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Synthesis of New Trioctahedral Mg-Smectite

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New trioctahedral Mg-smectites were synthesized hydrothermally from homogeneous Mg-Si precipitates having a wide range of compositions, i.e., from Mg=3.2 to 6, vs. Si=8 in the atomic ratios. Dispersed solutions of the synthetic smectites formed transparent gels possessing good rheological properties.

Because of their cation-exchange properties and their ability to swell in water and to form organic and inorganic interlayer complexes, smectites have been of interest as the possible materials for industrial applications.[1] In Japan, a few of purified smectite products[2] made from bentonites have been utilized in cosmetics, medicines, gel agents, etc. The demand for those products, however, has been limited because of their expensive production cost and their inferior properties inherited from the raw bentonites, e.g., low whiteness, low transparency of the dispersions, high content of impurities, etc. Although many synthetic studies of smectites have been carried for mineralogical studies, few experiments have been made with the interest of preparing synthetic smectites as industrial raw materials.[3] The present paper is concerned with the synthesis of new trioctahedral smectites having attractive good properties for industrial applications.

The synthesis procedure is as follows: (1) a Mg-Si solution is prepared having desired Mg/Si atomic ratio by dissolving magnesium salts, such as chloride, sulfate, nitrate, etc., in an acidic solution containing sodium silicate; (2) Mg-Si precipitates are formed by mixing the above Mg-Si solutions with alkali solutions; (3) the Mg-Si precipitate is washed and filtered to remove secondary products; (4) a slurry is prepared from the Mg-Si precipitate, NaOH, and HF, etc.;

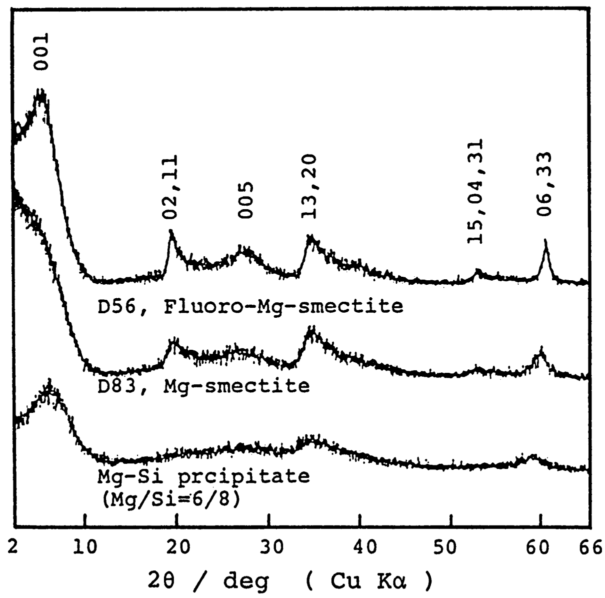

Fig. 1. X-Ray powder diffraction patterns of typical synthetic Mg-smectites and the initial Mg-Si precipitate.

Table 1. Magnesium composition and layer charge of expanding layer minerals containing only silicon and magnesium in 2:1 layers

Mineral	Number of specimens	Atomic ratio of Mg vs. Si=8	Cation exchange capacity (mequiv./100 g)	Layer charge vs. Si=8
Mg-smectite[a)]	4	3.2 - 5.84	78 - 100	0.57-0.90
Stivensite[4)]	3	5.31 - 5.76	36.0 - 45.4	0.30-0.42
NTSM[b)]	2	5.16 - 5.28	———	1.44-1.68

a) Data from Fig. 3.

b) Na-fluor-tetrasilicic mica.[5)]

(5) smectites are formed hydrothermally in an autoclave at 150-250 °C under the water vapour pressure for 1-3 h and (6) products are dried and powdered.

X-Ray powder diffraction (XRD) patterns of typical products obtained from the systems with or without fluorine and the Mg-Si precipitate are shown in Fig. 1. The XRD pattern of the Mg-Si precipitate produced at room temperature shows that this precipitate has a poorly crystalline smectite-like structure. Thus, trioctahedral Mg-smectites of good quality appear to have formed in a short time under the relatively mild hydrothermal conditions of this study. Chemical analyses of the products were nearly the same as the compositions expected.

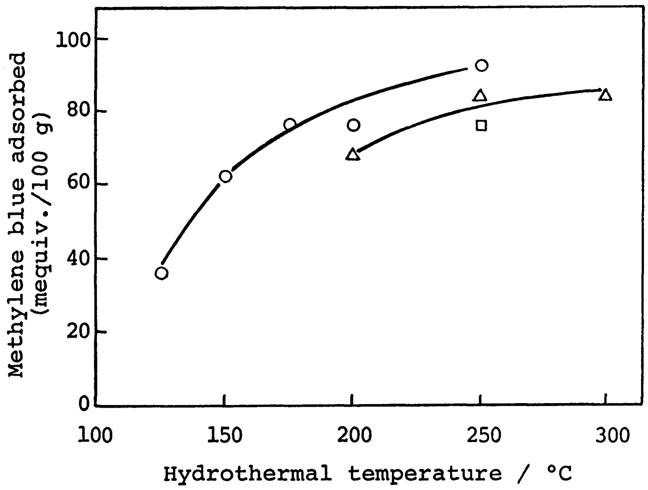

Fig. 2. Effect of hydrothermal temperature on the methylene blue adsorption of synthetic Mg-smectites. Treating time: ○ 24 h; △ 3 h; □ 2 h.

Expandable phyllosilicates have a structure composed of alternating 2:1 layer, which consists of two sheets of linked SiO_4 tetrahedra sandwiching octahedral cations between them, and an interlayer. The 2:1 layers, which have a net negative charge (layer charge), are loosely tied together by interlayer cations. Water also is present between the layers. Stevensite $[Na_{0.33}Mg_{5.84}Si_8O_{20}(OH)_4]$[4)] and Na-fluor-tetrasilicic mica (NTSM) $[Na_2Mg_5Si_8O_{20}F_4]$[5)] have been reported as expandable phyllosilicates contain only silicon and magnesium in 2:1 layers. The negative charge of the 2:1 layer of the Mg-smectites reported in this paper is considered to be due to gaps in the octahedral positions, i.e., vacancies in the octahedral sites, as in stevensite and NTSM.

The Mg composition and layer charge of the Mg-smectite are quite different from those for stevensite and NTSM (Table 1). Mg compositions of stevensite and NTSM are limited to a narrow range, but that of the Mg-smectites ranges from 3.20

Table 2. Effect of fluorine addition on the methylene blue adsorption, transmittance, and rheological properties of synthetic Mg-smectites[a)]

Lot.No.	Amount of F[b)]	MB adsorbed (mequiv./100 g)	Transmittance[c)] %	Rheological properties[d)] AV(mPa·s) 600 rpm	AV(mPa·s) 6 rpm	PV (mPa·s)	YV (Pa)	GS(Pa) 10"	GS(Pa) 10'
D83	0	84	8.4	2	25	1.5	48	24	48
D83[e)]	0	84	18.8	18	250	10	720	140	340
D82	1	92	64.0	13	100	8	430	96	140
D55	2	90	67.4	17	500	8	860	430	1920
D56	3	96	79.5	23	1450	6	1580	1960	4210
D169	4	92	18.1	20	1200	6	1290	1770	3400
NTSM	-	0	0.6	6	—	5	48	24	48
NTSM[e)]	-	0	0.3	7	25	6	96	48	72
Kunipia F	-	112	0.8	8	50	7	96	24	24

a) Preparation composition: Si:Mg:Na= 8:6:0.7; hydrothermal condition: 200 °C, 3 h.

b) Atomic ratio versus Si=8.

c) Measured with 500nm light transmitted through the 1% dispersive solution against water=100%.

d) Measured 2.5% gel solution at 25 °C with Van VG meter. AV: Apparent viscosity; PV: Plastic viscosity; YV: Yield value; GS: Gel strength.

e) Dispersive solution heated at 80 °C for 16 h.

and 5.84 versus Si=8. The layer charges of Mg-smectites correspond closely to the smectite group, which has layer charge between 0.4 and 1.2 per formula unit.[6)] Stevensite has about half the layer charge of normal smectite (ideal: 0.67), and the layer charge of NTSM is larger than that of the smectite group.

The properties of the Mg-smectite were affected by the preparation compositions of starting materials and the hydrothermal conditions. The effect of hydrothermal temperature and time on the methylene blue (MB) adsorption of the synthetic products is shown in Fig. 2. The slurry composition used was Si:Mg:Na= 8:5.33:1.33. Above 200 °C, the MB adsorption was >68 mequiv./100 g even at a treatment time of <3 h. Table 2 shows the effect of fluorine addition on the properties of Mg-smectites along with those of a purified bentonite product, "Kunipia F",[2)] and NTSM. Fluorine-free Mg-smectite (Lot. No. D83) showed a weak gel formation ability, but, if the gel solution had been heated to 80 °C, it became more viscous than the dispersions of NTSM or Kunipia F. The addition of fluorine to Mg-smectites improved markedly the properties of their dispersions as shown in Table 2. At fluorine addition values of 3 versus Si=8, transparency and rheology improved significantly. The effect of hydrothermal temperature on the properties for the fluorine Mg-smectite is shown in Table 3. The optimum synthesis temperature appeared to be about 200 °C.

Figure 3 shows the compositional range for fluorine Mg-smectite formation. Fluorine Mg-smectites could be synthesized in the composition range Mg=3.2-6

Table 3. Effect of hydrothermal temperature on the amount of methylene blue adsorbed, transmittance, and rheological properties of synthetic fluorine Mg-smectites[a)]

Lot.No.	Temp °C	MB adsorbed (mequiv./100 g)	Transmittance %	Rheological properties[b)] AV(mPa·s) 600 rpm	AV(mPa·s) 6 rpm	PV (mPa·s)	YV (Pa)	GS(Pa) 10"	GS(Pa) 10'
D107	150	68	9.8	4	25	3	48	72	380
D108	180	88	67.5	19	1150	6	1200	1720	3740
D56	200	96	79.5	23	1450	6	1580	1960	4210
D109	250	98	56.0	13	450	6	670	380	1770

a) Preparation composition: Si:Mg:Na:F= 8:6:0.7:3; hydrothermal time: 3 h.

b) AV: Apparent viscosity; PV: Plastic viscosity; YV: Yield value; GS: Gel strength.

versus Si=8. If Mg was in excess of the octahedral composition, the Mg ion may have occupied the interlayer space as an exchangeable cation and/or as a magnesium hydroxide layer, similar to that found in chlorite minerals. Thus, this new material appears to be structurally intermediate between stevensite and NTSM, but it has better gel properties than either of those materials.

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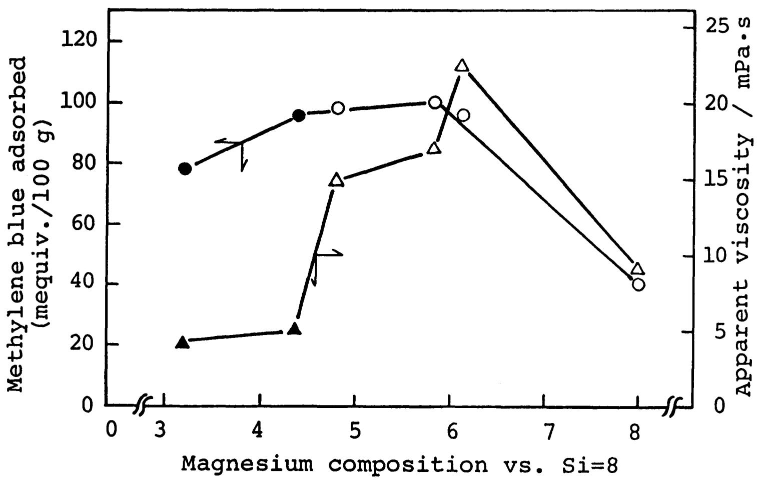

Fig. 3. Effect of magnesium composition on the properties of synthetic fluorine Mg-smectites. Compositions and synthetic condition: Black symboles Si:Na:F= 8:0.7:2, 250 °C, 2 h. White symboles Si:Na:F= 8:0.7:3, 200 °C, 3 h.

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