TRIETHYLENE DIAMINE–CLAY COMPLEXES AS MATRICES FOR ADSORPTION AND CATALYTIC REACTIONS*

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Abstract—Complexes of 1,4-diazabicyclo [2.2.2] octane (triethylene diamine) with smectite and vermiculite were made for the purpose of exposing the internal surfaces of the clays for adsorption of gases and possible catalytic activity. When the diprotonated form of the amine saturated the exchange sites, internal surfaces of the clays were found to be available to nitrogen, ethane, and 2,4-dimethyl pentane. Proton lability in the smectites was studied with NH_3, D_2O, and C_6D_6 experiments. Catalytic function was demonstrated in the conversion of acetonitrile to acetamide in the smectite.

INTRODUCTION

The objective of this work was to place materials within the interlamellar spaces of layer lattice silicates such as smectite and vermiculite which would hold the sheets apart a significant amount, yet were small enough to permit interlamellar penetration by liquid or gaseous molecules for the purpose of adsorption and/or catalytic reactions. It was found that the small "cage" compound 1,4-diazabicyclo [2.2.2] octane also called triethylene diamine (TED) fulfilled these objectives better than any of the others considered. The molecule has a bulky shape which prevents it from assuming a position parallel with the clay surface which would cover surfaces and also result in small distances between adjoining silicate layers. In addition its cationic form is divalent so each molecule neutralizes two exchange sites. When it is the exchange cation, these properties, together with its small crossectional area ($28 Å^2$), permit the internal surface of smectite and vermiculite to be available to many molecules. Results obtained in this study include X-ray and infrared absorption properties, gas adsorption isotherms, and catalytic abilities.

METHODS

The clays utilized in this work were smectite from Upton, Wyoming and vermiculite from Libby, Montana. The clay fraction was obtained by dispersion and sedimentation methods. The diprotonated form of the triethylene diamine (TED) was obtained by adding HCl to a water solution of the amine to a pH of 2.1. Titration of the amine indicated protonation of one nitrogen at about 6.5 pH and the other

at about a pH of 2.5. The sodium forms of the clays were treated with an excess of the amine salt, then washed with distilled water until no free chloride was found. Complexes of the amine with Cu and Na smectite were accomplished by treating these homoionic clays with the molecular amine in water solutions. After complexing, they were washed with distilled water. Micro-Kjeldahl analysis of the clays saturated with the chloride salt of the amine gave 0.99 and 1.14 m-equiv. N/g for the smectite and vermiculite respectively.

I.r. spectra were obtained on self-supporting films of the smectite and vermiculite placed in the sample beam of a Beckman IR-7 spectrophotometer. X-ray powder diffraction data obtained on thin films of clay mounted in a Philips diffractometer utilizing Ni filtered copper radiation. Nitrogen adsorption data at liquid nitrogen temperatures were obtained with a Perkin-Elmer sorptometer and surface areas calculated from the resulting isotherms. Adsorption isotherms of ethane and 2,4-dimethylpentane were obtained at 25°C on freeze-dried samples of the clays mounted on quartz helices in a vacuum system. After overnight degassing, the weight of material adsorbed was measured with a cathetometer as a function of the pressure of the gas supplied. Water is very weakly held by the TED^{2+}–clays, and the degassing procedure used, was effective in dehydrating the clay. I.r. spectroscopic data indicated all the water was removed by heat treatment at 100°C.

RESULTS

X-ray powder diffraction. The spacings obtained for smectite and vermiculite treated with either molecular TED or the diprotonated species, were rather uniform. When TED^{2+} was the saturating cation on the exchange complexes, a 14.2 Å spacing was obtained for both smectite and vermiculite when dry. When
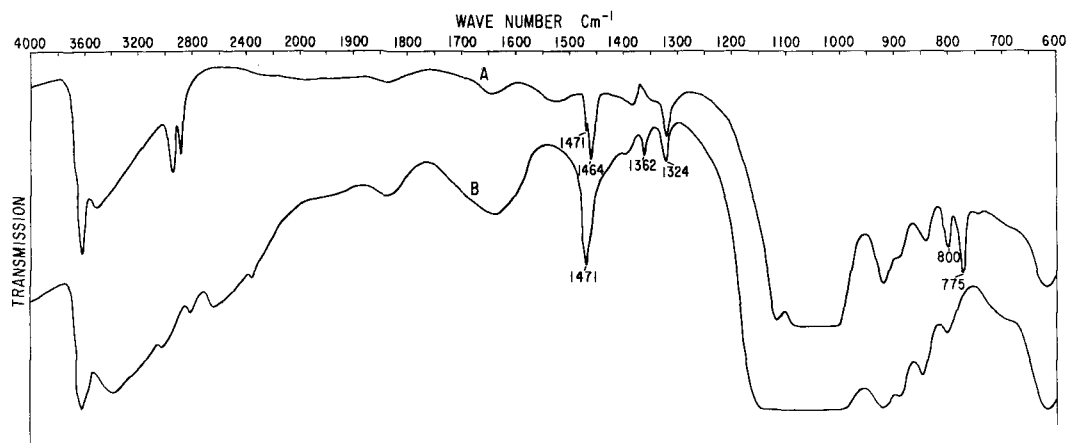
WAVE NUMBER Cm⁻¹

Fig. 1. I.r. spectra of TED-Cu(II)–smectite—A; and TED²⁺–smectite—B.

wet, the smectite exhibited a slightly higher spacing of 14.9 Å. When Cu(II) smectite was treated with molecular TED, the resulting complex had a spacing of 14.8 Å, while the TED-Cu(II) vermiculite was 14.4 Å. All of the spacings exhibited rationality and thus demonstrated the homogeneity of the TED-clay complexes.

I.r. spectra. The i.r. spectra of TED²⁺-smectite and Cu(II) smectite treated with molecular TED appear in Fig. 1. The protonated form distinguishes itself chiefly by the band at 1471 cm⁻¹ while the molecular form does the same with a band at 1463 cm⁻¹. When Na(I) smectite is complexed with a molecular TED, only the 1463 cm⁻¹ band is present. The smectite with cationic TED on the exchange sites has a strong 1471 cm⁻¹ band while the Cu(II) smectite treated with molecular TED has a strong 1463 cm⁻¹ band but also a weaker peak at 1471 cm⁻¹. In the latter case it appears that the Cu(II)-clay surface is acid enough to protonate some TED while the rest of it is likely coordinated to the copper exchange ion. The latter conclusion is supported by a blue color typical of Cu(II) amine complexes. Studies on clay films normal and at 45° to the i.r. beam failed to show appreciable pleochroic character for any bands in any of the complexes.

Nitrogen and alkane adsorption. Utilizing nitrogen adsorption isotherms, surface areas were calculated with the Langmuir equation. Earlier results (Knudson and McAtee, 1972; and Clementz and Mortland, 1974) have indicated that the Langmuir equation is obeyed better than the Brunauer Emmett Teller (BET) equation when internal surfaces of smectite accounts for most of the adsorption. These calculations gave values of 280 M²/g and 144 M²/g for TED²⁺ saturated smectite and vermiculite respectively. Figure 2 shows adsorption isotherms for 2,4-dimethylpentane on the TED²⁺ saturated smectite and vermiculite while Fig. 3 shows similar data for the adsorption of ethane. When surface areas are calculated from the 2,4-dimethylpentane isotherms with the Langmuir equation, values of 199 M²/g and

116 M²/g are obtained for the smectite and vermiculite respectively. The ethane isotherms could not be used for this purpose since the isotherms were obtained at very low partial pressures, only going up to about $P/P_0 = 0.02$. The solid points at zero partial pressures in Figs. 2 and 3 are obtained upon pumping the systems at high vacuum overnight after obtaining the adsorption isotherms. In Fig. 3 it is obvious that all the ethane is removed upon degassing but in Fig. 2 very appreciable amounts of 2,4-dimethylpentane remain.

Deuterobenzene and deuterium oxide experiments. Experiments were performed on the TED²⁺-smectite to see whether or not hydrogen deuterium exchange takes place between the clay and D₂O and also with deuterobenzene. The measure of exchange was determined by observing the degree of deuteration of structural hydroxyl groups utilizing i.r. spectroscopy. At 100°C, at least half of the structural hydroxyls became deuterated upon reaction of the TED²⁺-smectite with
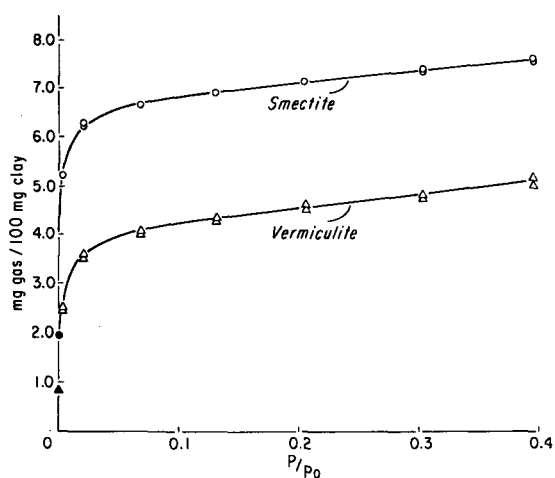

Fig. 2. Adsorption isotherms (25°C) of 2,4-dimethylpentane on TED²⁺–smectite and TED²⁺–vermiculite. The solid points represent gas remaining after extensive degassing.
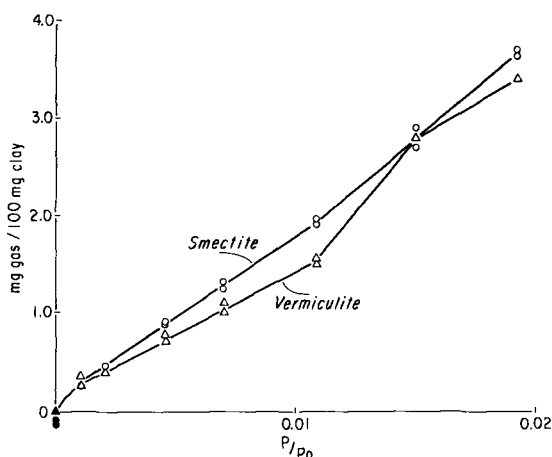
Fig. 3. Adsorption isotherms (25°C) of ethane on TED^{2+}–smectite and TED^{2+}–vermiculite. The solid points are obtained upon extensive degassing after ethane adsorption.

D_2O in a 16 hour time period. This agrees with previous results (Russell and Fraser, 1971 and Yariv and Heller-Kallai, 1973) indicating smectites with high Bronsted acidity may easily exchange protons from structural hydroxyls with surface hydrogen ions. Isotopic exchange reactions of benzene over zeolites have been studied (Venuto and Landis, 1968) where zeolites with D^+ as the exchange cation were utilized. In this work deuterobenzene was utilized and the degree of exchange monitored by observing the appearance of deuterated structural hydroxyl groups. When the TED^{2+}–smectite was refluxed (80°C) with deuterobenzene for several days only a trace of OD stretching vibrations appeared probably representing hydroxyl groups exposed at the edge of the clay platelets. In a bomb only small amounts of exchange took place at 115°C over a 16 hour period. However at 189°C, considerably more exchange occurred and the structural integrity of the TED^{2+} remained, as indicated by i.r. spectroscopy. At 220°C, about one-third of the structural hydroxyls were deuterated. However, there was some indication from i.r. that the TED^{2+} was beginning to decompose. For comparison, bomb experiments were performed with Al^{3+}– and Na$^+$–

smectites at 220°C. In the case of the Al^{3+}–smectite, about the same amount of exchange took place as with the TED^{2+} system, however the Na$^+$ system produced only trace amounts of exchange. When deuterobenzene or D_2O was reacted with TED^{2+}–vermiculite, very little deuterium exchange with lattice hydroxyls was observed.

Catalytic studies with acetonitrile. In an effort to demonstrate some catalytic properties of the TED^{2+}–smectite system, reactions with acetonitrile were performed. The hydrolysis reaction goes according to the following equation: $CH_3CN + H_2O \rightarrow CH_3CONH_2$. Sanchez et al. (1972) found that some nitriles were catalyzed to produce amides on smectite surfaces, the rates being related to the kind of exchange ion and thus proportional to the acidity of the surface. Figure 4 shows the i.r. spectrum of air-dry TED^{2+}–smectite reacted in a cell with acetonitrile at 20°C for 24 hr. The strong band appearing at 1600 cm^{-1} in spectrum B is suggested to be that of the amide I (CO stretching) band of acetamide and the shoulder near 1600 cm^{-1} that of the amide II band. These results demonstrate a catalytic ability of the TED^{2+}–smectite. In contrast, the TED^{2+}–vermiculite did not produce appreciable acetamide upon reaction with acetonitrile. Several attempts to obtain isomerization of 1-hexene by refluxing the liquid in the presence of TED^{2+}–smectite, were unsuccessful.

DISCUSSION

The X-ray powder diffraction data show that the TED^{2+} ion can keep the smectite and vermiculite sheets apart under dehydration conditions and the surface area determinations with both N_2 and 2,4-dimethylpentane demonstrate the accessibility of these molecules. The nitrogen analyses (0.99 m-equiv./g) of the TED^{2+}–smectite prove that the divalent organic cation is in fact neutralizing two exchange sites on the clay since the cation exchange capacity determined from other methods is found to be 0.92 m-equiv./g. Similarly, the vermiculite had 1.14 m-equiv. N/g and its measured CEC was 1.15 m-equiv./g. The higher charge density of the vermiculite means a greater population of TED^{2+} ions per unit area with resulting lower amounts of surface available for adsorption in comparison experiments. The low CEC values for this vermiculite as compared with pure vermiculites are the result of its inhomogeneity since it contained a mica component.

Sieving effects of the TED^{2+}–clays were not demonstrated for the three gases used since the internal surfaces were available to all, as indicated by the isotherms. However it is very likely that there would be great differences in retention times due to differential diffusion rates within the interlamellar spaces.

The (001) spacing of 14.2 Å for the TED^{2+}–smectite and vermiculite indicate the organic ion is oriented with the axis of the two nitrogens parallel with the z axis of the clay platelets since this dimension is
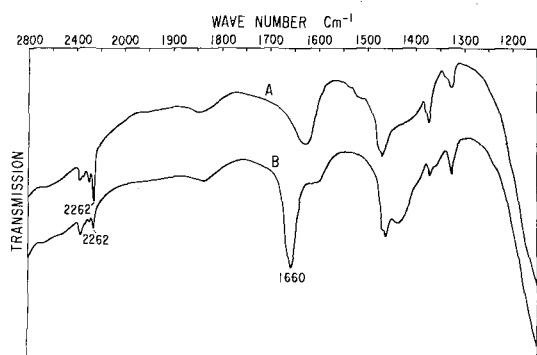

Fig. 4. I.r. spectra of air-dry TED^{2+}–smectite treated with acetonitrile. At zero time—A, after 24 hours—B.

about 4.6 Å compared with about 5.5 Å for a minimum dimension at right angles to the nitrogen–nitrogen axis. Since the silicate structure itself is about 9.6 Å, the conclusion as to the orientation seems reasonable.

The proton lability of the TED^{2+}–clays was demonstrated directly by i.r. spectroscopy when thin films of the complexes were exposed to NH_3 gas and the formation of large quantities of NH_4^+ were observed along with the concomitant disappearance of TED^{2+} and the appearance of molecular TED. The high degree of isotopic exchange of H from lattice hydroxyls of TED^{2+}–smectite when exposed to D_2O at 100°C confirms the lability of H^+ associated with the TED^{2+} cations. The more limited proton transfer observed with C_6D_6 however, may suggest a lower proton lability than that of some zeolites (Venuto and Landis, 1968). A number of attempts to obtain isomerization of 1-hexene on the TED^{2+}–smectite were unsuccessful, again suggesting a limited Bronsted acidity for this system. However, the formation of acetamide from acetonitrile demonstrates a significant catalytic function.

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