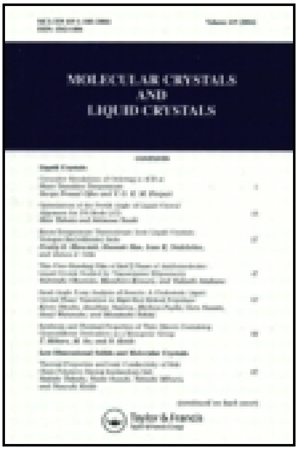

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Orientation of Guest Molecules and Formation of Mesoporous Silica Induced by Layered Silicate-Organic Interactions

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Orientation of Guest Molecules and Formation of Mesoporous Silica Induced by Layered Silicate-Organic Interactions

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This paper summarizes some of our recent results on layered silicate-organic systems. Unique nanomaterials are prepared by the interactions between layered silicates and organic species. The structural control of guest molecules and the structural transformation of host silicates have been accomplished by choosing appropriate layered silicates. One way for specific orientation of guest molecules is to utilize a layered clay mineral kaolinite. A kaolinite-*p*-nitroaniline intercalation compound was successfully prepared by using a kaolinite-methanol intercalation compound as a versatile intermediate. Kanemite, a layered polysilicate composed of single layered silicate sheets, was structurally transformed on intercalation of organoammonium ions, which produced a mesostructured precursor for ordered mesoporous silica.

Keywords: layered silicate; intercalation; silicate-organic systems; kaolinite; kanemite; mesoporous silica

INTRODUCTION

Inorganic layered materials have been utilized to accommodate and organize organic guest species in their interlayer spaces to form supramolecular inorganic-organic hybrid systems[1]. Among a large number of inorganic layered materials, natural and synthetic layered silicates play a major role in intercalation chemistry. Kaolinite, a layered aluminosilicate, has a unique structure because the interlayer region is sandwiched between hydroxyl groups of the $AlO_2(OH)_4$ sheets in one side and the oxide arrangements of the silicate sheets in the other (Figure 1a), affording an asymmetric nanoenvironment. It has been known that small polar guest molecules such as *N*-methylformamide

(NMF) and dimethyl sulfoxide (DMSO) are intercalated and aligned in one direction between the layers of kaolinite[2]. Thus, kaolinite is an excellent host for organizing guest species, although the reactivity is rather low compared with those of the smectite group of clay minerals like montmorillonite. Hence, intercalation reaction of kaolinite can be extended by a guest displacement method in which new guest species can be intercalated by displacing previously-intercalated species.

One of the advantages of the use of layered materials is to confine guest species in their two-dimensional regions to induce selective orientations. One of the typical fields demanding unidirectional orientation is nonlinear optics using organic molecules with hyperpolarizabilities like *para*-nitroaniline (*p*NA) which needs to be oriented noncentrosymmetrically. Consequently, a successful formation of a kaolinite-*p*NA intercalation compound is valuable for future nanomaterials design.

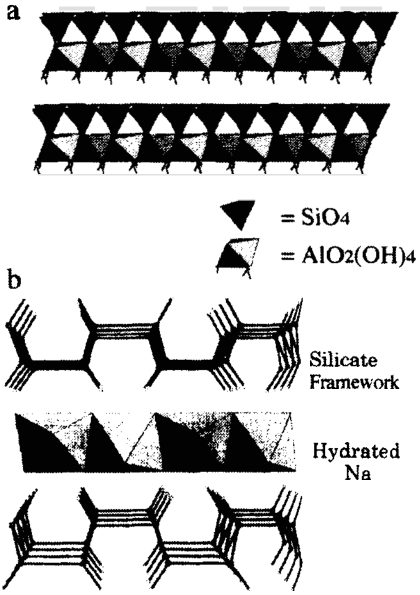

FIGURE 1 Structural model of a) kaolinite and b) kanemite[3].

On the other hand, we have found that a layered polysilicate kanemite ($NaHSi_2O_5 \bullet 3H_2O$, Figure 1b), which is composed of single layered silicate sheets[3], exhibits a structural transformation when organoammonium ions are intercalated between the layers of kanemite[4]. The resultant silicate-organic mesostructures are converted to mesoporous silica by calcination[4]. After the discovery, various mesoporous silicas have been synthesized. In this paper, mesoporous silica derived from kanemite is also briefly presented.

KAOLINITE-*p*-NITROANILINE INTERCALATION COMPOUND

Kaolinite (ideal chemical formula, $Al_2Si_2O_5(OH)_4$) used was KGa1, well-crystalline Georgia kaolinite. *p*NA has been reported not to be intercalated into kaolinite even by a conventional guest displacement method. Therefore, a fine guest displacement method by using a kaolinite-methanol intercalation compound as the intermediate[5] was applied. A kaolinite-methanol intercalation compound was prepared as reported previously and the wet intercalation compound was stirred in a dichloromethane solution of *p*NA at room temperature for 3 days for the intercalation.

All the results by powder XRD, ^{13}C and ^{29}Si solid state NMR, IR, CHN analysis and SHG intensities confirmed the intercalation of *p*NA into kaolinite. The basal spacing of the product increased to 1.50 nm. The value was larger than that of the kaolinite-methanol intercalation compound (1.11 nm). The basal spacing of kaolinite is 0.72 nm, and the increase by 0.78 nm after intercalation is smaller than the length of *p*NA molecule (0.90 nm). Considering the amount of *p*NA (0.6 *p*NA/$Al_2Si_2O_5(OH)_4$), *p*NA molecules are thought to take a monomolecular arrangement with their molecular axis inclined to the aluminosilicate layers. In the ^{13}C CP/MAS NMR spectrum of the product, typical four signals due to the carbons of *p*NA were observed at 112, 128, 135 and 155 ppm. A signal due to $\underline{C}H_3O$- was observed at 49 ppm, suggesting that a small amount of methanol or methoxy groups attached to the octahedral sheets were present.

Two orientations of *p*NA molecules in the interlayers are possible; that is, NO_2 and/or NH_2 groups are oriented toward hydroxyl groups of the gibbsitic ($AlO_2(OH)_4$) sheets. In the present system, NO_2 groups in *p*NA are hydrogen bonded with hydroxyl groups of kaolinite, which is supported by intercalation behavior of nitrobenzene and aniline using a kaolinite-methanol intercalation compound as the intermediate. It was found that nitrobenzene molecules were intercalated between the layers of kaolinite whereas aniline molecules were not. This difference between nitrobenzene and aniline for intercalation strongly suggests that the interactions between OH groups in kaolinite and NO_2 groups in *p*NA molecules are thought to be a main driving force for the intercalation of *p*NA.

Solid state ^{29}Si NMR spectroscopy revealed that the chemical shift due to Si in the tetrahedral sheets is the same as those observed for kaolinite-alkylamine intercalation compounds where NH_2 groups interact with the silicate sheets, suggesting similar interactions between NH_2 groups and the silicate sheets. The IR spectrum of the kaolinite-*p*NA intercalation compound indicates the presence of weaker hydrogen bondings between NH_2 groups and the silicate sheets as compared with those in *p*NA crystals.

The kaolinite-*p*NA intercalation compound is SHG active and its intensity is similar to that of urea. Because the signals of both raw kaolinite and several mixtures of kaolinite and *p*NA crystals were very low, the SHG intensity of the intercalation compound is almost ascribable to *p*NA molecules in the interlayer space of kaolinite. The unique interlayer structure of kaolinite should play a major role in the noncentrosymmetric orientation of *p*NA molecules.

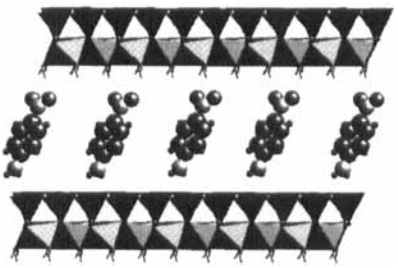

FIGURE 2 Schematic representation of the kaolinite-*p*NA intercalation compound.

On the basis of these results, the alignment of *p*NA molecules is schematically represented as shown in Figure 2. Although there are no definitive data whether the *p*NA molecules in the interlayer space are fully unidirectionally oriented, the present results have clarified that kaolinite is an excellent host immobilizing photofunctional materials in its unique interlayer region. Various inclusion hosts have already been applied for the arrangement of molecules such as *p*NA and stilbazolium ions. However, an outer electrical field[6] and guest-guest interactions[7,8] are required for the alignment of molecules in layered materials (such as saponite, layered double hydroxide, and $MnPS_3$) because the interlayer spaces are sandwiched between the same surfaces of adjacent layers. The present results show that the asymmetric environment in the interlayer region of kaolinite induces a spontaneous orientation of guest molecules.

KANEMITE-DERIVED MESOPOROUS SILICA

There have been keen interests in ordered mesoporous materials for potential applications such as adsorption, catalysts, catalyst supports, hosts for inclusion of quantum wires, new reaction media, and so on, since we discovered mesoporous silicas derived from a layered polysilicate kanemite (called FSM later). The studies on both the formation process by *in-situ* powder X-ray diffraction[9] and the detailed characterization of as-synthesized products have clarified the uniqueness of this system. Progress has also been made in the fields of adsorption and modification of pore structures. For example, taxol, an anticancer substance, was adsorbed into FSM-type mesoporous silicas with the pore sizes larger than 1.8 nm, while it was not adsorbed into the channels with the pore size less than 1.6 nm, indicating that mesoporous silicas have a molecular sieving property for relatively large molecules[10]. Inner surface modification with silylating agents and alcohols have been successfuly performed[11]. The assembling ability of surfactants is also effective for the formation of various ordered mesostructured metal oxides with lamellar, hexagonal and cubic phases in addition to silica mesophases.

Although various mesoporous silicas have been synthesized, all the structures reported so far have been governed by the geometrical packing of surfactants because the formation of inorganic-organic mesostructured precursors relies on the cooperative organization of inorganic species and surfactants. We have recently noticed that a novel mesoporous silica can be prepared by using kanemite and surfactants, which cannot be derived by the reported cooperation of surfactants and soluble silica sources.

A layered hexadecyltrimethylammonium-kanemite intercalation compound was prepared at first and it was transformed to a mesostructured precursor for a novel mesoporous silica by acid treatment. Intralayer condensation was indicated by ^{29}Si MAS NMR and the bending of the silicate sheets were clearly observed by TEM. The novel mesoporous silica has lozenge one-dimensional channels derived from kanemite, which cannot be derived by the reported cooperation of surfactants and soluble silica sources. The details will be reported in near future.

CONCLUSIONS

A couple of examples of the interactions of layered silicates with organic substances have been presented. A spontaneous arrangement of guest molecules by the interlayer surface structure of kaolinite is a new step toward highly selective reactions and the formation of molecular assemblies with specific chemical, photochemical, and electrical properties. Careful selection of both the kind of layered silicates and the synthetic conditions leads us specific structural and orientational control of intercalated guest molecules. Structural transformation of host structures occurs when the silicate structure is flexible enough to correspond to the interactions with guest organic assemblies. Controlling nanostructures based on layered silicate-organic systems in higher order is surely a direction for future nanomaterials design.

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