Clays and Clay Minerals, Vol. 29, No. 2, 153–156, 1981.

PROPERTIES OF SILICA-INTERCALATED HECTORITE[1]

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Abstract—Silica-intercalated hectorite with an 001 spacing of 12.6 Å and a N_2 BET surface area of 220 m^2/g was prepared by hydrolysis and oxidation at 500°C of hectorite containing a silicon acetylacetonate complex. The intercalate swelled to higher spacings upon adsorption of water, glycerol, and pyridine, but the silica was not expelled when the interlayers swelled and contracted in successive adsorption/desorption cycles. The surface area measured by isobutane adsorption agrees with the N_2 BET surface area, suggesting that the interlayers are available for adsorption of aliphatic hydrocarbons. The intercalated silica did not inhibit the ability of the interlayers to enter into cation-exchange reactions, as judged from Cu^{2+}-binding experiments. Infrared studies of NH_3-, pyridine-, and NO_2-adsorption indicate the presence of Bronsted acidity and the absence of Lewis acidity in the interlayer regions.

Key Words—Acidity, Hectorite, Infrared spectroscopy, Intercalation, Silica, Surface area.

INTRODUCTION

Recent work by Endo *et al.* (1980) indicated the feasibility of incorporating silica between the layers of swelling clays. They showed that silicon could be introduced into the interlamellar regions by ion exchange of tris(acetylacetonato)silicon(IV) cations ($Si(acac)_3{}^+$), by *in situ* reaction of acetylacetone-solvated clays with $SiCl_4$, or by formation of polychlorosiloxanes $(-SiOCl_2-)_n$. Upon hydrolysis and/or oxidation of these systems at high temperatures (i.e., 500°C), a silica residue remained between the smectite layers which resulted in a d(001) spacing of 12.6 Å. The present study reports some chemical and physical properties of a smectite-silica intercalate prepared by the hydrolysis and oxidation of $Si(acac)_3{}^+$-hectorite.

METHODS

A natural hectorite from Hector, California, supplied in spray-dried from by Baroid Division of NL Industries, was used in this study. The sodium form of the mineral as an oriented film or in powder form was solvated with acetone and treated with $[Si(acac)_3][HCl_2]$ dissolved in a minimum amount of acetone. The ratio of $Si(acac)_3{}^+$ to cation-exchange capacity (CEC) equivalents of the clay was 5:1. After a two-week equilibration at room temperature, the clay was washed with acetone, air dried, and then heated in air at 500°C for 5 hr. The resulting material had a d(001) spacing of 12.6 Å. A diffraction pattern showing four orders of 001 reflections was published previously (Endo *et al.*, 1980). A specific surface of 220 m^2/g was measured by N_2 adsorption at liquid nitrogen temperatures. X-ray powder diffraction (XRD) data were obtained with a Philips diffraction unit using CuKα radiation. Infrared spectra (IR) were obtained using a Beckman IR-7 spectrophotometer. Chemical analyses of completely digested samples were carried out by Galbraith Laboratories, Knoxville, Tennessee.

RESULTS AND DISCUSSION

Infrared absorption spectra

Figure 1 shows the IR spectrum of (A) Na^+-hectorite and (B) the hectorite-silica intercalate. The bands near 800 cm^{-1} and 1200 cm^{-1} in (B) were attributed to the intercalated silica. The single band at 800 cm^{-1} can be found in several forms of silica, such as amorphous silica, cristobalite, and tridymite (Farmer and Palmieri, 1975). The shoulder near 1200 cm^{-1} can also be found in some silica compounds, many with a layer-type structure (Farmer, 1974). The strong, broad band at 1600 cm^{-1} and the broad absorptions between 1550 and 1300 cm^{-1} were not identified, but may be combinations or overtone bands of the intercalated silica. Clearly, the peak at 1600 cm^{-1} is not the deformation band (ν_2) for water because the corresponding OH-stretch vibrations were essentially absent in spectrum (B). Most of the hydroxyl groups initially associated with the Si after hydrolysis of the acetylacetone ligands were destroyed

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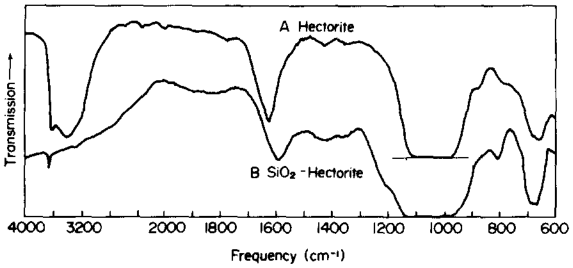


Figure 1. Infrared spectra of oriented film samples of (A) air-dry Na^+-hectorite and (B) the hectorite-silica intercalate after firing at 500°C.

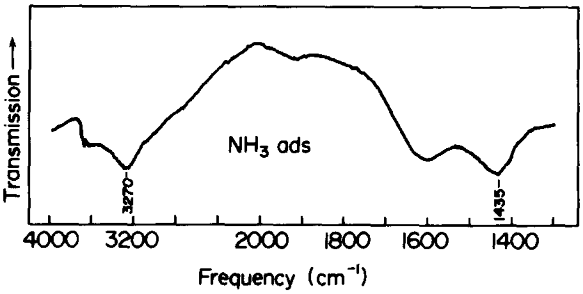


Figure 2. Infrared spectrum of ammonia adsorbed on hectorite-silica intercalate. The intercalate was dried at 400°C before being exposed to anhydrous ammonia gas.

at the high temperatures (500°C) and were converted to siloxane bonds.

Swelling properties

The 12.6-Å spacing of the hectorite-silica complex persisted under dehydration conditions, but hydration of the complex at high humidities and in liquid water led to higher spacings. The 001 reflections of the complex under various hydration conditions indicate interstratified systems containing varying proportions of water layers within the interlamellar regions. When these systems were again dehydrated, the original 12.6 Å spacing was re-established. The XRD results indicate that, although the hectorite-silica complex was able to swell, the silica was not expelled from the interlayers when the clay swelled and contracted.

Other polar molecules, such as glycerol and pyridine, caused the hectorite-silica complex to swell. Spacings of 18 Å were obtained with glycerol, very near the value obtained for ordinary smectites possessing two layers of glycerol. Pyridine adsorption by the hectorite-silica complex resulted in a 001 spacing of 14.7 Å.

Adsorptive and ion-exchange properties

Endo *et al.* (1980) pointed out earlier that different levels of silica intercalation may be obtained depending upon reaction conditions. Varying the amount of silica in the interlayers is expected to alter the surface area and other properties of the intercalation complex. The specific surfaces of the intercalate examined in the present study is 220 m^2/g for nitrogen adsorption and 183 m^2/g for isobutane adsorption, indicating that interlamellar areas are available to molecules as large as isobutane.

Because the cation-exchange properties of the smectite-silica intercalate are of interest, a sample of the intercalate was allowed to equilibrate in 0.4 N $Cu(NO_3)_2$ overnight. The clay was then washed exhaustively with water, dried, and analyzed for Cu^{2+} and Na^+. The results indicated the presence of 79.5 and 10.7 meq/100 g for Cu^{2+} and Na^+, respectively; the sum of these values is close to the CEC of the original material. Thus, the smectite did not lose much of its CEC as a result of silica intercalation, and most of the exchange sites were apparently not occluded by silica. The presence of Na^+ in the calcined product indicates that not all of the sodium ions were replaced in the exchange reaction with $Si(acac)_3^+$. It is possible that some Na^+ was trapped by the interlamellar silica.

The Bronsted acidity of the smectite-silica complex was investigated by heating a film of the material to 400°C, cooling it, and then exposing it to NH_3 gas for several hours. The IR spectrum of the product is shown in Figure 2. The bands at 1435 and 3270 cm^{-1}, respectively, are attributed to the bending and antisymmetric stretching modes of NH_4^+. The presence of NH_4^+ provides direct evidence for the presence of dissociable protons in the system. When the smectite-silica complex reacted with liquid pyridine, an IR band was observed near 1550 cm^{-1}, which is characteristic of pyridinium ion (Farmer and Mortland, 1966).

The source of the protons which are able to protonate NH_3 and pyridine is open to question. Although the hydroxyls present in pure hydroxylated silicas are not strong enough Bronsted acids to furnish protons for protonation of NH_3, silica-alumina will cause the ammonium ion to form (Little, 1966). The Bronsted sites in the smectite-silica complex are likely to be protons that were generated when the $Si(acac)_3^+$ hydrolyzed, and that neutralized the layer charge of the mineral.

Reaction with NO_2

Because the interlamellar surfaces of hectorite consist of oxygen atoms bridging mainly silicon in tetrahedral positions and because intercalated silica should be coordinately saturated, an appreciable concentration of Lewis acid sites would not be expected in the interlayers of the silica-hectorite intercalation complex. IR studies of NO_2 adsorption can be helpful in probing the presence or absence of Lewis acid sites. Parkyns (1973) showed that dry alumina and silica-alumina adsorb NO_2 exclusively by a dissociative mechanism that involves NO^+ and NO_3^- formation. The NO_3^- that is strongly bound to vacant coordination positions on the surface can be readily identified by strong IR absorptions near 1600 and 1220 cm^{-1}. Thus, it was

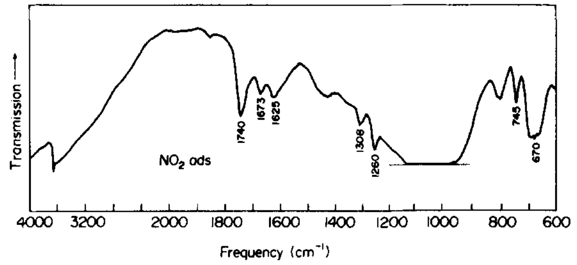
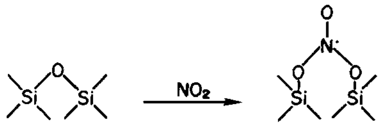


Figure 3. Infrared spectrum of NO_2 adsorbed on a silica-intercalated hectorite film. The sample was heated to 400°C to remove water prior to exposure to dry NO_2.

of interest to examine the mode of NO_2 adsorption on the silica-hectorite complex.

Figure 3 shows the IR spectrum of the silica-intercalated hectorite after adsorption of dry NO_2. Prior to exposure to NO_2, the sample was heated at 400°C to remove water. The most intense band in the spectrum occurred at 1740 cm^{-1} which, along with bands at 1260, 745, and 670 cm^{-1}, are near those observed for free N_2O_4 (Perkins and Wilson, 1952) and can be assigned to physically adsorbed N_2O_4 molecules. The bands at 1625 and 1308 cm^{-1} are in the region expected for NO_2 molecules in equilibrium with N_2O_4 on the surface (Millen and Watson, 1957). No strong absorptions occurred in the region expected for coordinated NO_3^-. Thus, no Lewis acidity was apparent in the interlamellar region.

The band at 1673 cm^{-1} could not be assigned to physically adsorbed NO_2 or N_2O_4 or to NO_3^- complexed to a Lewis acid site. Parkyns (1973) observed a similar band near 1658 cm^{-1} for NO_2 chemisorbed to silica and suggested that it may result for the insertion of NO_2 into a strained surface Si–O–Si bond:



A similar reaction may have occurred between NO_2 and intercalated silica.

CONCLUSIONS

The results suggest that the silica incorporated in swelling clays is relatively inert. Its main function is to act as a prop separating the silicate layers. The clay interlayers, after intercalation with silica, can still be swelled by polar solvents, and the silicate layers retain their cation-exchange function. The silica was not expelled from the interlayers as the silica-smectite complex swelled and contracted in successive adsorption/desorption cycles. The 12.6-Å spacing of the complex is sufficient to permit molecules as large as pyridine and isobutane to penetrate the interlamellar region. The presence of dissociable protons in the interlayer was indicated by the protonation of adsorbed NH_3 and pyridine. These acid sites probably arose as a result of protons formed in the hydrolysis of the $Si(acac)_3^+$ species used in the synthesis, and which subsequently neutralized charge arising from the smectite structure. The NO_2-adsorption studies indicate that adsorption occurred through a non-dissociation mechanism. No Lewis acidity was apparent in the interlamellar region, as expected from structural considerations. The presence of Bronsted acidity without Lewis acidity may impart desirable properties for the use of silica-intercalated smectites as catalysts.

ACKNOWLEDGMENT

Partial support of this research by National Science Foundation grant CHE-8002413 is gratefully acknowledged.

REFERENCES

Endo, T., Mortland, M. M., and Pinnavaia, T. J. (1980) Intercalation of silica in smectite: *Clays & Clay Minerals* **28,** 105–110.

Farmer, V. C. (1974) The layer silicates: in *The Infrared Spectra of Minerals,* V. C. Farmer, ed., Mineralogical Society, London, 331–364.

Farmer, V. C. and Mortland, M. M. (1966) An infrared study of the coordination of pyridine and water to exchangeable cations of montmorillonite and saponite: *J. Chem. Soc. (A),* 344–351.

Farmer, V. C. and Palmieri, F. (1975) The characterization of soil minerals by infrared spectroscopy: in *Soil Components Vol. 2, Inorganic Components,* J. E. Gieseking, ed., Springer-Verlag, Berlin, 573–670.

Little, L. H. (1966) *Infrared Spectra of Adsorbed Species:* Academic Press, New York, 185–193.

Millen, D. J. and Watson, D. (1957) The ionization of dinitrogen tetroxide in nitric acid. Evidence from measurements of infrared spectra and magnetic susceptibilities: *J. Chem. Soc.,* 1369–1372.

Parkyns, N. D. (1973) Adsorption sites on oxides. Infrared studies of adsorption of oxides of nitrogen: *Proc. 5th Internatl. Cong. Catalysis* **12,** 255–266.

Perkins, W. D. and Wilson, M. K. (1952) The vibrational spectrum of dinitrogen tetraoxide: *Phys. Rev.* **85,** 755.

(Received 30 October 1980; accepted 10 December 1980)

Резюме—Гекторит с кремнезёмными включениями с (001) параметром решётки 12,6 Å и площадьы поверхности N_2 БЭТ 220 м²/г был приготовлен путем гидролиза и окисления при 500°C гекторита, содержащего кремне ацетилацетоновый комплекс. Включения набухали (параметр решетки увеличивался) путем адсорбции воды, глицерина и пиридина, но кремнезём не вытеснялся, когда прослойки набухали и сжимались во время чередующихся циклов адсорбции/десорбции. Площадь поверхности, измеренная путем адсорбции изобутана, находилась в согласии в площадью поверхности N_2 БЭТ, указывая на то, что прослойки доступны для адсорбции алифатических углеводородов. Кремнезёмные включения не мешают проходить катионообменным реакциям, о которых можно судить по экспериментом Cu^{2+} связи. Изучение адсорбции NH_3, пиридина, и NO_2 путем инфракрасной спектроскопйй указывает на присутствие в области прослоек кислотности Бронстеда и отсутствие кислотности Льюиса. [E.C.]

Resümee—Hektorit mit eingelagertem Siliziumdioxid, der einen 001 Abstand von 12,6 Å und eine N_2 BET Oberfläche von 220 m²/g aufwies, wurde aus Hektorit, der einen Siliziumacetylaceton-Komplex enthielt, durch Hydrolyse und Oxidation bei 500°C hergestellt. Die Einlagerung quoll nach der Adsorption von Wasser, Glycerin, und Pyridin auf größere Abstände. Das Siliziumdioxid wurde jedoch nicht verdrängt, wenn die Zwischenlagen in aufeinander folgenden Adsorptions/Desorptionszyklen quollen und kontrahierten. Die Oberfläche, die mittels Isobutan-Adsorption gemessen wurde, stimmt mit der N_2 BET Oberfläche überein. Dies deutet darauf hin, daß die Zwischenlagen aliphatische Kohlenwasserstoffe adsorbieren können. Das eingelagerte Siliziumdioxid hinderte die Zwischenlagen nicht, an Kationenaustauschreaktionen teilzunehmen, wie aus Cu^{2+}-Bindungsexperimenten hervorgeht. Infrarotuntersuchungen der NH_3-Pyridin-, und NO_2-Adsorptionsprodukte deuten auf die Gegenwart von Brönstedsäure und auf die Abwesenheit von Lewissäure in den Zwischenschichtregionen hin. [U.W.]

Résumé—De l'hectorite intercalée de silice avec un espacement (001) de 12,6 Å et une aire de surface de N_2 BET de 220 m²/g a été préparée par hydrolyse et oxidation à 500°C d'une hectorite contenant un complexe acétylacetonate de silice. L'intercalé a gonflé à de plus hauts espacements lors de l'adsorption d'eau, de glycérol, et de pyridine, mais la silice n'a pas été rejetée quand les intercouches ont gonflé et se sont contractés dans les cycles successifs d'adsorption/désorption. L'aire de surface mesurée par l'adsorption d'isobutane est en accord avec l'aire de surface N_2 BET, suggérant que les intercouches sont disponibles pour l'adsorption d'hydrocarbones aliphatiques. La silice intercalée n'a pas inhibé l'abilité des intercouches d'entrer dans les réactions d'échange de cations, comme il l'a été jugé à partir d'expériences liant le Cu^{2+}. Des études à l'infrarouge de l'adsorption de NH_3, de pyridine et de NO_2 indiquent la présence d'acidité Bronsted et l'absence d'acidité Lewis dans les régions intercouches. [D.J.]