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Control of Interlayer Microstructures of a Layered Silicate by Surface Modification with Organochlorosilanes

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The preparation of solids which accommodate guest species with controlled interactions between the surface and the adsorbed species at a molecular dimension is an important subject from a wide range of scientific and practical viewpoints. Microporous inorganic materials such as zeolites are the materials studied most extensively due to the rigidity and stability of their microstructures.[1,2] Analogous microporous structures based on organic building blocks have the potential for more precise rational design.[3−5] However, these frameworks are capable of binding only small molecules or ions. Here we report the preparation of layered inorganic−organic nanocomposites, which exhibit novel guest binding properties, from a crystalline layered silicate magadiite[6] by silylation of interlayer silanol groups with organochlorosilanes. The surface properties were designed to bind guest species by controlling the degree of silylation as well as the use of organochlorosilanes with different functionality. The inorganic−organic host structures bind guest species in their expandable interlayer spaces with the cooperative effects of the organophilic octyl groups and possible hydrogen bonding.

The reactions between organochlorosilanes and hydroxylated surfaces lead a creation of organically modified surfaces where organic moieties are covalently attached. Modification of silicas with variable geometry such as porous silica gels for the chromatographic stationary phase[7] and flat substrates for constructing molecular devices[8] has been investigated extensively. The silylation of the interlayer silanol groups of layered silicates may lead to novel functional inorganic−organic supramolecular systems.

The silylation of the silanol groups in the interlayer spaces of Na-magadiite was achieved by utilizing the dodecyltrimethylammonium (abbreviated as C_{12}TMA)-exchanged form as the intermediate.[9] The C_{12}TMA-magadiite was prepared by an ion exchange between Na-magadiite[10] and an aqueous C_{12}TMA chloride solution.[9,11] The C_{12}TMA-magadiite, $\{(C_{12}TMA)_{1.8}\cdot Si_{14}O_{29}\cdot nH_2O\}$, with the basal spacing of 2.79 nm, was suspended in a mixture of an organochlorosilane, octyldimethylchlorosilane ($C_8H_{17}(CH_3)_2SiCl$; abbreviated as $1C_82C_1SiCl$) or octyltrichlorosilane ($C_8H_{17}SiCl_3$; abbreviated as $1C_8Si3Cl$), and toluene under nitrogen flow for 48 h and the product was separated by centrifugation. When $1C_8Si3Cl$ was used, the silylated product was washed with an acetone/water mixture to remove chlorines from the residual SiCl of the attached organosilyl groups. The basal spacing decreased upon the silylation to 2.33 and 2.18 nm for $1C_82C_1SiCl$ and $1C_8Si3Cl$ systems, respectively. The amounts of the attached organosilyl groups were determined to be 1.84 and 1.94 per $14SiO_2$ (molar ratio) for $1C_82C_1SiCl$ and $1C_8Si3Cl$ systems, respectively. The deintercalation of C_{12}TMA during the silylation was shown by the absence of N in the elemental analysis. The expanded interlayer space of the C_{12}TMA-magadiite made it possible to introduce bulky organosilyl groups in the interlayer space as reported for diphenylmethylsilylation of magadiite.[9]

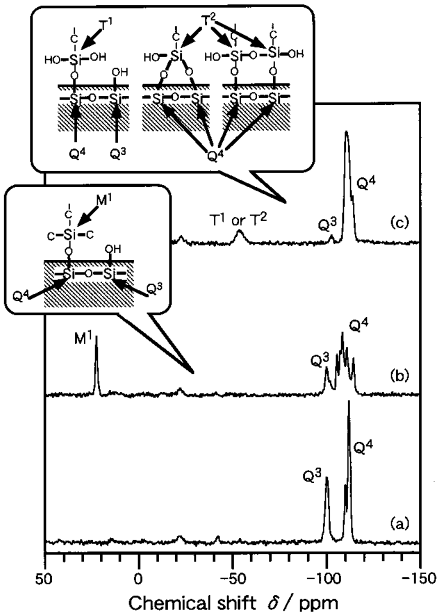

Figure 1. ^{29}Si MAS NMR spectra of (a) C_{12}TMA-magadiite, (b) $[1C_8\text{-}2C_1Si]_{1.84}$-magadiite, and (c) $[1C_8Si]_{1.94}$-magadiite. Inset: Schematic structures of the states of the organosilyl groups in the interlayer space.

In the ^{29}Si MAS NMR spectra of the silylated products (Figure 1, parts b and c), signals due to the organosilyl groups appeared at 22.6 and −55.0 ppm for $[1C_82C_1Si]_{1.84}$- and $[1C_8Si]_{1.94}$-magadiite, respectively. The signal at 22.6 ppm was due to the M^1 environment of silicon, showing the silylation of the surface silanol group with $1C_82C_1SiCl$. The broad signal observed at −55.0 ppm in the spectrum of the $[1C_8Si]_{1.94}$-magadiite was ascribable to cyclic T^2 and/or T^1 environments of silicon,[7,12] indicating that the silicon atom in the organosilyl group is attached as a dimer or bridged to two adjacent surface silanol groups of magadiite with a hydroxyl group (shown in the Figure 1 inset).

These two differently modified magadiites exhibited different adsorption behavior. The adsorption of *n*-alkyl alcohols was carried out by immersing the silylated derivatives into liquid *n*-alkyl alcohols. After the mixtures were stirred for 2 days, the products were centrifuged and the resulting slurries were examined

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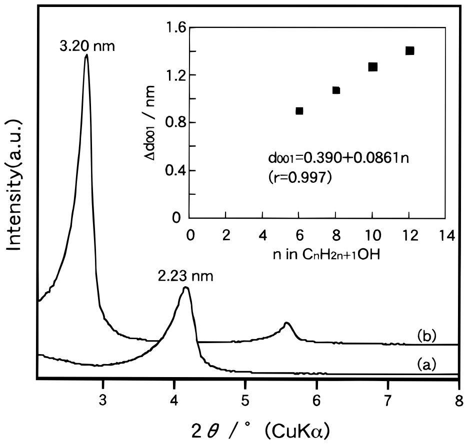

Figure 2. X-ray diffraction patterns of (a) $[1C_8Si]_{1.94}$-magadiite and (b) *n*-octyl alcohol treated $[1C_8Si]_{1.94}$-magadiite.-

by XRD. Figure 2 shows the change in the XRD patterns after the reaction with *n*-octyl alcohol. The basal spacing of the $[1C_8Si]_{1.94}$-magadiite increased from 2.18 to 3.20 nm by reaction with *n*-octyl alcohol, while that of the $[1C_82C_1Si]_{1.84}$-magadiite did not change significantly. It is difficult to determine the amount of intercalated *n*-octyl alcohol, since the differentiation of the intercalated and the externally adsorbed *n*-octyl alcohol was difficult in the present experiments. Supposing that the interlayer packing density of organic groups did not change with the presence of *n*-octyl alcohol, the molar ratio of *n*-octyl alcohol to the $Si_{14}O_{29}$ unit of magadiite was roughly estimated to be 1.9. To evaluate the guest inclusion quantitatively, further study on the adsorptive properties is being made and will be reported subsequently.

The difference in the microstructures was thought to affect the notable difference in the reactivity toward the adsorption of *n*-alkyl alcohols. Silanol groups were thought to exist in the interlayer surface of the $[1C_8Si]_{1.94}$-magadiite (Figure 1 inset), while the surface was effectively covered with organic groups (octyl and methyl groups) in the interlayer space of the $[1C_82C_1Si]_{1.84}$-magadiite. Considering the fact that *n*-decane did not intercalate into both of the derivatives, the interactions between the hydroxyl groups of alcohols and the surface SiOH groups were thought to be concerned with the adsorption of alcohols. Thus, the introduction of the trifunctional silane opens up a new opportunity to obtain novel adsorbents for polar organic molecules. It should be noted here that *n*-alcohols do not intercalate into Na- and H-magadiites under the experimental conditions employed in the present study. Consequently, the cooperative effect of hydrophobicity of the octylsilyl groups and the hydrogen bonding with silanol groups played a dominant role for the observed guest binding.

n-Alkyl alcohols with different alkyl chain lengths were intercalated into the interlayer space of the $[1C_8Si]_{1.94}$-magadiite. There is a linear relationship between the basal spacings and the alkyl chain length of the alcohols (Figure 2 inset), indicating that the intercalated alcohols take a paraffin-type arrangement with the attached octyl groups in the interlayer space of magadiite. The linear relationship also suggests that the alkyl chain length did not affect the molar ratio of the adsorbed alcohol to silicate layer. The variation in the basal spacings with the size of adsorbates is worth noting as a merit of swellable layered solids for adsorbents. The adsorbed alcohols are thought to orient by the interactions between polar head and the interlayer surface, probably silanol groups, to produce an anisotropic molecular assembly. Change in the *d* spacing can be explained by the arrangement of the interlayer organic groups. Organosilyl groups are thought to form an interdigitated monolayer by the silylation. When alcohols are intercalated, the interlayer alcohols and organosilyl groups are thought to rearrange to form a bilayer to expand interlayer spaces.

The surface properties have also been controlled by changing the surface coverage with the organosilyl groups. By the reaction of the C_{12}TMA-magadiite with a semiquantitative amount of $1C_8$-$2C_1$SiCl and $1C_8$Si3Cl, silylated derivatives, the $[1C_82C_1Si]_{1.34}$- and $[1C_8Si]_{1.17}$-magadiites with basal spacings of 2.23 and 1.81 nm, respectively, were obtained. The basal spacings were different from those of the derivatives with a different degree of silylation, indicating that the arrangements of the attached organosilyl groups varied depending on the composition. Supposing that the attached octyl groups distribute homogeneously, the average area occupied by each octyl group in the $[1C_82C_1Si]_{1.34}$-magadiite is estimated to be 1.4 times larger than that in the $[1C_82C_1Si]_{1.84}$-magadiite. The difference in the density of the octyl group on the interlayer surface of magadiite is expected to affect the adsorptive properties.

The $[1C_82C_1Si]_{1.34}$- and the $[1C_8Si]_{1.17}$-magadiites adsorb *n*-octyl alcohol in the interlayer spaces with the expansion of the basal spacings to 2.74 and 3.18 nm, respectively. This observation suggests that the silanol groups at the interlayer surface of magadiite can interact with alcohol molecules when the surface was not fully covered with organic groups. In the studies on the selective adsorption of organic molecules into the layered metal phosphonates, the distance between adjacent organic groups was thought to be responsible for the selectivity.[13,14] In the present system, the organic modification at a controlled degree of surface coverage is an effective way to control the guest binding properties of layered silicates. The change in the basal spacings by the *n*-octyl alcohol intercalation (2.18 to 3.20 nm and 1.82 to 3.18 nm for the $[1C_8Si]_{1.94}$- and $[1C_8Si]_{1.17}$-magadiites, respectively) strongly suggests that the adsorbed amount of alcohols are affected by the surface coverage with organosilyl groups.

We have demonstrated the synthesis of a new type of adsorbents of inorganic−organic nanocomposites with controlled interlayer microstructure and guest binding properties. The cooperative effects of the geometry and chemical nature of the modified surface on the guest binding have been achieved by a surface modification applied for the layered silicate. The adsorbents derived from layered solids are promising materials due to the combination of the confined microstructures, the stability, and the variety of surface properties.[1,15] The adsorption properties of organoammonium−smectites have been reported so far.[16−18] However, the origin of the different ability of adsorbents is not fully understood and the adsorbed organoammonium ions may deintercalate in aqueous media. Although the silylated derivatives of layered silicic acids[19−21] are expected to behave differently from the organoammonium clays, their application as adsorbents has not been reported so far. The present paper shows the first successful application of the organically modified layered polysilicates as adsorbents. Not only the adsorption selectivity but also the adsorbed state of the guest species is worth investigating since the states and the orientation of the guest species are controlled by the host−guest interactions.[22,23] Clay−polymer nanocomposites have been prepared from organoammonium−silicates.[24] Further variation of organic moieties and the extent of the surface coverage should lead to another type of selective guest inclusion with the controlled host−guest interactions.

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