Synthetic allophane from high-concentration solutions: nanoengineering of the porous solid

F. OHASHI[1],*, S.-I. WADA[2], M. SUZUKI[3], M. MAEDA[1] AND S. TOMURA[1]

[1]*Ceramics Research Institute, AIST Chubu, Shimo-Shidami, Moriyama, Nagoya 463-8560,* [2]*Agricultural Department, Kyushu University, 6-10-1 Higashi, Hakozaki, Fukuoka 812-8581, and* [3]*Research Center for Deep Geological Environments, AIST Tsukuba, 1-1-1, Higashi, Tsukuba 305-8567, Japan*

ABSTRACT: The amorphous aluminosilicate allophane was synthesized by rapid mixing of inorganic solutions with high initial concentrations ($10-100$ mmol/l) followed by hydrothermal treatment. X-ray diffraction (XRD) and transmission electron microscopy (TEM) revealed homogeneous products having a hollow spherical amorphous structure with a particle diameter of $3-5$ nm. The amorphous products had a high BET specific surface area ($490-552$ m^2/g) in comparison with natural allophane and had a narrow pore-size distribution ($2-5$ nm in diameter). The results of water vapour adsorption isotherm studies showed a gradual increase over the range of relative water vapour pressure of $0.6-0.9$ and reached a maximum of ~85 wt.%. The synthetic allophane shows promise as an adsorbent material because of its high adsorption-desorption capacity and its unique structure.

Allophane, which exists naturally, is an aluminosilicate hydrate produced by weathering, e.g. of pozzuolanas on the Earth's surface, and the chemical composition gives an Si/Al ratio typically of $0.5-1.0$ (Henmi *et al*., 1976). The aluminosilicate hydrate comprises hollow spherical particles with diameters of 3.5 to 5 nm (determined by TEM), and the walls of the particles are thought to consist of two sheets: an octahedral Al sheet and a tetrahedral Si sheet with accessible open pores 0.35 nm in diameter (Wada & Wada, 1977; Wilson *et al*., 1986). For allophane, both XRD and electron diffraction data indicate no repeat of structural units in any of the three dimensional space. Therefore non-crystalline is more appropriate than short-range order in the definition of allophane (Van der Gaast

et al., 1985). Since the term short-range order has been used for a wide range of crystallinity, it would be confusing to use the term in the definition of allophane (Wada, 1989). Allophane is a cluster material which is produced naturally. It is important in that it exerts considerable control on the physical and chemical characteristics of soil. Because of the particle shape and the resultant high degree of surface activity, gas and liquid can be adsorbed easily onto the particle, both inside and out. The adsorption capacity is also increased by the hydroxyl groups that exist on the surface (Clark & McBride, 1984). Therefore, there is a wide range of uses in industry, e.g. as a catalyst carrier, as a deodorizer, as a humidity-controlling material, and as a CO_2 separation membrane. However, because it has a non-crystalline structure, a complete three-dimensional structural analysis is not possible. The particle size and the composition distribution vary widely because it is produced naturally. The

synthesis of allophane has succeeded only when using a dilute solution of ~2−4 mmol/l (Wada *et al*., 1979, 1988). Such experiments give extremely low yields of allophane and the unexpected formation of boehmite and amorphous silica produced in this method were noted by Wada *et al*. (1979). In general, amorphous silica and aluminium hydroxide precipitated first if the starting solutions were were mixed gradually in low concentrations at near-equilibrium conditions and the pH was not neutralized gradually with the alkaline solution. It was extremely difficult to obtain a high yield of the desired material using the above-mentioned method.

In this research, the authors attempted to synthesize allophane in amounts appropriate for the industrial and environmental uses listed above.

MATERIALS AND METHODS

The experimental procedure is shown in Fig. 1. Four synthetic allophane products were created, firstly by preparing separate Si-source and Al-source solutions of various concentrations. The initial concentrations of 100, 50, 30 and 10 mmol/l of sodium orthosilicate and aluminium chloride hexahydrate, respectively, were prepared. The Si- and Al-source solutions were weighted at the atomic ratio of Si/Al = 0.75 for each initial concentration. Both source solutions were mixed together rapidly and stirred for 1 h at room temperature to synthesize the allophane precursor. Sodium chloride formed as a by-product in the mixed suspension was removed by centrifugation. The white precursors obtained were autoclaved by performing the hydrothermal reaction for 2 days at 100°C. The resulting materials were washed with distilled water repeatedly until they came to neutral pH. Subsequently, washed samples were dried at 40°C in an electric oven. Natural allophane (Ki-P) taken from the Kitakami pumice bed was used as a reference material.

Powder X-ray diffraction measurement was carried out by RINT-2100V/PC diffractometer (Rigaku Corp.) using Ni-filtered Cu-*K*α radiation at 30 mA and 40 kV. The morphology of the products was examined using a transmission electron microscope with an accelerating voltage of 100 kV (JEM-200CX, JEOL Ltd.). The Si and Al contents in the products were determined by X-ray fluorescence (XRF) analysis using a MESA-500 device (Horiba Ltd). Fourier transform infrared (FTIR) spectra were obtained from KBr discs incorporating air-dried samples using a Perkin-Elmer FTIR Spectrum 2000 spectrometer. The Brunauer-Emmett-Teller (BET) surface area of the products was determined by means of nitrogen adsorption at liquid nitrogen temperature ($T = -195°C$). Pore-size distribution was measured by the Cranston-Inkley method using a nitrogen adsorption isotherm (Carlo Erba Instruments Co., Sorptomatic-1900). The isotherm of water vapour adsorption was determined using an adsorption isotherm analyser (Tokyo Shikenki Manufacturing Co., EAM-01S) using ~0.3 g of product, which had been under vacuum at 25°C for 1 day. After complete evacuation, the relative humidity in the chamber was gradually increased from 10 to 90%. During this process, the increase in the sample weights represented the amount of water vapour adsorbed.

$$Na_4SiO_4 + 4H_2O \rightarrow Si(OH)_4 + 4NaOH$$
$$AlCl_3 \rightarrow Al^{3+} + 3Cl^-$$
$$Na_4SiO_4 + 4/3\ AlCl_3 \rightarrow SiO_2 \cdot 4/3\ Al_2O_3 + 4NaCl$$

Sodium orthosilicate Na_4SiO_4 Aluminium chloride $AlCl_3 \cdot 6H_2O$

Initial concentrations of the solutions: 10, 30, 50 and 100 mmol/l

Mixing (Si/Al = 0.75)
Agitation (R.T., 1 h)

Allophane precursor

Desalination (centrifugation)
Hydrothermal reaction (100°C, 48 h)

Synthetic allophane

Measurements
X-ray diffraction, FTIR spectra, TEM, specific surface area, pore-size distribution, water vapour adsorption isotherm
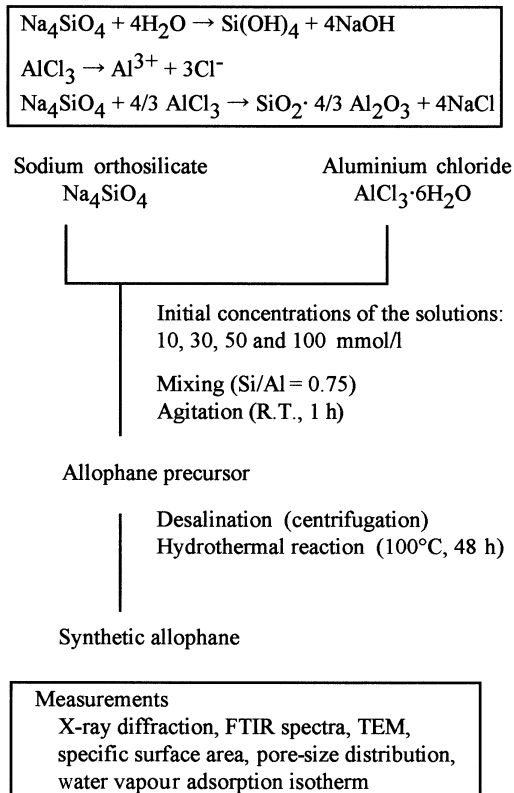
FIG. 1. Experimental procedure of the synthesis method of allophane.

RESULTS AND DISCUSSION

Figure 2 shows the XRD profiles of the synthetic allophanes. The profiles of the synthetic allophanes exhibited broad reflections centred at 0.34 and 0.22 nm, typical of natural allophanes as well as X-ray amorphous aluminosilicates. Amongst these peaks, is one which is specific to spherical hollow particles and which originates in the SiO_4 tetrahedral sheet of allophane, especially the diffraction area of 0.33−0.35 nm. The diffraction peak of the silica gel, which consists of the polymerized SiO_4 tetrahedra, appears nearby at ~0.39 nm. Therefore, the allophane has a different structure from that of silica gel (Henmi, 1987). Moreover, the peak that originated in the aluminium hydroxides (boehmite and gibbsite) was not observed. The TEM images of typical synthetic allophanes are given in Fig. 3. As anticipated, aggregated ring-shaped particles were observed in the synthesized samples and had structures similar to those described for allophanes, which have a hollow spherical structure unit, the external diameter of which is 3−5 nm. In FTIR spectra for the synthetic allophanes, typical absorption bands based on aluminosilicate are clearly observed, i.e. characteristic absorption centred at 3500 cm^{-1} (assigned to structural OH-stretching vibration), at ~900 cm^{-1} (Al or Si−O stretching), and in the region 800−400 cm^{-1} (Si−O−*X* (*X*: Si or Al) stretching) are confirmed in Fig. 4. An absorption band due to the -OH-bending vibration of adsorbed water appeared at 1650 cm^{-1}. Wada *et al.* (1988) noted that natural allophane and imogolite show a distinctive broad absorption centred at 570 cm^{-1} with weak shoulders at 670 and 430 cm^{-1}, suggesting that the wall structure of the synthesized allophanes possess imogolite-type $((OH)Si(OAl_{oct})_3)$ framework structures. Boehmite and gibbsite were recognized, using XRD and FTIR, as co-products by Wada *et al.* (1979) and Tomura *et al.* (1996), but were not observed here, suggesting that allophane was synthesized efficiently from higher-concentration solutions, using this method. The pore-size distribution curves of the natural and synthetic allophanes calculated by the Cranston-Inkley method, are shown in Fig. 5. The synthetic specimens exhibited relatively narrow
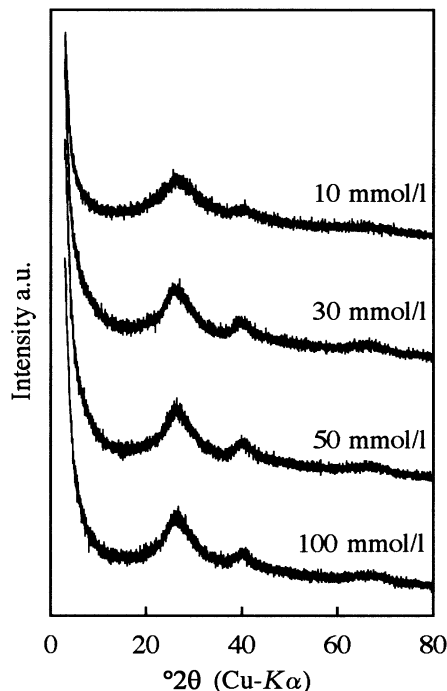

FIG. 2. XRD profiles of the synthetic allophanes from solutions with various initial concentrations.
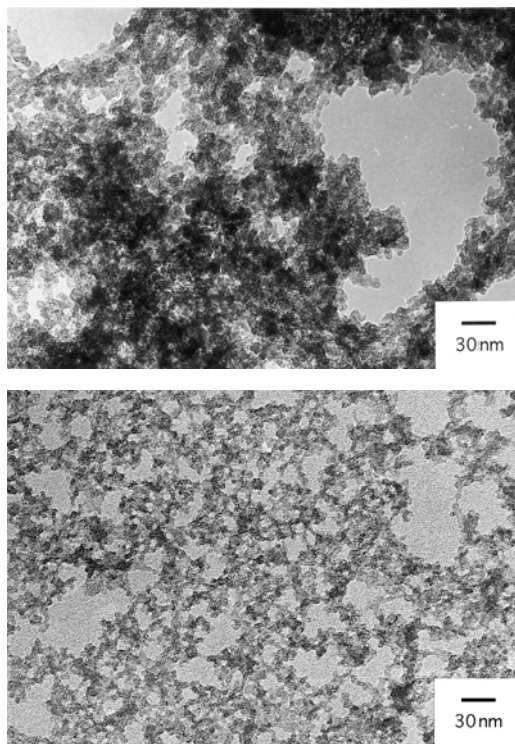

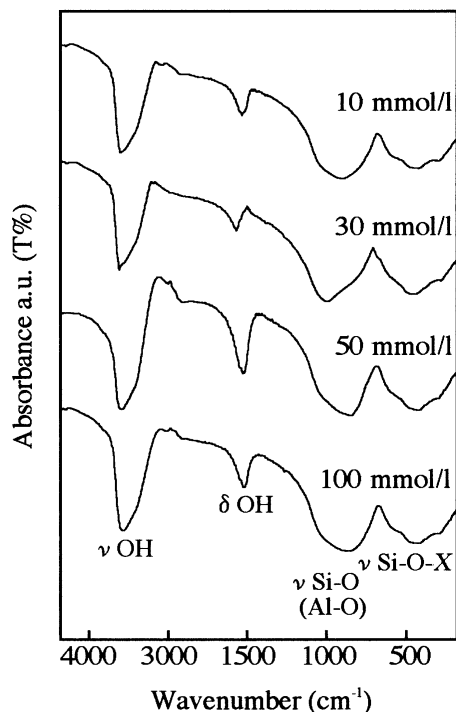FIG. 3. Typical TEM images of synthetic allophane (initial concentration 10 mmol/l).

FIG. 4. FTIR spectra of the synthetic allophanes from solutions with various initial concentrations.

FIG. 5. Pore-size distribution curves of the synthetic allophanes and the reference materials (C.I. method).

distribution curves. The synthetic allophanes have a much larger peak centred at 4 nm, which results from a much larger fraction of microporosity compared to the natural allophane. The differential pore volume within the pore diameter range of $10-30$ nm increased as the initial concentration was increased. Though the nitrogen isotherm is not shown here, the adsorption isotherm of the synthetic allophane showed type I behaviour with an H2 hysteresis loop. This indicates the presence of micropores; the pore diameter was ~0.4 nm. This value corresponds to the size of the accessible open pores in the allophane spherical wall. These results suggest that the pore distribution of such homogeneous porous materials can be controlled and adjusted using the initial reaction concentrations. The Si/Al ratio analysed by XRF, the specific surface area (BET method), the pore volume and the average pore diameter (C.I. method) of the synthesized samples and the references are listed in Table 1. All quantities tended to increase with increasing initial concentration of the starting solution. These remarkably large values of specific surface area and total pore volume are greater than
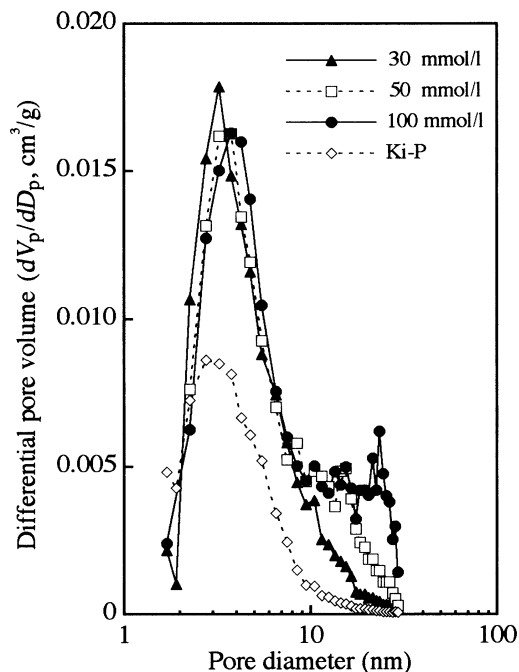
those of natural allophane (265 m^2/g, 0.15 cm^3/g). The specific surface area ranged from 490 to 552 m^2/g. The combination of having a high surface area and a relatively narrow pore-size distribution, indicates that most of the surface area is probably attributable to the uniform arrangement of the internal surfaces. The average pore diameters also increase with initial concentration. The reason is the change in the aggregation of the allophane particles. We suggest that the reason for the increasing Si/Al ratio is that 3-D networks were developed between the allophane particles, and that synthetic allophane may have excellent adsorption capacity as a consequence. The water vapour adsorption isotherms are shown in Fig. 6. The synthetic products exhibited quite distinct adsorption-desorption curves which have an inflection characteristic of capillary condensation within opened pores. The adsorption isotherms of the synthetic allophanes showed an isothermal line with a narrow hysteresis loop. Water molecules were adsorbed in type IV isotherms. The small hysteresis observed in those isotherms would be attributed to the capillary condensation phenomenon, because the water contact angles at adsorption and

TABLE 1. Characteristic data of natural and synthetic allophanes from various initial concentrations.

Specimen (initial conc.)	Specific surface area (m^2/g)*	Pore specific volume (cm^3/g)**	Average pore diameter (nm)**	Elemental Si/Al ratio
Natural allophane				
Ki-P	265	0.15	1.81	0.70
Synthetic allophane				
(30 mmol/l)	490	0.47	2.48	0.82
(50 mmol/l)	504	0.61	3.12	0.92
(100 mmol/l)	552	0.78	3.70	0.94

* BET adsorption method using N_2 gas
** Cranston-Inkley method

desorption were almost the same. The water vapour adsorption isotherm of natural allophane showed an approximately isothermal line where the amount of the absorbed water increased in a straight line with the increase in the relative water vapour pressure: the maximum amount of absorbed water was ~30 wt.%. The results indicated that the sample of initial concentration of 100 mmol/l absorbed water

FIG. 6. Water vapour adsorption isotherms of the synthetic allophanes and the reference material.

rapidly by ~0.8−1.0 relative water vapour pressure and showed the hysteresis loop. The maximum amount of water adsorption achieved was ~85 wt.% when the relative vapour pressure reached 0.95. The total amount of adsorbed water was restricted by the specific surface area and the pore volume. These quantities control the effective surface available for water vapour adsorption. From these results, in order to obtain a large amount of water adsorption and high humidity-control ability, it is necessary to control the pore diameter, the BET surface area and the pore volume. Moreover, the humidity control efficiency is better for the synthesized products than for the reference materials. However, the synthesized materials have an associated hysteresis loop. This phenomenon might be due to the difference between condensation and evaporation of the liquid water meniscus, and/or some of chemically adsorbed water molecules connected to the Si (or Al) atoms as silanol (or aluminol) groups (Iler, 1979). From the above-mentioned results, the synthetic allophane might become a possible intelligent humidity-controlling material. Establishing the method of synthesizing allophane has led to the development of a multipurpose adsorbent.
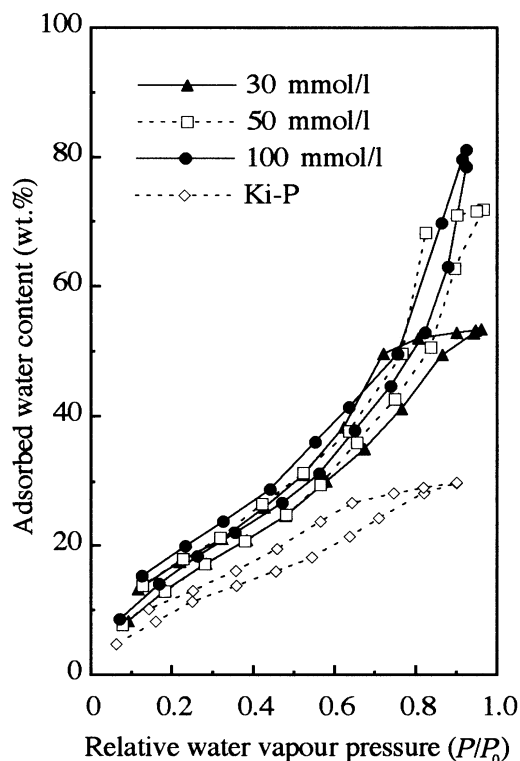
CONCLUSIONS

Allophane was synthesized by a hydrothermal reaction of inorganic solutions with various higher initial concentrations than was previously thought possible. Transmission electron microscopy and FTIR spectroscopy revealed that uniform hollow spherical aluminosilicate clusters were formed after the hydrothermal synthesis. The synthetic allophanes have short-ranged mesostructured architecture in

which the pore diameter was dependent on the initial solution concentrations. The products showed greater maximum water vapour adsorption than did natural allophane, and the isotherm curves increased to 0.6−0.9 of relative water vapour pressure. Some additional properties relevant to practical applications will be examined in the future.

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