

¹³C CPMAS NUCLEAR MAGNETIC RESONANCE STUDY OF THE ADSORPTION OF 2-PHENETHYLAMINE ON CLAYS

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Abstract—2-Phenethylamine ¹³C-enriched in the beta position was adsorbed on four different aluminum-exchanged clays: hectorite, Barasym, Laponite RD, and lithium taeniolite. The sites for adsorption were characterized by ¹³C high-resolution cross-polarization magic angle spinning nuclear magnetic resonance (CPMAS-NMR) spectroscopy. Using differences in chemical shift values and linewidths, three different types of bound ammonium compounds and a motionally restricted bound compound were identified. Correlation with charge effects indicated that one of the clay sites was extremely acidic.

The important catalytic sites for the different clays, the edge or platelet face, interlamellar and some combination of both, were probed by using the trimethylsilyl group as a clay-blocking agent. Silylation of aluminum-exchanged Laponite RD and Li taeniolite had little effect on amine adsorption. This indicates that, for these clays, amine adsorption occurred mainly at interlamellar sites. For hectorite, amine adsorption occurred at both surface and interlamellar sites, and silylation had the effect of reducing surface adsorption. Silylation of Barasym resulted in a very interesting shift of adsorption from one kind of surface site to a more acidic surface site.

Key Words—Amine reactions with clays, Clay acidic sites, Solid state NMR.

INTRODUCTION

The lack of good crystalline order in sheet silicates is probably the source of their catalytic behavior, but it also leads to a complex array of possible sites for reaction (Theng, 1974). These sites include edge, interlayer, defect, and ion-exchange. Moreover, the adsorbed species may be any combination of surface-contact (physiosorbed), ion-exchanged, or for basic compounds such as amines, protonated, or Lewis acid adducts. For species contained in the interlayer, there is also the possibility of dynamics involving lateral diffusion and oriented species with movement about a specific axis (Pinnavaia, 1983; Laszlo, 1986).

The structural diversity makes clay catalysts potentially powerful; however, the question remains as to how to maximize the active sites to achieve the greatest efficiency for a given reaction. This requires methods to detect and to characterize the active sites and the adsorbed species. Of the many techniques that have been applied, high-resolution cross-polarization magic-angle spinning-nuclear magnetic resonance (CPMAS-NMR) spectroscopy of solids has proved to be very useful in studies of metal ions in and/or on clays (Bank *et al.*, 1989; Weiss Jr. *et al.*, 1990; Laperche *et al.*, 1990). Differences in chemical shifts and linewidths provided information about the structure of the clay and the chemical environment of the metal ions.

The present study extends the use of CPMAS-NMR spectroscopy to characterize the possible sites for amine adsorption on four clays: hectorite, Barasym, Laponite RD, and Li taeniolite. These clays have an array of surface areas, particle sizes, and interlayer sites.

2-Phenethylamine was chosen as the amine because it combines the high base strength ($pK_b = 4.17$; see Carothers *et al.*, 1927) and, thus, the high reactivity of an aliphatic amine with the substantial chemical shift change upon complexation for the beta carbon. The amine was prepared with ¹³C-enrichment in the beta position to enhance the sensitivity for CPMAS-NMR analysis. The aromatic carbon atoms of 2-phenethylamine are in a chemical shift region substantially removed from the aliphatic carbon atoms and the nitrogen atom. Thus, while the chemical shift values do not change upon bonding to the nitrogen, they do provide an independent method for assessing the degree of motional restriction from steric crowding in the interlayer sites.

EXPERIMENTAL METHODS

Materials

Laponite RD, a synthetic hectorite clay with a very large surface area (Table 1), was provided by Laporte Laponite Products of Bala Cynwyd, Pennsylvania. Li taeniolite, a synthetic fluormica with water-swelling properties and the largest cation exchange capacity (CEC) of the clays studied (Table 1), was provided by Dr. Jack Johnson of Exxon in Annandale, New Jersey. Barasym and hectorite were obtained from the Source Clay Repository of the Clay Minerals Society. Barasym is a synthetic mica-montmorillonite with a mixed (2:1) non-expandable:expandable layer structure. Hectorite is a naturally occurring, Li-containing trioctahedral smectite.

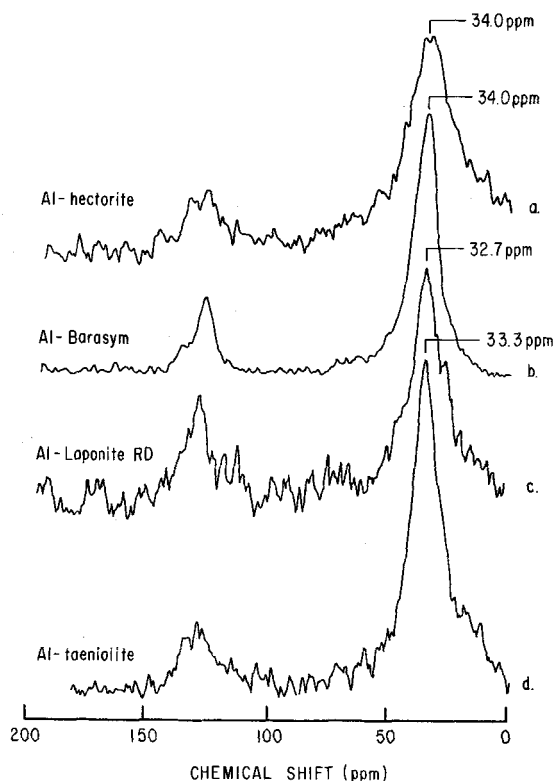


Figure 1. ^{13}C CPMAS-NMR spectra of ^{13}C -enriched 2-phenethylamine adsorbed on Al-clays. The chemical shift values of the beta carbon atom are for the centers of the signals containing multiple components in ppm referenced to tetramethylsilane. The linewidths at 25 MHz are: a) 350 Hz; b) 250 Hz; c) 312 Hz; and d) 312 Hz. The linewidth at 75.5 MHz is 600 Hz for (a). The values are compared to the solid complexes of 2-phenethylamine with: HCl, 33.5 ppm, 117 Hz at 25 MHz, 245 Hz at 75.5 MHz; SnCl_4 , 35.1 ppm, 135 Hz at 25 MHz, 280 Hz at 75.5 MHz; and AlCl_3 , 33.5 ppm, 140 Hz at 25 MHz, 300 Hz at 75.5 MHz. Each spectrum contains 8000 transients.

Preparations

^{13}C -enriched 2-phenethylamine was prepared from benzyl alcohol ^{13}C -enriched at the benzylic position (Aldrich Chemical Co.) (1.1 g, 0.01 mol) and benzyl alcohol (2.2 g, 0.02 mol) in conc. HCl (15 ml, 0.174 mol). The mixture was refluxed for 4 hr, extracted with chloroform, washed with water, and dried. The resulting chloride (3.74 g) was converted to the nitrile by heating at 55°C with NaCN (4 g, 0.08 mol) and Bu_4NBr (0.1 g, 0.3 mmol) in 50% ethanol-water (28 ml). The nitrile (3.3 g) was reduced with lithium aluminum hydride (4.0 g, 0.105 mol) in 150 ml of diethyl ether at 0°C. The crude amine was distilled in a Kuglerohr apparatus, and the fraction at 80°C and 4 mm Hg gave 2 g, 0.017 mol, 57% yield. The ^{13}C NMR spectrum of this material in CDCl_3 had signals at 140.0, 128.7, 128.3, 126.0, 43.6, and 40.2 ppm. The integrated area of the beta carbon peak at 40.2 ppm relative to the

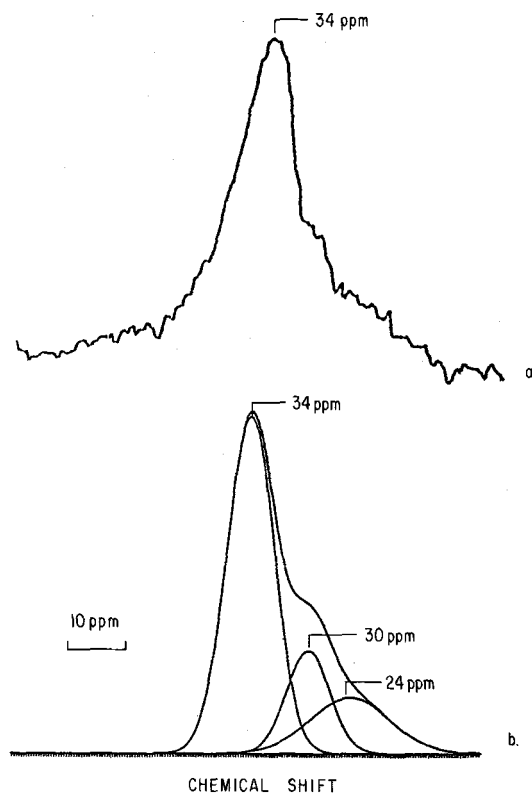


Figure 2. ^{13}C CPMAS-NMR spectrum for a) the beta carbon region shown in Figure 1a compared to b) the lineshape deconvolution showing the sum of three components.

aromatic carbon peak confirmed the overall 33.3% enrichment of this carbon.

Al-exchanged clays were prepared by heating 5 g of each clay with 50 mL of 0.10 M $\text{Al}(\text{NO}_3)_3$ at 90°C for 1 hr, then centrifuging and washing the pellet with water until the pH was neutral. The solid was dried at 80°C for 24 hr and then calcined at 200°C for 2 hr in air. X-ray fluorescence analyses of the major oxides were performed by the Geochemical Laboratories at McGill University.

Silylated clays (the Al-exchanged clays as well as the original materials) were prepared from 0.5 g of clay and trimethylchlorosilane (2 ml, 0.016 mol) in 5 ml of dichloromethane. Excess silane and solvent were removed on a rotary evaporator, and the residue was dried at 40°C in air for 30 min.

The amine adsorbed on clays was prepared by adding 2-phenethylamine (0.1 ml, 0.8 mmol) dissolved in 5 ml dichloromethane to 0.5 g of Al-exchanged or silylated Al-exchanged clays, stirring for 2 hr, removing the solvent and unadsorbed amine *in vacuo*, and drying the adsorbed clays at 40°C for 2 hr.

^{13}C CPMAS-NMR spectroscopy

CPMAS-NMR spectroscopy was done on a modified Jeol 60FX spectrometer with a Chemagnetics probe.

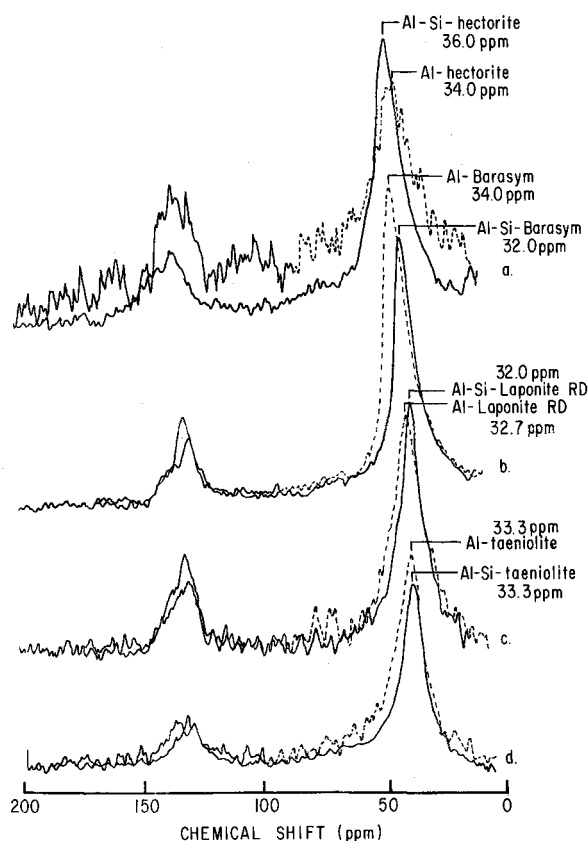


Figure 3. ^{13}C CPMAS-NMR spectra of ^{13}C enriched 2-phenethylamine adsorbed on Al-Si-clays (solid lines) compared to Al-clays unsilylated (dashed lines): a) hectorite; b) Barasym; c) Laponite RD; and d) taeniolite. Each spectrum contains 8000 transients.

Kel-F rotors were used with spinning speeds of 2.5–3.5 kHz. The single pulse sequence used a contact time of 1 ms (unoptimized) and a recycle time of 2 s. Line broadening of 25 Hz was applied, and all spectra were referenced to tetramethylsilane. The solution ^{13}C NMR spectra were obtained at 75.5 MHz using a Varian XL300 at 7.05 T and Waltz proton decoupling.

RESULTS

The CPMAS-NMR spectra of 2-phenethylamine adsorbed on the Al-exchanged clays (Al-clay) showed multiple peaks (Figure 1) with increased linewidths relative to pure solids such that distinguishing between Bronsted and Lewis bound species was not possible. In this paper, we will refer to the chemically adsorbed species as the ammonium compound, although we recognize that Lewis acid contributions are also possible.

The spectrum corresponding to Al-hectorite (Figure 1a) shows the greatest increase in line width. Deconvolution (Figure 2) of the spectrum characterizes three components with chemical shift values of 34, 30, and 24 ppm. By varying the concentration of the adsorbed

amine, we were able to isolate the species at 34 ppm with 100 Hz linewidth at low concentrations. At higher concentrations of the amine on the clay, the broad component at 24 ppm with a 350 Hz linewidth was evident.

The CPMAS-NMR spectrum of the amine adsorbed on Al-Barasym reveals multiple components as well (Figure 1b). Contact time variation in the pulse sequence resolved two components. In going from 75 to 2000 μs , there was a modest but significant shift in spectral detail. The optimum contact time is around 500 μs with about a 20% loss of signal intensity at 1000 μs . At the shortest contact time, the predominant peak is the one at 34 ppm; whereas, at increasing contact times, the second peak emerges at 29 ppm. At a contact time of 250 μs , the two major components are separated by 5 ppm with a linewidth of 250 Hz. Moreover, the broad component at 25 ppm does not appear at all at short contact times, and it only becomes evident at a contact time of 500 μs .

The CPMAS-NMR spectra for the amine adsorbed on Al-Laponite RD and Al-taeniolite (Figures 1c and 1d) show a signal maximum at 32.7 ppm with a linewidth of 312 Hz and 33.7 ppm with a linewidth also of 312 Hz, respectively. Deconvolution of the spectra confirmed the presence of multiple components (spectra not shown).

Adsorption of 2-phenethylamine on silylated Al-hectorite (Al-Si-hectorite) has a remarkable effect on the CPMAS-NMR spectrum (Figure 3a). The beta carbon region is narrower, but the overall signal intensity is comparable to the corresponding unsilylated clay. The spectrum is still characterized by multiple components with similar chemical shifts, but the linewidths are different and lead to an overall linewidth at half-height of 250 Hz. The resulting spectrum greatly resembles those of Al-Si-Laponite RD and Al-Si-taeniolite (Figures 3c and 3d). The effect of amine concentration was examined. At the lowest coverages narrower linewidths were found; and, in fact, these were similar to those observed for the pure solid amine compounds. As the amount of coverage increases, the linewidths increase and the chemical shift maximum moves to lower shielding (i.e., to a greater value for ppm).

The CPMAS-NMR spectrum of the amine adsorbed on Al-Si-Laponite RD (Figure 3c) is similar in major details to that of the corresponding unsilylated clay. There is some narrowing of the beta carbon signal and concomitant small loss of overall signal intensity for the same number of transients. The absence of a silylating effect on the chemical shift is significant since silylation of Al-Laponite RD is quite extensive as determined by ^{13}C CPMAS-NMR spectroscopy. The spectral changes for Al-Si-taeniolite closely resemble those of the Laponite RD sample. There is a linewidth narrowing to 240 Hz and some loss of overall signal without a significant change in chemical shift. In con-

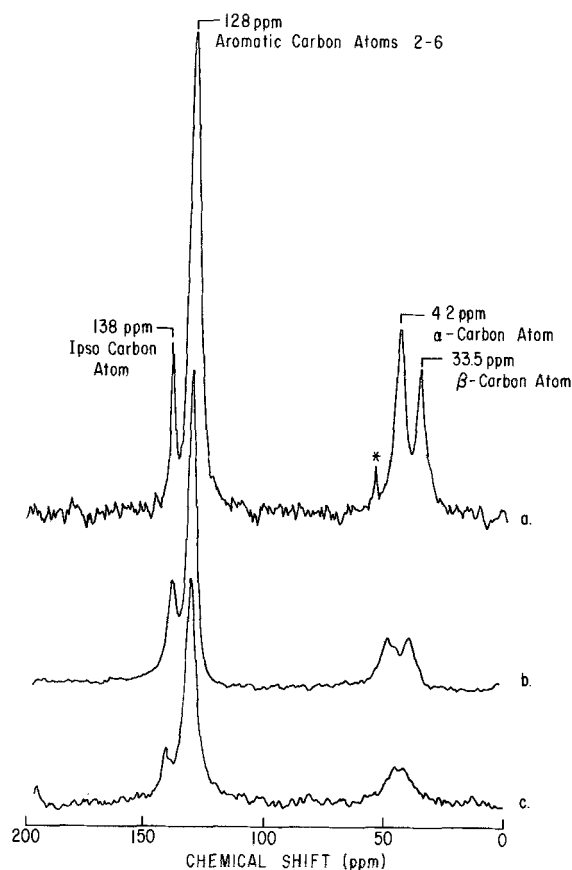


Figure 4. ^{13}C CPMAS-NMR spectra of isotopically normal 2-phenethylamine in solid complexes compared to Al-Barasym: a) pure 2-phenethylammonium chloride; b) pure 2-phenethylamine-tin tetrachloride; and c) 2-phenethylamine-Al-Barasym. The peak designated by * is a spinning sideband. Spectra (a) and (b) contain 8000 transients; spectrum (c) contains 32,000 transients.

trast to Laponite RD, this clay has a low surface area and the extent of silylation is modest.

In contrast to the above, silylation of Al-Barasym changes the available distribution of sites. The spectrum (Figure 3b) shows a narrowing of the linewidth and significant loss of signal intensity. The peak maximum for the beta carbon has moved to greater shielding from 34 to 32 ppm with a change in linewidth from 250 to 165 Hz. This indicates a change in the major adsorption component.

Spectral region for aromatic carbon atoms

The naturally abundant ^{13}C amine rather than the ^{13}C -enriched beta carbon amine was used for this part of the study. The spectral region of interest is that which is assigned to the ipso carbon (138 ppm; see Figures 4a and 4b) and the other five carbon atoms in the phenyl ring (128 ppm; Figures 4a and 4b). The spectra for pure 2-phenethylammonium chloride (Figure 4a)

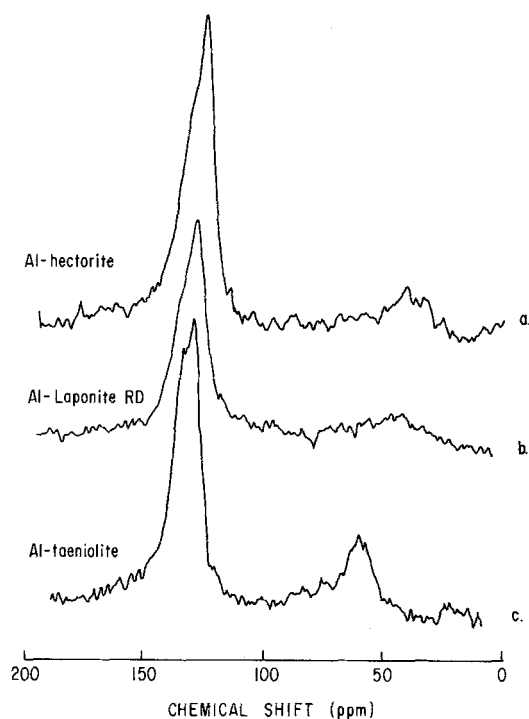


Figure 5. ^{13}C CPMAS-NMR spectra of isotopically normal 2-phenethylamine adsorbed on clays showing the greatly broadened region for the aromatic carbon atoms: a) Al-hectorite; b) Al-Laponite RD; and c) Al-Taeniolite. Each spectrum contains 32,000 transients.

and the pure solid complex of 2-phenethylamine with tin tetrachloride (Figure 4b) show linewidths of about 100 Hz. The spectrum for 2-phenethylamine adsorbed on Al-Barasym (Figure 4c) is similar and has a linewidth of 125 Hz for the peak that corresponds to the five aromatic carbon atoms.

In contrast, the spectra for the other clays under similar conditions (Figure 5a-c) show greatly broadened linewidths of the order of 400 Hz. This increased linewidth involves a complex envelope of multiple chemical shifts.

The above data suggest that, for Al-Laponite RD, Al-taeniolite, and Al-hectorite, the adsorbed amine occupies interlayer sites. These sites probably include ion-exchange sites based on the following CPMAS-NMR experiment. An authentic ion-exchanged sample, Laponite RD (not Al-exchanged) was ion-exchanged in aqueous solution with 2-phenethylammonium chloride. The resulting spectrum (not shown) was identical to that of the spectrum obtained when 2-phenethylamine was adsorbed on Al-Laponite RD.

All of the spectra described above were obtained using cross-polarization, i.e., the excitation magnetization is transferred from the proton to the carbon. This method results in a signal for solidified or immobilized material only. In a Bloch decay NMR ex-

periment, the excitation magnetization is direct to the carbon. In general, occupied sites that have some motion involved are better detected with Bloch decay experiments, and significant differences in the spectra between the excitation methods reveal differing site adsorptions with differing motion. A Bloch decay experiment was performed to assess the efficiency of cross polarization in sampling the sites and the effect of motion. For Si-Al-hectorite adsorbed with 2-phenethylamine, the comparison of the Bloch decay spectra with that of a cross-polarization experiment (not shown) revealed no differences in the chemical shift of the beta carbon atoms with a somewhat greater linewidth (20%) for the Bloch decay spectrum. Thus, the Bloch decay experiment does sample a somewhat greater range of amine adsorption sites, but the effect is not large.

DISCUSSION

CPMAS-NMR spectroscopy has been used successfully in characterizing solid amine adducts and amine adsorbed on alumina using as a diagnostic the alpha and beta carbon atoms of butyl amine (Dawson *et al.*, 1981) and pyridine on silica alumina (Maciel *et al.*, 1983). Recently, Ofori-Okai and Bank (1992) found that the chemical shift of the alpha and beta carbon atoms of 2-phenethylamine undergoes characteristic changes upon protonation or Lewis acid formation. We, therefore, predicted that, for amine adsorbed on clays, it would be possible to distinguish between the adsorbed neutral amine and the protonated or Lewis acid bound amine from the chemical shift values.

The possible presence of multiple species was addressed in three ways. First, deconvolution of the signals was performed by mathematical simulation. Second, we used concentration variation to isolate a more strongly adsorbed component at low concentrations revealing that the components had different adsorption patterns. Finally, it was possible to demonstrate that the multiple components had differing sensitivities to contact time variation in the CPMAS-NMR pulse sequence. Each of these methods is of comparable value in designating multiple sites although experimentally one or the other may prove more feasible in given instances depending upon the number of transients required and the chemical shift separation of components. In the case of Al-Laponite RD and Al-taeniolite, there were clearly multiple peaks, indicating that the method of deconvolution served well and multiple experiments were not required. For Al-Barasym, the broad, relatively shapeless peak required the more time-consuming multiple experiments, each at a specific contact time. For Al-hectorite, the contact time variation would have been prohibitively long and, thus, concentration variation was used to separate the components.

Maciel *et al.* (1983) have noted that intramolecular chemical shift differences for individual carbon atoms

eliminate the ambiguities caused by different changes and errors due to external referencing. In our system, the center of the aromatic signal serves as an internal reference since this peak always appears at 1284 ± 1 ppm in a wide variety of solution and solid-state spectra of 2-phenethylamine and its complexes.

Chemical shift changes from sites of different acidities

The free amine has a chemical shift for the beta carbon of 40.2 ppm. Protonation of nitrogen leads to increased shieldings of the beta carbon by 7 ppm relative to the free amine for the solid hydrochloride salt (Ofori-Okai and Bank, 1992). Relative to the chemical shift of the beta carbon of the amine, the smallest increase in shielding that we observe is for a signal at a chemical shift of 33 ppm for one of the species, which agrees well with that of the solid ammonium compound. The other two species, chemical shifts of 30 and 24 ppm, are more shielded. Dawson *et al.* (1981) similarly found multiple resonances for the beta carbon of butyl amine adsorbed on alumina. They attributed this to the fact that the surface acid was indeed a stronger acid than the model solid reference compound. Similarly, for the clay these more shielded resonances denote amine bound to sites of greater acidity than HCl.

The chemical shift of the beta carbon has been correlated with charge effects and modeled with semiempirical calculations (Linares *et al.*, 1980; Dawber and Massey-Shaw, 1989). The chemical shift of these sites at 30 and 24 ppm, respectively, indicate considerably greater charge on the nitrogen atom in the clay bound species than is observed in any of the solid complexes of the amine studied so far. While the detailed nature of these sites giving rise to these species is not now known, it is clear that clays have distinct sites of differing acidities. Moreover, some of these sites are very acidic.

Amine-ammonium complexes

The physisorbed amine is expected to have a chemical shift similar to that of the free amine (40 ppm) based on results for pyridine on silica-alumina (Maciel *et al.*, 1983). In all spectra at low concentrations of amine, we do not see significant signals at 40 ppm. Given the linewidths, identification of small contributions from the amine could not be assessed; however, in several of the spectra, there were distinct signals at 36–37 ppm, i.e., chemical shift values midway between the protonated and non-protonated forms. These signals could be the result of an amine-ammonium complex. Infrared spectral data support the importance of such species on clays (Farmer and Mortland, 1965) and recent studies of ^{15}N CPMAS-NMR spectroscopy indicated a related species in the

bis(dimethylamino) naphthalene complex (Grech *et al.*, 1990).

Multiple species

The linewidths of the beta carbon signals on the clays are greater than those of the pure compounds, sometimes as much as three times greater. The two common sources of linewidth increases are chemical shift dispersion and motion. Results from butyl amine on alumina (Dawson *et al.*, 1981) where motion has been ruled out demonstrate that the line broadening is from chemical shift dispersion, indicating the presence of multiple species. We think this is most probably the case here because of the following experiments (see also Meinhold *et al.*, 1986).

In Table 1, we reported the linewidths of several samples at two field strengths, at 2.35 and 7.05 T. For both the pure compounds and the amine adsorbed on clays, the effect of field strength on linewidth was approximately 2.3. This similar effect of field strength on the observed linewidth is compatible only with a chemical shift dispersion explanation for the increased linewidths of the clay samples. Moreover, work in progress with ^{15}N -labeled amine shows individual components as a result of the smaller linewidths. The smaller linewidths found in the ^{15}N CPMAS-NMR spectra are caused by the absence of quadrupolar broadening that occurs with the ^{14}N isotope. Finally, the similarity of the Bloch decay and the CPMAS experiments indicate that there is not extensive motion occurring, but rather that there are multiple sites.

Blocked sites

A procedure was used to block certain sites on the clays as a method to characterize the adsorption process. Trimethylsilyl chloride is known to react with hydroxyl protons (Maciel *et al.*, 1981), and, in reactions with clays, the hydroxyl protons at edge and/or defect sites are the only ones involved because of the steric requirements for the reagent. First, the extent of silylation for each clay was determined by ^{13}C CPMAS-NMR spectroscopy using the intensity of the signal for the methyl carbon at around 0 ppm. Each spectrum consisted of a single peak of linewidth 30 ± 5 Hz with the following signal intensities expressed as signal to noise ratios (S/N) normalized to the number of transients: Laponite RD, 57; Barasym, 30; hectorite, 17; taeniolite, 12. Thus the amount of silylation of the clays that we determined generally followed the extent of reported surface area of the clay (Table 1). Comparison of the spectra for 2-phenethylamine adsorbed on Al-clays and Al-Si-clays indicates the relative importance of the edge and/or the defect site hydroxyl groups available for reaction with the amine. It also reflects the relative number of more acidic sites on the surface of the clays.

Table 1. Surface areas, layer spacings, particle size diameters, and cation exchange capacities of the clays.

Clay ³	Surface area (m ² /g)	Layer ² spacing (Å)		Part. diameter (Å)	CEC (meq/100 g)
		w/amine	w/o amine		
Laponite RD	370 ¹	15.8	?	300 ¹	55 ¹
Hectorite	63 ¹	14.9	14.4	3000 ¹	52 ¹
Barasym	133 ¹	12.6	11.5	1000 ¹	57 ¹
Li-Taeniolite	10 ²	14.8	12.7	50,000 ²	120 ²

¹ Cenens and Schoonheydt (1988).

² J. Johnson, personal communication.

³ Chemical composition (weight %) determined by X-ray fluorescence analysis. Laponite: RD SiO₂, 59.35; Al₂O₃, 5.51; TiO₂, 0.02; Fe₂O₃, 0.08; MgO, 20.74; CaO, <0.01; Na₂O, 0.16; K₂O, <0.01. Hectorite: SiO₂, 34.70; Al₂O₃, 4.09; TiO₂, 0.04; Fe₂O₃, 0.02; MgO, 15.30; CaO, 23.40; Na₂O, 1.26; K₂O, 0.13. Barasym: SiO₂, 49.06; Al₂O₃, 39.09; TiO₂, 0.01; Fe₂O₃, 0.07; MgO, <0.01; CaO, <0.01; Na₂O, 0.25; K₂O, 0.01. Taeniolite: SiO₂, 64.71; Al₂O₃, 2.67; TiO₂, 0.01; Fe₂O₃, 0.08; MgO, 21.72; CaO, 0.14; Na₂O, 0.19; K₂O, 0.05.

The effect of silylation of the clays and subsequent amine adsorption fall into two main categories. For Al-Si-taeniolite and Al-Si-Laponite RD, the small line narrowing and loss of signal are ascribed to the loss of the minor contribution from edge sites. For the naturally occurring clay hectorite, there are both interlayer and edge sites for amine adsorption, although the edge or dislocation sites contribute more in the unsilylated clay. Silylation of hectorite results in fewer edge sites, and the interlayer sites dominate giving rise to a spectrum that resembles Al-Si-taeniolite and Al-Si-Laponite RD.

In contrast, silylation of Al-Barasym brings about a change in the chemical shift; therefore, the silylating agent has reacted with the kinds of sites that preferentially bind the amine. This selectivity reveals that Al-Barasym has distinctly different kinds of acidic sites.

Location of acidic sites

For the clay Al-Barasym, adsorption of 2-phenethylamine involves only edge sites or platelet faces. We base this conclusion on the following observations. First, edge adsorption involves unrestricted aromatic rotation, which is consistent with our CPMAS-NMR spectral linewidths in the aromatic region. Rapid motion causes the chemical shifts of the two ortho and meta carbon atoms to be isotropically averaged and leads to narrow linewidths. Second, the layer spacing of the Al-Barasym with the amine is 12.6 Å, which is typical of a mixed-layer clay with only minor expansion of the expandable layers. This is in contrast to an expansion to layer spacings of 14.8–15.8 Å for the other expandable clays upon amine adsorption. And finally, for Barasym, evidence indicates that most of the catalytic activity is associated with the edge sites (Wright *et al.*, 1972). Nevertheless, these sites are far from homogeneous and instead represent an array of acidities. By

using the silylating agent, some of the sites can be selectively blocked.

The remaining clays, Al-Laponite RD, Al-taeniolite, and, to a lesser extent, Al-hectorite, all involve mostly interlayer adsorption as seen from the greater change in layer spacing upon amine adsorption and the increase in linewidths of the aromatic carbon atoms resulting from restricted aromatic motion in the interlayer. Motional restriction comes about from steric crowding of some solid structures (Occelli *et al.*, 1989; Resing *et al.*, 1979). If the aromatic ring cannot undergo rotation rapidly, then the signals for the ortho and meta carbon atoms will each be seen as a pair of signals. Depending upon the chemical shift differences and linewidths, this could easily be observed as significant broadening in the region. This is not the case for the para or ipso carbon signals, and these should remain as sharp as in the freely rotating compound. Fortunately, the chemical shift of the ipso carbon is sufficiently removed from the other aromatics that we can observe the linewidths of the ipso carbon unaffected. An analogy to the use of a sterically derived change in spectra to distinguish between internal and external surface adsorption is the blue and red shifts in the visible spectroscopy of methylene blue on clays (Cenens and Schoonheydt, 1988). These shifts were used to characterize the planarity and to assign the internal and external sites for the amine adsorption.

For the clays we have studied, hectorite is the only naturally occurring clay, and it has the broadest range of different sites. Both surface sites and interlayer sites contribute to the amine adsorption. Silylation decreases the available edge sites, and the interlayer sites then predominate giving the CPMAS-NMR spectrum similar to those of Al-Si-Laponite RD and Al-Si-taeniolite. Heterogeneity and irregularity for the natural clay may render some sites more difficult to access because of dislocations.

SUMMARY

In applying the results of this study for possible insight in clay catalysis, the most striking features come from Al-Barasym and Al-hectorite. For Al-Barasym, acid surface sites of very different reactivities are available for bonding to bases. Moreover, these sites can be preferentially selected by reaction with trimethylsilyl chloride. It is very likely that some combination of reagent size and site location play important roles in the selection process, and modifying the silylating reagents with increased steric demands should provide even greater selectivity. With a narrower band of amine sites available, catalytic selectivity could be improved.

For Al-hectorite, a naturally occurring expandable clay, there is a significantly greater heterogeneity of sites for amine adsorption than is available for synthetic clays. These differences are far greater than typical physical property data would indicate and are very

possibly due to the irregularities in the natural material. Two things are relevant. First, this behavior is likely to be true for many naturally occurring clays; and second, this heterogeneity can be controlled by surface treatment and monitored by CPMAS-NMR spectroscopy. With a method to control the heterogeneity of available sites and the means to assess this control, it should be possible to study these effects on reactivity.

Finally, the far greater similarity of the spectra for Al-Laponite RD and Al-taeniolite with and without silylation lead to the conclusion that edge sites contribute far less to the amine adsorption. This is particularly important for Al-Laponite RD, where the ¹³C CPMAS-NMR spectrum of the silylated clay reveals a high concentration of silylated sites as is consistent with the greater surface area of this clay. In this regard, Al-Laponite RD and Al-taeniolite offer an opportunity to assess the relationship between catalytic activity and sites which are predominantly interlayer.

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