Research paper

Effects of fluoride and urea on the crystal growth of a hectorite-like layered silicate on a silica surface

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ABSTRACT

Dissolution of the silica substrate has been considered to be the initial reaction step in the in situ crystallization of hectorite-like layered silicate (Ht) on a silica surface in an aqueous urea solution at 373 K, occurring before the reactions with LiF and $MgCl_2$. However, the effects of the quantities of fluoride and urea on Ht crystal growth are unclear. Here, magnetite particles encapsulated inside silica microcapsules were used as an indicator of silica dissolution to elucidate the mechanism of Ht growth. When large quantities of LiF and urea were used, the amount of crystallized Ht increased but the magnetization (at 12 kOe) of the sample was reduced, showing erosion of the occluded magnetite particles after dissolution of a certain proportion of the hollow encapsulating silica grains. Hence, the observed reduction in magnetization was adopted as a means to estimate the degree of dissolution of silica during Ht formation. Appropriate concentrations of urea and fluoride were used in the aqueous dispersions to control the amount of Ht formed in the heterogeneous nucleation reactions without the need for excess quantities of silicate, Li^+, and Mg^{2+}.

1. Introduction

There has been growing interest in the heterogeneous nucleation reactions of layered inorganic crystals on bulk solid substrates as a consequence of their practical importance in the production of mechanically improved supporting materials, especially for separation and catalysis in flow systems. The solid substrate has been used as a source for the layered materials; the other chemicals are supplied from the solution media. The choice of the solid substrate chemical present in solution can lead to the formation of various fine crystals such as titanosilicate–silica fibers (Pérez-Carvajal et al., 2013), M(= Ni, Zn)/Al layered double hydroxides (LDH)–Al_2O_3 plates (Chen et al., 2006; Zhang et al., 2008), and M(= Mg, Zn)/Al LDH–Al_2O_3 fibers (Zhang et al., 2013, 2014). The reactions at the interface lead to the formation of fine crystals on the substrate, while preserving the shape of the substrate (the so-called sacrificial template or self-template).

The smectite group of layered clay minerals has long been studied in various materials' application, because of their swelling and cation exchange abilities, and structural/compositional versatility (Theng, 1974; Barrer, 1989; Ogawa and Kuroda, 1995; Bergaya et al., 2006; Okada et al., 2012a, 2014a, 2015a; Takagi et al., 2013). Synthetic smectites, which possess swelling properties similar to those of natural smectites,

have been widely studied and used (Newmann and Sansom, 1970; Torii and Iwasaki, 1986; Carrado et al., 1991, 1993, 1997; Tateyama et al., 1996; Kloprogge et al., 1999; Carrado, 2000; Reinholdt et al., 2001; Jaber and Miehé-Brendlé, 2005, 2008; Stöter et al., 2013). Recently, the heterogeneous nucleation reactions of fine crystals of hectorite-like (Okada et al., 2012b, 2015b, 2016a, 2016b; Okada and Suzuki, 2015) and saponite-like (Okada et al., 2015c) layered silicates have been investigated on an amorphous silica substrate. The silica substrate acts as a sacrificial template and functions as the source of the layered silicates through partial dissolution without loss of morphology. The size and shape of the silica substrate (e.g., fiber and sphere) alter the characteristics of the final product, and unique and useful phenomena/functions have been reported, including ready recovery from aqueous media (Okada et al., 2012b), topochemical intercalation (Okada et al., 2015b), filtration (Okada et al., 2016a), rapid chiral discrimination (Okada et al., 2016b), and controlled release (Okada et al., 2015c). Hence, silica substrates offer many advantages as heterogeneous nucleation media for the construction of a hierarchically designed supporting material.

The mechanism of the heterogeneous nucleation reactions of a hectorite-like layered silicate (Ht) with the ideal formula $Li_x[Mg_{6-x}Li_xSi_8O_{20}(OH)_4 \cdot nH_2O]$ on amorphous silica particles has been discussed (Okada et al., 2012b, 2015b, 2016a). In addition to silica, the required chemical reagents are LiF, $MgCl_2$, and urea. Hydrolysis of urea at 373 K increases pH in aqueous solution to yield the crystal embryo;

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because the dissolved silica is consumed during the Ht formation, the compositional balance of silica, LiF, and $MgCl_2$ should be responsible for the heterogeneous nucleation. In a recent report describing the heterogeneous nucleation of Ht on a silica fiber, spherical silica particles co-precipitated through the polycondensation of silica oligomers as a side reaction when an excess amount of urea was added to the starting solution (Okada et al., 2016a). In addition, the presence of fluoride (LiF) in the initial solution should catalyze the hydrolysis of silica substrates. The concentrations of urea and fluoride are thus expected to play a dominant role in the dissolution of silica. Although the quantity of silica supplied by the dissolution is important in precisely designing the Ht crystals including the thickness of the Ht layer on the silica surface, it is difficult to estimate the quantity of silica dissolved during the hydrothermal reactions. Hence, an indicator of the amount of dissolved silica substrates is required to discuss the mechanism of in situ crystallization.

Here, the correlation between silica substrate dissolution and crystal growth of Ht is determined under hydrothermal conditions (373 K for 48 h) using magnetite particles occluded in hollow amorphous silica microcapsules. In an alkaline hydrothermal environment, magnetite is readily eroded (Uchida et al., 2011) and loses its magnetism. Hence, the reduction in the degree of microcapsule magnetization predicts the degree of silica dissolution. A systematic experiment using this material was conducted by changing the quantities of fluoride and urea in the starting mixture.

2. Experimental

2.1. Materials

Iron(III) nitrate nonahydrate (99%), lithium fluoride (99.9%), sodium chloride (99.5%), calcium chloride (95%), lithium chloride (99.0%), magnesium dichloride hexahydrate (98.0%), urea (99.0%), methylene blue tetrahydrate (95.0%), and isooctane (2,2,4-trimethylpentane) were purchased from Wako Chemical Co., Ltd. Octyltrichlorosilane (OTCS) and methyltrichlorosilane (MTCS) were purchased from Aldrich Chemical Co., Ltd., and Shin-Etsu Chemical Co., Ltd., respectively. These materials were used as received.

2.2. Preparation of silica-encapsulated magnetite particles

The silica microcapsules used as the starting material were prepared according to a literature procedure (Okada et al., 2014b), which is described reproduced here in detail. Water droplets in a water-in-oil (W/O) emulsion were used as templates for the silica microcapsules as follows. MTCS (9 mmol) in isooctane (10 mL) was poured into a W/O emulsion prepared by mixing water (0.22 mL), an aqueous solution of $Fe(NO_3)_3$ (0.75 mL, 3.0 mol/kg), and OTCS (12 mmol) in isooctane (50 mL) under magnetic stirring. The mixture was stirred at room temperature for at least 3 h to form polymethylsiloxane shells around the aqueous droplets. After filtration, the product was washed with isooctane and dried at 323 K for 1 day. The dried product was heated at 393 K in air, and then calcined at 873 K in an electronic furnace. The calcined solid was treated under a flow of H_2 gas at 583 K and was subsequently heated to 973 K in a flow of N_2 gas. After cooling in the N_2 flow, the resulting product was stirred with 1 M HCl for 1 day. The acid-treated sample was recovered using neodymium magnets, whose surface magnetic field was 3.8 kOe, located at both sides of a glass vial (outer diameter of 21 mm). The magnetic field gradient from the center of the glass bottle to the magnet was 1.9×10^2 kOe/m. The recovered samples were thoroughly washed with water before further magnetic recovery. Hereafter, the product is denoted as $Fe_xO_y@SiO_2$.

The amount of Fe in $Fe_xO_y@SiO_2$ was 6 mass% (ICP analysis). The magnetization at 12 kOe (Ms), remanence, and coercive force were 4.0 emu/g, 1.3 emu/g, and 0.3 kOe, respectively. The average grain size of the $Fe_xO_y@SiO_2$ was 0.6 μm, and almost all grains were less than 3 μm in size (Okada et al., 2014b).

2.3. Heterogeneous nucleation reactions of Ht on the silica microcapsules

The typical molar ratio of $LiF:MgCl_2:SiO_2:urea$ in the starting mixture was 0.21:0.8:8:8 (Okada et al., 2015b), where the Li and Mg salts were diminished to 15% from the ratio of Li:Mg:Si = 1.4:5.6:8.0 used in a synthetic procedure using a silica sol (Ogawa et al., 2008). The magnetic silica microcapsules were immersed in a Teflon-lined autoclave containing 0.05 L of an aqueous solution of LiF, $MgCl_2$, and urea for every gram of microcapsules; the mixture was then heated at 373 K for 48 h. After the reaction vessel was cooled in an ice bath, the resulting dispersions were collected using neodymium magnets as described above. Hereafter, the product is abbreviated as F15, where "15" refers to the estimated amount of Ht in the sample. The different molar ratios of $LiF:MgCl_2:SiO_2:urea$ are summarized in Table 1. When the quantities of LiF and $MgCl_2$ were doubled, the sample name is given as F30. The subscript (1/4 or 1/800) represents the molar ratio of urea with respect to the typical ratio (i.e., Si:urea = 1:1).

2.4. Cation-exchange capacity

The cation-exchange capacity (CEC) of the Ht hybrid samples was determined from the quantity of calcium exchanged (Ogawa et al., 1992). Each sample grains (0.1 g) was immersed in an aqueous $CaCl_2$ solution (0.2 mM, 25 mL). The solution was regenerated twice and used after washing with deionized water until a negative $AgNO_3$ test was obtained. The Ca-exchanged form was repeatedly washed with an aqueous solution of NaCl (0.4 mM, 25 mL) in order to replace the entrained Ca^{2+} ions with Na^+ ions, and ion chromatography was used to determine the concentration of Ca^{2+}.

2.5. Adsorption of MB

The adsorption of cationic methylene blue (MB) dye was investigated using a batch test. A small (0.05 g) sample of either F15 or $Fe_xO_y@SiO_2$ was reacted with 5 mL of an aqueous MB solution (0.1 mM) in a glass vessel for 2–24 h at room temperature, and the resulting solid was then separated using neodymium magnets.

2.6. Equipment

X-ray powder diffraction (XRD) patterns were obtained using a Rigaku RINT 2200 V/PC diffractometer (monochromatic Cu Kα radiation) operated at 20 mA and 40 kV in the 2θ range from 2° to 70°, where the sampling step and counting time were 0.01° and 1.0 s, respectively. Scanning electron micrography (SEM) images were captured on a Hitachi SU-8000 field-emission scanning electron microscope (operated at 1 kV) after applying an osmium plasma coating to the samples. The transmission electron micrographs with energy dispersive X-ray (EDX) mapping were obtained on a Hitachi High-Tech HD-2300A spherical aberration corrected scanning transmission electron microscope (STEM) equipped with an EDAX Genesis XM 4 EDX spectrometer (accelerating voltage of 200 kV). The sample powder was deposited on a TEM Cu grid. Magnetization curves were obtained from a Toei Kogyo VSM-5S vibrating sample magnetometer (VSM). Ion

Table 1
Sample name, chemical composition of the starting mixture, CEC, and the magnetization at 12 kOe (Ms) for the silica-encapsulated magnetic particles and the Ht-coated particles prepared in this study.

Sample	$LiF:MgCl_2:SiO_2:urea$	CEC [10^{-5} eq/g]	Ms [emu/g]
$Fe_xO_y@SiO_2$	–	–	4.0
F15	0.21:0.8:8:8	2.9	0.78
F15-1/4	0.21:0.8:8:2	1.6	3.4
F15-1/800	0.21:0.8:8:0.01	0.36	4.0
F30	0.42:1.6:8:8	6.1	0.71
F30-1/4	0.42:1.6:8:2	4.3	0.85