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Novel Two-Dimensional Molecular Space Material with Regular Double Bonds

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Nanospace materials can be used to influence and control chemical processes in their nanospaces, because they provide molecular reaction spaces with special properties. Layered materials, such as clay minerals and layered double hydroxides (LDHs), have been investigated extensively as nanospace materials, as they provide a stable two-dimensional nanospace for chemical processes.[1−17] A variety of molecules can be intercalated into the two-dimensional interlayer space of layered materials. The two-dimensional layer structure of layered materials is expandable with the size of the intercalated molecule. The intercalated molecule can form monolayers or bilayers in the interlayer space of layered materials independent of molecular size, due to the interaction between the layer plate and the molecule. Some novel chemical and physical properties can be obtained in two-dimensional layered molecular spaces that are different from the macroscopic space.[18−31] Thus, two-dimensional layered materials

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are promising materials for influencing and controlling molecular reaction processes in the interlayer spaces.

However, it is difficult to influence and control molecular reaction processes in the interlayer space utilizing current layered materials as a result of a lack of functional properties and unchangeable layer structure. Therefore, it is very important to synthesize novel two-dimensional layered materials with regular functional groups in the layer structure to influence and control the molecular reaction processes in the two-dimensional layer space. The regular arrangement of functional groups is a key point to influence and control molecular reactions in the two-dimensional molecular space. The regular arrangement of functional groups in the two-dimensional structure would form a controllable molecular reaction space through utilization of the interaction between the regular functional groups and the guest molecule.

Previously, we reported a novel layered aminophenylsilica material (Cl$^-$/NH$_3^+$C$_6$H$_4$SiO$_{1.5}$, APhTMS-Cl) with amino groups in the layer structure.[32,33] APhTMS-Cl exhibited a stable layer structure and better intercalation response. Here, we report the development of a novel two-dimensional molecular space material with regular double bonds. Layered acrylamidephenylsilica (C$_2$H$_3$CONHC$_6$H$_4$SiO$_{1.5}$, AAPhS) was synthesized by liquid−solid reaction between layered aminophenylsilica and acrylic acid. The two-dimensional layered molecular space with regular double bonds can be used as a functional molecular reaction space for chemical and physical processes by utilization of the functionality of double bonds. The double bonds regularly arranged in the two-dimensional layer space can be used in end-functionalized polymerization and addition reactions with other functional molecules.

The layered APhTMS-Cl was prepared as described previously.[32,34] Layered AAPhS was synthesized by adding 1.303 mL of acrylic acid to a mixture of 0.168 g of APhTMS-Cl and 84 mL of deionized water, and the suspension was stirred at room temperature for 2 days. The reactant changed color from red to yellow. The precipitates were then filtered, washed with deionized water and ethanol, and then dried in vacuum.

The solid-state ^{13}C NMR spectra of APhTMS-Cl and AAPhS are shown in Figure 1. Only two resonances were observed at 125 and 135 ppm referenced to tetramethylsilane (TMS) for APhTMS-Cl (Figure 1a). This was attributed to the superposition of resonances of carbon species in the aromatic rings of APhTMS-Cl due to the aromatic rings fixed in the framework of silica as a layer plate and NH$_3^+$ ions formed. The resonances at 125 and 135 ppm were assigned to the carbon species connecting with amino groups and other carbon species in the aromatic rings of APhTMS-Cl, respectively, as shown in Figure 1a.

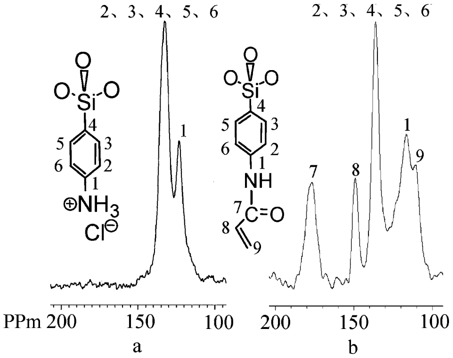

Figure 1. Solid-state ^{13}C NMR spectra of (a) layered APhTMS-Cl and (b) layered AAPhS.

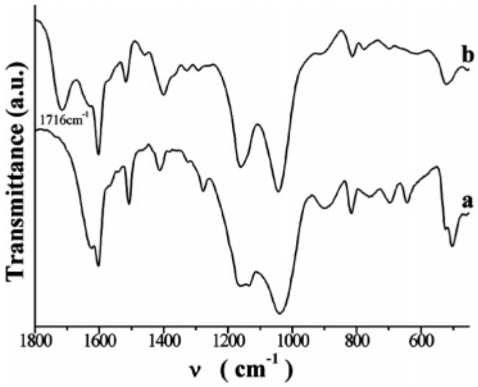

Figure 2. IR spectra of (a) layered APhTMS-Cl and (b) layered AAPhS.

The solid-state ^{13}C NMR spectrum of AAPhS clearly indicated amide formation and the presence of double bonds in the structure, as shown in Figure 1b. The new resonances at 176.5, 149, and 110.7 ppm were observed corresponding to $C(=O)-N$, $-CH=$ and $=CH_2$ from the acrylic acid moiety in AAPhS, respectively (Figure 1b). The aromatic peaks shifted from 135 and 125 ppm in APhTMS-Cl (Figure 1a) to 136 and 116.4 ppm, respectively, as a result of amide formation in AAPhS (Figure 1b).

The IR spectra were also used to examine amide formation between the amino group of layered APhTMS-Cl and the carboxyl group of acrylic acid. A new peak appeared at 1716 cm^{-1} in the IR spectrum of AAPhS compared with APhTMS-Cl (Figure 2). The peak at 1716 cm^{-1} was assigned to the amide formed between the amino group of layered APhTMS-Cl and the carboxyl group of acrylic acid. The carbonyl peak at a higher wavenumber in the IR spectrum of AAPhS was considered to be due to the existence of vinyl groups and the carbonyl groups fixed in the layer structure of AAPhS. The double bonds could not be clearly confirmed in the IR spectrum of AAPhS, because the stretching vibration peak (1680−1620 cm^{-1}) of vinyl groups was covered by the other peaks in layered aminophenylsilica. However, the solid-state ^{13}C NMR spectrum of layered AAPhS clearly confirmed the

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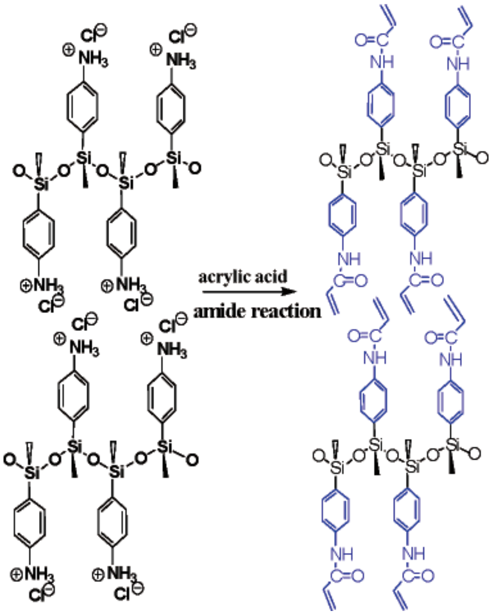
(34) The layered aminophenylsilica was synthesized by the slow titration of HCl into a mixture of *p*-aminophenyltrimethoxysilane (APhTMS, 2.78 mmol) and sodium dodecyl sulfate (2.92 mmol) in aqueous solution with stirring at room temperature (pH 2−3). The APhTMS−dodecyl sulfate complex (APhTMS-DS) was obtained as a light pink precipitate. The layered APhTMS-Cl was obtained from the APhTMS-DS by washing with a mixture of hydrochloric acid and ethanol. All the reagents were purchased from the Aldrich Chemical Co.

Scheme 1. Schematic Illustrations of the Layered APhTMS-Cl Organosilica and Layered AAPhS Organosilica



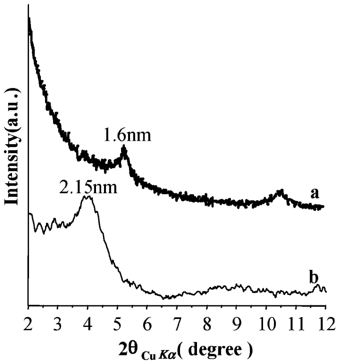


Figure 3. Powder XRD patterns of (a) layered APhTMS-Cl and (b) layered AAPhS.

existence of vinyl groups in the layer structure, as described above.

The results of solid-state ^{13}C NMR and the IR spectrum of AAPhS indicated that the amino group in the layered APhTMS-Cl reacted with the carboxyl group of acrylic acid at room temperature and the vinyl groups were arranged as end-functional groups in the layer structure, as shown Scheme 1. The better responses of solid-state ^{13}C NMR and the IR spectrum showed the stable chemical structure of AAPhS and better liquid−solid reactive behavior between the layered APhTMS-Cl and acrylic acid

The X-ray diffraction (XRD) pattern of AAPhS was clearly different from that of APhTMS-Cl. The diffraction peak assigned to the 001 reflection was shifted from $2\theta = 5.45°$ in APhTMS-Cl to $2\theta = 4.04°$ in AAPhS, as shown in Figure 3. The interlayer distance shifted from 1.6 nm in APhTMS-Cl to 2.15 nm in AAPhS. The change in the interlayer distance was consistent with the change in the molecular length from APhTMS-Cl to AAPhS, as shown in Scheme 1. The better XRD response indicated that the layer structure had been retained during the formation of layered AAPhS by the liquid−solid reaction between layered APhTMS-Cl and acrylic acid and the double bonds were arranged regularly in the layer structure of layered AAPhS.

Table 1. Elemental Analysis Results of AAPhS

sample	C (wt %)	N (wt %)	attempted formula
AAPhS	40.31	5.29	$(CH_2{=}CHCONHC_6H_4)_{0.96}(Cl^-NH_3^+C_6H_4)_{0.04}SiO_{1.5}\cdot 3.7H_2O$

The results of elemental analysis of layered AAPhS shown in Table 1 indicated that about 96% of the amino groups in layered APhTMS-Cl reacted with the carboxyl groups of acrylic acid to form amides in layered AAPhS. The higher liquid−solid reactive efficiency between layered APhTMS-Cl and acrylic acid further confirmed that the double bonds were regularly arranged in the layer structure of layered AAPhS.

Layered AAPhS was synthesized by liquid−solid reaction between layered APhTMS-Cl and acrylic acid, and better liquid−solid reactive behavior was obtained. The results of solid-state ^{13}C NMR, the IR spectrum, and the XRD pattern indicated that layered AAPhS has functional regular double bonds and a stable layer structure, as shown in Scheme 1. The results of elemental analysis also further confirmed that the amino groups in layered APhTMS-Cl were almost completely transformed to amide and the double bonds were regularly arranged in the layer structure of layered AAPhS. Otherwise, the regular vinyl groups in the layer structure of AAPhS can easily be polymerized after treatment with $K_2S_2O_8$. The polymerization of regular double bonds in the layer structure of AAPhS can be confirmed by spectral analysis. The interlayer distance of layered AAPhS decreases after polymerization of regular double bonds in the layer structure of AAPhS. The reaction processes and structure with regard to polymerization of layered AAPhS will be reported in detail elsewhere.

The novel two-dimensional molecular space with regular double bonds can be used as a functional molecular reaction space by utilization of the functionality of regular double bonds. The distances and the amounts of regular double bonds in the layer structure can be understood and used as key points to influence and control molecular reaction processes in the two-dimensional molecular space. The double bonds regularly arranged in the two-dimensional layer space can polymerize and react with other organic molecules through liquid−solid reaction. A series of novel layered materials with regular functional groups can be synthesized by hybridizing various types of organic groups in the layer structure of layered acrylamidephenylsilica. The chemical and physical processes in the two-dimensional molecular space can be influenced and controlled by utilization of two-dimensional layered materials with regular functional groups.

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