

# Synthesis of Transparent Magadiite–Silica Hybrid Monoliths

Koichi Kikuta,<sup>†</sup> Keiko Ohta,<sup>†</sup> and Katsuhiko Takagi<sup>\*,†,‡</sup>

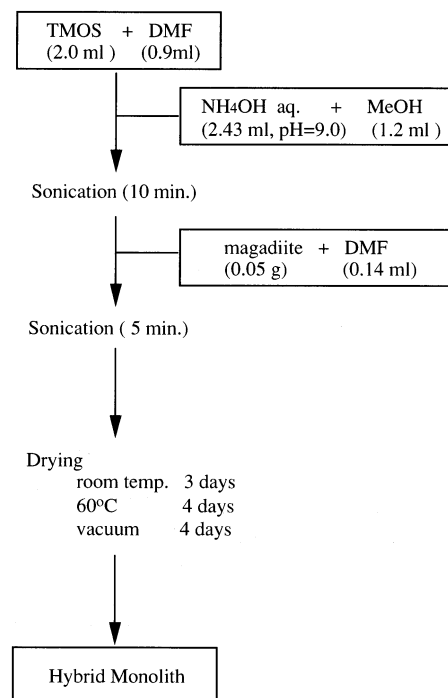
Department of Crystalline Materials Science, School of Engineering, Nagoya University, and CREST, JST (Japan Science and Technology), Furo-cho, Chikusa, Nagoya, 464-8603 Japan

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The synthesis of optically transparent magadiite–silica hybrid monoliths was investigated by the incorporation of delaminated magadiite powders into a sol–gel-derived silica matrix obtained by hydrolysis and condensation of tetramethoysilane (or tetramethyl orthosilicate or TMOS). The delamination of sodium magadiite was accomplished by the intercalation of laurylpyridinium ions (LPy<sup>+</sup>) into the particles followed by ion exchange with Na<sup>+</sup>. The resulting fine platelike crystallites was found to be useful in obtaining a magadiite–silica monolith. The present procedures were effective in the preparation of homogeneous and transparent magadiite–silica monoliths and were found to be significantly superior to the conventional method of alkylsilylation with hexamethyldisilazane (HMDS).

## Introduction

There have been many studies on the intercalation of organic molecules or ions into various kinds of inorganic layered compounds such as clay minerals.<sup>1–3</sup> In fact, we have reported on the processing of organic-clay hybrid compounds such as viologen-intercalated montmorillonite for applications in photofunctional materials.<sup>4</sup> Kuroda and co-workers have also reported in detail on the intercalation behavior and chemical modification of magadiite.<sup>5,6</sup> The layered silicate reported is a rather stable host material in acidic or basic conditions compared to other conventional clay minerals such as montmorillonites and is also usually optically transparent in the visible light region. In the present study, we have investigated a synthetic method for the hybridization of magadiite particles in polysilicate matrixes by adjusting the condensation conditions of TMOS. Sol–gel-derived silica monoliths were prepared in both acidic and basic conditions in the presence of a drying control chemical additive (DCCA), which remarkably reduces the stress during the drying process. In the absence of additives such as layered minerals, Adachi and Sakka were able to prepare transparent amorphous silica monoliths under a weak basic condition. Here, we have also applied a weak basic condition to suppress the exchange reactions of the intercalated ions in the magadiite interlayers.<sup>7</sup> As a result, we were



**Figure 1.** Experimental procedure for making hybrid gel monoliths.

successfully able to obtain new functional hybrid compounds as monolithic materials, significantly, for applications in functional optical systems.

## Experimental Section

**Hydrothermal Synthesis of Sodium Magadiite.** Sodium magadiite ( $\text{Na}_2\text{Si}_{14}\text{O}_{26}(\text{OH})_6 \cdot 6\text{H}_2\text{O}$ , Na–magadiite) was obtained by the hydrothermal reaction of fine silica powder (Wako Co., Ltd.) mixed with NaOH (Nakarai Co., Ltd.) in a molar ratio of 1:0.23:18.5 for  $\text{SiO}_2$ , NaOH, and  $\text{H}_2\text{O}$  in an

\* To whom correspondence should be addressed. Phone: +81-52-789-4584. Fax: +81-52-789-5581. E-mail: kik@apchem.nagoya-u.ac.jp.

<sup>†</sup> Nagoya University.

<sup>‡</sup> JST.

(1) Bala, P.; Samantaray, B. K.; Srivastava, S. K. *Mater. Res. Bull.* **2000**, *35*, 1717–1724.

(2) Ogawa, M.; Ishikawa, A. *J. Mater. Chem.* **1998**, *8*, 463–467.

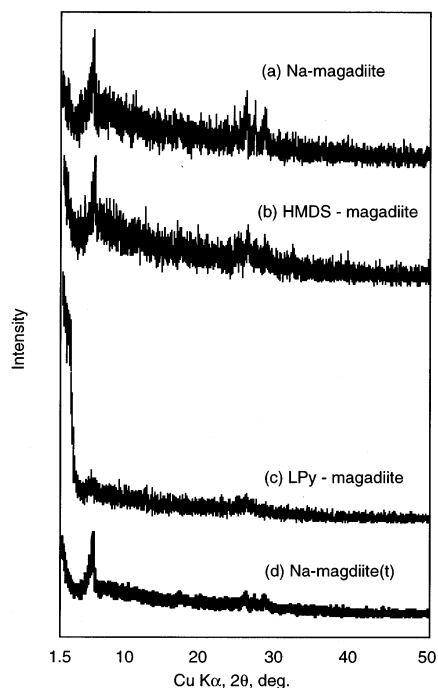
(3) Drljaca, A.; Spiccia, L.; Anderson, J. R.; Turney, T. W. *Inorg. Chim. Acta* **1997**, *254*, 219–224.

(4) Sonobe, K.; Kikuta, K.; Takagi, K. *Chem. Mater.* **1999**, *11*, 1089–1093.

(5) Ogawa, M.; Okutomo, S.; Kuroda, K. *J. Am. Chem. Soc.* **1998**, *120*, 7361–7362.

(6) Isoba, K.; Kuroda, K.; Ogawa, M. *Chem. Mater.* **2000**, *12*, 1702–1707.

(7) Adachi, T.; Sakka, S. *J. Non-Cryst. Solids* **1988**, *100*, 250–253.



**Figure 2.** XRD profiles of magadiite powders. (a) Hydrothermally prepared sodium magadiite. (b) Magadiite powder treated with HMDS. (c) Magadiite powder intercalated with LPy<sup>+</sup>. (d) Sodium magadiite prepared from LPy-magadiite.

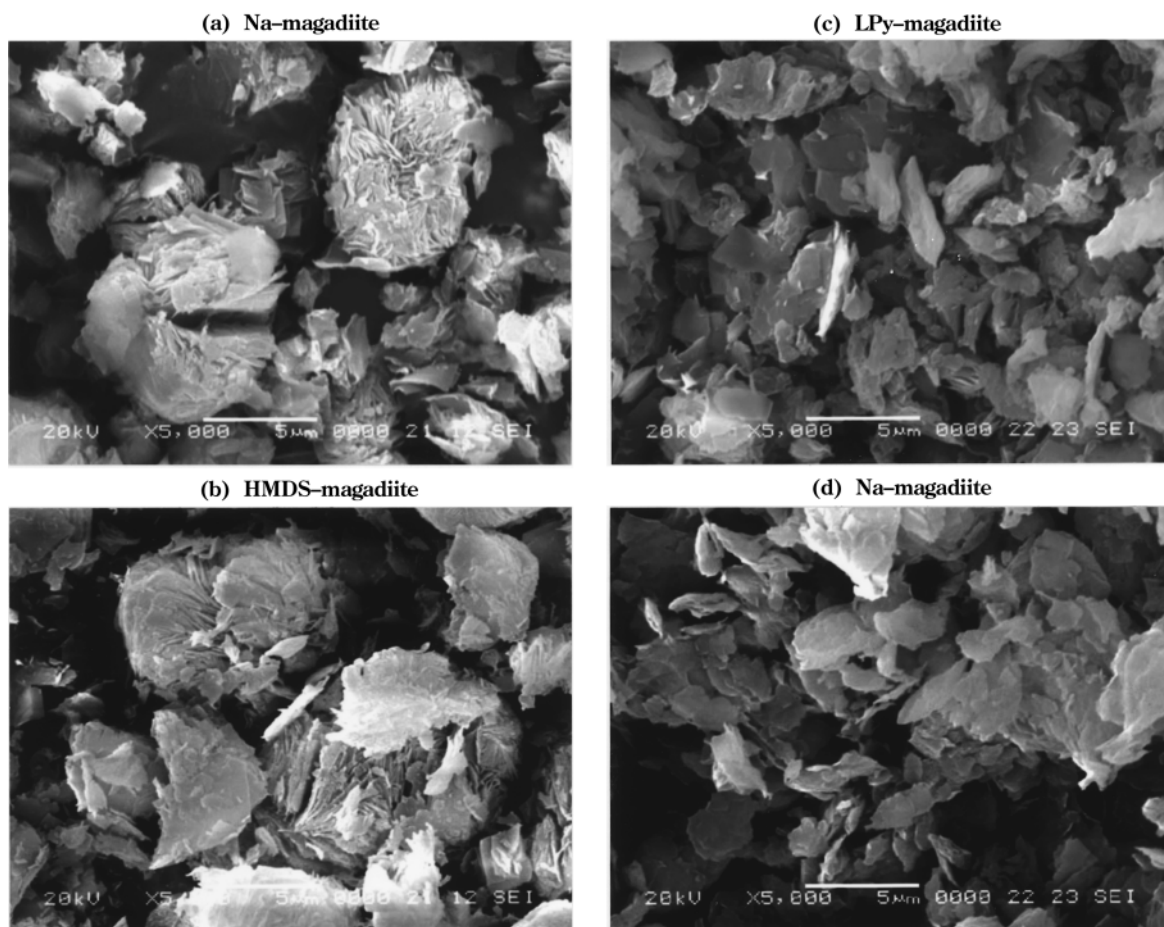
autoclave sealed stainless tube according to previous literature.<sup>8</sup> The hydrothermal reactions were carried out at 170 °C

for 18 h accompanied by stirring at 300 rpm. The obtained reaction mixture was then washed with a dilute NaOH aqueous solution and dried at 50 °C for 48 h. The resulting white powder was analyzed by X-ray powder diffractometry (Rigaku Co., Ltd., Rint 2100V) operated at 40 kV and 40 mA using a scanning rate of 1°/min and a scan step of 0.01°. Its morphology was also investigated by SEM (JEOL, JSM-6300).

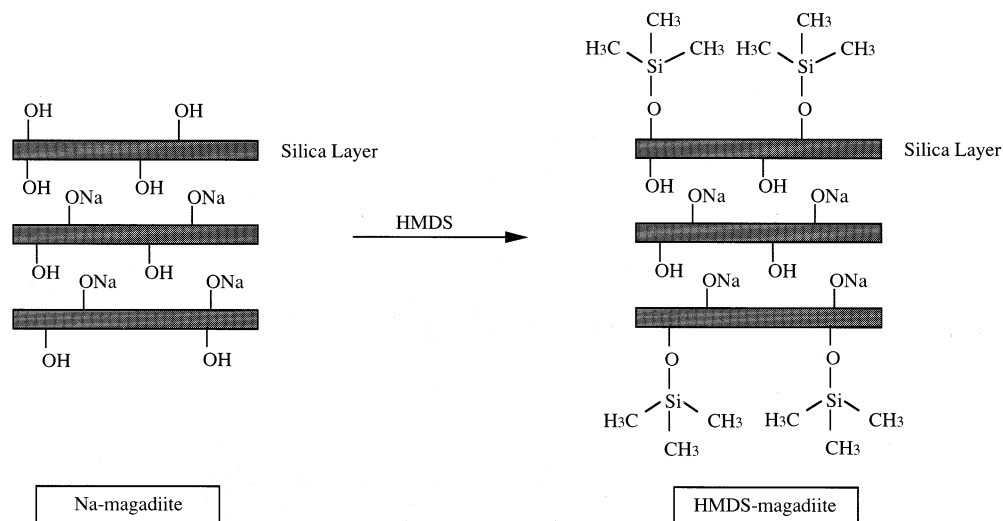
**Trimethylsilylation of Magadiite.** To modify the surface nature of magadiite, hexamethyldisilazane (HMDS, 20 mL) was treated with the magadiite (1 g) suspension in absolute toluene (10 mL) and was refluxed for 48 h. After the reaction, the prepared sample was filtered off and washed three times with hexane. The amounts of the trimethylsilyl group were determined by elemental combustion analyses of the carbon and nitrogen contents.

**Intercalation of Organic Guests into the Magadiite Interlayers.** The intercalation of laurylpyridinium chloride (LPyCl) into the magadiite interlayers was carried out in an aqueous suspension by heating at 60 °C for 2 days and with the addition of LPyCl of 10% excess compared to the amounts of intercalated silanol groups of magadiite. The degree of intercalated LPy<sup>+</sup> ions in the magadiite interlayers was evaluated by measurements of the absorbance of the remaining LPy<sup>+</sup> ions in the filtrate with an UV-vis spectrometer (Jasco, V-550).

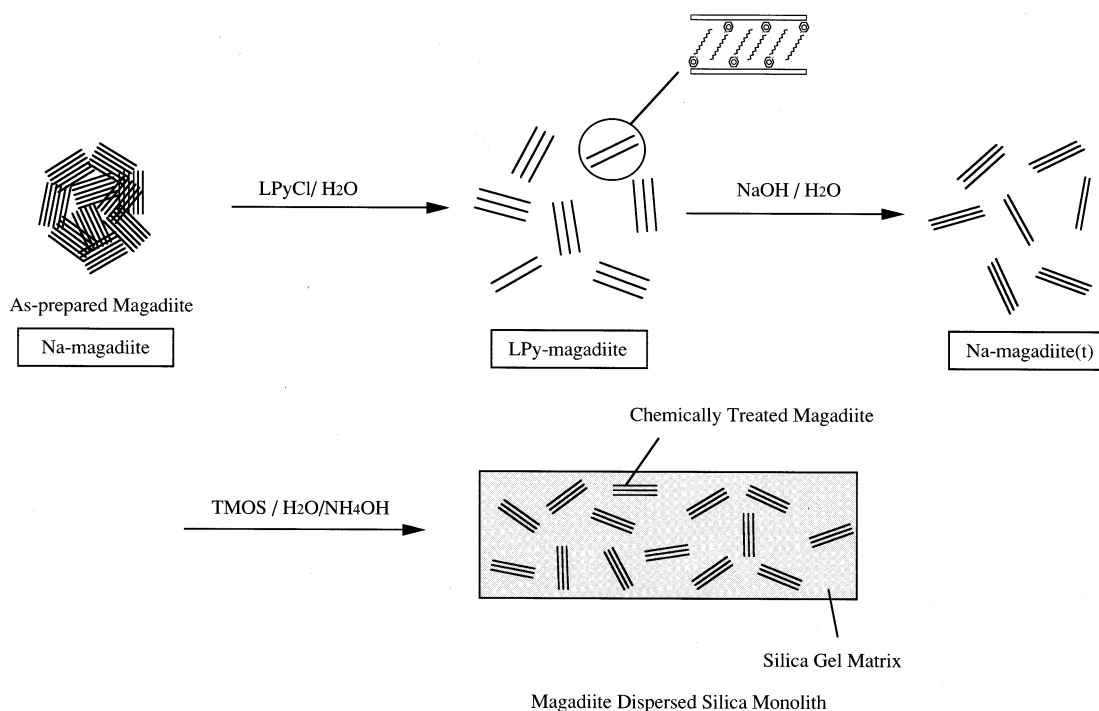
**Preparation of the Silica Monolithic Gel.** To obtain a transparent monolithic gel even under acidic and basic conditions, it has been reported that the addition of DCCA can avoid cracking. Because reactions such as protonation in the clay interlayers need to be suppressed during preparation of the silica monolithic gel, a mild alkaline condensation condition was applied in accordance with a report by Adachi and Sakka.<sup>7</sup> The experimental flowchart was indicated in Figure 1. Tet-



**Figure 3.** SEM photographs of magadiite powder. (a) Hydrothermally prepared sodium magadiite. (b) Magadiite powder treated with HMDS. (c) Magadiite powder intercalated with LPy<sup>+</sup>. (d) Sodium magadiite prepared from LPy-magadiite.



**Figure 4.** Schematic model of the chemical modification of magadiite with HMDS; procedure (A).



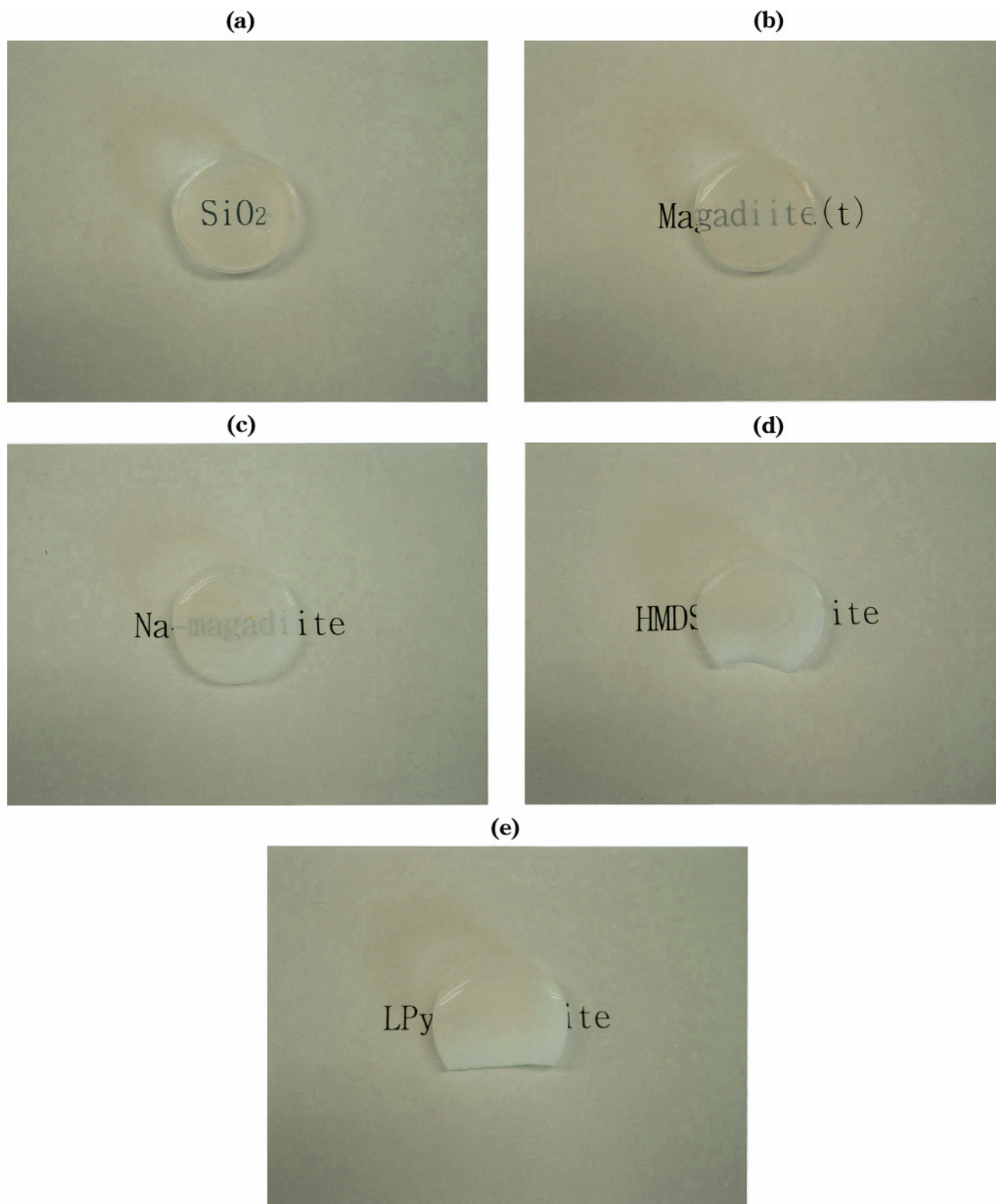
**Figure 5.** Chemical reaction of magadiite and its application for the syntheses of magadiite-dispersed silica monoliths; procedure (B).

ramethoxysilane (TMOS, 2 mL) and *N,N*-dimethylformamide (DMF, 0.9 mL) were mixed with 1.2 mL of methanol and a dilute ammonia aqueous solution (2.4 mL, pH = 9). The solution was then sonicated for 10 min. A dispersion of sodium magadiite or chemically treated magadiite powders (50 mg) in DMF (0.14 mL) prepared by trimethylsilylation or intercalation–deintercalation processes, as mentioned above, were added into the TMOS/DMF mixed solution under ultrasonication. After sonication for 5 min, the suspended solutions were poured into a Teflon container with a diameter of 30 mm. The samples were kept under ambient conditions for 4 days and then placed in an oven at 50 °C for an additional 3 days, followed by complete drying under vacuum for 4 days. The structural analysis of the dried gel monoliths were performed by SEM investigations.

## Results and Discussions

**Alkylsilylation of Magadiite.** To obtain homogeneous and optically transparent gel monoliths, two approaches were examined for the hydrothermally prepared sodium magadiite powder (Na–magadiite). Procedure (A) involves the trimethylsilylation of the surface silanol groups of magadiite using hexamethyldisilazane (HMDS) for the purpose of hydrophobic modification of the surface. The XRD profile of HMDS–magadiite in Figure 2b was almost comparable to that of the starting magadiite in Figure 2a, suggesting that HMDS reacted with the silanol groups only on the surface of the magadiite particle but not with those in the interlayers because no change in the basal spacing of the resulting magadiites could be observed. The IR spectrum of the powder indicates the existence of trimethylsilylated





**Figure 6.** Photographs of silica- and magadiite-dispersed silica monoliths. (a) Pure silica gel monolith. (b) Hybrid gel monolith dispersed with Na-magadiite. (c) Hybrid gel monolith dispersed with Na-magadiite (t). (d) Hybrid gel monolith dispersed with HMDS-magadiite. (e) Hybrid gel monolith dispersed with LPy-magadiite.

silanol by weak absorptions at  $2970\text{ cm}^{-1}$  assigned to the methyl group. The composition of the HMDS-magadiite could be estimated as  $\text{Na}_2\text{Si}_{14}\text{O}_{26}(\text{OH})_{6-x}\cdot 6\text{-H}_2\text{O}\cdot 0.13\text{Si}(\text{CH}_3)_3$  based on the elemental analysis.

Procedure (B) involves the preintercalation process of the cationic surfactant molecules. Significant mor-

phological change was observed as a result of the intercalation of  $\text{LPy}^+$  ions into the magadiite interlayers. A strong diffraction line due to the basal plane of the magadiite was observed around  $2\theta = 2.2^\circ$  in Figure 2c, which corresponds to a distance of  $40.8\text{ \AA}$ , suggesting that a swelling of the magadiite took place by the

introduction of the  $\text{LPy}^+$  ions and opening of the interlayers. The intercalated  $\text{LPy}^+$  ions amounted to more than 80% based on the CEC by analysis of the UV–vis measurements of the filtrate. The  $\text{LPy}^+$  ions intercalated in magadiite could be replaced again by  $\text{Na}^+$  with the addition of the NaOH solution ( $\text{Na-magadiite(t)}$ ), as shown in Figure 2d.

The morphology of the magadiite powders was studied by SEM observations, as shown in Figure 3. The as-prepared sodium magadiite ( $\text{Na-magadiite}$ ) consists of large agglomerates with a characteristic round-shape and lamella structure, as can be seen in Figure 3a. A similar spherical shape can also be seen in the HMDS–magadiite hybrid powder, indicating that HMDS only reacts with the surface silanol groups, as illustrated in Figure 4. On the other hand,  $\text{LPy}^+$ –magadiite can be seen as small platelike crystallites with a piled structure, which resulted in a favorable orientation in the XRD profile. During the intercalation procedure, delamination of the magadiite layers occurred together with the swelling of the hybrid particles. Further treatment with a NaOH aqueous solution resulted in the complete exchange of  $\text{LPy}^+$  ions to sodium ions while keeping the platelike morphology ( $\text{Na-mag(t)}$ ). This chemical process is illustrated in Figure 5. The results suggest that such  $\text{Na-mag(t)}$  can be useful in incorporating functional guest molecules when dispersed in the silica matrix.

The resulting magadiite powders were used for the preparation of the magadiite–silica monolithic gels by dispersion in the silica matrixes. In general, the most serious problem that needs to be avoided is the cracking of the monoliths. Figure 6a shows the transparent silica gel monolith obtained using the same preparation procedures, however, in the absence of magadiite. The hybrid monoliths with a diameter of 17 mm and a thickness of 3.5 mm were successfully prepared without any cracks. However, hybridization with the magadiite caused a significant decrease in the optical transparency. For example, the silica monolith incorporated with the as-prepared  $\text{Na-magadiite}$  is translucent because of the large magadiite particles precipitated toward the bottom of the monolith, as shown in Figure 6b. In the case of HMDS–magadiite and  $\text{LPy-magadiite}$  in parts

d and e of Figure 6, the synthesized monoliths became opaque, although the particles were homogeneously dispersed throughout the matrix. The opaqueness may come from the existence of fine air bubbles generated in the silica matrix during the gelation process. In contrast, for the case of the  $\text{Na-mag(t)}$ , a clear and transparent monolith could be synthesized, as shown in Figure 6c. The homogeneous dispersion of the treated magadiite powder in the silica matrix was concluded to be crucial in the effective hybridization of the magadiite silica. The swelling character of the resulting magadiite was also examined by XRD analysis during the hydrolysis and the condensation of TEOS. Thus, the synthesis of such new materials as these magadiite powders by combining functional organic molecules with layered oxide hybrids was possible for applications in optical devices.

### Conclusions

Two chemical modification processes were investigated for the preparation of a fine magadiite platelike crystal. Our studies revealed that the intercalation of  $\text{LPy}^+$  ions followed by resubstitution with  $\text{Na}^+$  was more effective than the conventional method of trimethylsilylation of the surface silanol groups of the magadiite particles in the formation of well-isolated crystallite layers. To prepare highly transparent magadiite– $\text{SiO}_2$  monoliths, the suppression of the segregation of the magadiite particles in the sol–gel-derived silica matrix was also found to be vital. A rather transparent monolith including the isolated fine magadiite particles could be synthesized using a  $\text{Na-magadiite(t)}$  under weak basic conditions without cracking or the formation of bubbles.

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