Ion-exchangeable Layered Aminophenylsilica Prepared with Anionic Surfactant Templates

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The synthesis of a novel anion-exchangeable nanostructured aminophenylsilica with a well-ordered layer geometry was demonstrated by utilizing the sol-gel reaction of *p*-aminophenyltrimethoxysilane in the presence of an anionic surfactant micelle under acidic conditions

Inorganic materials with layered nanostructures, such as clay minerals and perovskites, have been extensively investigated in the field of materials chemistry.[1] They can adsorb various organic and inorganic species into their interlayer nanospace by an intercalation reaction. The chemical and physical environment of the interlayer changes depending on the type and the amount of the intercalants. Interactions of the intercalants with the inorganic layer and with each other also affect the properties of the intercalation compounds. According to this intercalation capability, these materials found a wide variety of important applications as adsorbents, rheologically control agents, reaction media, and organic–inorganic nanocomposites.

The surfactant-templated sol-gel method has been most widely applied to synthesize the nanostructured silica materials.[2] The key process of this method is the formation of the cooperative organization between silane compounds and cationic or neutral surfactants through ionic or hydrogen bond interactions.

We have proposed a novel strategy for the synthesis of nanostructured organosilica, which utilizes the ionic interaction between ionic surfactants and the ionic organofunctional group of an organoalkoxysilane. The novel nanostructured aminopropylsilica synthesized according to this strategy possessed a well-ordered layer structure with a two-dimensional (2-D) inorganic framework constructed with a hexagonal network of Si–O–Si linkages.[3] The aminopropyl groups were regularly arranged on both sides of the silica layer. The layered nanostructure was retained even after the removal of the template surfactants. Various kinds of anionic species can be intercalated into the interlayer of this material. The estimated density of the anion-exchangeable sites is quite high (8.99 mmol g^{-1}).

In this communication, we demonstrate the availability of the strategy by employing a different starting material, *p*-aminophenyltrimethoxysilane (APhTMS). The resulting nanostructured aminophenylsilica is expected to show different physical and chemical properties from those of the aminopropylsilica, because the polarity, mutual interaction, and arrangement of the aminophenyl moieties as well as their reactivity are definitely different from those of the aminopropyl groups.[3]

The layered aminophenylsilica was synthesized by the slow titration of HCl (0.5 mol dm^{-3}) into a mixture of APhTMS (2.78 mmol), 0.84 g of SDS (2.92 mmol), and 30 cm^3 of deionized water with stirring at room temperature (pH 2–3). APhTMS-dodecyl sulfate complex (APhTMS-DS) was obtained as a light pink precipitate and washed with deionized water and ethanol, then dried in a vacuum. The powder X-ray diffraction pattern of APhTMS-DS exhibits a sharp diffraction peak at $2\theta = 2.22^\circ$ ($d = 4$ nm), suggesting that at least one of the lattice parameters of the obtained material is large (Figure 1a). The assignment of this peak will be discussed later. The elemental analysis results show that APhTMS-DS is composed of the dodecyl sulfate anion ($C_{12}H_{25}OSO_3^-$) and $NH_3^+C_6H_4SiO_{1.5}$ in a 1:1 molar ratio.[4]

The template surfactant could be removed from the APhTMS-DS by washing with a mixture of hydrochloric acid and ethanol. The complete replacement of dodecyl sulfate anions by chloride anions was confirmed by elemental analysis as well as solid state ^{13}C CP/MAS NMR. APhTMS-Cl is composed of Cl^- and $NH_3^+C_6H_4SiO_{1.5}$ in a 1:1 molar ratio.[4] The resulting material is abbreviated APhTMS-Cl hereafter. The XRD pattern of APhTMS-Cl was different from that of APhTMS-DS (Figure 1b). Two diffraction peaks were observed at $2\theta = 5.45^\circ$ ($d = 1.6$ nm) and 10.8° ($d = 0.82$ nm). The assignment of these peaks will be discussed later.

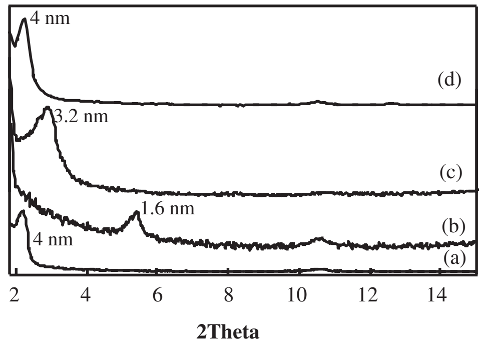

Figure 1. Powder X-ray patterns: (a) APhTMS-DS, (b) APhTMS-Cl (c) APhTMS-OS and (d) APhTMS-DSI (Intercalation compound).

The structures of APhTMS-DS and APhTMS-Cl were further studied by transmission electron microscopy (TEM). Stacked plate-like materials with an average 2-D size of about 100 nm were observed for both samples. A typical TEM micrograph of APhTMS-Cl is shown in Figure 2. The selected area electron diffraction (SAD) pattern of this plate showed a clear hexagonal pattern (Figure 2, inset). A similar SAD pattern was also observed from APhTMS-DS. This pattern indicates that the aminophenylsilica layer has a pseudo-hexagonal structure resembling to that of certain types of clay minerals. The lattice parameters of the *a* and *b*-axes calculated from the SAD pattern was 0.52 and 0.90 nm, respectively. It is worth noting that the SAD pattern was identical with that of the layered aminopropylsilica reported earlier.[3] The lattice parameters are very close to those of the layered silicates (talc and pyrophyllite). Therefore, it is considered that the layer structure of aminophenylsilica is constructed with a hexagonal Si–O network as illustrated in Figure 3a. It is considered that the aminophenyl groups are alternately arranged on both sides of the sheet in order to reduce the steric repulsion between the aminophenyl groups (Figure 3b). From the structure model shown in Figure 3b, the thickness of the aminophenylsilica layer was estimated to be about 1.5 nm. The main diffraction peak of APhTMS-Cl that appeared at $2\theta = 5.45^\circ$ ($d = 1.6$ nm) is therefore assigned to the 001 reflection. The assignment of the small diffraction peak that appeared at $2\theta = 10.8^\circ$ ($d = 0.82$ nm) is not definite at present, but might be attributed to the 001 reflection from the interdigitated structure. The structure of APhTMS-DS is illustrated in Figure 3c. The estimated basal spacing (4.1 nm) shows good agreement with the observed d value (4 nm) of APhTMS-DS. The sharpness of the reflection peak indicates the high regularity of the stacking of layers in APhTMS-DS. It would be the result of the strong interaction between the hydrocarbon chains of the dodecyl sulfate anions.

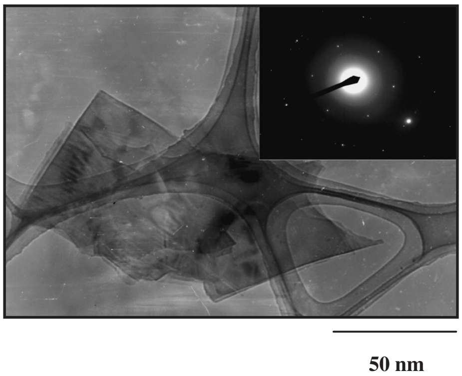

Figure 2. Transmission electron micrograph of APhTMS-Cl. The inset shows the selected area electron diffraction pattern.

The anion-exchange capability of APhTMS-Cl was examined by the intercalation experiments of the octyl sulfate (OS) and dodecyl sulfate (DS) anions. APhTMS-Cl was treated with aqueous solutions of the alkyl sulfates at room temperature for 5 h. The elemental analysis results showed that the chloride anions were completely exchanged by the alkyl sulfate anions in both cases.[4] The intercalation of the alkyl sulfate anions was confirmed by the XRD spectra. The XRD pattern of APhTMS-DS after re-intercalation (APhTMS-DSI, Figure 1d) was almost identical to that of the as-prepared APhTMS-DS (Figure 1a). The increase of the basal spacing from APhTMS-Cl (1.6 nm) to APhTMS-DSI (4 nm) was 2.4 nm, which corresponded well to the length of two DS anions (1.3 nm × 2). Similarly, the observed basal spacing of APhTMS-OS (3.2 nm) was very close to the sum of the basal spacing of APhTMS-Cl (1.6 nm) and the length of two OS anions (0.9 nm × 2). The anion exchange capacity of the layered aminophenylsilica is calculated to be 6.89 mmol g^{-1}.

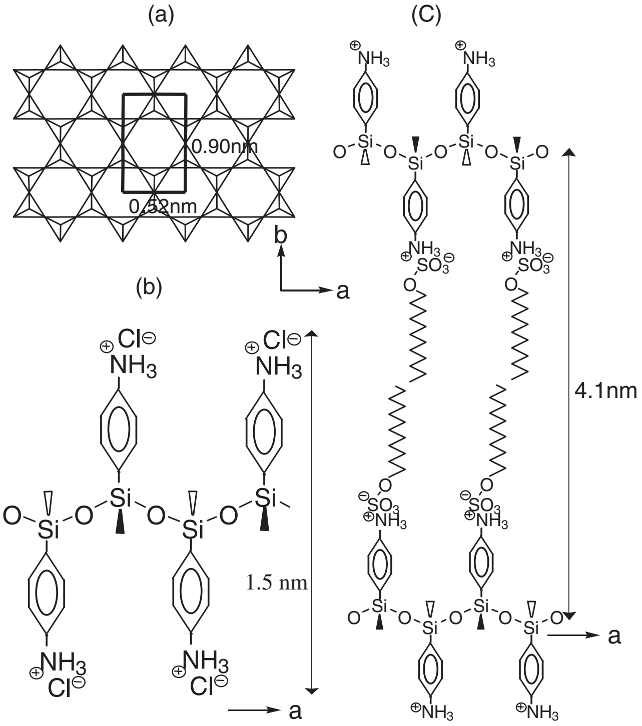

Figure 3. Schematic illustrations of the APhTMS organosilica. (a) Top view of Si–O hexagonal sheet. (b) Vertical cross-section view of APhTMS-Cl. (c) Vertical cross-section view of APhTMS-DS.

In summary, the novel nanostructured aminophenylsilica with a layered geometry has been prepared by utilizing the ionic interaction between the anionic surfactant and the cationic group of organoalkoxysilane. The resulting material has a large anion exchange capacity and was stable during the ion exchange process. A series of novel nanostructured organosilica materials can be synthesized by utilizing this strategy.

References and Notes

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4 Elemental analysis result: APhTMS-DS: N: 0.0307 g/g; S: 0.0708 g/g. APhTMS-Cl: N: 0.063 g/g; S: 0 g/g; Cl: 0.1572 g/g. APhTMS-OS: N: 0.0352 g/g; S: 0.081 g/g, Cl: 0 g/g; APhTMS-DSI: N: 0.0306 g/g; S: 0.0701 g/g; Cl: 0 g/g.

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