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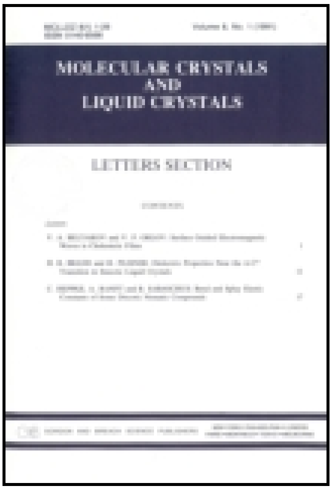

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Strain Energy and Structural Property of Methyl Substituted Imogolite

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Aluminosilicate mineral, imogolite, with chemical composition [$(OH)_3Al_2O_3SiOH$] has high monodispersity of diameter originated by the arrangements of inner hydroxyl (OH) groups that induced the strain energy minimum due to hydrogen bond networks. We have successfully synthesized substituted imogolite with methyl groups (Me-imo) instead of inner hydroxyl groups. While imogolite prefers zigzag chirality, Me-imo prefers armchair chirality which was confirmed by the simulation and the x-ray diffraction (XRD) pattern. Me-imo has larger specific surface area and less hydrogen bond contribution than that of imogolite, which was confirmed by the Barrett-Joyner-Halenda (BJH) pore size distribution.

Keywords Imogolite; methyl imogolite; hydrogen bonding; chirality

Introduction

Nanotubes have been increasingly investigated as building blocks due to their potential applications in nanofluidic devices, [1–4] electronics, photonics, chemical separation, photo catalysis and biotechnology [5–9]. Imogolite, aluminosilicate nanotubes, is a naturally occurring hydrous aluminosilicate found in soils of volcanic origin with a net composition $(HO)_3Al_2O_3SiOH$. Recently, the direct synthesis method of imogolite containing covalently attached organic groups has been reported by Bottero et al. [10] who successfully synthesized imoglite-like material with the inner surface completely lined by methyl groups substituting for the hydroxyl species (Me-imo). Although there are methyl groups instead of hydroxyl groups on the inner surface, meaning of the absence hydrogen bond network, Me-imo has perfectly tubular structure. Therefore, in this work, we have systematically analyzed the substitution and the tubular structure formation. To support the systematical analysis with experimental data, Me-imo is synthesized and confirmed with powder X-ray diffraction (XRD), and pore size distribution with Barrett-Joyner-Halenda (BJH) plot.

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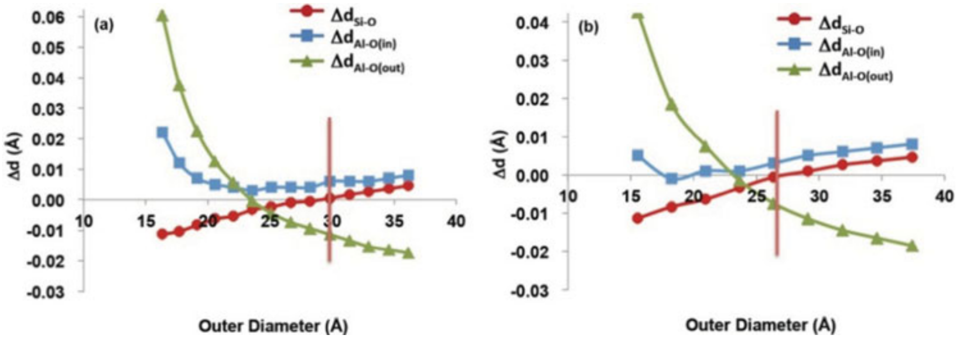

Figure 1. The variations of outer, $\Delta d_{Al-O(out)}$, and inner Al—O, $\Delta d_{Al-O(in)}$, and Si—O, Δd_{Si-O}, bond distances compared to outer diameter of Me-imo (a) zigzag and (b) armchair.

Preparation of Methyl-imogolite (Me-imo)

According to Bottero method, [10] Al(s-butoxide)$_3$ and triethoxymethylsilane (TEMS) are added to the 75 mM aqueous solution of $HClO_4$, the molar ratios Si:Al:$HClO_4$ = 1:2:1. The solution is stirred for 18 h, diluted to 20 mM in Al, refluxed at 100°C for 4 days, dialyzed for 4 days against de-ionized water, and then impurities in the solution is removed with centrifugation. The final product is obtained after freeze drying.

The Simulation Results of Imogolite and Me-imo

Imogolite is a single-walled nanotube that consists of a curved layer of aluminum (III) hydroxide ($Al(OH)_3$) on the outer wall with silanol ($(SiO_3)OH$) groups substituted on the inner wall. In the case of Me-imo, however, the hydroxide groups are substituted by methyl groups on the inner wall. Me-imo has larger diameter (26.38Å, imogolite = 16.99Å) due to the substitution of methyl groups. There are two kinds of factors to make imogolite tubular structure. One is the arrangements of inner hydroxyl (OH) groups that make hydrogen bond (HB) networks. Another is the variations of inner and outer Al—O and Si—O bond distances. We have reported that the HB networks is the origin of the strain energy minimum (i.e., highly monodispersed in diameter) and the preference for zigzag chirality, even though the relaxation of inner and outer Al—O bonds and Si—O bond distances is the driving force for the tubular imogolite formation. [11] However, Me-imo having inner methyl groups is only affected by the second factor which has no HB contribution. Figure 1 shows the calculated variations of outer, $\Delta d_{Al-O(out)}$, and inner Al—O, $\Delta d_{Al-O(in)}$, and Si—O, Δd_{Si-O}, bond distances of Me-imo. Imogolite has minimum values of $\Delta d_{Al-O(in)}$ at N = 8 induced by HB networks.[11] $|\Delta d_{Al-O(in)}|$, $|\Delta d_{Al-O(out)}|$, and $|\Delta d_{Si-O}|$ in Me-imo, in Figure 1 monotonically decrease with increases in the tubular curvature because the curvature decreases with increasing diameter. However, $|\Delta d_{Si-O}|$ is 0 at 26 and 30Å. It means that strain energy is minimum at the points. This value is corresponded with the diameter of Me-imo, so bond length relaxation is the factor of tubular formation in Me-imo.

XRD Pattern of Imogolite and Me-imo

Figure 2 shows the XRD patterns of Me-imo and imogolite. Powder XRD pattern of imogolite is similar to the literature data [12]. There are four 2 theta peaks on imogoltie at

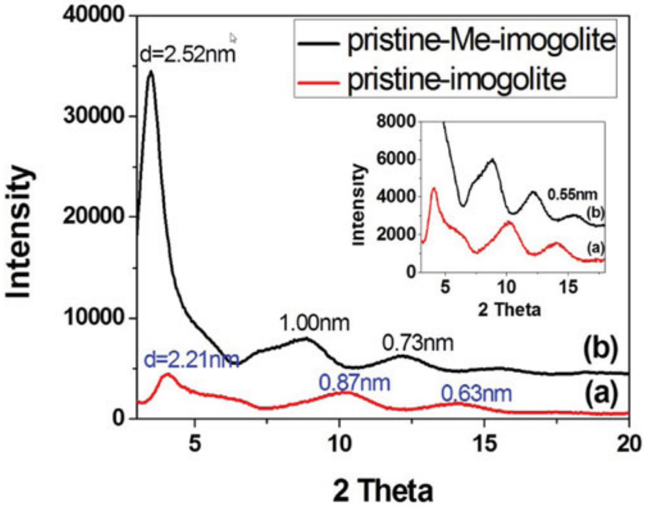

Figure 2. Powder X-ray diffraction pattern of (a) pristine-imogolite and (b) pristine-Me-imo.

4°, 6°, 10° and 14.2° which represent crystalline aluminosilicates. Me-imo, otherwise, has five peaks that are 3.5°, 7.6°, 8.85°, 12.25° and 15.6°. In the pattern, all peaks of Me-imo are more intense than them of imogolite as reported, especially the peak assigned the (100) reflection at 3.5° with Me-imo. Although the reason has been inferred in previous works as an increase in ordered packing of the nanotubes, no evidence has been reported. The (100) reflection, the cell parameter *a*, corresponds to a center-to-center distance between two nanotubes. The cell parameter *a* values in Me-imo and imogolite are 25.21Å and 22.06Å, respectively. And the calculated diameters of Me-imo and imogolite are 26.38Å and 16.99Å, respectively. It means that Me-imo is more strongly interacted with each other because of electronic imbalance between inner and outer surface molecules. Generally, O atom has stronger electronegativity than C atom, so it induces the imbalance. It is remarkable that the peak at 15.55° in Me-imo corresponding the cell parameter *c* and the aluminum hydroxide repeat unit, which is 5.5Å coincided with armchair chirality. The strain energy changes of Me-imo in zigzag and armchair chirality are shown in Figure 1. According to the calculated strain energy for the armchair chirality, the strain energy is slightly lower at 26–30Å which is similar to the experimental diameter. Me-imo could be synthesized with armchair chirality as a result of strain energy.

BJH Pore Size Distribution

The adsorption pore distribution curves of the samples were estimated by the BJH analysis method. According to the BJH plots of imogolite in Figure 3, the pore size distributions of Me-imo show similar behaviors depending on the degassing temperature. Comparing both pristine and degassed nanotubes at 300°C, the specific surface area of imogolite is 2.11 m^2/g and 430.13 m^2/g, respectively, and that of Me-imo is 516.42 m^2/g and 732.73 m^2/g, respectively. The specific surface area difference between pristine and degassed Me-imo is ca. 1.5 times, but in the case of imogolite, the difference is ca. 215 times. It could be suggested that pristine imogolite is affected by the physisorbed water molecules, but Me-imo is not affected by the water molecules due to the absence of HB.

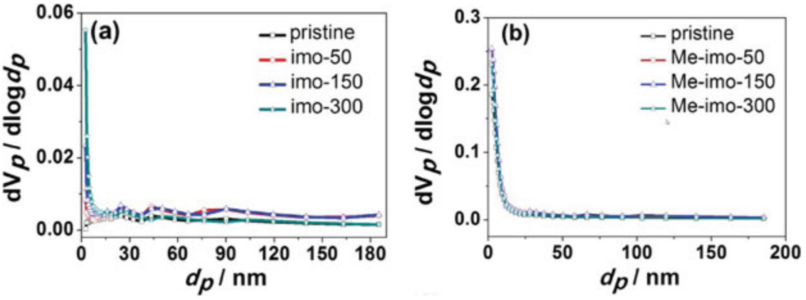

Figure 3. BJH pore size distribution plot: (a) pristine-imogolite (squares) and imogolite degassed at 50°C (circles), 150°C (triangles) and 300°C (stars); (b) pristine-Me-imo (squares) and Me-imo degassed at 50°C (circles), 150°C (triangles) and 300°C (stars).

Me-imo was successfully synthesized by the regular synthesis method for imogolite using carbon instead of silicon. Hydrogen bonding and water contents on the tubular structure control the pore size distribution and the size of the nanotube. Characteristics of the prepared Me-imo are well agreed with the simulated data.

Acknowledgments

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