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Effects of Dialysis on the Formation of Imogolite from Highly Concentrated Hydroxyaluminum-Silicate Solution

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To examine the effects of dialysis on the formation of imogolite and the stability of imogolite precursor, a highly concentrated Si and Al mixed solution was dialyzed against distilled water for several tens of hours and heated at 98°C after various time durations. Imogolite was synthesized from the solutions dialyzed for 48–108 h, irrespective of the duration, within 6 days after dialysis. For dialysis times of over 120 h, imogolite was not synthesized for the 6 day duration.

Key words: imogolite, hydroxyaluminum-silicate, instantaneous mixing, dialysis, highly concentrated solution

Introduction

Imogolite is a nanotube-like aluminum silicate that exists in natural soil [1]. It has an outer diameter of about 2.0 nm, an inner diameter of about 1.0 nm, and length ranging from several dozen nanometers to a few micrometers [2]. The chemical composition of imogolite includes a Si/Al molar ratio of 0.5. The structural unit of imogolite has a circumference in the range of 10 to 12 gibbsite unit cells, as well as monosilicate anion bonds on the vacant site of gibbsite displacing three OH groups [3].

Because of its unique morphology and structure, imogolite not only has a high specific surface area but also shows excellent adsorption characteristics and a high affinity for water. Therefore, it is expected to be used as a heat exchange material and a desiccant [4]. It has also been studied as an inorganic polymer suitable for the preparation of inorganic-organic polymer hybrids [5] [6]. Imogolite, however, does not exist in abundance naturally; therefore, a method for producing large quantities of imogolite using low-cost inorganic materials needs to be developed.

Imogolite can be synthesized in a short time simply by boiling partially neutralized solutions of monosilicic acid and aluminum salts [2]. The imogolite yield gradually decreases as the concentration of the starting solution increases, probably because coexisting anions, such as chlorides and sulfates seriously hamper the growth of imogolite tubes [7]. Farmer and Fraser synthesized imogolite using tetraethoxysilane and aluminum-s-butoxide solutions having an Al concentration of 60 mmol L^{-1}, without the presence of coexisting ions such as Na and Cl ions [8] [9]. Currently, imogolite is obtained by desalting several times through a centrifugation mixture of sodium orthosilicate and

aluminum chloride solutions, followed by dropwise addition of sodium hydroxide and heating at 100 ℃. Using this procedure, it is possible to synthesize imogolite from the unheated solution with an Al concentration of around 10 mmol L^{-1}.

In the present study, we synthesized imogolite from a concentrated hydroxyaluminum-silicate solution in which the coexisting ions concentration was decreased by dialysis [10]. The Si and Al concentrations of a dialyzed solution were around 25 mmol L^{-1} and 50 mmol L^{-1}, respectively. These are the highest concentrations ever used in inorganic solutions. Imogolite however was not formed when the hydroxyaluminum-silicate solution was subjected to excessive dialysis. This is likely because the precursor of imogolite might be unstable and is dissociated by long dialysis durations in the presence of low coexisting ion concentrations.

To examine the effects of dialysis on the formation of imogolite and aging of dialyzed solutions, we prepared the solutions after 12–144 h dialysis from hydroxyaluminum-silicate solution and heated them under various aging duration conditions.

Experimental

Synthesis

A sodium orthosilicate solution was prepared from reagent grade Na_4SiO_4 in distilled water with a concentration of 0.49 mol L^{-1}. A 1.0 mol L^{-1} aluminum chloride solution was prepared by dissolving special grade $AlCl_3 \cdot 6H_2O$. After verifying the concentrations of the two starting solutions by Inductively Coupled Plasma – Atomic Emission Spectrometry (ICPS-7000; Shimadzu Corp.), the solutions were diluted to 100 mmol L^{-1} (Na_4SiO_4) and 200 mmol L^{-1} ($AlCl_3$) immediately before use. The Na_4SiO_4 solution was fortified with NaOH to obtain OH/Al ratios of 2.40 of the mixed solution. A hydroxyaluminum-silicate solution was synthesized by mixing 500 mL portions of the diluted Na_4SiO_4 and $AlCl_3$ solutions instantaneously in a 1000 mL beaker followed by aging for 90 min with continuous vigorous stirring.

30 mL portions of the hydroxyaluminum-silicate solutions were placed in cellulose tubes (UC36-32-100; Viskase Sales Corp.). These tubes were dialyzed in 2 L distilled water for 12 to 144 h. During dialysis, the distilled water was replaced once every 24 hours. Each dialyzed solution was aged at room temperature (20°C) for 0–6 days. 5 mL portions of each dialyzed solution were then placed in bottles and heated at 98°C for 5 days.

Characterization

The pH of each dialyzed solution was measured (pH/Cond Meter D-54; Horiba Ltd.). Si, Al, Na and Cl concentrations in the dialyzed solutions were determined by ICP-AES (ICPS-7000; Shimadzu Corp.) and ion chromatography (Prominence; Shimadzu Corp.). XRD was carried out on the dried products from these solutions on slide glasses, using a diffractometer (RINT 2000 V; Rigaku Corp.).

Results and discussion

Immediately after mixing the Na_4SiO_4 and $AlCl_3$ solutions, the mixed solution became opalescent, but became clear 40 min after mixing.

Figure 1 presents XRD patterns of the end products prepared by (a) no aging and (b) aging for 6 days. Characteristic peaks of synthetic imogolite were detected at around $2\theta = 4.0°$, 10°, and 14.0°. For 48–108 h dialysis times, imogolite was synthesized from the dialyzed solutions. Although XRD patterns of the end products after 1–5 days aging are omitted here, similar patterns were obtained for these as for no aging and 6 days aging. Aging after 48–108 h dialysis did not affect the synthesis of imogolite within 6 days. For these dialysis times, the imogolite precursor in the dialyzed solutions remained

stable for at least 6 days. However, when the dialysis time was more than 120 h, the three distinctive peaks of imogolite became weaker, and the intensity of one characteristic peak of boehmite at $2\theta = 14.5°$ grew increasingly. Finally, the three imogolite peaks disappeared, leaving only the boehmite peak. The spectra of the products from the over 120 h dialysis were very different between the no aging and the 6 days aging solutions. This suggests that the stability of the imogolite precursor decreased after 120 h and 132 h dialysis for 6 days aging, probably because the Cl concentration was too low to maintain its stability.

Table I shows the pH, Si, Al, Na and Cl concentrations of each dialyzed solution, and the classification of the heated products from the solution. The crossbar signifies that the products in the solution state were not obtained because the solutions dried up completely during heating. The pH of the dialyzed solution was 5.06–5.72; its Cl concentration was around 5.0–10 mmol L^{-1} when imogolite was synthesized. In a previous study, imogolite was formed at a pH less than 5.0 [2][8][11]. Si and Al mixed solutions, especially with an Al concentration of 2 mmol L^{-1}, were found to synthesize imogolite at a Cl concentration less than 30 mmol L^{-1} [7][12]. Therefore, imogolite can be synthesized from solutions dialyzed for 12–36 h, based on these results. Appropriate pH values and Cl concentrations at which imogolite can be synthesized in this study differed from those described in previous reports. Future studies need be undertaken to identify factors or mechanisms related to imogolite synthesis conditions, including pH, coexisting ions and Al concentration in the precursor dispersion solution.

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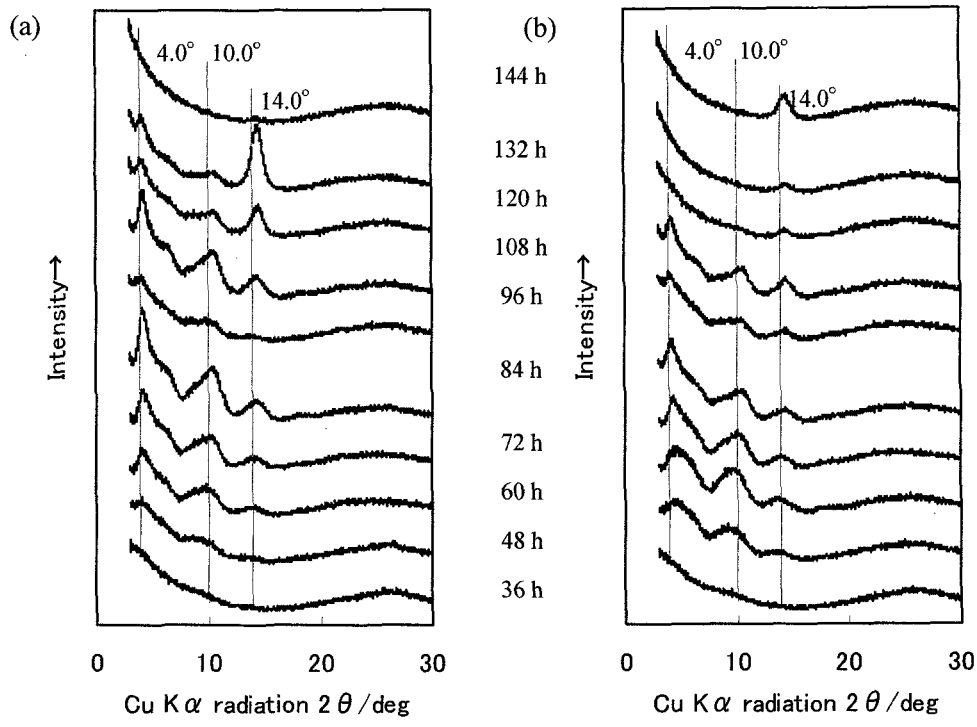

Fig. 1 XRD patterns of the heat treated products. The dialyzed solutions were prepared by (a) no aging and 6 days aging before heat treatment. The legend at the center shows the dialysis time for each pattern.

Table I Relationship between the dialysis time (D.T.) and products, pH, Si, Al, Na, Cl concentrations of the dialyzed solutions. A, amorphous; I, imogolite; B, boehmite

D.T. (h)	Aging Time (day) 0	1	2	3	4	5	6	pH	Si (mmol L^{-1})	Al (mmol L^{-1})	Na (mmol L^{-1})	Cl (mmol L^{-1})
0	A	A	A	A	A	A	A	3.55	50.0	100.0	211	300
12	A	A	A	A	A	A	-	4.18	37.9	65.6	2.60	21.31
24	A	A	A	A	A	A	-	4.39	35.3	61.2	2.70	19.85
36	A and I	A and I	A and I	A and I	A and I	-	A	4.80	29.8	53.5	0.35	11.89
48	I	I	I	I	I	-	I	5.06	26.9	48.2	0.29	9.84
60	I	-	I	I	I	I	I	5.18	27.2	50.0	0.23	8.42
72	I	I	I	I	-	I	I	5.41	26.5	48.9	0.22	7.01
84	I	I	I	-	I	I	I	5.46	26.9	50.0	0.22	5.72
96	I	I	I	-	I	I	I	5.49	27.3	51.4	0.30	5.64
108	I	I	-	I	I	I	I	5.72	28.3	53.2	0.18	4.94
120	I and B	I and B	-	I	I	I and B	A and B	5.95	25.7	48.8	0.20	4.08
132	I and B	-	I	A	I and B	I and B	A and B	6.12	27.2	52.8	0.11	3.96
144	A and B	-	A and B	A	A and B	A and B	A and B	6.37	27.5	53.4	0.29	3.91

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