

## EFFECTS OF SOLUTION CHEMISTRY ON THE HYDROTHERMAL SYNTHESIS OF KAOLINITE

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**Abstract**—The hydrothermal synthesis of kaolinite was examined in the  $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$  system to study inhibitory effects of additional ions on the formation of kaolinite. Syntheses were carried out with amorphous starting materials and salt solutions of various concentrations in Teflon pressure vessels at 220°C for 5 days. The reaction products were characterized by XRD, IR, DTA-TG, NMR and TEM. In all of the runs using solutions with cation concentrations less than 0.001 M, no significant effect on the formation of kaolinite was observed. The inhibitory effect of the univalent cations  $\text{Li}^+$ ,  $\text{Na}^+$  or  $\text{K}^+$  was less than that of divalent cations such as  $\text{Mg}^{2+}$  or  $\text{Ca}^{2+}$ . The addition of trivalent  $\text{Fe}^{3+}$  or excess  $\text{Al}^{3+}$  ions interfered with the formation of kaolinite significantly. Sulfate and acetate solutions interfered with the formation of kaolinite more than chlorides and nitrates. No crystalline product was obtained using a 1.0 M basic solution of carbonate or hydroxide. The addition of the lithium ion to the system affected the crystallization of kaolinite only slightly. The use of 0.1 M  $\text{LiCl}$  and  $\text{LiNO}_3$  solutions for the syntheses improved crystallization of kaolinite along the [001] direction.

**Key Words**—Effect of ions, Hydrothermal synthesis, Kaolinite, Solution chemistry.

### INTRODUCTION

Since the initial phase equilibrium studies of kaolinite,  $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ , by Roy and Osborn (1954), a number of studies have been reported on the formation mechanisms and kinetics of this mineral. Eberl and Hower (1975) synthesized kaolinite hydrothermally using amorphous gels with various Si/Al ratios. They reported that contamination by alkali ions inhibits the crystallization of kaolinite. De Vynck (1975, 1976) reported the hydrothermal transformation to kaolinite of aluminosilicate sols containing alkaline ions, such as  $\text{Li}^+$  or  $\text{K}^+$ . He determined the ratio ranges of Li or K:Al:Si for kaolinite formation.

In a previous study, we determined that the pH range of solutions suitable for the hydrothermal synthesis of kaolinite from amorphous alumina and silica to be within a range of 4.0 to 10.0 (Miyawaki *et al.*, 1989). However, kaolinite could not be produced using hydrothermal treatments in 1.0 M NaCl solution at neutral pH. This suggests that the presence of other ions in the reaction system interfere with the formation of kaolinite. Therefore, we systematically examined the effects of several cations and anions on the hydrothermal synthesis of kaolinite.

### EXPERIMENTAL

#### Materials

The amorphous gel used as the starting material was prepared from commercially available silica sol and alumina sol (Nissan Chemical Industries, Ltd., Snowtex-N and Aluminasol-200). The two sols were mechanically mixed at the Al/Si atomic ratio of 1:1. The mixture was heated at 600°C for 8 h to dry and decompose the acetic acid included as a sol deflocculant. The mixture was then crushed and passed through a 70 mesh sieve.

Solutions for the subsequent hydrothermal treatments were aqueous solutions of chlorides, nitrates, sulfates, acetates, carbonates, and hydroxides of lithium, sodium, potassium, magnesium, calcium, and iron. Solutions of aluminum salts were also examined because they cause the Al/Si atomic ratio to be greater than 1; the ratio of the ideal composition of kaolinite. The cation concentrations of the solutions were varied from 1.0 M to 0.0001 M. Distilled water was also used as an experimental solvent for reference purposes.

The syntheses were carried out by placing 4.0 g of the starting material and 16 ml of each solution into a Teflon pressure vessel with a capacity of 25 ml (San-AI Kagaku Ltd., HU-25). The reaction vessels were kept at 220°C for 5 days in an electric furnace. These experimental conditions are the same as those in the study on the growth of kaolinite by Tomura *et al.* (1985), and the duration period, 5 days, is the minimum period

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for the completion of kaolinite formation. The pH of the solution was measured with a pH meter (Horiba, M8 AD) before and after each hydrothermal experiment. The solid reaction products were separated from the solutions by filtration and were dried at 100°C for about 12 hr.

#### Analytical methods

The solid products were analyzed by X-ray powder diffraction (XRD), infrared absorption spectroscopy (IR), and differential thermal-thermogravimetric analysis (DTA-TG). The XRD patterns of random-mounted samples were obtained by step scanning (15 s per 0.02° step) with graphite monochromatized CuK $\alpha$  radiation (Rigaku, RAD-IIB). The DTA-TG curves were recorded by heating 40 mg of each sample from room temperature to 1150°C at a rate of 10 degrees per minute, using a Rigaku TG8110-TAS100 thermal analyzer. The kaolinite yield was not estimated from intensity of the XRD data, because the intensities were influenced by preferred orientation. It was estimated, instead, from the weight loss between 400°C and 1150°C, which corresponds to dehydration of the structural OH groups. Estimation of the kaolinite yield was carried out when both an endothermic peak at 540°C in the DTA curves and the X-ray diffraction pattern of kaolinite were clearly observed. Although the estimated value is affected by the coexistence of other phases, no correction was made for the overlapping weight loss of other phases. Infrared spectra were recorded on a Jasco IR-700 spectrophotometer using the KBr method.  $^{29}\text{Si}$  and  $^{27}\text{Al}$  nuclear magnetic resonance (NMR) spectra were obtained with a Bruker-MSL-200 spectrometer operated at 39.763 MHz for  $^{29}\text{Si}$  and 52.140 MHz for  $^{27}\text{Al}$ . Powdered samples were packed into rotors and spun in a magic-angle spinning probe at about 2.5 and 3.5 kHz for Si and Al, respectively. About 500 scans for  $^{29}\text{Si}$  and 120 scans for  $^{27}\text{Al}$  were accumulated. The magnetic field strength was 4.7 T. Chemical shifts were measured relative to TMS (tetramethylsilane) and  $\alpha\text{-Al}_2\text{O}_3$  for  $^{29}\text{Si}$  and  $^{27}\text{Al}$ , respectively. Some of the run products were observed by transmission electron microscopy (TEM) (JEOL, JEM-4000FX). The dry powder was sprinkled onto a carbon-coated Formvar-covered 150 mesh copper microgrid. The microscope was operated at 400 kV. Qualitative analysis of the samples was also carried out by energy-dispersive X-ray (EDX) analysis (Tracor-Northern TN-5500). The radius of the electron beam during analysis was ~50–500 nm.

## RESULTS

The products of the hydrothermal experiments as well as initial (pH<sub>S</sub>) and final (pH<sub>F</sub>) values for pH are listed for each run in Table 1. Figure 1 shows the kaolinite yield estimated from the TG curve, the intensity of the 020 reflection of kaolinite on the XRD pattern,

the Hinckley index, and the peak width at half height of the kaolinite 001 reflection. The kaolinite yield estimated from the TG curve must be higher than the true value, because no correction was made for other phases, such as amorphous or low-crystallinity materials, and alunite, as mentioned above. The 020 reflection of kaolinite in the XRD pattern is overlapped by smectite reflections. Therefore, three criteria were used for evaluating kaolinite formation without significant interference: 1) a yield greater than 80%, 2) an intensity for the 001 reflection higher than 300 cps, and 3) an intensity for the 020 reflection higher than 200 cps. Experimental runs that satisfy all of these criteria are indicated by **K**, with the values of pH in bold face in Table 1.

In all of the runs using solutions with 0.001 M and 0.0001 M cation concentrations, no significant effect on the formation of kaolinite was observed. The kaolinite yield decreased with an increase in the concentration of cations between 0.01 and 1.0 M. The final pH (pH<sub>F</sub>) of the runs in which kaolinite was synthesized without any considerable interferences (**K**, Table 1) were within a pH range from 2.0 to 4.0, except for runs using LiCl and NiNO<sub>3</sub> solutions. Smaller amounts of kaolinite were obtained in several runs out of the range.

The inhibitory effect on the formation of kaolinite by the addition of univalent Li<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup> cations was less than that of divalent cations such as Mg<sup>2+</sup> and Ca<sup>2+</sup>. Addition of trivalent Fe<sup>3+</sup> or excess Al<sup>3+</sup> interfered with the formation of kaolinite significantly. Sulfate and acetate solutions interfered with the formation of kaolinite more than chloride and nitrate solutions.

Increased Al<sup>3+</sup> concentration caused deviation from the ideal atomic ratio of Al/Si for kaolinite and interfered with the formation of kaolinite. The use of 1.0 M AlCl<sub>3</sub> solution caused formation of aluminum chloride hydroxide, whose X-ray diffraction pattern is close to those of Al<sub>11</sub>(OH)<sub>30</sub>Cl<sub>3</sub> and Al<sub>24</sub>O<sub>11</sub>(OH)<sub>44</sub>Cl<sub>6</sub> reported by Walter-Lévy and Breuil (1961) ("C," Table 1).

The kaolinite synthesized in 0.1 M LiCl or LiNO<sub>3</sub> solution gave a sharp 001 reflection, whereas nonbasal reflections were broad (Figure 2). The values for the Hinckley indices were lower than the other kaolinite samples (Figure 1a).

A phase with low crystallinity ("B," Table 1) that gives a reflection at 49.3°2 $\theta$  (CaCl<sub>2</sub> 1.0 M, Figure 3) was obtained by hydrothermal treatment in chloride, nitrate, sulfate, sodium acetate or potassium acetate solutions at higher concentrations (1.0 M, or in some cases 0.1 M). The pH values measured after the hydrothermal treatment of these runs, pH<sub>F</sub>, were generally lower than those of runs that produced kaolinite (Table 1). The major product synthesized with 1.0 M Fe<sup>3+</sup> solutions was hematite ("H," and "h," Table 1). Synthesis with 0.5 M K<sub>2</sub>SO<sub>4</sub> solution yielded alunite, and those with 0.5 M Li<sub>2</sub>SO<sub>4</sub> and Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> solutions

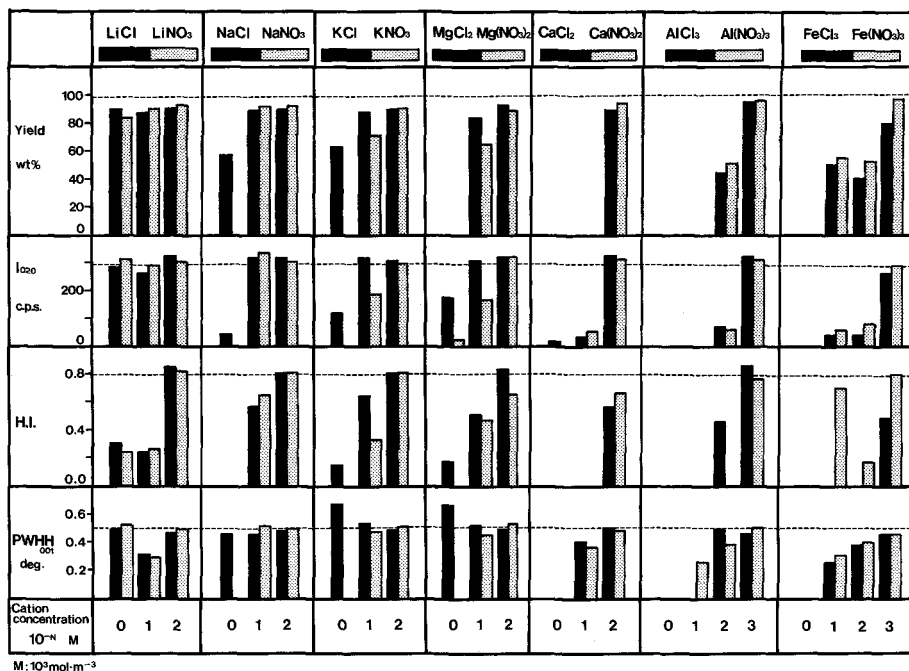


Figure 1a-c. Kaolinite yields estimated from TG curve, intensity of 020 reflection, Hinckley index, and peak width at half height of the 001 reflection. Broken lines indicate the values for kaolinite synthesized without additional ions.

yielded the  $\text{H}_3\text{O}^+$ -analog of alunite ("A," "a," Table 1). On the other hand, small quantities of smectite ("M," "m," Table 1) were obtained by syntheses with 1.0 M  $\text{Mg}(\text{SO}_4)$ , 0.5 M  $\text{Na}_2(\text{SO}_4)$  and 1.0 M  $\text{Mg}(\text{CH}_3\text{COO})_2$  solutions (see  $\text{Na}_2\text{SO}_4$  1.0 M, Figure 3). The basal spacing of these samples sprayed with ethylene glycol expanded to 17 Å. Except for  $\text{LiAlSiO}_4 \cdot \text{H}_2\text{O}$  and  $\text{Na}_{5.7}\text{Al}_{5.7}\text{Si}_{10.3}\text{O}_{32} \cdot 12\text{H}_2\text{O}$  ("D" and "E," respectively, Table 1), no crystalline products were obtained using basic solutions of carbonates and hydroxides at concentrations higher than 0.1 M (See KOH 1.0 M, Figure 3).

Figure 4 shows infrared spectra of the starting material, and products in 1.0 M  $\text{CaCl}_2$ , 1.0 M KOH, distilled water and 0.1 M LiCl (examples for "B," "X" and K, respectively, Table 1). The IR spectrum of synthetic kaolinite has absorption bands for O-H ( $3600\text{--}3700\text{ cm}^{-1}$ ), Si-O ( $1000\text{--}1100$ ,  $400\text{--}500\text{ cm}^{-1}$ ), Al-O ( $900\text{--}950\text{ cm}^{-1}$ ) and Al-O-Si ( $540\text{ cm}^{-1}$ ), similar to natural kaolinite (Van der Marel and Beutelspacher, 1976). No absorption was observed around  $540\text{ cm}^{-1}$  corresponding to the Al-O-Si absorption in the infrared spectrum of the starting material. The spectrum did show a broad absorption band for the OH group around  $3500\text{ cm}^{-1}$ , absorption bands for Si-O around 1100 and  $480\text{ cm}^{-1}$ , and small absorptions at 800 and  $900\text{ cm}^{-1}$ . The spectrum of the amorphous product in 1.0 M KOH, "X," showed some differences from that of the amorphous starting material. A broad Si-O absorption band was observed at lower wavenumber in

comparison to that of the starting material. Weak absorptions around 700, 600 and  $450\text{ cm}^{-1}$  were observed. The absorption around  $600\text{ cm}^{-1}$  is in the region of the Al-O-Si bond. The spectrum of phase "B" ( $\text{CaCl}_2$  1.0 M in Figure 4) showed a sharp absorption at  $1070\text{ cm}^{-1}$  overlapping a broad absorption, and another at  $750\text{ cm}^{-1}$ .

DTA-TG curves of synthetic kaolinite, the starting material, and the products in 1.0 M KOH and 1.0 M  $\text{CaCl}_2$  are given in Figure 5. The DTA curve of kaolinite synthesized in distilled water showed an endothermic peak at  $540^\circ\text{C}$  accompanied by weight loss, and an exothermic peak at  $990^\circ\text{C}$  corresponding to a spinel transition. The DTA curve of the starting material does not have a substantial exothermic peak for the spinel transition. The starting material lost 2.3% of its weight between 400 and  $1150^\circ\text{C}$ , corresponding to 16.5% of the kaolinite yield. The amorphous product in 1.0 M KOH, "X," showed a small endothermic peak at  $260^\circ\text{C}$ , and continuous weight loss was observed in the TG curve. The "B" phase with low crystallinity ( $\text{CaCl}_2$  1.0 M, Figure 5) showed two endothermic peaks at 110 and  $580^\circ\text{C}$  on the DTA curve, and two steps of weight losses in the TG curve. The product containing alunite or the  $\text{H}_3\text{O}^+$ -analog of alunite, "A," also showed considerable weight loss between 400 and  $1150^\circ\text{C}$ . Absolute values for the weight loss cannot be given since the pure "A" phase could not be obtained.

The  $^{29}\text{Si}$ -CP/MAS NMR spectra for synthetic kaolinite, the starting material, the product in 1.0 M KOH,

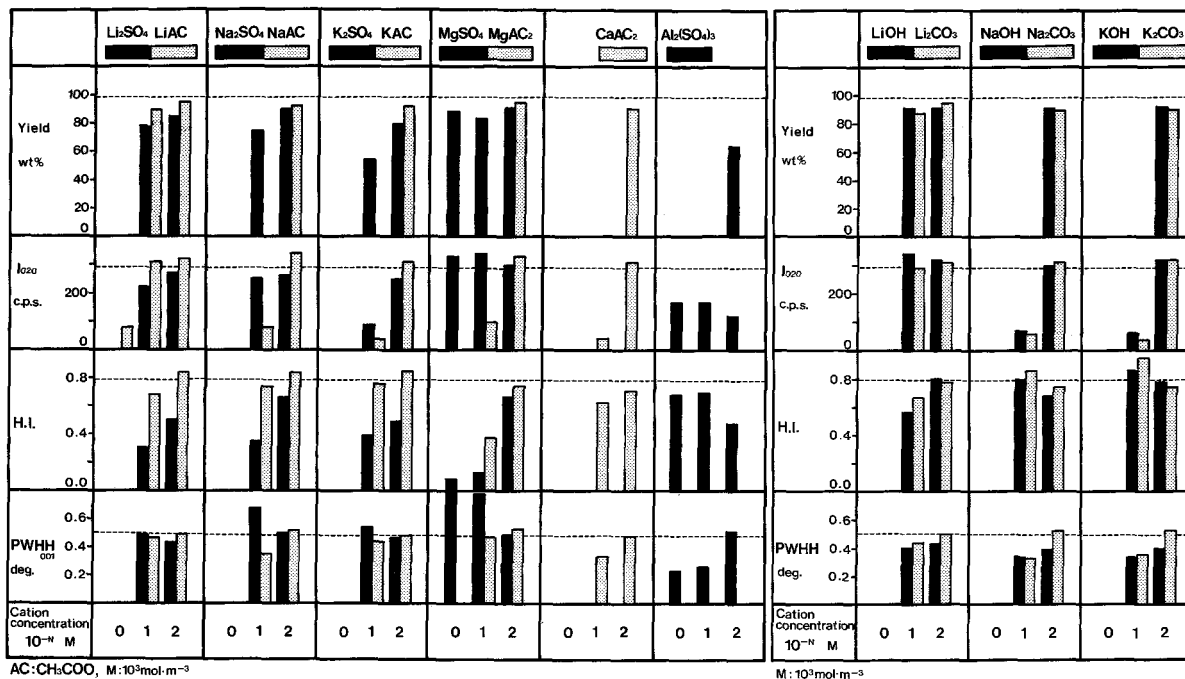


Figure 1a-c. Continued.

and that of 1.0 CaCl<sub>2</sub> are given in Figure 6. The spectrum for kaolinite synthesized with distilled water has a sharp Q<sup>3</sup> peak at -92 ppm. This indicates that oxygen atoms at three of the four corners of SiO<sub>4</sub> tetrahedra are shared with neighboring SiO<sub>4</sub> tetrahedra to form a two-dimensional phyllosilicate structure. The spectrum of the starting material has a peak at -115 ppm, corresponding to the Q<sup>4</sup> peak. The Q<sup>4</sup> peak suggests that the starting material has bridgings at all the oxygen

atom vertices of the SiO<sub>4</sub> tetrahedra with neighboring tetrahedra. On the other hand, the amorphous product in 1.0 M KOH, "X," showed a broad peak around -100 ppm. The spectrum of the product in 1.0 M CaCl<sub>2</sub>, "B," showed at least two peaks around -100 and -115 ppm.

<sup>27</sup>Al-MAS NMR spectra for the synthetic kaolinite (Figure 7) showed a broad signal around 0 ppm corresponding to six coordinated Al atoms, and two side

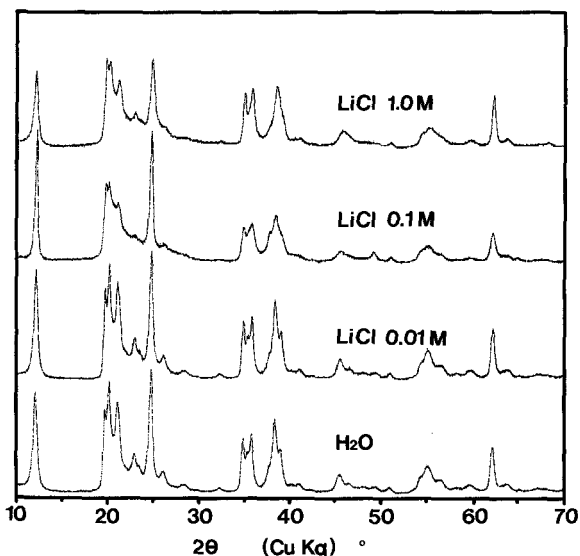


Figure 2. X-ray powder diffraction patterns of kaolinite synthesized with 1.0, 0.1, 0.01 M LiCl solutions, and without additional ions.

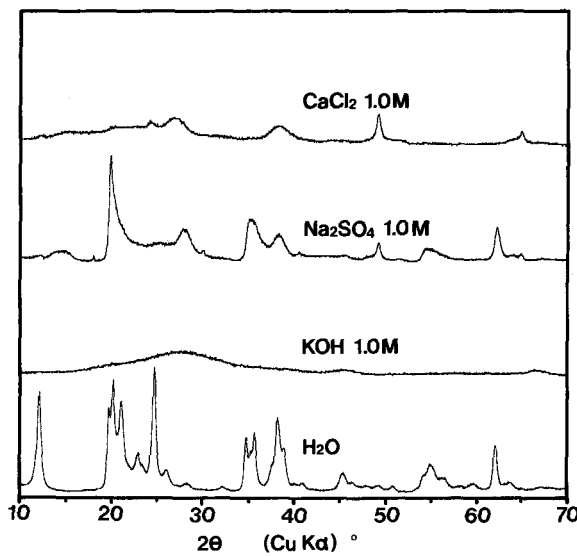


Figure 3. Selected X-ray powder diffraction patterns of the products.

Table 1. Phases for the products and pH values of the solvents, before and after syntheses.

Anion	Li <sup>+</sup>		Na <sup>+</sup>		K <sup>+</sup>		Mg <sup>2+</sup>		Ca <sup>2+</sup>		Al <sup>3+</sup>		Fe <sup>3+</sup>	
	CC	RP	pH <sub>0</sub> /pH <sub>f</sub>	RP	pH <sub>0</sub> /pH <sub>f</sub>	RP	pH <sub>0</sub> /pH <sub>f</sub>	RP	pH <sub>0</sub> /pH <sub>f</sub>	RP	pH <sub>0</sub> /pH <sub>f</sub>	RP	pH <sub>0</sub> /pH <sub>f</sub>	RP
Cl <sup>-</sup>	1	K	4.8/1.0	B	5.1/1.9	k, B	4.8/1.7	k, B	6.7/2.2	B	8.6/2.7	B, C	1.8/2.5	H, B
	0.1	K	5.5/1.4	K	4.7/2.1	K	5.1/2.0	K, B	7.0/2.8	k, B	6.0/2.9	B	3.0/2.4	B, h
	0.01	K	5.9/2.2	K	4.7/2.4	K	5.4/2.3	K	7.0/2.8	K	5.7/2.8	k, B	3.6/2.2	B
	0.001	K	6.1/2.5	K	5.0/-	K	5.8/2.5	K	7.1/-	K	5.7/3.2	K	4.0/3.1	K
NO <sub>3</sub> <sup>-</sup>	1	K	6.8/1.1	B	6.1/2.2	B	6.1/2.0	B	5.1/1.8	B	5.1/1.9	B	1.7/0.5	H, B
	0.1	K	6.7/1.6	K	6.3/2.8	k, B	6.1/2.7	k, B	5.8/2.4	B	5.7/3.0	B	3.2/-	k, B
	0.01	K	7.0/2.7	K	6.4/3.3	K	6.3/3.0	K	6.1/2.6	K	6.0/2.7	k, B	4.0/2.3	k, B
	0.001	K	7.1/3.1	K	6.5/3.2	K	6.3/3.6	K	6.1/3.0	K	6.6/3.1	K	4.6/3.1	K
SO <sub>4</sub> <sup>2-</sup>	1	k, a	5.9/1.5	B, M	6.2/1.7	A, B	6.4/2.2	M, k	5.6/2.2	M, k	5.6/2.2	A, k	2.7/-	A, k
	0.1	k, B	6.4/2.0	k, B	6.5/2.2	B, a	6.5/2.6	m, k, B	6.0/2.1	m, k, B	6.0/2.1	A, k, B	3.3/1.7	A, k, B
	0.01	K	6.8/2.5	K	6.9/2.8	K, B	6.7/2.8	K	6.1/2.6	K	6.1/2.6	k, B	3.7/2.3	k, B
	0.001	K	7.0/3.0	K	7.1/3.0	K	6.7/3.1	K	5.9/3.0	K	6.1/3.0	K	4.3/3.1	K
CH <sub>3</sub> COO <sup>-</sup>	1	k	8.4/4.7	B	8.3/4.8	B	7.9/4.8	M	8.4/3.8	X	7.6/4.7			
	0.1	K	7.8/2.6	k	7.8/4.0	k	7.5/3.6	k	7.9/3.6	k	7.6/3.2			
	0.01	K	6.9/2.8	K	6.9/3.2	K	6.9/3.0	K	7.1/2.9	K	7.2/2.8			
	0.001	K	6.4/3.1	K	6.3/3.2	K	6.3/3.1	K	6.5/3.0	K	6.5/2.6			
OH <sup>-</sup>	1	D	12.4/8.7	E	13.3/10.5	X	13.9/11.6							
	0.1	K	12.5/-	k	12.8/6.7	k	12.9/4.9							
	0.01	K	11.8/2.5	K	12.0/3.2	K	11.8/2.7							
	0.001	K	10.7/2.7	K	10.8/2.6	K	10.5/2.6							
CO <sub>3</sub> <sup>2-</sup>	1	K	12.0/2.5	X	12.0/7.1	X	12.4/7.1							
	0.1	K	11.4/2.3	k	11.9/5.2	k	12.0/4.3							
	0.01	K	10.5/2.6	K	10.5/2.6	K	10.4/2.6							
	0.001	K	10.5/2.6	K	10.5/2.6	K	10.4/2.6							

CC: Cation Concentration (M, mole per liter).

RP: Resulting Products.

A,a: alunite or H<sub>3</sub>O<sup>+</sup>-analog of alunite

B: low crystallinity phase (pseudoboehmite)

C: Al<sub>11</sub>(OH)<sub>30</sub>Cl<sub>3</sub> or Al<sub>12</sub>O<sub>11</sub>(OH)<sub>44</sub>Cl<sub>6</sub>

Lower case a, h, k and m, indicate phases with relatively lower intensities of XRD.

pH<sub>0</sub>: pH of solvent before mixing with the starting material; pH<sub>f</sub>: pH of solvent measured after the hydrothermal treatment.

-: not measured because of solution leak during hydrothermal treatment.

D: LiAlSiO<sub>4</sub>·H<sub>2</sub>OE: Na<sub>5</sub>Al<sub>5</sub>Si<sub>7</sub>O<sub>32</sub>·12H<sub>2</sub>O

X: amorphous phase

K,k: kaolinite

M,m: smectite

H,h: hematite



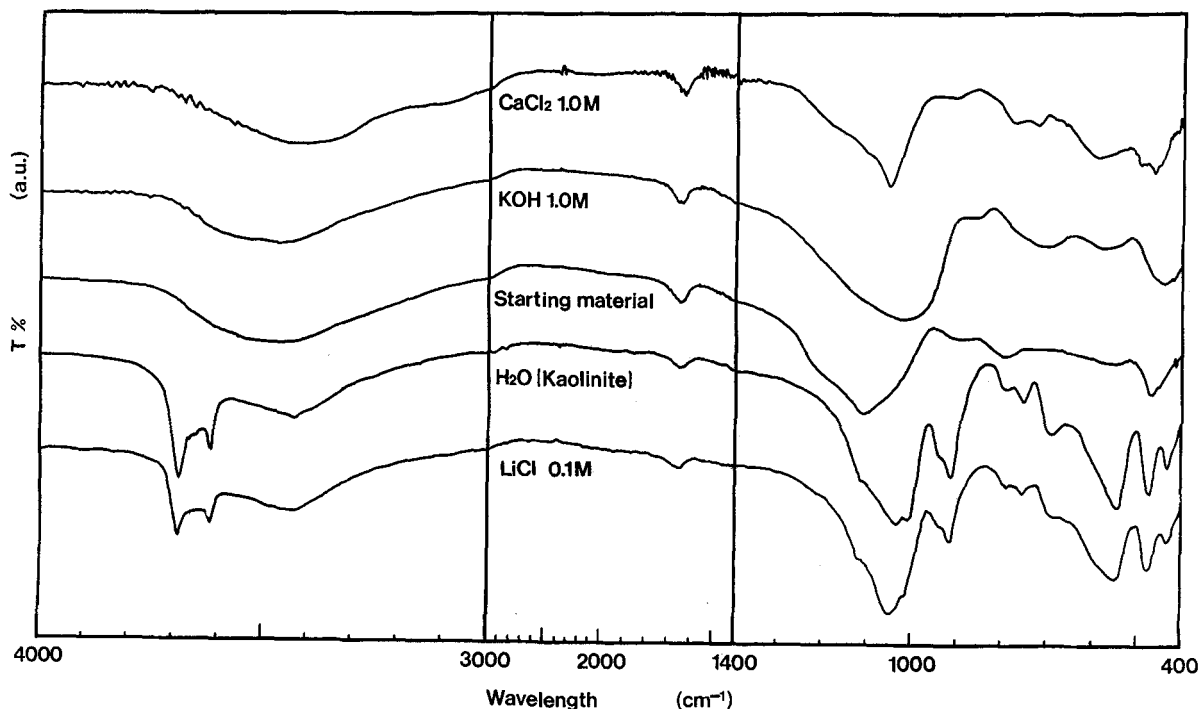


Figure 4. Infrared spectra of the starting material, an amorphous phase from a 1.0 M KOH solution, a low crystallinity phase (pseudoboehmite) synthesized with a 1.0 M  $\text{CaCl}_2$  solution, kaolinite hydrothermally synthesized without additional ions, and kaolinite synthesized in 0.1 M LiCl.

satellite band (SSB) signals. Although the starting material also showed a broad signal around 0 ppm, the left SSB signal is much higher than the right SSB signal. The signal around 60 ppm in the spectrum of the amorphous product in 1.0 M KOH, "X," corresponds to a signal for four-coordinated Al atoms. The signal of six-

coordinated Al atoms around 0 ppm was observed in the spectrum of the product with low crystallinity in 1.0 M  $\text{CaCl}_2$ , "B," as well as in those of synthetic kaolinite and well-crystallized boehmite obtained from the aluminum sol by hydrothermal treatment.

Figure 8 shows the TEM photographs of the starting material (a), the run products in 1.0 M  $\text{CaCl}_2$  (b, c), that in 1.0 M KOH (d), kaolinite synthesized in 0.1 M LiCl (e) and that in distilled water (f). The starting material (Figure 8a) consists of fine particles less than 30 nm. Two kinds of materials with different shapes were observed in the run products in 1.0 M  $\text{CaCl}_2$  (Figures 8b, c). Considerable Al, small amounts of Si, and trace amounts of Ca were detected in the material with thin, platy shapes (Figure 8b). The relative intensities of Si and Ca decreased and that of Al increased with increased focusing on the electron beam. The major components of the other run product in 1.0 M  $\text{CaCl}_2$  (Figure 8c) were Si and Al. Ca was also detected as a minor component. The EDX analysis revealed that the run product in 1.0 M KOH (Figure 8d) contains Si, Al and K. Hexagonal plate-shaped crystals of kaolinite were observed in the run products of both 0.1 M LiCl and distilled water (Figures 8e, f, respectively). The crystal sizes of the kaolinite synthesized in 0.1 M LiCl appeared to be smaller than that synthesized in distilled water. No definitive difference in the ratios of the characteristic X-ray of Al and Si was observed between

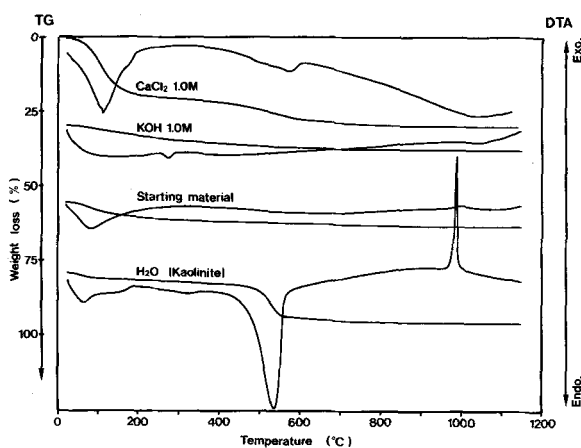


Figure 5. DTA-TG curves for the starting material, an amorphous phase from a 1.0 M KOH solution, a low crystallinity phase (pseudoboehmite) synthesized with 1.0 M  $\text{CaCl}_2$  solution, and kaolinite hydrothermally synthesized without additional ions.

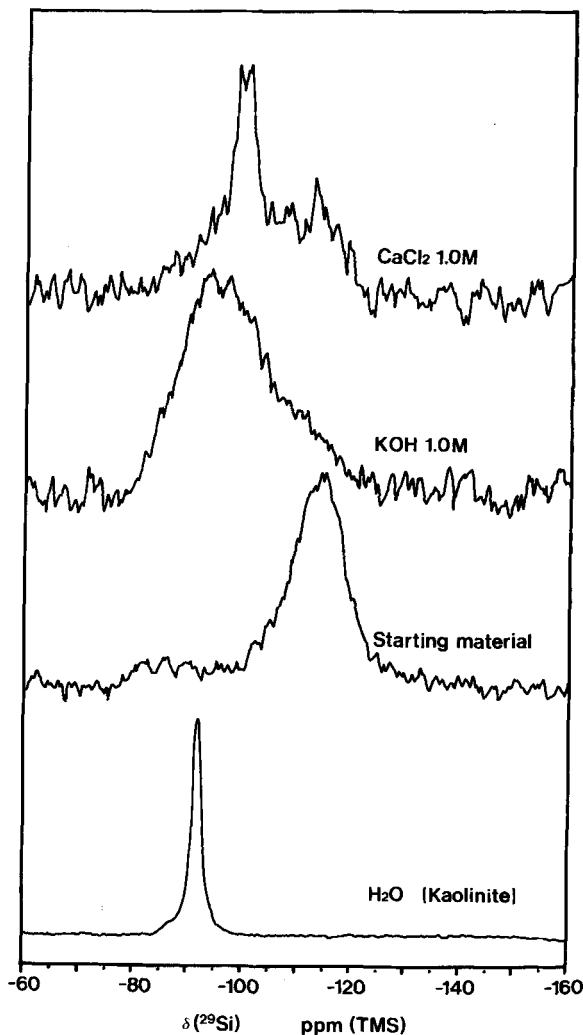


Figure 6.  $^{29}\text{Si}$  CP/MAS NMR spectra for the starting material, an amorphous phase from a 1.0 M KOH solution, a low crystallinity phase (pseudoboehmite) synthesized with 1.0 M  $\text{CaCl}_2$  solution, and kaolinite hydrothermally synthesized without additional ions.

kaolinite formed in 0.1 M LiCl and that in distilled water.

## DISCUSSION

### *The starting material*

The starting material is an amorphous powder consisting of silica and alumina. The IR absorption of the OH group (Figure 4) suggests that the starting material was hydrated. On the other hand, the infrared spectrum without the Al-O-Si absorption bands (Figure 4) and the DTA curve without the exothermic peak for a spinel transition (Figure 5) indicate that the starting material is not an aluminosilicate. A three-dimensional framework of  $\text{SiO}_4$  tetrahedra is suggested by the  $Q^4$

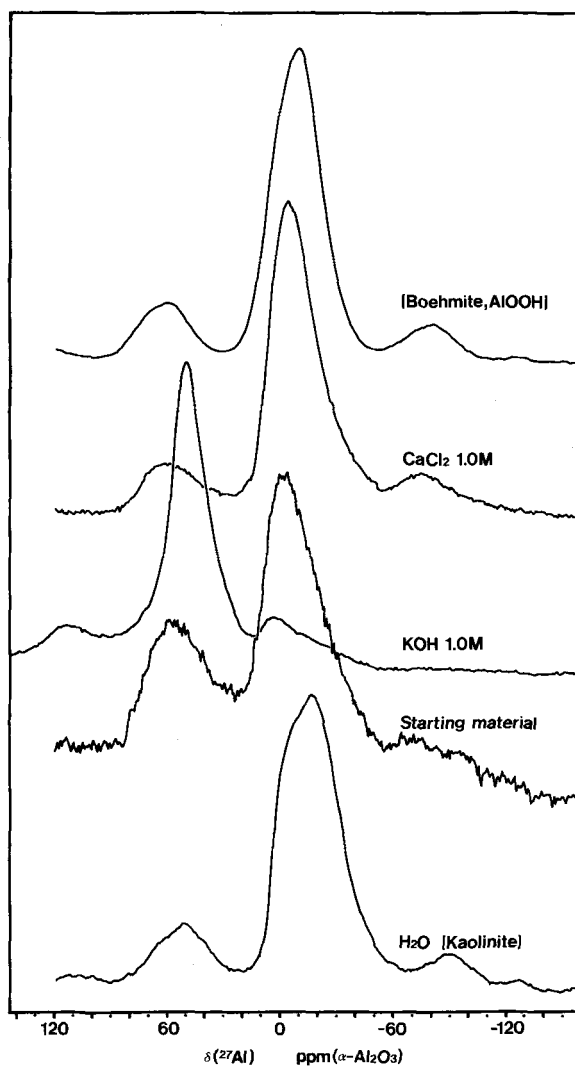


Figure 7.  $^{27}\text{Al}$  MAS NMR spectra of the starting material, an amorphous phase from a 1.0 M KOH solution, a low crystallinity phase (pseudoboehmite) synthesized with 1.0 M  $\text{CaCl}_2$  solution, kaolinite hydrothermally synthesized without additional ions, and boehmite, AlOOH.

peak in the  $^{29}\text{Si}$ -CP/MAS NMR spectrum (Figure 6). The unbalanced SSB signal in the  $^{27}\text{Al}$ -MAS NMR spectrum (Figure 7) may be caused by overlap from another signal. The signal around 60 ppm corresponds to four-coordinated Al atoms. It may be concluded that the starting material is a partially hydrated, simple mixture of silica with a three-dimensional framework and alumina with both six- and four-coordinated Al atoms. It is not an aluminosilicate.

The final pH values of the hydrothermal treatments with distilled water ranged from 2.5 to 3.5, although no ions were added into the reaction system. In a previous study (Miyawaki *et al.*, 1990), elution of  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  ions from the starting material into solution during the hydrothermal synthesis caused a decrease

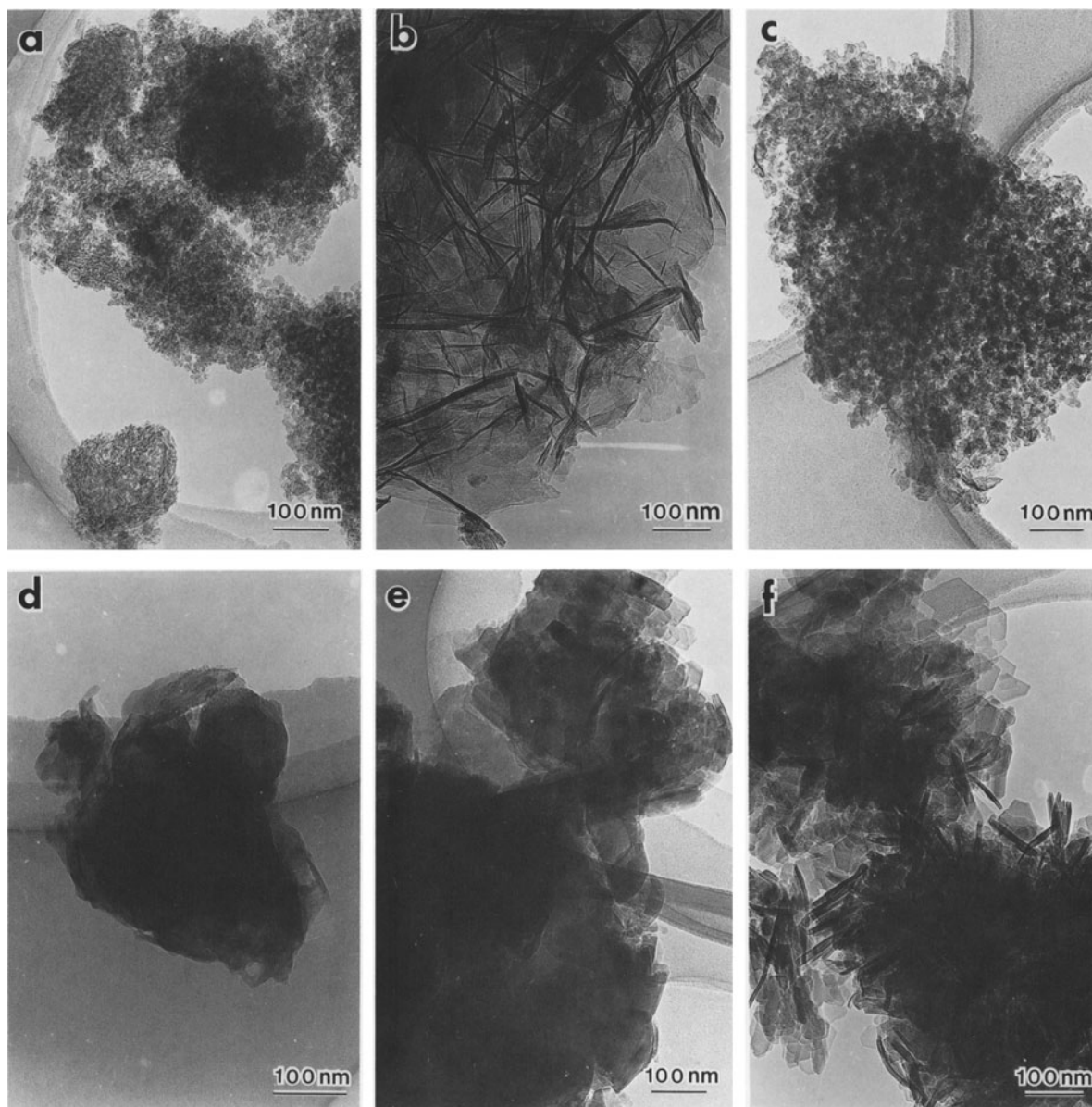


Figure 8. Transmission electron micrographs of the starting material (a), the run products in 1.0 M  $\text{CaCl}_2$ , "B" (b, c), that in 1.0 M KOH, "X" (d), kaolinite synthesized in 0.1 M LiCl, "K" (e), and kaolinite synthesized in distilled water, "K," (f).

in pH. Our starting material includes trace amounts (<0.1 wt%) of the impurities sulfur, chlorine and sodium. It should be noted that all of the results of the present experimental runs include the effects of these impurities.

#### *The amorphous product in alkaline solutions*

The EDX analysis of the amorphous phase, "X," synthesized with 1.0 M KOH showed that it consists of Al, Si and K. It is impossible to determine whether the amorphous product is an aluminosilicate or a mix-

ture because of a broad Al-O-Si band in the infrared spectrum (Figure 4) and the absence of a spinel transition peak in the DTA curve (Figure 5). However, the amorphous product shows a difference in the peak positions in both the  $^{29}\text{Si}$ - and  $^{27}\text{Al}$ -NMR spectra as compared with the amorphous starting material (Figures 6, 7). The resulting product using 1.0 M KOH is a typical example of the amorphous phase. The  $^{29}\text{Si}$ -CP/MAS NMR spectra of the amorphous phase gave a broad peak around  $-90$  ppm that is close to the  $\text{Q}^3$  peak of kaolinite ( $-92$  ppm). The  $^{27}\text{Al}$ -MAS NMR



spectra shows a peak around 60 ppm corresponding to four-coordinated Al atoms and two SSB signals. Consequently, phase "X" is an aluminosilicate or a mixture of an amorphous silicate and an aluminum compound consisting of four-coordinated Al atoms.

#### *The product with low crystallinity*

The X-ray powder diffraction pattern of product "B" showed only weak ( $<100$  cps) reflections at  $49.3$  and  $64.9^\circ 2\theta$  ( $\text{CuK}\alpha$ ), and extremely broad reflections around  $27$  and  $38.5^\circ 2\theta$  ( $\text{CuK}\alpha$ ) (Figure 3). The diffraction pattern of the product with low crystallinity in experimental runs at lower  $\text{pH}_F$  values is similar to those of the products formed under acidic conditions using the same starting material (Miyawaki *et al.*, 1989). Moreover, the XRD pattern of the low-crystallinity phase is very similar to that of pseudoboehmite (De Vijnck, 1973). The infrared spectrum without a distinct Al-O-Si band (Figure 4) and the DTA curve showing no spinel transition peak (Figure 5) suggest that the "B" phase does not have the Al-O-Si bond observed in kaolinite. Two different phases were observed during TEM analysis of the run product in  $1.0$  M  $\text{CaCl}_2$ . One (Figure 8c) consists of Si, Al and Ca. It may be an amorphous calcium aluminosilicate or a mixture of amorphous phases. The other phase with a thin, platy shape (Figure 8b) may be an aluminum compound covered with the Al, Si, Al, and Ca phase, because of variation in the relative intensities of Si, Al and Ca (See Results). On the other hand, the NMR spectra differ significantly from those of the starting material and phase "X." One of two peaks around  $-100$  ppm observed in the  $^{29}\text{Si}$ -NMR spectra (Figure 6) indicates a conversion from  $\text{Q}^4$  to  $\text{Q}^3$  during the hydrothermal treatment. The  $^{27}\text{Al}$ -NMR spectra of the low-crystallinity phase resembles that of boehmite (Figure 7). These results suggest that the low-crystallinity phase may be a mixture of pseudoboehmite and an amorphous silicate with  $\text{Q}^3$  and  $\text{Q}^4$  structures.

#### *Kaolinite synthesized in 0.1 M LiCl or LiNO<sub>3</sub>*

It is worth noting that the use of  $0.1$  M  $\text{LiCl}$  and  $\text{LiNO}_3$  solutions for the syntheses was effective in the crystallization of kaolinite in the  $[001]$  direction. Syntheses using  $\text{Li}^+$ , which is only slightly larger than  $\text{Al}^{3+}$ , produced kaolinite samples having lower values for the Hinckley indices (Figure 1a). Figure 9 is a plot of the kaolinite yield vs. the Hinckley index showing a positive correlation between the two parameters. However, kaolinite samples synthesized in only  $1.0$  and  $0.1$  M  $\text{LiCl}$ ,  $\text{LiNO}_3$ , or  $\text{MgSO}_4$  solutions do not match the correlation. The lower Hinckley indices and the higher yields for the products using  $1.0$  and  $0.1$  M  $\text{MgSO}_4$  solutions are due to coexistence of smectite (Table 1). Such characteristics observed in kaolinites synthesized in Li-bearing solutions, unaccompanied by smectite, are crystallographic abnormalities.

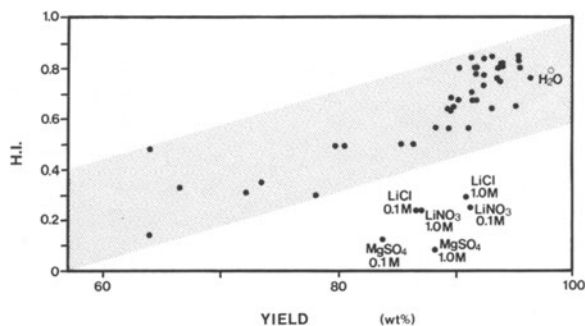


Figure 9. Relationship between kaolinite yields estimated from TG curves and the Hinckley indices.

Plançon *et al.* (1988) reported that the Hinckley index does not estimate the types or abundances of various structural defects, the classical "crystallinity," but is directly related to the proportions of two kinds of kaolinite, a low-defect kaolinite and a moderate- to high-defect kaolinite. The "Li-kaolinite" has a sharp 001 reflection in spite of the lower Hinckley index. The XRD peak width is a function of crystal size and strain. The lower Hinckley index and sharp 001 reflection suggest that the "Li-kaolinite" consists mainly of "moderate- to high-defect kaolinite" and is well developed in the  $[001]$  direction, and/or has low strain, compared with kaolinite synthesized without additional ions.

Two possibilities regarding the effects of  $\text{Li}^+$  ions can be presumed. One of these is isomorphous substitution with  $\text{Li}^+$  ion at the octahedral site. The other is an effect on crystallization of kaolinite, such as poisoning of crystal growth sites by  $\text{Li}^+$  ions outside the crystal.

If we assume isomorphous substitution of univalent  $\text{Li}^+$  for trivalent  $\text{Al}^{3+}$  at an octahedral site, the introduction of two  $\text{Li}^+$  ions into two vacant octahedral sites is necessary to compensate the charge. Disordered distributions of Al, Li and vacancy in the octahedral site would lower the Hinckley index. Moreover,  $\text{Li}^+$  ions increase the dimensions of the octahedral sheet, because of a larger ionic radius compared with  $\text{Al}^{3+}$  ( $\text{Li}^+$ :  $0.74 \text{ \AA}$  and  $\text{Al}^{3+}$ :  $0.53 \text{ \AA}$ , Shannon and Prewitt, 1968). Consequently, an octahedral sheet with a relatively smaller dimension fits better into a tetrahedral sheet with a larger dimension in order to help crystal growth and reduce strain in the  $[001]$  direction.

Unfortunately, the chemical composition of the "Li-kaolinite" could not be analyzed because the amorphous phase coexisting with the product could not be separated. No clear evidence was obtained by EDX analysis, because Li cannot be detected in that analysis. Moreover, the reduction of Al components suggesting an isomorphous substitution of Al with Li could not be observed, as mentioned earlier. Therefore, no clear evidence for the position of  $\text{Li}^+$  ions, in or outside the crystal, could be obtained.

### Solution chemistry

The reaction mechanism for the formation of the poorly-crystalline pseudoboehmite, "B," is estimated as follows. Cations react with the silica component of the starting material to form an amorphous material which gives the Q<sup>3</sup> peak in <sup>29</sup>Si-NMR spectra. Consequently, the reaction system becomes acidic due to remaining pairing anions such as Cl<sup>-</sup>. The solubility of silica is relatively low and that of alumina is relatively higher in acidic solutions at room temperature (Mason, 1966). Tsuzuki (1986) reported that the trend of solubilities for quartz and gibbsite under hydrothermal conditions is the same as that at room temperature, after calculations using thermodynamic data. Therefore, the alumina component of the starting material dissolves and reacts under the acidic conditions to form pseudoboehmite with six-coordinated Al atoms. With the addition of a salt of a strong acid, the silica and alumina components of the starting material alter independently to an amorphous phase and pseudoboehmite, respectively, and kaolinite cannot be synthesized.

During the synthesis using solutions of concentrated sulfate, alunite (or the H<sub>3</sub>O<sup>+</sup>-analog of alunite) was precipitated. In some cases, both kaolinite and the H<sub>3</sub>O<sup>+</sup>-analog of alunite were produced. A similar paragenesis of kaolinite and alunite has been observed in natural hydrothermal deposits (Nagasawa, 1978). The XRD peak intensities for both kaolinite and the H<sub>3</sub>O<sup>+</sup>-analog of alunite increased with increase in the concentration of Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. In this case, inhibition of kaolinite formation by the sulfate ion might be reduced because of the consumption of sulfate in the formation of the H<sub>3</sub>O<sup>+</sup>-analog of alunite.

The use of basic solutions of carbonates and hydroxides resulted in the formation of different products, amorphous phase "X." The coordination number of the aluminum atom is four in alkaline solutions (Baes and Mesmer, 1976), and, in fact, the Al-NMR spectroscopy revealed the coordination number of Al atoms in the phase "X" to be four. The formation of four-coordinated Al is incompatible with the synthesis of kaolinite.

### CONCLUSIONS

Divalent cations such as Mg<sup>2+</sup> or Ca<sup>2+</sup> interfere with the crystallization of kaolinite more than do univalent Li<sup>+</sup>, Na<sup>+</sup> or K<sup>+</sup> cations. The addition of Fe<sup>3+</sup> or excess Al<sup>3+</sup> ions interfered most with the formation of kaolinite. Among ions with the same valence, the larger the cation, the greater the inhibition in the formation of kaolinite. The use of 0.1 M LiCl and LiNO<sub>3</sub> solutions improved crystallization of kaolinite along the [001] direction. Sulfate and acetate solutions interfered with the formation of kaolinite more than did chlorides and nitrates. No crystalline product was obtained with ex-

remely basic solutions. In an extremely basic reaction system, the formation of 4-coordinated aluminum inhibited the crystallization of kaolinite. The higher solubility of alumina in extremely acidic systems promoted the formation of pseudoboehmite rather than kaolinite. It may be concluded that the pH of the reaction system should be kept between 2 and 4 in the hydrothermal reaction, except for runs in Li-bearing solutions.

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