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# INTERCALATION OF SILICA IN SMECTITE[1]

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**Abstract**—Silica has been intercalated in swelling clays by hydrolysis and/or oxidation of tris(acetylacetonato)silicon(IV) cations, $Si(acac)_3^+$, and polychlorosiloxanes, $(-SiOCl_2-)_n$, in the interlamellar regions of the minerals. The $Si(acac)_3^+$ ions have been placed on the interlamellar surfaces by ion exchange and by *in situ* reaction of the acetylacetone-solvated clays with $SiCl_4$. The $(-SiOCl_2-)_n$ polymers were formed in the interlayers by reaction of adsorbed benzaldehyde with $SiCl_4$. The optimum (001) spacing observed after firing the clays in air at 500°C (12.6 Å) corresponds to the presence of a monolayer of siloxane chains. Nitrogen BET surface areas range from 40 to 240 $m^2/g$, depending on the amount of internal surface covered by the intercalated silica. In some cases, highly ordered products were formed which exhibit four orders of (00$\ell$) reflection. Interstratified products with d(001) values between 9.6 and 12.6 Å exhibit surface areas consistent with the presence of a random mixture of totally collapsed interlayers and interlayers containing siloxane monolayers. Attempts to achieve silica intercalation by hydrolysis of $SiCl_4$ in the clay interlayers were not productive.

**Key Words**—Hectorite, Intercalation, Silica, Smectite, Vermiculite.

## INTRODUCTION

There has been considerable interest in introducing materials into the interlamellar regions of swelling clays in order to keep the layers apart when the solvent is removed, thus making internal surface available for adsorption and possible catalysis. A number of organic materials have been used quite successfully (Barrer and Macleod, 1951; Knudson and McAtee, 1973; Mortland and Berkheiser, 1976; Clementz and Mortland, 1974; Traynor *et al.*, 1978) to keep layers apart at low to moderate temperatures but which fail in the temperature range of 250–500°C. In these higher temperature ranges, success in keeping the layers apart have been reported by Lahav *et al.* (1978) utilizing aluminum hydroxides, by Yamanaka and Brindley (1979) using zirconyl chloride, and by Loeppert *et al.* (1979) using complex salts of bipyridyl or 1,10-phenanthroline and firing the materials to high temperatures (i.e., 550°C).

The present work attempts to intercalate silica within the interlamellar regions of swelling clays in order to keep the mineral layers apart at high temperatures. Aragon de la Cruz *et al.* (1973) reported the adsorption of chlorosilanes by smectite and vermiculite within the internal areas of the minerals, but no results were reported which might indicate the presence of intercalated silica after heating at high temperatures. The methods reported here indicate a degree of success in introducing silica within the internal surfaces with a resulting availability of a portion of that surface for adsorption.

## EXPERIMENTAL

Homoionic exchanged forms of montmorillonite from Upton, Wyoming (API Reference Clay No. 25), hectorite from Hector, California (supplied by Baroid Division of NL Industries), and vermiculite from Libby, Montana were prepared by equilibrating the <2-$\mu$m fraction of the minerals with aqueous solutions of the appropriate metal ion or alkylammonium salts, washing the clays free of excess salt, and freeze drying. Thin, oriented-film samples suitable for X-ray powder diffraction (XRD) or infrared (IR) absorption measurements were obtained by slow evaporation of aqueous suspension under ambient conditions. Reagent grade acetylacetone [H(acac)], benzaldehyde, and $SiCl_4$ were used without further purification.

The tris(acetylacetonato)silicon(IV) cation, $Si(acac)_3^+$, was prepared as the $HCl_2^-$ salt by reaction of $SiCl_4$ and acetylacetone in benzene according to the method of Riley *et al.* (1963). Ivory-colored crystals of the compound were obtained from benzene over a 3–7-day period. The crystals were washed with diethyl ether, immediately dried *in vacuo*, and stored at room temperature under vacuum or under an inert atmosphere. The compound was found to decompose over

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the temperature range 175–180°C (in a sealed capillary). Its IR spectrum in acetone and chloroform was identical to the spectrum reported by Thompson (1969) for $Si(acac)_3(HCl_2)$. The $Si(acac)_3^+$ cation was exchanged into freeze-dried or oriented-film samples of various swelling clays by dissolving in acetone a quantity of $Si(acac)_3(HCl_2)$ corresponding to 2.0 or more times the CEC equivalent of the clay and allowing the solution to equilibrate with the clay for two or more days. The clay then was washed with acetone and air-dried. Hydrolysis of the surface bound $Si(acac)_3^+$ cation was carried out in water or in aqueous suspension at pH = 9.0. Two to four days at room temperature were allowed for hydrolysis. The clays then were fired successively at 200–240°C for 10 hr and at 500–550°C for 3–5 hr in a muffle furnace.

A Philips X-ray diffractometer with Ni-filtered Cu K$\alpha$ radiation was used to measure basal spacings. IR spectra (4000–600 $cm^{-1}$) were obtained with a Beckman Model IR-7 spectrometer. Samples were examined as oriented thin films or incorporated into KBr disks. Surface areas were determined by $N_2$ adsorption at liquid nitrogen temperature by employing a Perkin-Elmer Shell Model 212-B sorptometer. Samples were degassed by heating at 150–160°C under flowing He as a carrier gas. The adsorption data were plotted according to the BET equation. Differential scanning calorimetry was carried out on a duPont Thermal Analyzer which was operated in air at a heating rate of 10°/min from room temperature to 350°C.

## RESULTS

### *Hydrolysis of intercalated $Si(acac)_3^+$ ions*

$Si(acac)_3^+$ has been known for some time to undergo hydrolysis in aqueous solution to form hydrous silica (Dhar *et al.*, 1959):

$$Si(acac)_3^+ + 5H_2O \rightarrow Si(OH)_4 + 3H(acac) + H_3O^+ \quad (1)$$

$$xSi(OH)_4 \rightarrow (SiO_2)_x(H_2O)_{2-y} + yH_2O \quad (2)$$

It was of interest in the present study to determine if $Si(acac)_3^+$ could be exchanged into swelling clays and then hydrolyzed on the exchange sites to form domains of siloxane chains in the interlayer regions.

Exchange reactions of $Ca^{2+}$- and $Al^{3+}$-montmorillonite, and $Na^+$-hectorite with $Si(acac)_3(HCl_2)$ in acetone solution does indeed lead to binding of complex cations. IR spectra of the exchanged clays contain well defined bands near 1555, 1540, 1390, 1350, and 1320 $cm^{-1}$ that are characteristic of $Si(acac)_3^+$ (Thompson, 1969). In some cases a band attributable to the keto form of free acetylacetone also is observed near 1730 $cm^{-1}$ ($\nu$(C=O)), perhaps resulting from partial hydrolysis of $Si(acac)_3^+$ by small amounts of water. In each case a basal spacing of 16.7 ± 0.3 Å is observed, suggesting that the $Si(acac)_3^+$ cation is intercalated.

Hydrolysis of the surface-bound $Si(acac)_3^+$ ions was carried out in water or in dilute NaOH (pH = 9.0). Hydrolysis of the complex was verified by the appearance of acetylacetone with $\lambda_{max}$ = 275 nm in the solution phase. The hydrolyzed clays then were heated successively at 200–240°C to oxidize any remaining acetylacetone and at 500–550°C in air. The basal spacings of the final products were in the range 12.1 to 12.6 Å. Since the observed spacings are considerably larger than the 9.8–10.0-Å spacings expected for totally collapsed interlayers, and the carbon contents are uniformly low (0.6–1.3 wt. %), it is apparent that silica has been intercalated.

Table 1 lists the basal spacings, carbon contents, and $N_2$-BET surface areas for the silica intercalates.

Differential scanning calorimetry of the freshly hydrolyzed $Si(acac)_3^+$-clays showed two endotherms. One endotherm at 100°C may be assigned to the loss of water of hydration; the second endotherm at 310°C may indicate the formation of siloxane bonds.

### *Reactions with acetylacetone and $SiCl_4$*

Since the above results for the hydrolysis of intercalated $Si(acac)_3^+$ indicated an encouraging degree of success in achieving silica intercalation in swelling clays, an attempt was made to form intercalated $Si(acac)_3^+$ ions *in situ* by the reaction of clays solvated with acetylacetone with $SiCl_4$ in benzene.

Two reaction schemes may be written for the anticipated reactions, depending on the ability of the initial exchange cation to complex acetylacetone. When the initial exchange ion is a non-complexing cation, the ion should be lost to solution to maintain charge balance in the clay:[2]

$$\overline{M^+ + 3H(acac)} + SiCl_4 \rightarrow \overline{Si(acac)_3^+} + M^+ + Cl^- + 3HCl \quad (3)$$

In the presence of a complexing cation, however, the ion may not leave the silicate surface:

$$\overline{M^{n+}} + nH(acac) \rightarrow \overline{M(acac)_n} + nH^+ \quad (4)$$

$$\overline{M(acac)_n + nH^+} + H(acac) + SiCl_4 \rightarrow \overline{M(acac)_n} + nSi(acac)_3^+ + nHCl \quad (5)$$

The reactions of surface metal ions with acetylacetone according to Eq. (4) have been investigated previously by Parfitt and Mortland (1968).

Several swelling clays containing non-complexing

[2] The bars in the following equations symbolize the clay surfaces.

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Table 1. Basal spacing, carbon content, and surface areas of silica-clay intercalates prepared by hydrolysis of $Si(acac)_3^+$-exchange ions.[1]

| Initial clay | d(001) (Å) | % C | Surface area ($m^2/g$) |
|---|---|---|---|
| $Na^+$-Hectorite | 12.6 | — | 50[2] |
| | 12.6 | 1.30 | 240 |
| | 12.6 | 0.95 | 150 |
| $Li^+$-Hectorite | 12.6 | 1.35 | 76 |
| $Al^{3+}$-Montmorillonite | 12.6 | 0.61 | 180[2] |
| | 12.1 | 1.41 | 100[2] |

[1] Basal spacings, carbon contents, and $N_2$-BET surface areas were determined after hydrolysis in water or at pH = 9 and subsequent heating in air at 200°–240° and 500°–550°C.
[2] These samples were hydrolyzed in water; all other samples were hydrolyzed at pH = 9.

ions ($Li^+$, $Na^+$, $Ca^{2+}$) and complexing ions ($Cu^{2+}$, $Al^{3+}$) were solvated with H(acac), allowed to react with $SiCl_4$ in benzene, dried in oxygen, heated in air at 200°C for 10–18 hr to oxidize the organic fraction, and then heated at 500°C for 3–5 hr in air. A similar series of experiments was conducted with homoionic montmorillonites containing the alkylammonium ions $(CH_3)_4N^+$, $(CH_3)_3NH^+$, and $H_2(DABCO)^{2+}$, where the latter species is the diprotonated cation of 1,4-diazabicyclo[2.2.2]octane. The alkylammonium clays were solvated with H(acac) and allowed to react with $SiCl_4$ in a manner analogous to the inorganic exchange forms, except that the hydrolysis was carried out in water for 21 days prior to heating in air at 500°C.

IR adsorption spectra indicate that all of the swelling clays adsorb free acetylacetone. In addition, the clays containing complexing cations ($Cu^{2+}$, $Al^{3+}$) exhibit the presence of coordinated acetylacetonate in accord with the earlier results of Parfitt and Mortland (1968). Upon reaction with $SiCl_4$, all of the H(acac) solvated clays show the presence of surface bound $Si(acac)_3^+$ in their IR spectra.

Table 2. X-ray diffraction and surface area data for products obtained by reaction of swelling clays with acetylacetone and $SiCl_4$.

| Initial clay | d(001) (Å) After solvation with H(acac) | d(001) (Å) After reaction with $SiCl_4$ | d(001) (Å) After heating to 500°C | Surface area ($m^2/g$) |
|---|---|---|---|---|
| $Al^{3+}$-Montmorillonite | 15.8 | 14.5 | 12.6 | — |
| $Cu^{2+}$-Montmorillonite | 13.0 | 12.8 | 10.0 | — |
| $Ca^{2+}$-Montmorillonite | 15.2 | 14.7 | 12.6 | — |
| $Li^+$-Montmorillonite | 13.2 | 13.4 | 9.6 | — |
| $Ca^{2+}$-Hectorite | 15.2 | 14.7 | 12.6 | — |
| $Na^+$-Hectorite | 14.7 | 14.4 | 12.6 | — |
| $Li^+$-Vermiculite | 15.2 | 14.5 | 12.6 | — |
| $H_2(DABCO)^{2+}$-Montmorillonite | — | — | 11.0 | 42 |
| $(CH_3)_3NH^+$-Montmorillonite | — | — | 11.8 | 91 |
| $(CH_3)_4N^+$-Montmorillonite | — | — | 12.6[1] | 174 |

[1] The carbon content of this product was 3.48 wt. %.

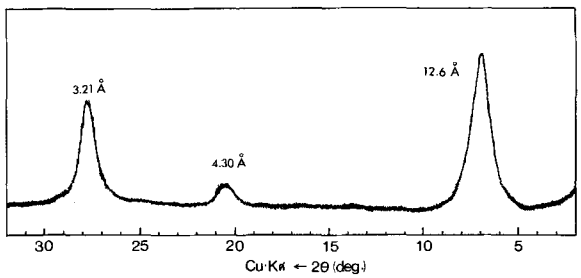



Figure 1. X-ray powder diffraction pattern of an oriented clay film sample with a silica intercalate. The sample was prepared by reaction of H(acac)-solvated $Na^+$-hectorite with $SiCl_4$ and subsequent hydrolysis or oxidation at 200° and 500°C.

Table 2 lists the d(001) values of the products obtained after solvation with H(acac), subsequent reaction with $SiCl_4$, and heating in air at 500°C. Included in the table are surface areas of selected products obtained after heating at 500°C. In most cases the (001) spacing is near 12.6 Å, indicating the presence of an intercalated monolayer of siloxane chains. Spacings corresponding to collapsed or nearly collapsed interlayers are observed for the products obtained from $Cu^{2+}$- and $Li^+$-smectites. It is possible that in these cases the initial clay is not sufficiently swollen by H(acac) to allow penetration of $SiCl_4$, and consequently the $Si(acac)_3^+$ observed by IR is present only at external surfaces.

Figure 1 illustrates the four orders of reflection for an oriented film sample of a silica intercalate obtained by reaction of $Na^+$-hectorite with H(acac) and $SiCl_4$. It is noteworthy that the fourth order reflection is exceptionally intense, suggesting important changes in the structure factor resulting from silica incorporation.

### *Reactions with benzaldehyde and $SiCl_4$*

Another promising approach to the intercalation of silica in layered silicates involves the reaction of benzaldehyde and $SiCl_4$ to give benzalchloride and a poly-

Table 3. X-ray diffraction and surface area data for the products obtained by reaction of swelling clays with benzaldehyde and $SiCl_4$.

| Initial clay | d(001) (Å) After solvation with $C_3H_5CHO$ | d(001) (Å) After reaction with $SiCl_4$ | d(001) (Å) After heating to 500°C | Surface area ($m^2/g$) |
|---|---|---|---|---|
| $Na^+$-Hectorite | 14.7 | 14.3 | 12.6 | 190 |
| $Li^+$-Vermiculite | 14.5 | 14.3 | 12.6 | — |
| $Al^{3+}$-Montmorillonite | 14.5 | 14.2 | 12.8 | — |

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chlorosiloxane (Zappel, 1955), which may be subsequently hydrolyzed to a hydrous silica:

$$SiCl_4 + C_6H_5CHO \rightarrow C_6H_5CHCl_2 + (-SiOCl_2-)_n \quad (6)$$

$$(-SiOCl_2-)_n + H_2O \rightarrow SiO_2 \cdot xH_2O + HCl \quad (7)$$

The attractive feature of Eq. (6) for forming interlamellar siloxane bonds is that both the products and reactants are neutral species. Therefore, no charge redistribution is required when the reaction is carried out in the interlayers of a clay mineral.

The reaction of benzaldehyde and $SiCl_4$ was carried out in the interlayers of three swelling minerals: $Na^+$-hectorite, $Li^+$-vermiculite, and $Al^{3+}$-montmorillonite. The reaction methods were exactly analogous to those described above for the *in situ* reaction of H(acac) and $SiCl_4$.

Table 3 provides the (001) spacings for the three clays after different stages of reaction along with the surface area of one of the products. The successful intercalation of a siloxane monolayer is again indicated by the 12.6-Å spacings and the relatively high surface area after heating to 500°C.

### *Hydrolysis of $SiCl_4$*

An attempt was made to prepare silica intercalates by reaction of various air-dry homoionic smectites ($Na^+$, $Ca^{2+}$, $Al^{3+}$, $(CH_3)_3NH^+$, $(CH_3)_4N^+$) with $SiCl_4$ vapor or $SiCl_4$ in benzene solution. It was hoped the $SiCl_4$ would diffuse into the interlamellar space and hydrolyze by reaction with residual water forming Si–OH groups which would then be converted to silica by heating at 500°C. However, in all cases (001) spacings near 9.6 Å were observed, indicating essentially complete collapse of the interlayer regions. It is possible that rapid hydrolysis of $SiCl_4$ occurs at edges of the clay particles and that $SiCl_4$ does not diffuse into the interlayer regions.

## DISCUSSION

The results presented here demonstrate that hydrolysis of $Si(acac)_3^+$ ions is an effective method for introducing silica in the interlayer region of swelling clays. The $Si(acac)_3^+$ may be introduced by ion exchange or by *in situ* reaction of H(acac) and $SiCl_4$ in the clay interlayers. The hydrolysis of chlorosiloxanes formed by the reaction of benzaldehyde and $SiCl_4$ in the interlayers is also a viable method for forming intercalated silica. However, the interlamellar hydrolysis of $SiCl_4$ was not productive in forming intercalated silica.

The highest d(001) value observed for the intercalated silica complexes is 12.6 Å, which corresponds to incorporation of a single sheet of siloxane. In some cases the (001) reflection was skewed toward lower $2\theta$ values, suggesting that some interlayers may have been formed that contained more than one siloxane sheet.

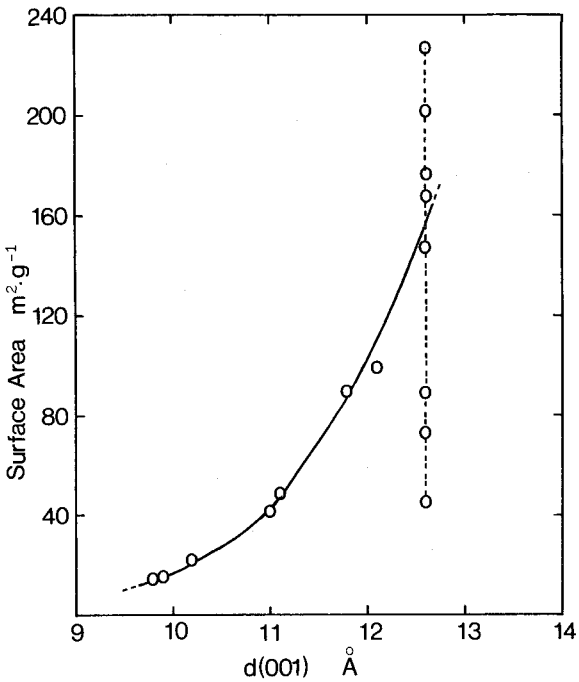



Figure 2. Relationship between surface area and (001) spacings for silica-clay intercalates prepared by hydrolysis/oxidation of $Si(acac)_3^+$ or $(-SiOCl_2-)_n$ polymers in the interlayers of swelling clays. The samples with d(001) values between 9.6 and 12.6 Å are presumed to contain varying proportions of collapsed layers (9.6 Å) and layers containing silica (12.6 Å).

By limiting the amount of silica incorporated in the interlayers, it is possible to form randomly interstratified systems with d(001) values between 9.6 and 12.6 Å. In these highly interstratified systems the (001) spacing should be reflective of the relative number of completely collapsed interlayers and those containing siloxane monolayers.

The expected relationship between available surface area and (001) spacing between 9.6 and 12.6 Å is verified by the plot shown in Figure 2. However, considerable variation in surface area is observed for the intercalates with (001) spacings equal to 12.6 Å. This variation in surface area probably arises from differences in the number of silica polymers within the interlamellar regions. Where most of the interlamellar space is filled, low surface areas would be expected. Where the interlamellar space is only partially occupied by silica, considerable internal surface would be available for adsorption.

The nitrogen desorption peaks observed in the surface area measurements were quite asymmetric which points to interlamellar adsorption. If nitrogen was adsorbed on only external surfaces, symmetrical peaks would result. The low carbon content of the samples is good evidence that residues from the decomposition of

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the organic reagents are not responsible for keeping the silicate sheets apart at the 12.6-Å position. When samples were heated to temperatures as high as 620°C, the 12.6-Å spacing was still maintained. Also, the development of a very intense fourth order reflection in the more highly ordered products (*cf.* Figure 1) is suggestive of important changes in the structure factor of the systems which could result from silica intercalation.

The very special chemical treatments required for silica intercalation suggest that this phenomenon is not a likely process in natural systems. However, the modification of swelling clays with these chemical methods may have relevance for industrial processes where the maintenance of an expanded layered silicate structure at high temperature may be of interest for selective adsorption and catalytic applications.

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**Резюме**—Кремнезем был включен в разбухающие глины с помощью гидролиза и/или окисления катионов три (ацетилацетоната) силикона(IV), $Si(acac)_3^+$, полихлоросилоксанов $(-SiOCl_2-)_n$ в межслойных областях минералов. Ионы $Si(acac)_3^+$ были помещены на межслойные поверхности ионным обменом и реакцией *in situ* глин, растворенных в ацетилацетоне, с $SiCl_4$. Полимеры $(-SiOCl_2-)_n$ образовывались в межслоях реакцией адсорбированного бензалдегида с $SiCl_4$. Оптимальные (001) промежутки, наблюдаемые после прокаливания глин в ваздухе при 500°C (12,6Å) соответствуют присутствию монослоя силоксановых цепей. Азотные BET поверхностные площади изменяются от 40 до 240 $m^2/г$, в зависимости от размера внутренней поверхности, покрытой внедренным кремнеземом. В некоторых случаях образуются высоко-порядковые продукты, которые проявляют четыре порядка отражения 001. Переслаивающиеся продукты с величинами d(001) в пределах 9,6 и 12,6Å прявляют поверхностные площади, согласующиеся с присутствием беспорядочной смеси полностью разрушенных межслоев и межслоев, содержащих силоксановые монослои. Попытки достичь интеркалации кремнезема гидролизом $SiCl_4$ в межслоях глины не дали результатов. [N. R.]

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**Resümee**—$SiO_2$ wurde in quellfähige Tone durch die Hydrolyse und/oder Oxidation von Tris(acetylacetonato)silicon(IV)-Kationen, $Si(acac)_3^+$, und Polychlorosilioxane $(-SiOCl_2-)_n$ in die Zwischenschichtbereiche der Minerale eingelagert. Die $Si(acac)_3^+$-Ionen wurden auf die Zwischenschichtoberflächen durch Ionenaustausch und durch die in situ Reaktionen von in Acetylaceton gelösten Tonen mit $SiCl_4$ aufgebracht. Die $(-SiOCl_2-)_n$-Polymere wurden in den Zwischenschichten durch die Reaktion von adsorbiertem Benzaldehyd mit $SiCl_4$ gebildet. Der optimale (001) Schichtabstand, der nach dem Erhitzen der Tone auf 500°C in Luft (12,6 Å) beobachtet wurde, stimmt mit dem Vorhandensein einer Monoschicht von Siloxanketten überein. Stickstoff BET Oberflächenbereiche reichen von 40–240 $m^2/g$, abhängig von der Größe der inneren Oberfläche, die durch das eingelagerte $SiO_2$ bedeckt ist. In einigen Fällen entstehen gut geordnete Produkte, die vier Ordnungen der $00\ell$-Reflexion zeigen. Wechsellagerungsprodukte mit d(001)-Werten zwischen 9,6 und 12,6 Å zeigen Oberflächenbereiche, die mit dem Vorhandensein einer unregelmäßigen Mischung aus volständig zusammengebrochenen Zwischenschichten und Zwischenschichten, die Siloxan-Monoschichten enthalten, übereinstimmen. Versuche, eine $SiO_2$-Einlagerung durch die Hydrolyse von $SiCl_4$ in den Tonzwischenschichten zu erreichen, waren nicht erfolgreich. [U.W.]

**Résumé**—La silice a été intercalatée dans des argiles gonflants par hydrolyse et/ou par oxidation des cations tris(acétylatonato)silicés(IV), $Si(acac)_3^+$, et polychlorosilioxanes, $(-SiOCl_2-)_n$, dans les régions interfolaires des minéraux. Les ions $Si(acac)_3^+$ ont été placés sur les surfaces interfolaires par échange d'ions, et par la réaction *in situ* des argiles dissolus à l'acétylatone avec $SiCl_4$. Les polymères $(-SiOCl_2-)_n$ ont été formées dans les intercouches par la réaction de benzaldehyde adsorbée avec $SiCl_4$. L'espacement (001) optimal observé après la cuisson des argiles à l'air à 500°C (12,6 Å) correspond à la présence d'une monocouche de chaînes siloxanes. Les régions de surface de nitrogène BET s'étagent de 40 à 240 $m^2/g$, dépendant de l'étendue de surface interne couverte par la silice intercalatée. Dans quelques cas, des produits qui exhibent 4 ordres de réflection $(00\ell)$ sont formés. Des produits interstratifiés avec des valeurs d(001) entre 9,6 et 12,6 Å exhibent des surfaces fidèles à la présence d'un mélange fait au hasard d'intercouches totalement effondrées et d'intercouches contenant des monocouches siloxanes. Des efforts faits pour obtenir l'intercalation de la silice par l'hydrolyse de $SiCl_4$ dans les intercouches d'argile ne se sont pas montrés productifs. [D.J.]

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