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Characterization of synthetic imogolite nanotubes as gas storage

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Imogolite is a naturally occurring hydrated aluminum-silicate polymer that consists of a tubular structural unit having an external diameter of 2.3–2.7 nm and an inner diameter of ca. 1 nm. The tube length is from about 400 nm to several micrometers. The tube walls are composed of curved gibbsite-like sheets with SiOH groups on the inside and AlOH groups on the outside, having a composition $(HO)_3Al_2O_3SiOH$ [1]. Imogolite is common in the clay fraction of soils derived from glassy volcanic ashes or pumice beds, and it has also been found in many podzols [2, 3]. Several investigations concerning natural imogolite have been published [4–6]. A synthetic route for production of imogolite was described in 1977 from dilute solutions of aluminum chloride and monosilicic acid [7]. Crystallization takes place at a lower concentration of the starting solutions and low pH under the boiling point treatment [8]. However, the above common process does not produce a high yield of well-crystallized imogolite tubes. Recently, nanotubes composed of various materials such as carbon, boron nitride, and oxides have been investigated [9–11], in particular, carbon nanotubes, which have great potential as materials with novel properties that are not found in conventional graphite or carbon fullerene [12]. For instance, since the suggestion of highly efficient storage of a natural gas with single walled carbon nanotubes, experimental determinations of the storage capacity and the mechanism of the storage have been performed extensively [13]. In the present work, the authors attempt to improve a synthetic method and to characterize an aluminosilicate mineral forming such hollow tubular structures for the purpose of gas storage.

Imogolite nanotubes were synthesized from a highly concentrated starting solution under hydrothermal conditions. In a typical synthetic procedure, 66.7 ml of Na_4SiO_4 solution (concn. 100 mmol/l) was mixed with the same amount of 150 mmol/l $AlCl_3$ solution, and then 1 mol/l NaOH was added dropwise (1 ml/min) into the above homogeneous solution under stirring until $pH > 6$. After the desalinization process, the precursor suspension was adjusted to $pH < 4$ using 5 mol/l HCl under stirring. The reaction mixture was autoclaved for 2 days at 100 °C, during which period the solution gradually cleared. After the solution was cooled, ca. 25 wt% of NH_4OH solution was added for flocculation until the pH value >8. Stiff transparent gels were collected by centrifugation. The resulting gel was dried at 100 °C for 24 h. The synthesized product and natural imogolite were analyzed by X-ray diffraction, N_2-adsorption, field emission-scanning electron microscopy (FE-SEM) observation, and ^{27}Al and ^{29}Si magic angle spinning (MAS) nuclear magnetic resonance (NMR) performed on Bruker MSL400 and ASX400, respectively, at room temperature (104.26 MHz for ^{27}Al and 79.49 MHz for ^{29}Si). The adsorption of methane was measured using a steel cell, and the pressure was monitored at 21 °C up to 8 MPa. The adsorbed amount was calculated by weighing the cell on a sensitive electronic balance. Before the adsorption measurement, the sample was degassed under vacuum at 125 °C for 3 h. The adsorption isotherm of water vapor was determined using a BELSORP-18 (Bel Japan, Inc.) at 25 °C. Natural imogolite separated from a Kitakami pumice bed was used as a reference material, named Ki-G.

The X-ray diffraction profiles of the synthetic and natural imogolites are shown in Fig. 1. The synthetic imogolite showed sharper characteristic diffraction peaks at $d = 2.00$, 0.90, 0.63 and 0.39 nm, which can be assigned to (010), (020), (030) and (032), respectively, for the cylindrical structure [8]. This profile is similar to that obtained for the natural imogolite, showing a narrow (010) reflection peak at a d value of about 2.0 nm. This value is larger than that of the natural imogolite (1.78 nm). It means that the synthetic tubes had greater diameters, i.e., longer distances between the centers of neighboring cylinders. These X-ray diffraction results indicated formation of a mesostructured well-crystallized synthetic imogolite

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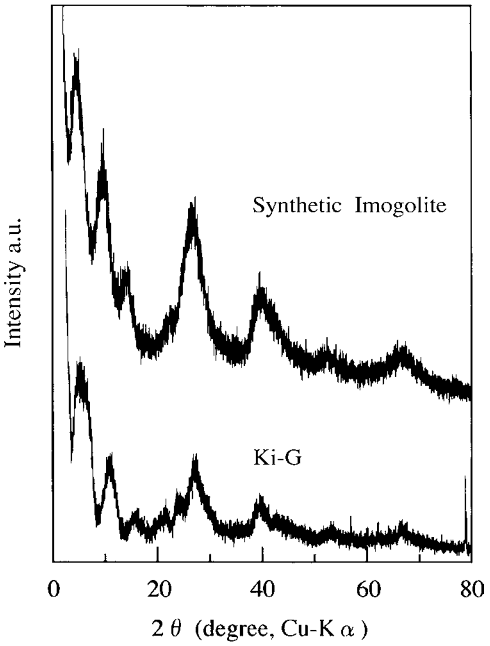

Figure 1 X-ray diffraction profiles of the natural and synthetic imogolites.

with higher mesoporosity. Fig. 2 shows that FE-SEM observation revealed the form of imogolite to be fibrous tube bundles, each containing many individual imogolite tubes (with ca. 2.5 nm outer diameters). The threads were curled and entangled forming web-like structures. This bundle was observed also in electron micrographs of natural imogolite. The pore-size distribution curves of the synthetic and natural imogolites were calculated by the Horvath-Kawazoe method [14] and are shown in Fig. 3. These specimens exhibited fairly narrow distribution curves. The nitrogen adsorption isotherm of the synthetic imogolite showed type I behavior, indicating a presence of micropores; the pore radius was ca. 0.4 nm. In contrast, the isotherms of the natural imogolite showed type IV behavior with an average pore radius of 0.55 nm. The synthetic imogolite has a much larger peak at 0.35 nm, which results from a much larger fraction of microporosity as compared to the natural sample. This sharp peak, observed at 0.35 nm, corresponds to the fine imogolite tubular structure. The specific (Brunauer-Emmett-Teller) surface areas were 297 and 222 m^2/g for the natural and synthetic imogolites, respectively. The ^{29}Si MAS NMR spectra for both samples exhibited sharp peaks centered at −79 ppm from tetramethylsilane. This ^{29}Si chemical shift is typical for the imogolite structures and originates from Si in a Q^0 site bonded to one OH group [15]. As other peaks were not detected, the chemical shift strongly suggested that the SiO_4 units were surrounded by mainly Al atoms. The ^{27}Al MAS NMR spectra of the synthetic and natural imogolites exhibited isotropic peaks centered at −4 ppm and 58 ppm with spinning sidebands on both sides, which indicated mainly the presence of octahedrally coordinated Al (VI) and a slight presence of tetrahedrally coordinated Al (IV). From these results, in imogolite, each Si is attached through oxygen to six octahedral Al atoms, and each Al is attached through oxygen to three Si atoms. The electronic environment of imogolite Si is due to the presence of four adjacent oxygens, one attached to hydrogen and the other three attached only to octahedral Al, i.e., $Si(OAl(VI))_3OH$. Adsorption isotherms of methane on the natural and synthetic imogolites were measured at 21 °C and pressures up to 8 MPa. The adsorption isotherm is the Langmurian type, indicating that methane adsorption is monolayer adsorption. The total methane storage capacity of the natural imogolite reached 42.5 mg/ml at 4.09 MPa. In the case of the synthetic imogolite it was 50.6 mg/ml at 4.05 MPa, higher than that of the usual compressed natural gas storage

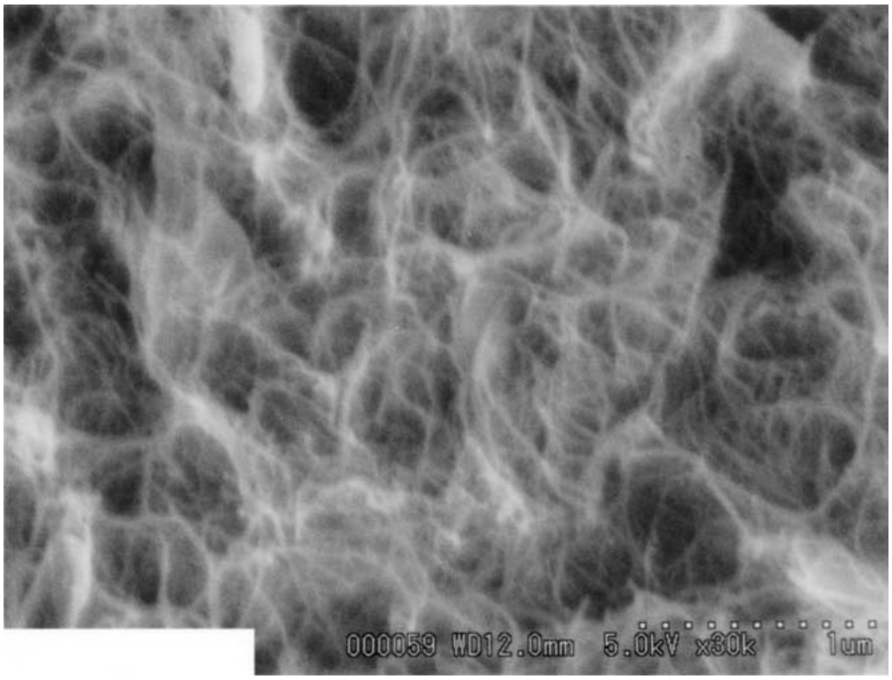

Figure 2 FE-SEM image of the synthetic imogolite.

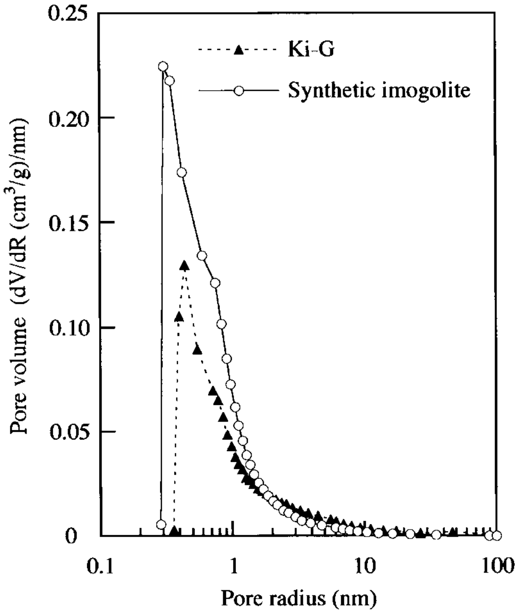

Figure 3 Pore size distribution curves of the natural and synthetic imogolites.

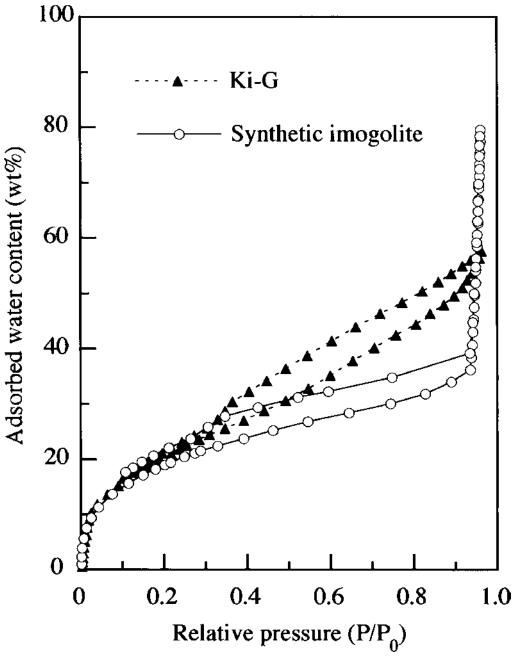

Figure 4 Water vapor adsorption isotherms of the natural and synthetic imogolites.

(28 mg/ml at 4.0 MPa). Fig. 4 illustrates the adsorption isotherms of water vapor. The natural imogolite showed an approximately isothermal line where the amount of adsorbed water increased in proportion to P/P_0: the maximum amount of adsorbed water was ca. 60 wt%. The synthetic imogolite showed a rapid increase over the range of P/P_0 of 0.9–0.95 and achieved a maximum of ca. 80 wt%. In order to obtain a large amount of water adsorption and a high methane storage capacity, it is necessary to control the *micro*/*meso* porous structure and the hydrophilic/hydrophobic surface affinity. A study on the surface modification of these aluminumsilicate nanotubes is now in progress. The synthetic imogolite might become a multipurpose adsorbent. Moreover, the high methane storage capacity of the synthetic imogolite is expected to considerably improve the adsorbed natural gas technology.

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