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Influence of Silica Contents in Hydrothermal Kaolin Synthesis

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Abstract

Kaolin mineral is hydrothermally synthesized from bayerite and alumina gel with different amounts of silica gel at temperatures from 180 to 214°C. Kaolin is formed readily at low silica hydrothermal runs. Thermodynamically, this is considered for ionization properties of bayerite and alumina gel. This suggests that kaolin is formed from bayerite and alumina gel with course of ionic precipitation.

1. Introduction

The conditions for kaolin** formation have been reported by many authors(MOREY et al., 1937; ROY et al., 1954), and the stability ranges of it have been defined. The mechanisms for kaolin formation are, however, not clear. Recently, HAWKINS et al. (1962) studied the kaolin formation from the viewpoint of ionic species and DEKIMPE et al. (1964) from that of alumina structure.

In this paper, the conditions for synthesis of kaolin from bayerite and alumina gel with silica gel are described, and the influence of SiO_2/Al_2O_3 for the kaolin formation is discussed.

2. Experimental

Starting materials are bayerite and alumina gel for alumina source, and silica gel for silica source. The bayerite and alumina gel are artificially formed from an aluminum plate. Metal mercury is scrubbed on the aluminum plate over 99.9% in purity forming amalgam, and then it put into deionized water for one day. White precipitates occurred in the water are bayerite. The amalgam is left in the air for few days, and they turn to alumina gel. The silica gel is a reagent of special grade and pulverized in an agate mortar.

Reactions were done for 30 or 15 mg of the bayerite and alumina gel to 30, 15, 10 and 5 mg of silica gel, and their SiO_2/Al_2O_3 are 4.35, 2.19, 0.73 and 0.36 (Mol. ratio). The reaction solution is deionized water of 3 ml for each run.

The Morey type autoclave is used for the experiment. Inside of the bomb was shielded with a teflon beaker of 5 ml capacity. The bomb is placed in an automatically controled electric furnace. The operating temperature is directly measured by a thermocouple and its accuracy is smaller than ±2°C. The operating temperatures are 160 to 214°C and durations are 7 to 13 days. The bomb is quickly quenched by cold water after the run. The products are

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** In this paper, the details of kaolin minerals are not inspected and the term kaolin means kandite (except halloysite) used by BROWN (1955).

examined by X-ray diffraction, infrared adsorption spectra and DTA.

3. Results

A summary of each run is shown in Table 1. Temperature and SiO_2/Al_2O_3 are changed for the runs. Kaolin is formed over 180 °C.

The results are plotted on the diagram shown in Fig. 1. In this figure, there is a tendency that kaolin is formed more easily in lower temperature side when the SiO_2/Al_2O_3 of starting material is low. Furthermore, alumina gel is more reactive than bayerite. They are proved by X-ray diffraction patterns and infrared adsorption spectra. The X-ray diffraction patterns of reaction products for 193 °C runs show that the 7Å peaks are pronounced in the low $SiO_2/$

Table 1 A summary of hydrothermal syntheses of kaolin.

Run No.	Starting materials	Reacting conditions			Reaction products	
		SiO_2/Al_2O_3	Temp. (°C)	Time (day)	Kaolin	Boehmite
11	Bayerite +Silica gel +H_2O	4.35	214	8	○	○
12		2.19	214	8	○	○
14		4.35	193	9	○	○
25		2.19	193	9	○	○
19		0.73	193	9	○	○
20		0.36	193	9	○	○
30		4.35	185	9	△	△
29		2.19	185	9	△	△
22		0.73	185	9	○	△
23		0.36	185	9	○	△
37		2.19	180	10	△	△
38		0.73	180	10	△	△
39		0.36	180	10	△	△
31		2.19	175	10	×	×
32		0.73	175	10	×	×
33		0.36	175	10	×	×
9	Alumina gel +Silica gel +H_2O	4.35	214	8	○	×
8		0.73	200	7	○	×
13		4.35	193	9	○	×
21		4.35	185	9	○	△
28		2.19	180	9	○	○
1		4.35	160	13	×	×
16		0.73	160	10	×	×
24		0.36	160	9	×	×

○ : Fair amount, △ : Very small amount, × : No detection

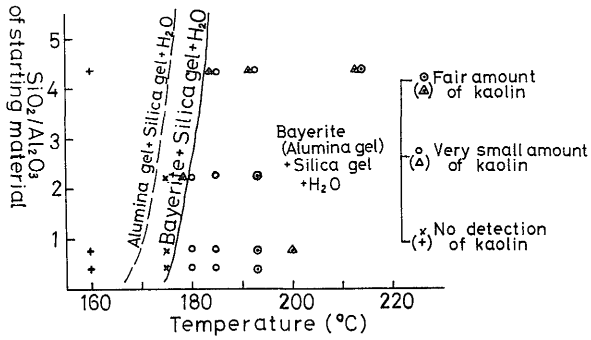
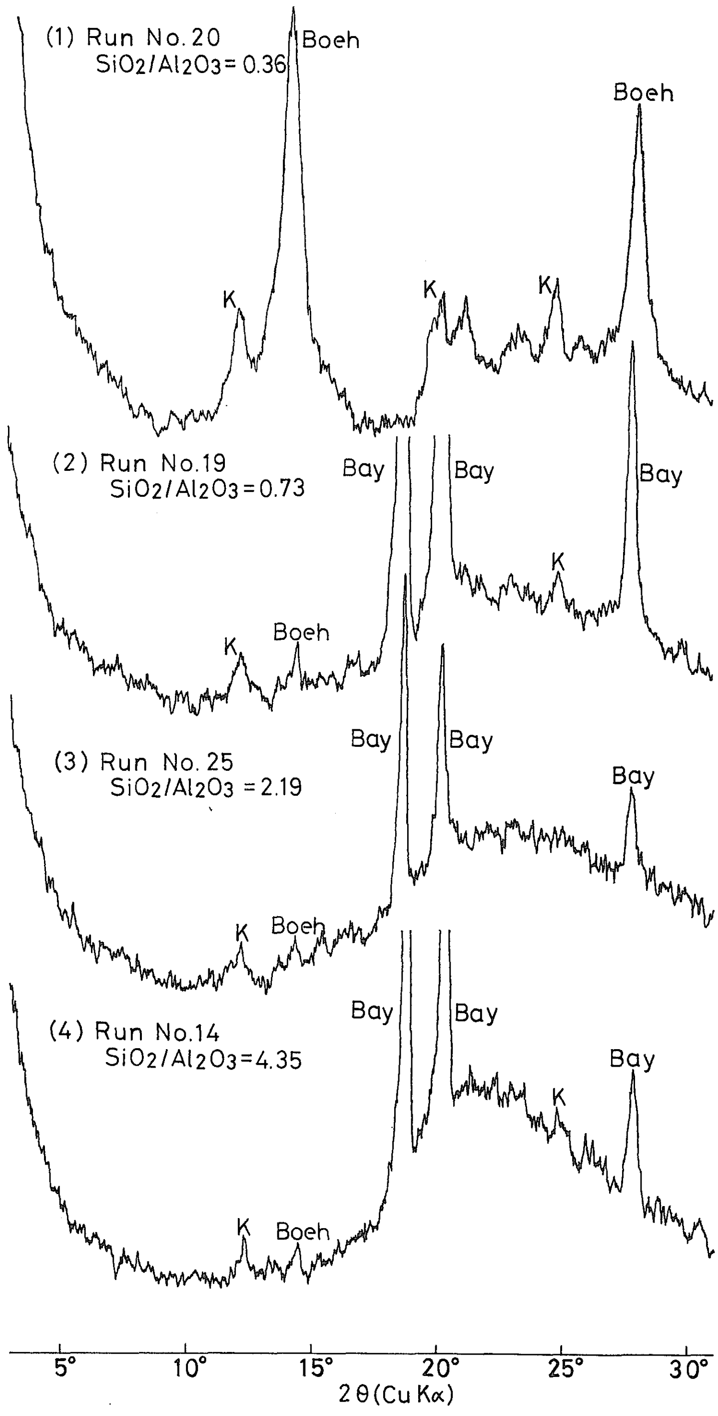


Fig. 1 Formation ranges of kaolin.



K: Kaolin, Boeh: Boehmite, Bay: Bayerite

Fig. 2 X-ray powder patterns of kaolin formed from bayerite and silica gel at 193 °C.

Al_2O_3 reactions (Fig. 2). The infrared adsorption spectra also show that the ratios of 3650 cm^{-1} peak (kaolin) to 3440 cm^{-1} peak (bayerite) are increased, with the decreasing of SiO_2/Al_2O_3 (Figs. 3 and 4).

The X-ray diffraction patterns of reactants from bayerite and alumina gel of same operating conditions show that the 7Å peaks are more pronounced for the reactant formed from alumina gel (Fig. 5).

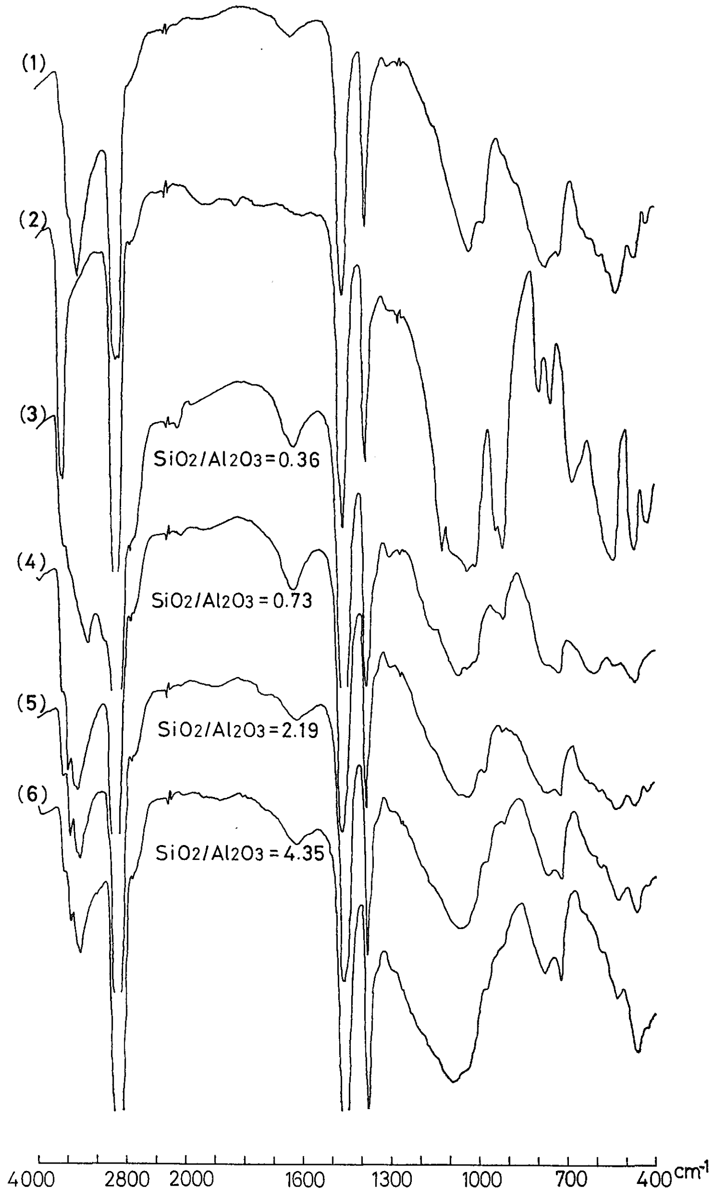


Fig. 3 Infrared adsorption spectra of bayerite, kaolin and reactants from bayerite and silica gel at 193°C.
(1): Bayerite, (2): Kaolin, (3): Run No. 20, (4): Run No. 19, (5): Run No. 25, (6): Run No. 14

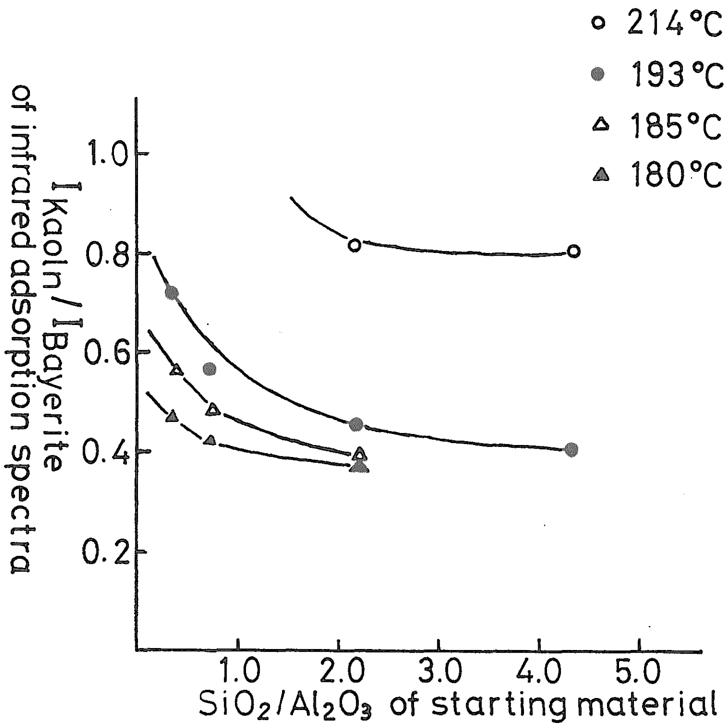


Fig. 4 Ratio of infrared adsorption of kaolin to SiO_2/Al_2O_3 of starting material on the reactants from bayerite and silica gel.

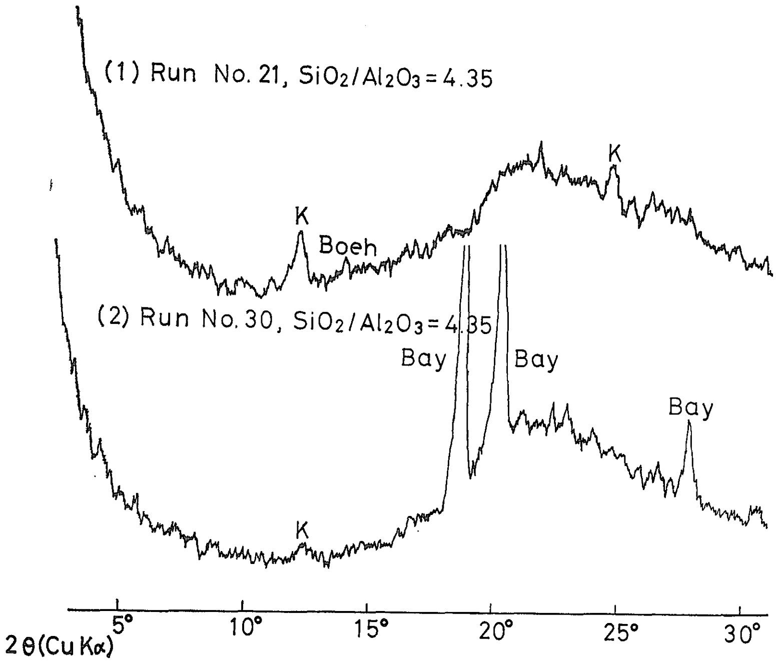


Fig. 5 X-ray powder patterns of kaolin at 185 °C runs.
(1): Kaolin formed from alumina gel and silica gel
(2): Kaolin formed from bayerite and silica gel

4. Discussion

The present results are thermodynamically considered.

Assuming the equilibrium among kaolin, bayerite, dissolved silica and water, the following equation can be written.

$$Al_2Si_2O_5(OH)_4 + 5H_2O = Al(OH)_3 + 2H_4SiO_4. \quad \cdots\cdots(1)$$

The equilibrium constant for equation (1) is

$$[H_4SiO_4]^2 = K.$$

Applying free-energy values to equation (1)

$$\Delta G°r = \Delta G°f\,\text{bayerite} + 2\Delta G°f\,H_4SiO_4 - \Delta G°f\,\text{kaolin} - 5\Delta G°f\,H_2O$$

$$\Delta G°r = 552.5 + 2(-300.3) - (-884.5) - 5(-56.69)$$

$$\Delta G°r = 14.85\ \text{kcal} = -1.364\ \log\,[H_4SiO_4]^2$$

$$\log\,[H_4SiO_4] = -5.44$$

$$K^{1/2} = [H_4SiO_4] = 10^{-5.44}$$

Consequently, equilibrium between kaolin and bayerite is attained at a fixed values of the activity of dissolved silica of 2.35 ppm as a H_4SiO_4. The H_4SiO_4 contents always exceed in the present runs. So, other ions have to be considered. GARRELS et al. (1965) present the following equations:

$$Al_2Si_2O_5(OH)_4 + 6H^+ = 2Al^{3+} + 2H_4SiO_4 + H_2O$$

$$Al_2Si_2O_5(OH)_4 + 3H_2O = 2H^+ + 2AlO_2^- + 2H_4SiO_4$$

and show the combination volume from these equations (Fig. 6). This figure shows that high concentration of AlO_2^- or Al^{3+} is required for the kaolin formation.

The present results show that the kaolin can be formed more easily from alumina gel than bayerite. This corresponds to the order of solubility of alumina form shown by WOLLAST (1967). So, low silica content may correspond to ionization of bayerite and alumina gel and be suitable

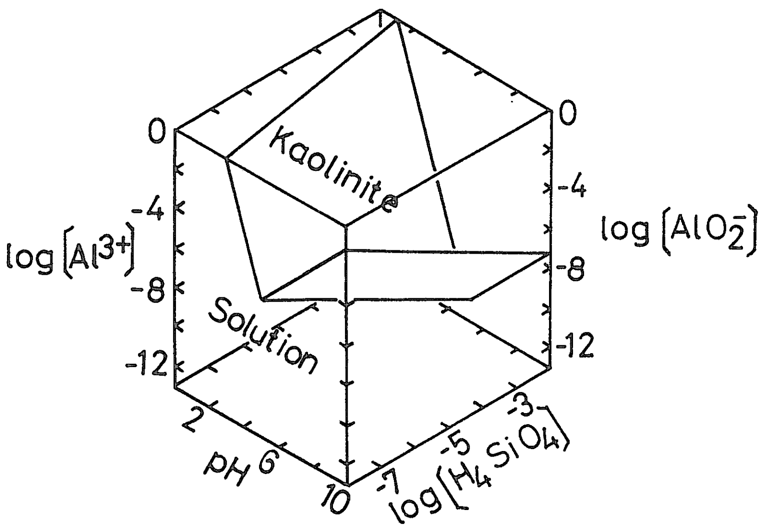


Fig. 6 Stability field of kaolin as defined by its dissociation ions AlO_2, Al, H and H_4SiO_4 at 25°C (after GARRELS et al. 1965).

for the kaolin formation.

If this is true, it is assumed that kaolin is precipitated easily from ionized species described by HAWKINS et al. (1962).

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カオリン合成におけるシリカ含量の影響

高 島 勲

要 旨

人工的に作ったバイエライトおよびアルミナゲルと，シリカゲルからカオリンを水熱合成した．このとき，シリカの含量が減少するにしたがってカオリンの生成が容易になった．この結果を熱力学的に考察した．

また，バイエライトとアルミナゲルの溶解度の差がオカリンの生成量とよく調和していることから，本実験におけるカオリンの生成は，アルミナ物質の結晶構造の違いよりも，イオン化の程度が違うことによる影響の方が強いように思われる．