Organic Derivatives of Layered Polysilicates. II.[1] Reaction of Magadiite and Kenyaite with Diphenylmethylchlorosilane

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Synopsis. Silanol groups on the interlayer surface of layered polysilicic acids (H-magadiite and H-kenyaite) were silylated by reaction with diphenylmethylchlorosilane. Dodecyltrimethylammonium magadiite and kenyaite intercalation compounds were used as the intermediates for the conversion. The interlayer modification was confirmed by XRD, IR, ^{29}Si-MAS NMR and elemental analysis.

Interlayer modification of layered materials by organic groups has attracted much attention from the viewpoint of the design of advanced materials with regulated structures. Layered polysilicates such as magadiite ($Na_2Si_{14}O_{29}\cdot xH_2O$) and kenyaite ($Na_2Si_{20}O_{41}\cdot xH_2O$) have exchangeable interlayer cations and acid treatment yields the corresponding layered polysilicic acids (H-magadiite ($H_2Si_{14}O_{29}\cdot xH_2O$) and H-kenyaite ($H_2Si_{20}O_{41}\cdot xH_2O$)). Since the layered polysilicic acids as well as the original layered polysilicates have interlamellar silanol groups,[2] they are expected to be one of the host materials for interlayer modification. In order to design the interlayer space freely, it is necessary to investigate the possibility of various types of interlayer modification. However, in the previous studies,[3,4] only trimethylsilylation was reported as the organic derivatizing method for polysilicic acids.

$$(\equiv Si\text{-}OH + ClSi(CH_3)_3 \rightarrow \equiv Si\text{-}O\text{-}Si(CH_3)_3)$$

These reports also showed that a bulky silylating agent such as diphenylmethylchlorosilane ($(C_6H_5)_2CH_3SiCl$, abbreviated as DPMCS) could not be intercalated.[4] These previous studies used only DMSO (or NMF) intercalated polysilicic acids as intermediates for the derivatization. In our previous study,[1] dodecyltrimethylammonium ($C_{12}H_{25}(CH_3)_3N^+$, abbreviated as DTMA) magadiite and kenyaite were preferable for the trimethylsilylation of the layered polysilicic acids. The advantage of the tetraalkylammonium intercalated polysilicic acids as intermediates for the organic derivatization was their relative stabilities and the variable enlargement of the interlayer space by variation in the number of carbon atoms in the organoammonium ions employed. Therefore, in this study, DPMCS was allowed to react with DTMA-magadiite and -kenyaite intercalation compounds and the silylated products were analyzed.

Experimental

Materials. The starting materials, Na-magadiite and K-kenyaite ($K_2Si_{20}O_{41}\cdot xH_2O$), were synthesized by the method described by Lagaly et al.[5,6] The exchange reaction of interlayer Na and K ions for DTMA ions to form the organoammonium intercalation compounds was also followed by the procedure by Lagaly et al.[5,7] The formation of the organoammonium intercalated compounds was checked by elemental analysis, X-ray, and IR data. Commercially available DPMCS was used in this study.

Silylation Reaction. The DTMA-magadiite and -kenyaite were mixed with DPMCS and the reaction mixtures were refluxed for 72 h. After the mixtures were filtered with suction, they were washed thoroughly with acetone and air-dried.

Analyses. X-Ray powder diffraction patterns were obtained by using Rigaku Rad IB (Cu $K\alpha$ radiation, Ni filtered). IR spectra were recorded on a Shimadzu IR-435 infrared spectrometer. ^{29}Si-MAS NMR spectra were obtained with a JEOL GSX-270 spectrometer at 53.67 MHz. The external standard was tetramethylsilane. Gated high power proton decoupling technique was employed with a 45° pulse, and the pulse repetition time was 7 s. Cross polarization (CP) technique with matched rf field amplitudes of 45 kHz was also employed. CP contact times were 5 and 8 ms, depending upon the sample, and the pulse repetition time was 5 s.

Results and Discussion

Table 1 shows the basal spacings of Na-magadiite, K-kenyaite, their DTMA complexes, and their silylated products. The spacing of DTMA-magadiite (29.4 Å) was larger than that of Na-magadiite (15.6 Å) by 13.8 Å. After the reaction with DPMCS, the spacing of the derivative decreased to 24.6 Å from 29.4 Å. However, the value was still larger than that of H-magadiite (11.2 Å) by 13.4 Å. The expansion of the layer spacing was retained after the heat treatment of the silylated products at 300—400 °C, suggesting the formation of $\equiv Si\text{-}O\text{-}SiCH_3(C_6H_5)_2$. The diphenylmethylsilylation of DTMA-kenyaite also gave similar results, although the d_{001} values were different because of the different layer thickness of kenyaite.

After the diphenylmethylsilylation, the IR absorption bands due to DTMA ions disappeared and new bands due to diphenylmethylsilyl (abbreviated as DPMS) groups appeared at 1430, 1270, 740, and 700 cm^{-1}. After the heat treatment up to 400 °C with a DTA instrument, the absorption peaks due to DPMS groups remained. Thus, these IR absorption peaks were not ascribed to by-products (ex. $(C_6H_5)_2CH_3SiOSiCH_3(C_6H_5)_2$) or the unreacted species, because

Table 1. Basal Spacings of Layered Polysilicates and Their Derivatives

	Na-magadiite(Å)	K-kenyaite(Å)
Original form	15.6	20.0
Dodecyltrimethylammonium exchanged form	29.4	35.6
Diphenylmethylsilylated form	24.6	31.4

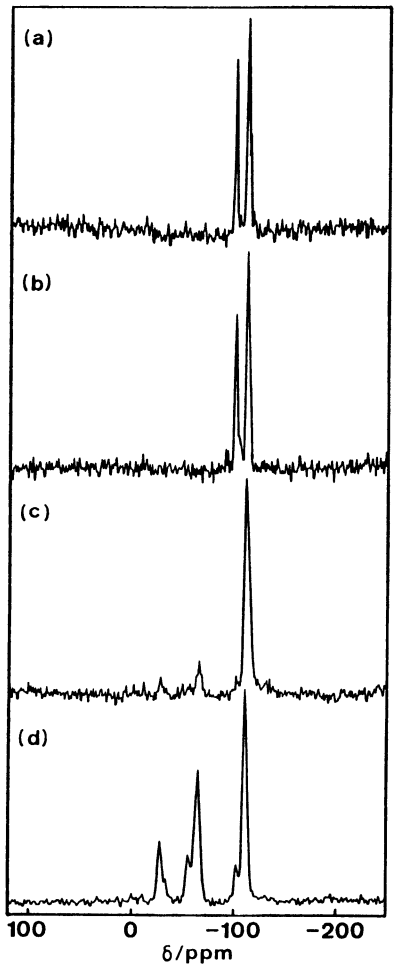

Fig. 1. ^{29}Si-MAS NMR spectra of (a) Na-magadiite, (b) dodecyltrimethylammonium magadiite, (c) and (d) diphenylmethylsilylated magadiite ((d): CP technique was used).

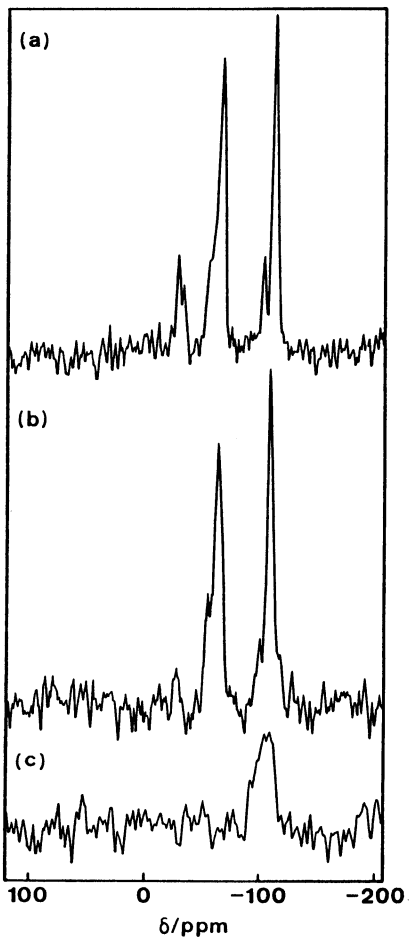

Fig. 2. ^{29}Si-CPMAS NMR spectra of heat treated diphenylmethylsilylated magadiite. (a) 300°C, (b) 500°C, and (c) 700°C.

their boiling points were lower than 350°C. The IR results of the silylated kenyaite also showed similar evidence of the linkage of the DPMS groups and the interlayer silanol groups.

Figure 1 shows the ^{29}Si-MAS NMR spectra of Na-magadiite, DTMA-magadiite, and the diphenylmethylsilylated magadiite. The NMR spectrum of Na-magadiite indicated the presence of two different SiO_4 units normally designated as Q^3 and Q^4 at −99.0 and −110.7 ppm, respectively. (Q^n means the SiO_4 having n siloxane bonds.) The spectrum was similar to the previous data reported by Pinnavaia et al.[8] The spectrum of the DTMA-magadiite did not show any significant changes in the chemical shifts and the intensities. However, in the spectrum of the diphenylmethylsilylated product, a remarkable change was observed. At first, the width of the peak due to Q^4 was broadened, indicating the presence of the newly formed Q^4 by silylation, (O_3SiOH (Q^3) →O_3SiO-SiR_3 (Q^4)). Secondly, the new peaks at −28 and −65 ppm appeared. With a further measurement using the cross polarization (CP) technique, these peaks were split, as shown in Fig. 1(d), although the reason for the splittings can not be explained definitely at present because the precise structure has not yet been clarified. The intensities of these peaks decreased with the combustion of the organic groups and finally unified into a single but relatively broad peak at −107 ppm (Fig. 2). Therefore, the peaks at −28 ppm were ascribed to the silicon atoms (Q^1) in the bonded DPMS groups. The latter signals at −65 ppm were thought to be assigned tentatively as the unsilylated Q^3 units strongly affected by the interlayer aromatic groups which usually caused an anisotropic magnetic effect. Possible bond distortion in the interlayer space may also influence the chemical shift.

Figure 3 shows the ^{29}Si-CP MAS NMR spectra of K-kenyaite, DTMA-kenyaite, and the silylated product. In the spectrum of the K-kenyaite, the Q^3 peak appeared at −98.5 ppm and the peak due to Q^4 at −109.7 ppm. In the spectrum of the DTMA-kenyaite, the peak due to Q^3 appeared at a similar position to that of K-kenyaite. However, the peak due to Q^4 was split into two peaks at −110.5 and −112.5 ppm. This difference between magadiite and kenyaite is probably ascribable to the difference in the layer structures. The spectrum of the silylated kenyaite indicated the presence of the Q^1 peak due to DPMS groups at −32.9 ppm. The signal at −64.9 ppm was tentatively assigned to Q^3. The peak due to Q^4 appeared at −110.2

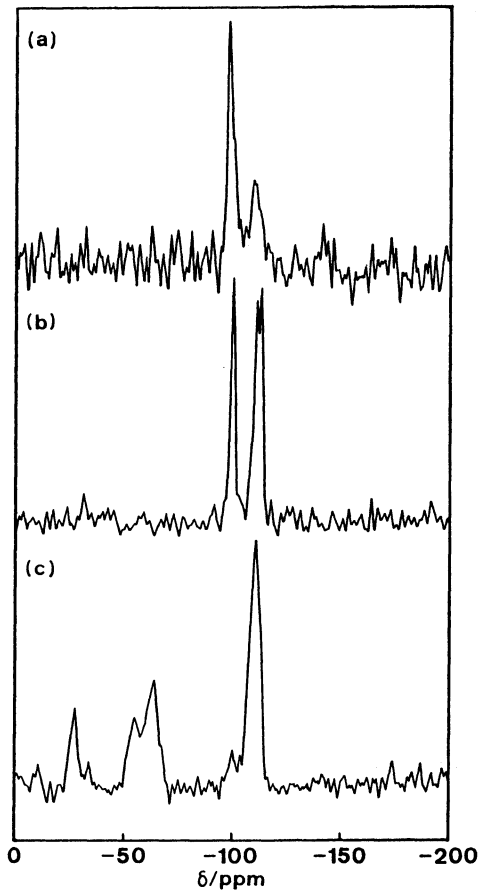

Fig. 3. ^{29}Si-CPMAS NMR spectra of (a) K-kenyaite, (b) dodecyltrimethylammonium kenyaite, and (c) diphenylmethylsilylated kenyaite.

ppm with a little broad peak width. These variations in the spectra corresponded to the partial diphenylmethylsilylation of interlamellar silanol groups.

The elemental analysis of the silylated magadiite and kenyaite also supported the silylation, though very small amounts of nitrogen due to remaining DTMA were detected. The H, C, and N contents (H, 2.01; C, 13.81; N, 0.15%) of the silylated magadiite indicated the ratio of DPMS group/$Si_{14}O_{29}$ was 0.79. The data of the silylated kenyaite (H, 1.39; C, 11.34; N, 0.10%) showed the ratio of DPMS group/$Si_{20}O_{41}$ was 0.92. As compared with the data on the trimethylsilylation of magadiite and kenyaite,[1] the values were lower because of the bulky nature of the DPMS groups.

The process of the diphenylmethylsilylation of DTMA-magadiite and -kenyaite can be expressed as a consecutive reaction. Since the silanol groups are present in the interlayer space of DTMA-magadiite and - kenyaite,[5,7] the silylating reagent can react with these silanol groups to form siloxane bonds;

$$\equiv Si\text{-}OH + (C_6H_5)_2CH_3SiCl \rightarrow \equiv Si\text{-}O\text{-}SiCH_3(C_6H_5)_2 + HCl.$$

The HCl produced can attack the DTMA silicate sites to form silanol groups. Then, the newly formed silanol groups can be silylated further.

In conclusion, the interlayer surface of magadiite and kenyaite was silylated with DPMCS using DTMA-magadiite and -kenyaite as intermediates, providing the possibility of various modifications of interlayer silanol groups.

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