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Heat–Induced Gelation of Hydroxy–Aluminosilicate Synthesized by Instantaneous Mixing of Sodium Silicate and Aluminum Chloride

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Imogolite is expected to be used as various industrial materials, but its mass production is needed before application. Imogolite is synthesized by heating solutions containing hydroxy–aluminosilicate (HAS) ions. It is possible to prepare fairly concentrated solutions of HAS ions. But heating the concentrated solution does not lead to the successful formation of imogolie. We prepared HAS solution containing 0.1 mol L^{-1} Al and heated it in erlenmeyer flasks with and without cover. Heating without cover induced heterogeneous cooling of the solution from the surface by the droplets of condensed water. Under this condition, HAS spontaneously coagulated to form transparent brittle gel, whereas the solution heated with cover became turbid uniformly. X–ray diffraction and infrared spectroscopy showed that the structure of the products were basically similar to that of allophane and imogolite. There was little structural difference between the products from different heating condition. The products were morphologically different from allophane and imogolite. Extremely small specific surface area of the products, 0.8 to 1.4 m^2 g^{-1}, suggested that the products were aggregates of HAS with strong inter particle bonding.

INTRODUCTION

Imogolite is a unique aluminum silicate having hollow tubular morphology (Wada, 1989). The structural unit of imogolite has a circumference of 12 gibbsite unit cells, with gibbsite *b* along the circumference and gibbsite *a* parallel to the tube axis. Each monosilicate anion attaches on the vacant site of gibbsite displacing three OH groups. The remaining Si–O points away from the sheet to form an Si–OH group (Cradwick *et al.*, 1972). Allophane is also an aluminum silicate mineral that is usually associated with imogolite in soils derived from volcanic eruptives (Wada, 1989). Although its structure has not been elucidated, basic structure, particularly the configuration of silicate anion, is common to that in imogolite.

Recently imogolite is gaining increasing interest from materials scientists as an inorganic polymer suitable for preparation of inorganic–organic polymer hybrids (Yamamoto *et al.*, 2004, 2005) and liquid crystals (Davidson *et al.*, 1997). Allophane and imogolite can be synthesized in a short time simply by boiling neutralized and partially neutralized solutions of monosilicic acid and aluminum salts, respectively (Farmer *et al.*, 1977; Wada and Wada, 1979). Wada and Wada (1980) showed that ionic compounds made up of monosilicate and polymerized hydroxyl aluminum ion form when solutions containing monosilicic acid and aluminum ion are partially neutralized. The compounds, which are termed hydroxy–aluminosilicate (HAS) ions, have been believed to be the precursor of imogolite.

Due to the interference from co–existing anions, however, increasing concentration of the starting solution for synthesis leads to serious decrease in imogolite yield (Farmer and Fraser, 1979; Wada and Sakimura, 2000). Another problem in imogolite synthesis is that monosilicic acid solutions having concentrations higher than 2 mmol L^{-1} are not stable and tend to form polysilicic acid. Farmer and Fraser (1979) solved the problem partly by using organic silicon and aluminum compounds for the preparation of HAS ions. They could successfully synthesized imogolite using tetraethoxysilan and aluminum–s–butoxide solutions having an Al concentration of 60 mmol L^{-1}. Ohashi *et al.* (2002) found that concentrated HAS solutions can be obtained by instantaneously mixing solutions of sodium orthosilicate and aluminum salts. They successfully obtained allophane from starting solutions containing 0.1 mol L^{-1} Al. Kondo *et al.* (2003) prepared HAS solutions containing up to 0.1 mol L^{-1} Al and heated them at boiling point. Probably due to the high concentration of co–existing NaCl, detectable amount of imogolite did not formed.

In the course of a series of synthetic experiments following the procedure described by Kondo *et al.* (2003), we found that HAS in solutions prepared by the instantaneous mixing method spontaneously coagulate on heating to form soft, brittle and transparent gel. Chemical analysis of the solutions and the gel showed that more than 90% of Si and 80% of Al were incorporated into gel and the gel could be separated from the solutions simply by sieving. In the present study, the conditions for the gel formation and the composition and structure of the gel material were explored by combination of X–ray diffraction (XRD), Fourier transform

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infrared spectroscopy (FTIR), electron microscopy (EM), water vapor and nitrogen adsorption.

MATERIALS AND METHODS

A stock sodium orthosilicate solution was prepared by dissolving reagent grade Na_4SiO_4 in deionized water. Stock aluminum chloride solution was prepared from special grade $AlCl_3 \cdot 6H_2O$. The solutions were diluted to 100 mmol L^{-1} (Na_4SiO_4) and 200 mmol L^{-1} ($AlCl_3$) just before use. To give OH/Al ratios of 2.40 of the mixed solution, the working Na_4SiO_4 solution was fortified with NaOH. HAS solutions were synthesized by mixing 500 mL portions of the diluted Na_4SiO_4 and $AlCl_3$ solutions instantaneously in 1000 mL beaker followed by aging for 90 minutes with continued vigorous stirring.

One hundred and fifty mL portions of the prepared solutions in 250 mL erlenmeyer flasks were heated with reflux condensers on an electric plate heater at 100 °C for 144 h with and without wrapping with aluminum foil. The wrapped solutions were homogenously heated. In the unwrapped solutions, on the other hand, the solution temperature at the surface of the solution was lower than that at the bottom. To examine the effect of aging time, the solutions were equilibrated for 0 h, 1 day, 5 and 10 days before heating.

Products formed by heating were separated from leachate by filtration using a plastic net with an opening of 0.15 mm or filtration with 0.45 μm membrane–filters under suction. The volume of the leachate was measured and Si contents were determined by colorimetry (Jackson, 1973). The Al concentration was determined by 8–hydroxyquinolinolate extraction method (Bloom *et al.*, 1978). These collected products were placed in a dialysis tubes (Seamless cellulose tubing UC36–32–100 from Viskase Sales co.) and dialyzed against deionized water to remove NaCl and unreacted H_4SiO_4 for 3 days and freeze–dried. The dried products were characterized by XRD and FTIR. The XRD was carried out on dried products packed in glass holders with Rigaku RINT 2000 V diffractometer. The FTIR spectra were recorded by KBr methods on pressurized KBr discs containing 2 mg of samples per 500 mg of KBr with Jasco FT/IR–460PLUS spectrophotometer. Small portion of the products were re–dispersed in deionized water and examined in a transmission electron microscope (Jeol Co., JEM 200CX). Water and nitrogen adsorptions were determined by a vapor adsorption apparatus (Bel Japan, Belsorp 18) and a nitrogen adsorption apparatus (Carlo Elba Instruments, Sorptmatic 1900).

RESULTS AND DISCUSSION

Immediately after mixing the $AlCl_3$ and Na_4SiO_4 solutions, the combined solution became opalescent but it cleared shortly. Upon heating the solutions in erlenmeyer flasks without cover, the solutions became slightly opalescent again and transparent gelatinous film developed on the surface of the solutions after 36 h. The film developed with time, several pieces of gel fall on the bottom of the flasks after about 48 h, and the amount of the gel on the bottom increased afterwards. The settled gel flakes were more brittle than gelatinous films of natural imogolite (Miyauchi and Aomine, 1966). Fig. 1 shows a photograph of the solution in an erlenmeyer flask after about 50 h heating on an electric hot plate without cover, where transparent gelatinous material floating on the solution surface can clearly be seen. The aging time before heating had no effect on the mode of formation of the gelatinous film. In flasks with aluminum foil cover, the solutions became slightly opalescent and small gelatinous films also formed on the surface of the solutions in 36 h. After that, however, the gelatinous films on the solution surface did not spread and merged into solution. After 48 h, the whole solution became strongly turbid with fluffy precipitates settled on the bottom of the flasks.

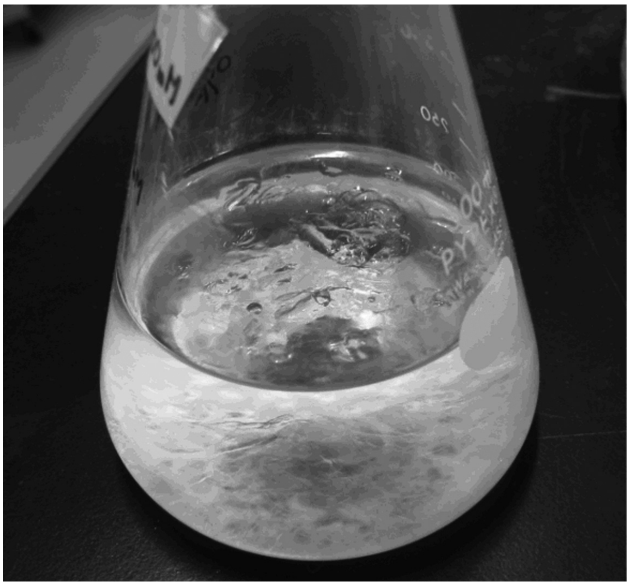

Fig. 1. Heating the instantaneously mixed solution in Erlenmeyer flask without cover yielded transparent gelatinous material floating on the solution surface.

The observation of the flasks during heating showed that many water droplets formed on interior wall of the uncovered flasks and they flew down onto the solution surface. It was noticed that the gelatinous film started to grow from the periphery of the solution surface. This suggests that the cooling of the solution by the condensed water triggered the gel formation. No condensation of water was noticed in the erlenmeyer flasks covered with aluminum foil.

The pH of the instantaneously mixed solution was 3.56 before heating and the aging at a room temperature for up to 10 days had little effect on the pH. The pH of the solutions after heating increased slightly and ranged from 3.80 to 3.90, indication no net proton release took place during heating. Wada *et al.* (1979) reported that the pH decreased significantly when imogolite formed and increased when allophane formed. The present results on solution pH suggest that imogolite is not likely to have formed in the solutions.

The amounts of Si and Al incorporated in the gel were calculated by subtracting their concentrations in

Table 1. Percentages of Si and Al found in the gel and Si/Al molar ratio of gel

Aging time/d	Uncovered			Covered with Al foil		
	% Si in gel	% Al in gel	Si/Al ratio	% Si in gel	% Al in gel	Si/Al ratio
0	94.7	84.0	0.564	97.6	88.4	0.552
1	96.4	86.1	0.560	98.6	89.9	0.548
5	93.1	83.0	0.561	98.6	88.9	0.555
10	97.1	85.8	0.556	98.6	87.7	0.562

the filtrates from the total Si and Al concentrations in the starting solution. The percentages of Si and Al found in the gel as well as the Si/Al molar ratio of the gel materials are listed in Table 1. Table 1 shows that 93–98% of Si and 83–90% of Al were incorporated in the gels and the Si/Al ratio of the gels materials are in a range from 0.55 to 0.56. The recovery of Al was significantly lower for gels formed in flasks without cover. The Si/Al molar ratios of natural imogolite specimen is in a range form 0.525 to 0.575 (Wada, 1989) and the Si/Al molar ratio for the proposed structural model is 0.5. The calculated Si/Al molar ratios of the present gel materials are within the range of natural imogolite samples. There was no noticeable relationship among the aging time, Si and Al recovery and the Si/Al ratios of the gel materials.

Wada and Wada (1980) showed that the degree of hydrolytic polymerization of Al ions is solely determined by the OH/Al molar ratio and the presence of Si does not affect the degree. In the present experiment the OH/Al molar ratio of the starting solution was set to 2.40. This value and the 'calibration curve' proposed by Wada and Wada (1980) give the estimate of the polymerized Al percentage of 81%. The percentages if Al incorporated in the gel materials, i. e. polymerized Al, are a little higher than the estimate, particularly for solutions heated with cover. The hydrolytic polymerization reaction of Al accompanies net proton release. It is puzzling that the solution pH did not decrease during heating.

Fig. 2 shows XRD patterns of the reaction products from instantaneously mixed solutions after heating. The eight diffraction patterns shown in Fig. 2 resembled each other. They showed broad diffraction band centered at about 0.34 and 0.22 nm. These peaks were a little sharper than those of natural allophone (Wada, 1989). In addition to these broad bands, they exhibited weak peaks at 2.2 and 1.2 nm. Although these diffraction peaks at low angles suggest the presence of imogolite, no imogolite was detected by electron microscopy (photos are not shown).

The FTIR spectra of the dried products are shown in Fig. 3. The FTIR spectra of all products showed broad and strong bands centered at 965 and 430 cm^{-1}, which are characteristic to allophane (Wada and Wada, 1979; Wada, 1989). Bands centered at 570 cm^{-1} are much broader than those of allophane and imogolite. All of the products exhibited a shoulder at 1200 cm^{-1}, which is not seen in the spectra of allophane and imogolite. The absorption bands in a region ranging from 500 to 700 cm^{-1} and that from 1000 to 1200 cm^{-1} were broader than those of allophane and imogolite.

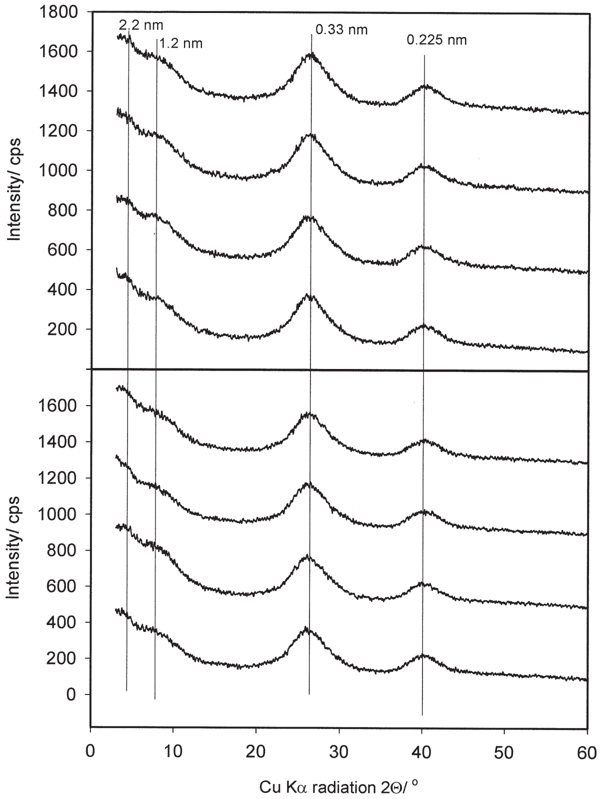

Fig. 2. XRD patterns of the reaction products formed by heating with (below) and without (above) cover. Aging time of solution was 0, 1, 5, 10 days in each group (from top to bottom).

Figs. 2 and 3 show that the eight products obtained in the present synthetic experiment resembled each other in terms of XRD and FTIR. The aging time before heating and the mode of heating, i. e. with or without cover, had little effect on the structure of the reaction products. The difference in the appearance of the reaction products is probably due simply to the difference in the mode of association of 'unit' particles.

The water vapor adsorption isotherms are shown in Fig. 4. Since there were only small differences among the samples, the isotherms for the products heated after 10 days of aging with and without cover are shown. The slope of the isotherms for adsorption process was high at a relative humidity (RH) range of 0 to 15% and much lower at RH >20%. The water adsorption was about 14% for all of the samples, which is a little lower than

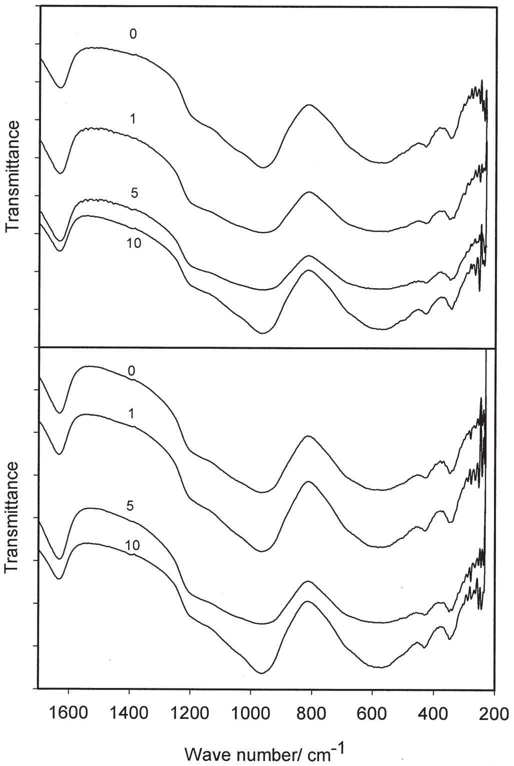

Fig. 3. Infrared spectra of the dried products formed by heating with (below) and without (above) cover.

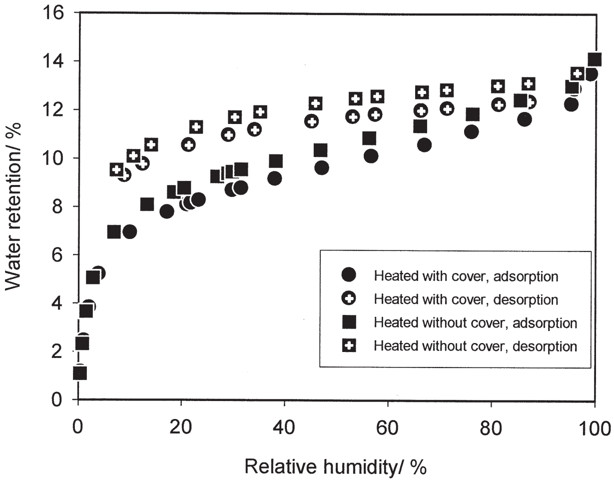

Fig. 4. Water vapor adsorption isotherms of the products heated after 10 days of aging with and without cover.

natural allophane and much lower than natural imogolite and synthetic allophanes (Ohashi *et al.*, 2002). The hysterisis of the isotherms indicate that the adsorption and desorption processes are not completely reversible. The observed irreversibility is similar to natural and synthetic allophane and imogolite.

The specific surface area based on the N_2 adsorption data was 0.83 m^2 g^{-1} for the product heated without aging without cover, 1.40 m^2 g^{-1} for that heated without aging with cover, 0.86 m^2 g^{-1} for that heated after 10 days of aging without cover, and 1.36 m^2 g^{-1} for that heated after 10 days of aging with cover. These values shows that the surface area is surprisingly small and the products recovered as a transparent gel have even smaller specific surface area. The specific surface area of natural and synthetic allophane reported by Ohashi *et al.* (2002) ranged from 265 to 552 m^2 g^{-1}.

Electron microscopic examination of the samples that were dispersed in water by ultrasonic treatment showed that the product contained circular or semicircular particles having diameters of about 0.1 to 1 μm. The examination at higher magnification suggested that the particles consisted of finer particles but it was difficult to define the detailed morphology of the 'unit' particles.

The results from XRD and FTIR indicate that the structure of the present synthetic products is basically similar to that of allophane and imogolite. The water adsorption characteristics of the products were not very much different from that of natural allophane. Striking difference was in their specific surface area. The extremely small specific surface area suggests that HAS coagulated during heating to form larger particles with strong inter particle bonding. The mode of heating affected the macroscopic morphology of the aggregates.

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