



Crystal architectures of a layered silicate on monodisperse spherical silica particles cause the topochemical expansion of the core-shell particles



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ABSTRACT

Anisotropic structural changes in an expandable layered silicate (directed towards the *c*-axis) occurring on isotropic and monodisperse microspheres were detected by measurable increases in the grain size. The hierarchical changes were observed through pursuing the sophisticated growth of expandable layered silicate crystals on monodisperse spherical silica particles with diameters of 1.0 μm; the core-shell hybrids with a quite uniform grain size were successfully produced using a rotating Teflon-lined autoclave by reacting spherical silica particles in a colloidal suspension with lithium and magnesium ions under alkaline conditions at 373 K. The size distribution of the core-shell particles tended to be uniform when the amount of lithium ions in the initial mixture decreased. The intercalation of dodecyltrimethylammonium ions into the small crystals through cation-exchange reactions expanded the interlayer space, topochemically increasing the grain size without any change occurring in the shapes of the core-shell particles.

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1. Introduction

It is an attractive proposition to use the expandable two-dimensional nanospaces in layered materials to organise guest organic species to add to the possibilities that are already available, which are to use ordered and constrained nano-environments and well-established nanoporous materials (e.g. zeolites and mesoporous solids) [1–4]. Inorganic–organic periodic materials such as metal–organic frameworks, porous coordination polymers [5,6] and crystal-like periodic organosilicas [7,8], have been of increasing interest because the organic moieties are spatially arranged in regular patterns in these materials. Nanosheet components have recently been used as scaffolds to create nanospaces to accommodate guest species [9,10]. However, nano-architectures involving the intercalation of organic moieties into two-dimensional expandable interlayer spaces in inorganic layered solids have long been studied. Nanospaces in interlayer space have been controlled by controlling the spatial distributions of the organic moieties by varying the numbers, positions and sizes

(molecular geometries) of the organic moieties [11–17]. This nanostructural versatility has encouraged us to seek further applications for these systems in selective adsorption, separation, catalysis and photochemical reactions [16].

The smectite group of layered clay minerals has been more extensively studied than have other layered inorganic solids [18,19]. Smectites are composed of ultrathin (*ca.* 1.0 nm) crystalline silicate layers separated by hydrated interlayers [19,20]. A silicate layer is composed of two silicon tetrahedral sheets and one aluminium (or magnesium) octahedral sheet. A negative charge in a silicate layer, generated through isomorphous substitution (e.g. the substitution of Si⁴⁺ with Al³⁺ in a tetrahedral sheet or of Mg²⁺ with Li⁺ in an octahedral sheet), will be compensated for by the presence of an interlayer alkali metal cation. Cation-exchange reactions between the interlayer cations and organoammonium ions are well known, and they are used in such applications as modifying surfaces, producing hydrophobic and microporous inorganic–organic hybrids for the uptake of specific molecules [21,22], producing controlled release materials, achieving selective catalysis and achieving efficient photo-induced processes. [16,23]. The cation exchange capacity (CEC), which directly correlates with the negative-layer charge density, is an important determiner of the distance

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between adjacent interlayer cations (the spatial density). Achieving an appropriate distance can allow the material to act as a molecular sieve for nonionic organic compounds [24–29] or to improve the photofunctions of photoactive molecules [30–34]. It has therefore been recognised that one of the advantages smectites offer (in addition to the many other important properties of smectites and their intercalation compounds) is that the CEC can be varied in order to control the spatial distribution of organic moieties [35]. Hectorite [36] and saponite [37] are layered clay minerals in the smectite family that have variable CECs. Hectorite and saponite have been synthesised for use precisely controlling cationic dye distributions [37] and adsorbing organic molecules [38].

The ability to control the morphology (i.e., grain size and shape) of a smectite is vital to achieving the optimum performance of a molecularly recognizable smectite-based hybrid. Quite fine crystals of synthetic smectites are generally obtained [39,40]. The shapes required have been produced through the bottom-up self-assembly of silicate layers by freeze-drying hydrogels [41–43], moulding non-cordierite honeycomb monoliths [44] and using optically transparent films [45–48] fabricated using various techniques (including depositing a smectite suspension on a substrate, using the Langmuir–Blodgett technique to exfoliate platelets [49–51] and using a layer-by-layer deposition technique [52–54]). The deposition of smectite silicate layers on different particles using an alternating adsorption technique [55] has recently allowed another class of multifunctional materials with hierarchical hybridizations to be produced. We have described the *in situ* crystallization of a smectite-like layered silicate on spherical silica particles. In that process the silica particles were found to be consumed through hydrothermal reactions without losing the silica morphology, and the silica that was consumed was found to be used as the source of the smectite [56]. Core–shell hybridization is not like the *papier mâché* method (but the so-called sacrificial template or self-template method), and it is possible to avoid flakes falling off the silica particles even in aqueous media. The monodisperse core–shell particles produced using the sacrificial template method could be used as host materials and/or building units in future separation, sensor, optics and electronic applications because the periodic arrangement of smectite (or a related layered solid) particles with defined shapes is key to achieving more sophisticated functional materials [57,58].

Here, we describe the sophisticated crystal growth of a hectorite-like layered silicate (abbreviated to Hect) with the ideal formula $\text{Li}_x(\text{Mg}_{6-x}\text{Li}_x\text{Si}_8\text{O}_{20}(\text{OH})_4) \cdot n\text{H}_2\text{O}$ on monodisperse amorphous spherical silica particles (abbreviated to Silica@Hect) using a sacrificial template method. Changing the LiF/MgCl₂ molar ratio in the starting mixture allowed the size of the Hect on the silica to be the negative-layer charge density of the Hect on the silica to be varied, from 0.5 to 0.9 mEq/g of Hect. The topochemical expansion of the Silica@Hect core–shell particles occurred when cationic surfactants were intercalated into the Hect via ion–exchange reactions.

2. Experimental section

2.1. Materials

Lithium fluoride, magnesium dichloride hexahydrate, urea, dioctadecyldimethylammonium (abbreviated to 2C₁₈) bromide, and methylene blue (abbreviated to MB) were purchased from Wako Pure Chemical Ind., Ltd. Monodispersed spherical silica powder with the grain size of 1.0 μm (KE–S100, Nippon Shokubai Co., Ltd.) was used as the source of hectorite-like silicate. All these chemicals were used without further purification.

2.2. Fabrication of Silica@Hect core–shell particles

A typical procedure was reported that described in the previous paper [56]. Here we modified the hydrothermal reaction conditions including chemical compositions and the heat treatment. A typical example of the LiF:MgCl₂:SiO₂:urea molar ratio in the starting mixture was 0.21:0.8:8.0:8.0, where the amounts of the Li and Mg sources added relative to the amount of SiO₂ were decreased by 15% from the Li:Mg:Si ratio of 1.4:5.6:8.0 [36]. Urea (2.16 g), MgCl₂·6H₂O (0.73 g) and LiF (0.024 g) were dissolved in water (80 mL). The resulting solution was mixed with an aqueous suspension of spherical silica particles (2.16 g in 20 mL of water) using a mechanical homogenizer (at 4600 revolutions per minute) for 30 min at room temperature. The slurry was transferred to a Teflon-lined autoclave and heated to 373 K for 48 h. The autoclave was rotated at 15 revolutions per minute using a hydrothermal synthesis reactor unit (Hiro Company) during the heat treatment. The slurry was then cooled in an ice bath and centrifuged (at 1400 g for 20 min), then the precipitate was collected and dried at 323 K. The LiF:MgCl₂:SiO₂ molar ratio in the starting mixture was changed as summarised in Table 1 to vary the CEC of the product.

2.3. Adsorption isotherms of MB on Silica@Hect from aqueous solution

Silica@Hect core–shell particles (0.05 g) were reacted with 20 mL of aqueous MB solution (0.13–0.75 mM) in a glass vessel with magnetic stirring for 1 day at 25 °C. To estimate the adsorption of MB to the vessel, blank samples containing 20 mL of aqueous MB solution with no adsorbents were also prepared. After centrifugation (1400 g, 20 min), the concentration of MB remaining in the supernatant was determined by Vis. spectroscopy (λ = 665 nm).

2.4. Cation-exchange reactions of Silica@Hect with a cationic surfactant

2C₁₈ bromide (15 mg) in a mixture of water and ethanol (10 mL, 50/50 v/v) was allowed to react with Silica@Hect (0.1 g) by magnetic stirring at room temperature for 1 day. The product was collected by centrifugation (1400 g for 20 min); this was followed by repeated washing with the mixture of water and ethanol. Finally, the washed solid was dried at 323 K.

2.5. Equipments

X-Ray powder diffraction (XRD) patterns were obtained by a Rigaku RINT 2200V/PC diffractometer (monochromatic Cu Kα radiation), operated at 20 mA, 40 kV. Thermogravimetric-differential thermal analysis (TG-DTA) curves were recorded on a Rigaku TG8120 instrument at a heating rate of 10 K/min and using α-alumina as the standard material. Nitrogen adsorption–desorption isotherms were measured at 77 K on Belsorp–mini (BEL Japan, Inc.). Before the adsorption experiment, the samples were heat-treated at 393 K under a reduced pressure. Scanning electron

Table 1
Sample list in the present study.

molar ratio of the starting mixture LiF:MgCl ₂ :SiO ₂ :urea	Sample name
0.21:0.80:8.0:8.0	Silica1.0@Hect1
0.42:0.69:8.0:8.0	Silica1.0@Hect2
0.63:0.69:8.0:8.0	Silica1.0@Hect3
0.84:0.69:8.0:8.0	Silica1.0@Hect4

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