

EFFECTS OF ACIDITY ON THE HYDROTHERMAL SYNTHESIS OF KAOLINITE FROM SILICA-GEL AND GIBBSITE

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Abstract—A comparative study is reported in which kaolinite has been hydrothermally synthesized at several pH conditions. The syntheses were carried out at 220 °C for 3 to 10 d with distilled water or acidic solutions using a mixture of silica-gel derived from alkoxide and gibbsite with a Si/Al ratio of 1:1 as the starting material. Use of acidic solution for the synthesis promotes the dissolution of the starting materials and leads to kaolinitization at an earlier stage of the reaction. However, the rate of kaolinitization is found to be rather slow, in comparison to the reaction with distilled water. The synthetic kaolinite was characterized by X-ray powder diffraction pattern. Kaolinite synthesized with distilled water was poorly grown for direction of the stacking. For example, crystallite size along the *c**-axis = 155 Å, whereas kaolinite synthesized with acidic solution gave a higher crystallite size along the *c**-axis, such as 253 Å in the case of the synthesis with 0.1 N HCl. Hinckley index of the synthetic kaolinite was varied from 0.35 to 0.80 by the acidity of the reaction. Different kaolinitization processes are implied by differences observed in the rate of kaolinitization, which has an influence on the nature of the stacking faults of the kaolinite.

Key Words—Crystallite size, Crystallization, Hydrothermal synthesis, Kaolinite, pH, Stacking fault.

INTRODUCTION

Hydrothermal syntheses of kaolinite have revealed that pH is one of the most important factors controlling the formation of kaolinite (De Kimpe et al. 1964; De Kimpe 1967; La Iglesia et al. 1973; Rodrique et al. 1973). Kaolinite generally crystallizes under acidic or neutral conditions from silica-alumina starting materials. The low pH favor formation of six-fold coordinated Al ion, which is effective for the crystallization of kaolinite. The effect of pH on the synthesis of kaolinite is not clear, because the process of kaolinitization and properties of synthetic kaolinite are also influenced by other factors, such as the structure and chemical composition of starting materials as well as hydrothermal conditions (Eberl and Hower 1975; Satokawa et al. 1994). Prior study shows that kaolinite crystallizes from an amorphous gel of silica and alumina within a pH range of 4 to 10 (Miyawaki et al. 1989). Kaolinite also crystallizes from a mixture of silica and alumina in a strong acid solvent (Osaka and Kato 1984). These two examples suggest that the suitable pH condition for the kaolinite formation depends upon the starting materials. The use of simple starting materials should be investigated to determine the effect of pH on

the formation and the properties of the synthetic kaolinite. The present study deals with the formation process and the nature of the stacking defects of the kaolinite synthesized at several pH ranges from a simple mixture of pure silica-gel and pure aluminum hydroxide.

EXPERIMENTAL METHODS

Synthesis

The starting material used for this study was a mixture of pure silica-gel and gibbsite (Si/Al atomic ratio = 1.0). The silica-gel was a spherical porous amorphous silica (Tosoh, 99.9% purity, separation material grade for chromatography) derived from tetraethyl orthosilicate. The gibbsite was a commercially available reagent, Al(OH)₃ (Sumitomo Chemical Industry, 99.9% purity). The hydrothermal treatment was carried out with 2 g of this mixture and 18 ml of a solvent in a 25 ml PTFE pressure vessel (San-ai Kagaku, HU-25). Distilled water, 0.001 to 1.0 N of hydrochloric acid (HCl) solution, or 0.001 to 1.0 N of nitric acid (HNO₃) solution was used as a solvent in the hydrothermal treatment. The pressure vessel was kept at 220 °C for 3 to 10 d. Solid products were separated by filtration, washed with distilled water and dried at 100 °C for 1 d.

Analytical Methods

The pH of the sample slurry was measured with a pH meter (Horiba, M8 AD) before and after the hydrothermal treatment. XRD patterns were obtained us-

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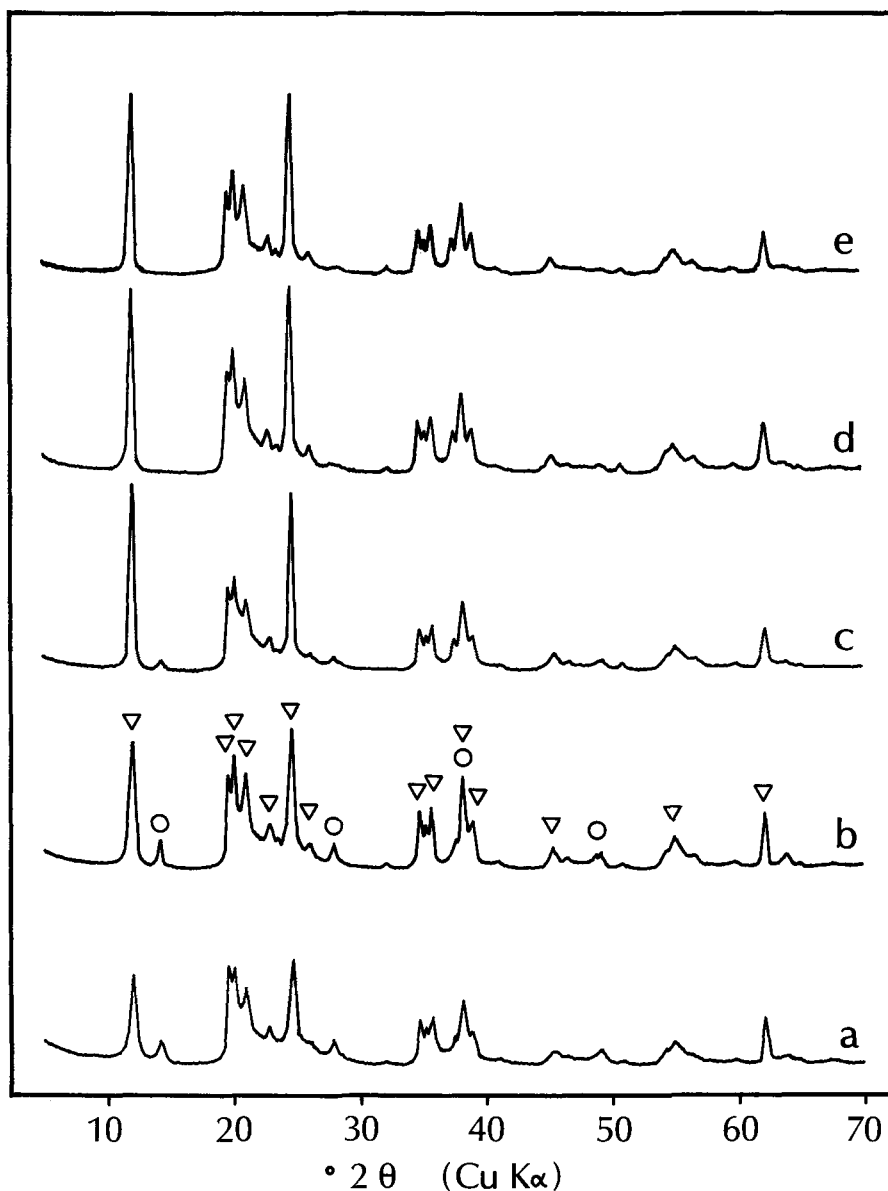


Figure 1. X-ray diffraction patterns of products synthesized at 220 °C for 10 d with a) distilled water, b) 0.01 N HCl, c) 0.1 N HCl, d) 0.2 N HCl and e) 0.5 N HCl. Selected diffraction peaks are indicated as follows: ∇ = kaolinite; \circ = boehmite.

ing a Rigaku RAD-IIB diffractometer that employed graphite monochromatized $\text{CuK}\alpha$ radiation with a step scanning technique (15 s for every 0.02° step). The crystallite size along the c^* -axis was calculated by the Scherrer equation (Brindley 1980). The nature of stacking defects of the synthetic kaolinite were characterized using the Hinckley index (Hinckley 1963), which shows the proportion of low-defect kaolinite in the synthetic samples (Plançon et al. 1988). The morphology of the kaolinite was observed with transmission electron microscopy (TEM) using a JEOL JEM-2000FX operating at 100 kV. Specific surface area was measured by N_2 gas adsorption (the B.E.T. method)

using a Carlo Erba Sorptomatic 1800 analyzer for the samples dried at 100 °C in vacuo. The chemical compositions of the solid products were analyzed by atomic absorption analysis for Al and Si using samples dissolved in hydrofluoric acid.

RESULTS

Characterization of Synthetic Kaolinite

The XRD patterns of products synthesized at 220 °C for 10 d with distilled water and 0.01 to 0.5 N HCl are shown in Figure 1. Kaolinite is the main phase and some boehmite was observed as a minor phase.

Table 1. Phases, pH values and crystalline data of the products (220 °C–10 d).

Solvent	pH ¹	pH ²	Product	S.S.A. ³ (m ² /g)	Si/Al	Crystallite size (Å)	Hinckley Index
Distilled water	7.0	4.8	Ka + (Bo)	64.9	1.00	155	0.49
0.001N-HCl	4.5	4.5	Ka + (Bo)	47.8	1.01	180	0.63
0.01N-HCl	2.2	2.7	Ka + (Bo)	48.6	1.00	176	0.80
0.1N-HCl	1.2	1.4	Ka + (Bo)	34.4	0.99	253	0.45
0.2N-HCl	0.7	1.4	Ka	27.3	1.02	231	0.65
0.5N-HCl	0.3	0.8	Ka	43.2	1.16	245	0.78
1.0N-HCl	0.2	0.5	Ka + am	56.6	1.62	238	0.76
0.001N-HNO ₃	4.5	4.1	Ka + (Bo)	52.9	1.02	180	0.65
0.01N-HNO ₃	2.2	3.9	Ka + (Bo)	60.4	1.02	162	0.66
0.1N-HNO ₃	1.2	1.4	Ka + (Bo)	29.4	1.00	279	0.35
0.2N-HNO ₃	0.6	1.0	Ka	29.2	1.03	253	0.45
0.5N-HNO ₃	0.4	0.6	Ka	40.4	1.11	245	0.50
1.0N-HNO ₃	0.2	0.4	Ka + am	47.6	1.47	231	0.79

Ka = Kaolinite; Bo = Boehmite; am = amorphous.

¹ pH = pH value before the reaction.

² pH = pH value after the reaction.

³ S.S.A. = specific surface area.

Phases, specific surface areas and Si/Al atomic ratios of all the solid products, and the crystallite size (CS) along the *c**-axis and Hinckley Index (HI) of synthesized kaolinite for the products, are summarized in Table 1 along with the pH data. Variations in the CS and

HI of the synthetic kaolinite are plotted against the pH values measured after the reaction in Figure 2. Kaolinite synthesized with dilute acid solution, for example, 0.01 N HCl (pH = 2.7) or 0.01 N HNO₃ (pH = 3.9) had higher HI than that with distilled water. The reaction with more concentrated acid solution, for example, 0.1 N HCl (pH = 1.4) or 0.1 N HNO₃ (pH = 1.4) led to an increase in the CS but a decrease in the HI. The products synthesized with more concentrated solution, 0.2, 0.5 and 1.0 N HCl (pH = 1.4, 0.8, 0.5) or 0.2, 0.5 and 1.0 N HNO₃ (pH = 1.0, 0.6, 0.4) gave higher CS and higher HI. The synthetic kaolinites could be classified into four types according to their characters: 1) type A with low CS and low HI, for example, synthesized with distilled water (pH = 4.8); 2) type B with low CS and high HI, synthesized with 0.01 N HCl (pH = 2.7); 3) type C with high CS and low HI, for example, synthesized with 0.1 N HCl (pH = 1.4); and 4) type D with high CS and high HI, for example, synthesized with 0.5 N HCl (pH = 0.8).

The TEM photographs of the four types of products are shown in Figure 3. Thin leaves of variable shape are observed for type A (Figure 3a), while relatively small platy particles are observed for type B (Figure 3b), whereas hexagonal plates that correspond to typical well grown kaolinite are observed for types C and D (Figures 3c and 3d).

The Si/Al atomic ratios of the solid products of hydrothermal treatment were approximately 1.0 the same as starting mixtures, except for the products synthesized in 1.0 N HCl (Si/Al = 1.62) and 1.0 N HNO₃ (Si/Al = 1.47), which were greater than that of the other products.

Intermediate Products

The XRD patterns of products reacted at 220 °C for 3 to 8 d with distilled water or 0.01 to 0.5 N HCl are

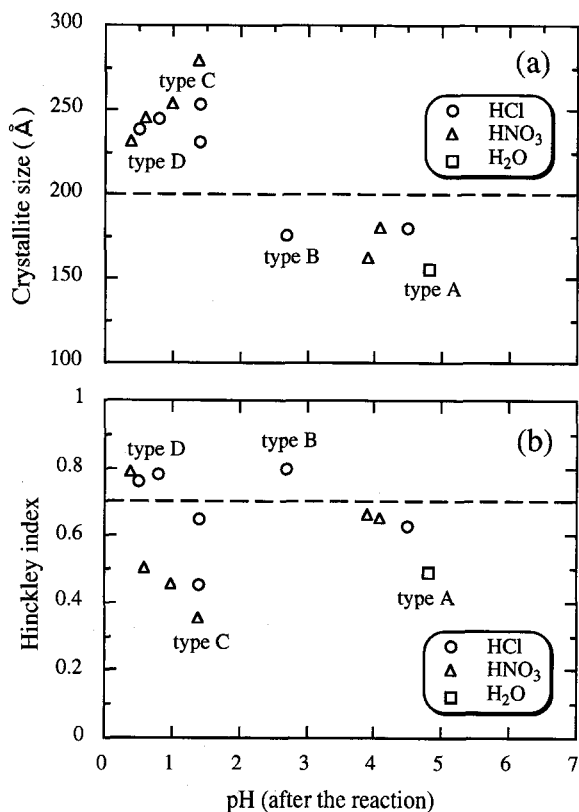


Figure 2. Relationships between properties of synthetic kaolinite and pH values measured after the reaction: a) crystallite size along the *c**-axis and b) Hinckley index.

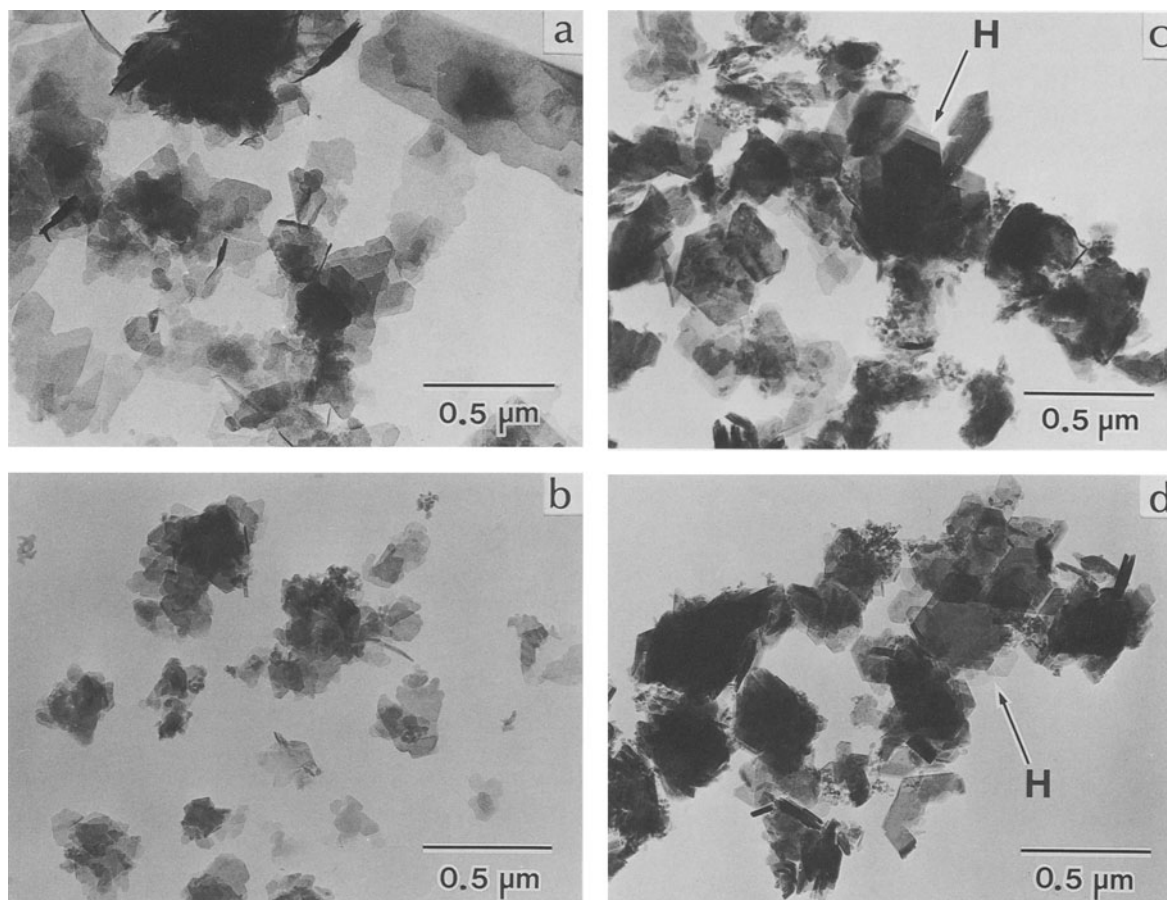


Figure 3. Transmission electron micrographs of products synthesized at 220 °C for 10 d with a) distilled water, b) 0.01 N HCl, c) 0.1 N HCl and d) 0.5 N HCl. These correspond to types A, B, C and D, respectively. Arrows indicate typical samples with hexagonal plates.

shown in Figure 4. The XRD pattern of the product obtained with distilled water for 6 d with gibbsite peaks (Figure 4a) indicated that some of the starting material, gibbsite, remained in the product. However, a drastic change was observed from the XRD patterns, the disappearance of the gibbsite peaks, between 6 and 8 d (Figures 4a and 4b), that is, the starting materials transformed into kaolinite abruptly during this period. Conversely, kaolinite peaks were observed within the XRD patterns of the products synthesized with the HCl solutions for 3 d, and no peaks of the starting material (gibbsite) were detected. Boehmite, for the case of 0.01 and 0.1 N HCl, or pseudoboehmite, for the case of 0.5 N HCl, was detected as an intermediate or coexisting phase within the products reacted with the HCl solutions.

Variation of the pH values and the rate of kaolinitization calculated with the relative intensity of the (001) peak of kaolinite from the XRD are plotted against the reaction time in Figure 5. The intensity for 10 d reaction of each treatment was normalized to 1.0.

The pH value of the reaction with distilled water was decreased over 3 d, after which it remained constant at about 4.8. The induction period, the length of time before crystallization begins, with distilled water was much longer than that for the acidic solution, although the slope of the kaolinitization curve of the reaction with distilled water was steeper than those with the acidic solutions.

DISCUSSION

Crystallization Processes

The kaolinitization processes are classified into two types according to the length of the induction periods, long, which correspond to the synthesis with distilled water or short, synthesis with acidic solution (Figure 4). The XRD patterns of the products synthesized with distilled water showed that the starting material virtually remained unchanged after the hydrothermal treatment at 220 °C up to 6 d, although the pH values had decreased over 3 d. The pH change must be in-

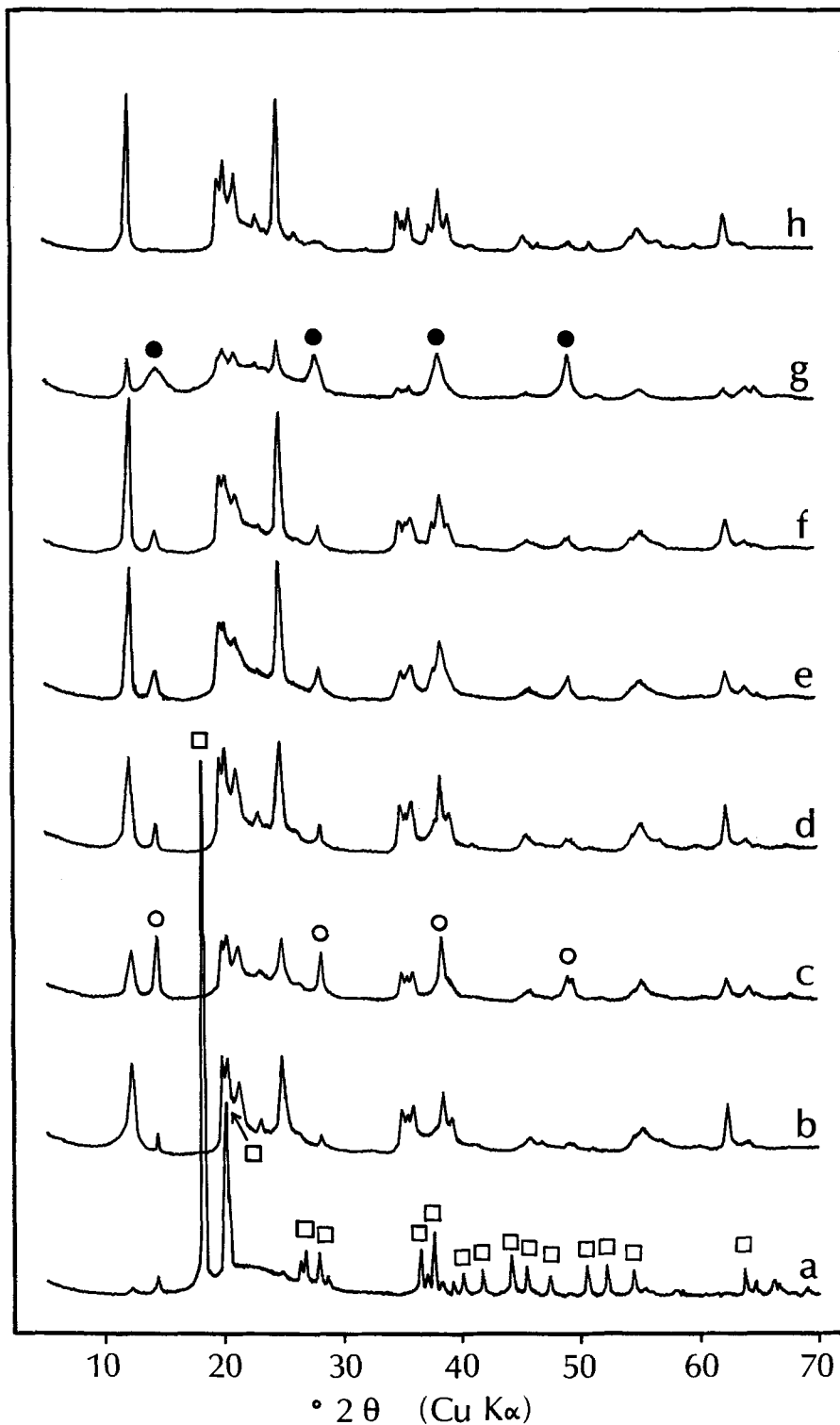


Figure 4. X-ray diffraction patterns of intermediate products synthesized at 220 °C with distilled water for a) 6 d and b) 8 d, those with 0.01 N HCl for c) 3 d and d) 5 d, those with 0.1 N HCl for e) 3 d and f) 5 d and those with 0.5 N HCl for g) 3 d and h) 5 d. Selected diffraction peaks are indicated as follows: ○ = boehmite; ● = pseudoboehmite; □ = gibbsite.

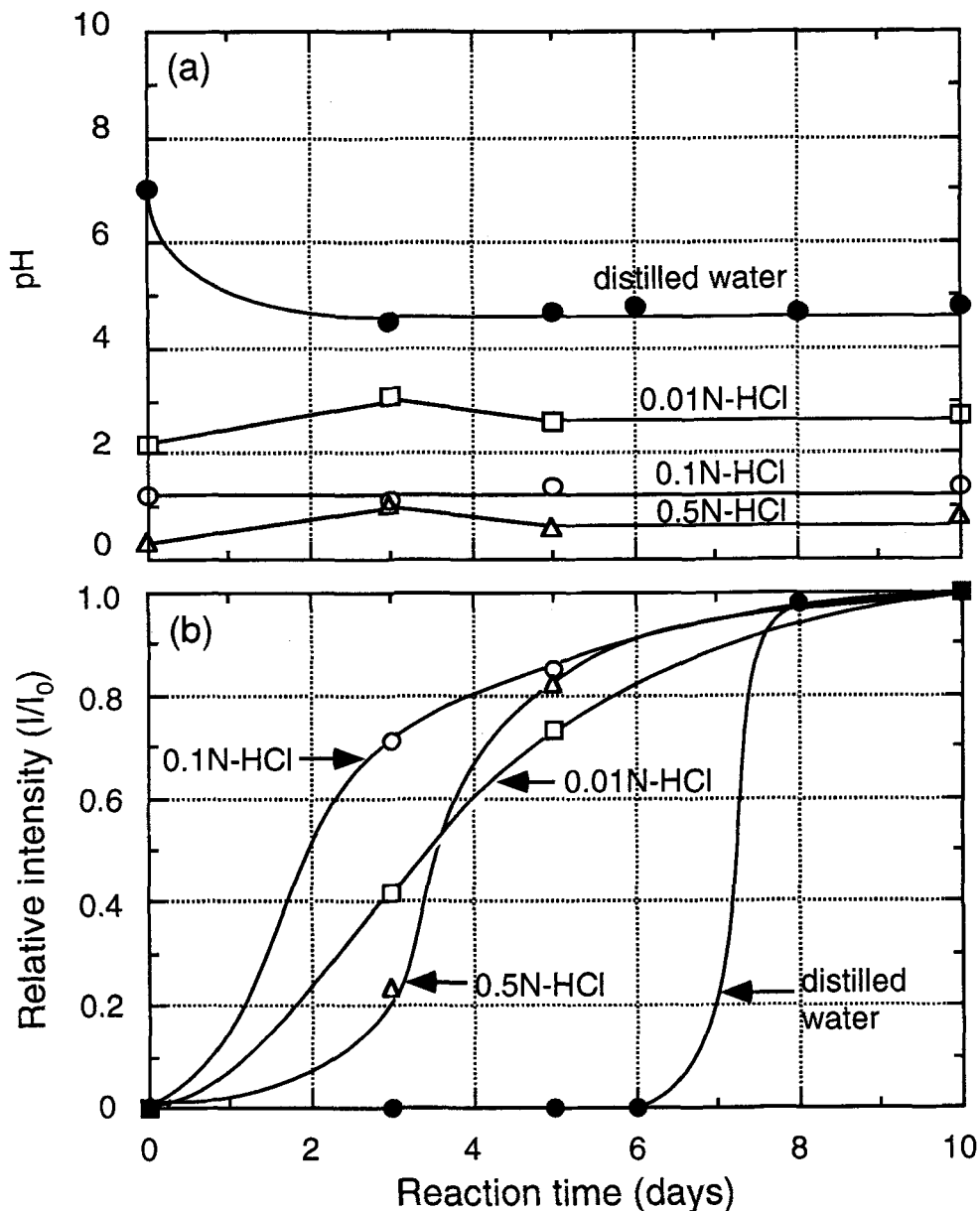


Figure 5. Variation in a) pH values and b) the rate of kaolinitization estimated by the relative intensity of (001) peaks in XRD patterns of the kaolinite synthesized with distilled water (corresponding to type A), with 0.01 N HCl (type B), with 0.1 N HCl (type C), and with 0.5 N HCl (type D) against the reaction time.

dependent of the crystallization of kaolinite, because the drop in pH and the kaolinitization were not synchronized.

The induction periods of the reactions resulting with the final pH values lower than 3.0, for example, reaction with 0.01 to 0.5 N HCl, were shorter than that of the reaction resulting with the final pH value greater than 4.0, reaction with distilled water. Since the solubility of gibbsite increases with decreasing pH within the acidic range (Kennedy 1959), the length of the induction period should be divided by the pH value of

the reaction system. The final pH value of the reaction with 0.001 N HCl (pH = 4.5) was similar to that of the reaction with distilled water (pH = 4.8). Therefore, the product synthesized with 0.001 N HCl is suggested to be classified as a type A.

The XRD peaks of boehmite from the products of 3 d reaction were stronger than those of 5 d reaction from the acidic solutions (Figures 4c–4h). Therefore, the kaolinitization within the acidic range should be carried out through boehmite as an intermediate phase. Satokawa et al. (1994) proposed that the kaolinite with

platy morphology should crystallize on the basis of the sheet structure of boehmite. Tsuzuki (1976) reported that the sequence of precipitation from a solution of silica and alumina to kaolinite through boehmite could be shown from solubility diagrams defined by $\log [Al^{3+}]$ and $\log [H_4SiO_4]$ at 200 °C and pH = 4.

Stacking Faults

The Hinckley index is related to the proportion of low-defect and moderate to high-defect kaolinites (Plançon et al. 1988). The kaolinite synthesized with several acidic conditions can be divided according to the HI. The proportion of low-defect kaolinite was low (HI < 0.5) for the samples of types A and C, whereas the proportion of low-defect kaolinite was relatively high (HI > 0.7) for the samples of types B and D. The nature of the stacking faults of the kaolinite are influenced by the pH conditions of the reactions. Conversely, the synthetic kaolinite can also be divided into two groups according to the CS. The values of CS of the synthetic kaolinites are much greater than 200 Å for the cases of the reaction solutions of pH < 2.0 (types C and D), whereas those are lower than 200 Å for the cases of the reaction solution of pH > 2.0 (types A and B). The tendency of the variation for HI and CS are quite similar for both kaolinites synthesized with HCl and HNO₃ solutions. The low pH condition for the synthesis of kaolinite is favorable for the dissolution of raw materials and improved crystallization of kaolinite along the *c**-axis (the stacking direction).

For type A, dissolution of the starting material, gibbsite, takes a long time, more than 6 d, whereas the crystallization of kaolinite is almost complete within 48 h, between the 6th and the 8th d of reaction. This abrupt crystallization should increase the proportion of the moderate or high-defect kaolinite. The smaller CS, 155 Å, and larger specific surface area, 64.9 m²/g, with variable particle shape indicate that kaolinite crystals of type A are poorly grown. The gradual crystallization was observed from the syntheses of types B–D (pH < 3.0). For type C, the relative intensity of the (001) reflection of kaolinite increased during the first 3 d, and the crystal growth of kaolinite was indicated by higher CS, 253 Å, smaller specific surface area, 34.3 m²/g, and hexagonal plates as observed by TEM (Figure 3c). For type D, low-defect kaolinite with typical hexagonal shape (Figure 3d) was formed from the strong acid condition, pH = 0.5. The process for type D is adequate for the crystal growth of kaolinite. However, the extremely low pH condition, pH = 0.2, is inadequate for crystallization of kaolinite by the deviation of the Si/Al atomic ratio, Si/Al = 1.62, observed for the product in 1.0 N HCl.

CONCLUSION

The rate of kaolinitization is affected by the pH condition of the reaction system. However, the variations of the properties of synthesized kaolinite, the proportion of low-defect kaolinite and crystallite size along the *c**-axis, cannot be simply explained by the difference in the rate of kaolinitization. It was found that at least the use of appropriately acidic conditions promotes the dissolution of the starting materials and the crystal growth of the kaolinite.

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