 3 OH bridges could accomodate NH_3 molecules without much hindrance. Thus, the model explains a strong sorption of 3 molecules/cluster for the ethyl clusters and predicts the strong sorption on the *n*-butyl cluster to be no more than 2.0 in agreement with the observed value of 1.8 ± 0.3 molecules/cluster. The sorption model qualitatively predicted the IR results. Both Lewis acidity and that associated with OH bridges (defined here as protonic acidity), were predicted by the model for the ethyl clusters whereas only protonic acidity was predicted for the *n*-butyl clusters.

The subtle changes in the moles of strongly sorbed NH_3/mol of cluster as the cmi was changed from Al, Cr, to Fe was *characteristic* of the intrinsic cluster sorption properties. Thus, the Langmuir constant, *n*, described the average number of strong sorption sites/cluster (Table 2) having the *minimum* energy to retain NH_3 under the purge conditions. This strong site density (not to be confused with the actual number of ions/cluster) was observed to increase from 2.2 to 3.0 as the cmi was changed. These data were explained by the ligand theory adopted for use here. Changing the cmi was assumed to change the molecular orbitals (MO's) of the cluster. The ability of the cupric ions to accept ligand electrons and the lability of the hydroxide protons were influenced by the cluster MO. Thus, the acidity of the cupric ions/hydroxide protons was altered by changing the cmi which itself did not chemisorb NH_3. Finally, the acidity of these sites determined the number of sites having the required energy to retain the NH_3. It was expected that clusters showing the highest site density for strong sorption would also show the highest, average activation energy for desorption (E_d).

Temperature-programmed desorption. The E_d for NH_3 desorption from Cab-O-Sil-supported clusters (31–32 wt%) increased from 11.9 ± 1.7, 14.8 ± 1.3, to 16.0 ± 1.6 kcal/mole as the cmi was changed from Al, Cr, to Fe. Thus, the TPD and strong sorption data suggested the cluster containing Fe showed the highest average acidity followed by the chromium cluster, and the aluminum cluster.

For the 10 wt% catalysts, the E_d for the exposed Cab-O-Sil surface contributed to the reported E_d for the sample. Thus, an attempt was made to subtract the Cab-O-Sil contribution to the TPD spectra. These data of T_m vs β for each difference spectrum showed "cluster" E_d of 21.8 ± 3.1 for FE/C.10, 19.8 ± 4.5 for CE/C.10, and 11.9 ± 1.8 kcal/mole for AE/C.10. As expected the "cluster" E_d changed in a manner before for the samples at 32 wt%. Since the 31–32 wt% samples were assumed to cover completely the Cab-O-Sil, no subtraction of the Cab-O-Sil spectrum was necessary.

However, these "cluster" E_d showed the combined effects of all sites. To calculate the E_d for desorption from the cupric ion, the TPD spectra of the blocked Cu^{2+} sample was subtracted from that of the unblocked sample to generate the difference TPD spectrum. The two peaks observed in Fig. 8C were assigned to NH_3/Cu^{2+} for the higher temperature, positive peak and NH_3/OH for the lower temperature, negative peak. The negative peak showed the *n*-butyl catalyst allowed more NH_3 sorption to the OH bridges than the ethyl catalyst in accordance with the hindered sorption model. For the Fe–Cu catalyst the cupric ion showed an E_d of 32.0 ± 3.0 kcal/mole whereas the OH bridge showed an E_d of 17.6 ± 0.3 kcal/mole.

CONCLUSIONS

Polynuclear metal complexes were suitable model acid catalysts to study the ligand effect in mixed metal oxides. The strong sorption site density per cluster and the activation energy for desorption changed with the cmi. The acidity was attributed to the combined sorptions to metal ion CUS and OH bridges; however, it was not possible to determine which of the sites were influenced most by changing the cmi. A model involving sterically hindered sorption to selective sites explained the available data of site density and energy of desorption.

APPENDIX: NOMENCLATURE

β	temperature programming rate, K/min
E_a, E_d	activation energies for adsorption desorption, kcal/mole
k_1, k_2	rate constants for adsorption, desorption, moles/time-g-Torr, moles/time-g
k_1^0, k_2^0	preexponential factors for adsorption, desorption, moles/time-g-Torr, mol/times-g
K^*	ratio of rate constants, k_1,k_2, Torr^{-1}
n	moles NH_3 sorbed/mole cluster
p	partial pressure of gas, Torr
r	net sorption rate, moles/time-g
T	temperature, K
t	time, s
θ	fractional coverage of surface, unitless
v_m	monolayer coverage, moles/g
x	degree of cluster association, unitless

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