Topochemical Transformation of Phyllosilicate Clay into Chlorite and Brucite

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Manipulation of two-dimensional layer structures has attracted a great deal of interest due to their importance in academic and industrial fields.[1] To date, the layer manipulation has been approached in two major directions, the modification of both intralayer surface and interlayer space[2−4] and the rearrangement of framework layers into other structures including amorphous phase.[5,6] The former leads to modified layer structures such as inorganic−organic hybrids, pillared clays, and nanocomposites without any changes in inherent framework of layers, whereas the latter accompanies the disintegration of the framework layer typically to be found in extraction of specific components and fabrication of functional materials from natural clays. As another new approach, here we have attempted to manipulate the framework layers composed of several polyhedral sheets, which not only allows a deep insight into layer structures but also offers unprecedented topochemical conversions of various natural clays into a number of advanced materials.

Framework layers of most natural clays are generated by a combination of octahedral and tetrahedral sheets.[7] Typically, silica is a main component of a tetrahedral sheet, although aluminate is frequently found in the tetrahedral sheet at various ratios. On the other hand, octahedral sheets comprise diverse elements, among which aluminum and magnesium are most rich.[6,7] A natural combination of tetrahedral and octahedral sheets occur in the specific ratios and modes, representatively grouped into structures such as mica, kaolinite, chlorite, and brucite. It is clear from these structures that the mica structure may be manipulated into either brucite or chlorite and kaolinite by selective removal of each tetrahedral sheet (Figure 1). Such sophisticated sheet-by-sheet manipulations could result in highly selective retrieval of the specific components as well as in unique topochemical transformation of framework layers, clearly distinguished from other selective leaching and conversion techniques.[5,6]

The sheet-by-sheet manipulation of framework layers would be possible only when the desired reaction occurs very homogeneously in interlayer space. Furthermore, it is also essential to control the reaction exactly. To meet these strict conditions, we develop a dry gel method that employs the partially hydrated (wet) strong base and the dry reaction. Our preliminary study revealed that neither solution-based nor solid reaction led to complete topochemical manipulation. In the dry gel method, however, mixing expandable clay with a wet base may facilitate rapid introduction of the base into an interlayer space of clay. Subsequent drying may lead to further, nearly complete, introduction and final thermal treatment allows a stoichiometric and homogeneous reaction in interlayer space. To our surprise, sheet-by-sheet removal of tetrahedral sheets in a mica-type clay is clearly visualized with a expandable fluoromica with a magnesia-base octahedral sheet by the dry gel method.

A synthetic clay, Na fluoromica (CO-OP Chemical Co., Japan) with the ideal chemical formula of $Na_{0.66}(Si_{3.98}Al_{0.02})[Mg_{2.68}]O_{10.02}F_{1.96}$, was used in this study to exclude possible impurity effects on the transformation process.[8] The mica gel, which is prepared by the addition of 150 wt % water, is well-mixed with solid NaOH by grinding in a mortar. This dry gel reaction method is adopted to selectively remove only a silica sheet from fluoromica with the different molar ratios of NaOH/clay. A gel mixture was aged for 30 min at room temperature and then treated in the dry gel state at 100 °C for 4 h under an ambient atmosphere. The reaction product is washed several times with 1 M NaOH solution and distilled water in order to completely remove the dissolved silicates from Na fluoromica, and then it was oven-dried at 60 °C for 12 h. Powder X-ray diffraction patterns of the samples were recorded on a Philips PW1830 automated powder X-ray diffractometer with Cu Kα radiation ($\lambda = 1.5418$ Å). High-resolution transmission electron microscopy (HRTEM) images were obtained with an FE-TEM (H-9000NA) operated at an accelerating voltage of 300 kV. The cross-sectional HRTEM specimens of the reaction products were prepared by ultramicrotome. To examine the presence of fluorine ions in the products, spatially resolved electron energy-loss spectroscopy (EELS) experiments were car-

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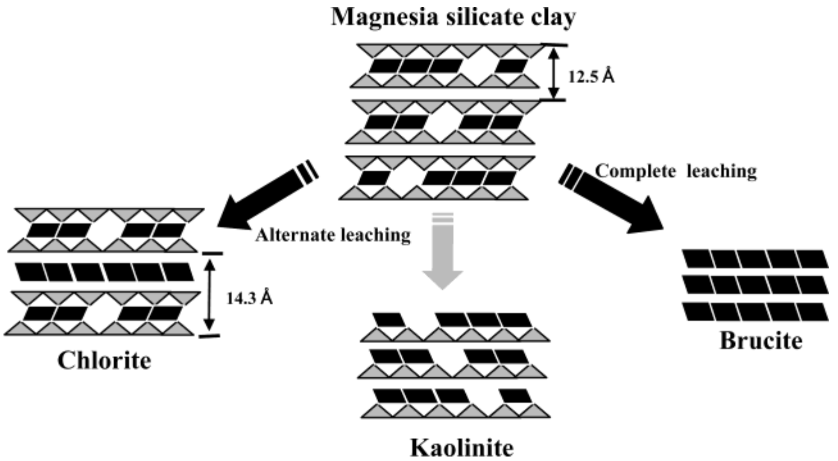

Figure 1. Schematic of topochemical transformation of a 2:1-type layered clay via selective leaching of silicate sheets.

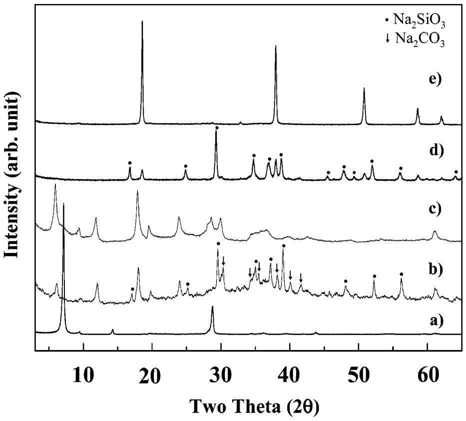

Figure 2. Powder X-ray diffraction patterns of (a) fluoromica and the reaction products obtained by selective leaching at 100 °C under an ambient atmosphere with the various OH^-/Si molar ratios: (b) chlorite before washing, (c) chlorite ($OH^-/Si = 1$), (d) brucite before washing, and (e) brucite ($OH^-/Si = 6$).

ried out in a Philips Tecnai UT-30 TEM operated in STEM mode and equipped with an Enfina system. The morphology and particle size for the products were investigated by an Hitachi S-4500 scanning electron microscopy (SEM) after the samples were coated with Pt/Pd alloy for 180 s with an E-1030 ion sputter.

Figure 2 shows the XRD patterns of the products obtained from a synthetic Na fluoromica with the various OH^-/Si molar ratios. Fluoromica is transformed either into chlorite or brucite, depending on the OH^-/Si molar ratio. In addition, it could be seen that the as-prepared samples (before washing) in both cases contain a noticeable amount of Na_2SiO_3, which is subsequently washed out. This result suggests that topochemical reassembly of sheets is accompanied by selective removal of each tetrahedral sheet. Chlorite is obtained when the OH^-/Si molar ratio is close to a value of 1. The characteristic (001) reflection of chlorite is observed at $d = 14.3 \pm 0.2$ Å, indicating that the octahedral $Mg(OH)_6$ sheets are regularly interstratified between 2:1 type layers.[9] On the other hand, a single-phasic brucite is attained when the OH^-/Si molar ratio is beyond a value of 6. The XRD pattern of brucite shows a strong peak at the (001) reflection along with the weak (101) one. This further indicates that the initial platelike morphology of fluoromica is well-preserved, even after complete transformation of the crystalline structure.

The water content of swellable clay gel was found to be a detrimental factor. When it was higher than 150 wt %, the complete transformation was not accomplished, even after a long reaction time up to 48 h. Moreover, the selective leaching did not occur in non-swellable phyllosilicates such as talc and biotite. When the gel mixture of talc and NaOH was treated at 100 °C for 4 h under an ambient atmosphere, any phase transformation was hardly observed. However, the topochemical transformation could be seen in other synthetic clay-like hectorite (Figure 1S in Supporting Information). This result indicates that the highly concentrated NaOH system is essential in the sheet-by-sheet manipulation. As well-documented,[7] Na clay quickly absorbs water molecules under high-humidity conditions to exhibit osmotic swelling property. It is, therefore, thought that, in the present process of preparing a gel mixture, NaOH would be partially hydrated by water molecules in the hydrated fluoromica gel one. The water content is insufficient to satisfy both full hydration of NaOH and the swelling capacity of fluoromica, and as a consequence the great difference in NaOH concentration across the border of fluoromica crystal would facilitate the rapid and homogeneous diffusion of partially hydrated NaOH into the interlayer space of mica rather than the desorption of interlayered water molecules. During thermal treatment, hydroxide anions supplied from partially hydrated NaOH in interlayer space selectively attack only the tetrahedral silicate sheets to dissolve into sodium silicates in the presence of sodium cations. On the other hand, $Mg(OH)_2$ octahedral sheets remain stable and finally rearrange into brucite structure under alkaline conditions because the magnesium hydroxide is highly stable in a strong alkaline environment.[10] In addition, EELS analyses indicate the presence of F^- not in the brucite but in the chlorite. This suggests that the substitution of hydroxide ions for the fluoride in an octahedral sheet take place simultaneously during the leaching of the silicate sheets in fluoromica. The degree of leaching could be precisely controlled by the stoichiometric reaction of partially hydrated NaOH in the interlayer with the silicate sheet,

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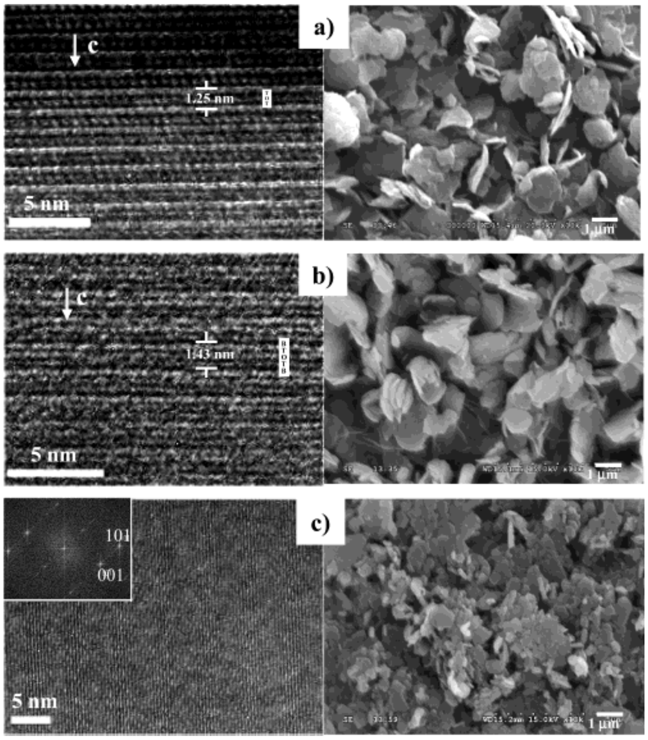

Figure 3. HRTEM and SEM images of (a) fluoromica, (b) chlorite, and (c) brucite. The inset shows its electron diffraction pattern.

which is clearly supported by its exclusive dependence on the OH^-/Si molar ratio. In addition, complete removal of both tetrahedral sheets from each layer seems to be favorable because of the structural default octahedral sheet in fluoromica, although a detailed study is needed to further understand why the chlorite-like structure is only available, not the kaolinite-like one.

As clearly demonstrated, the transformation reaction takes place via topochemical reaction, preserving the original two-dimensional morphology almost perfectly. The structural and morphological evolution of fluoromica is examined in detail with HRTEM and SEM. The original fluoromica shows a typical layer image of smectite structure, which has a unit layer consisting of an octahedral sheet between two sheets of tetrahedral silicate (Figure 3a). The light contrast in the HRTEM image displays the interlayer space between the layers. After alternative leaching of Si sheets, new dark fringes are observed in the layer lattice image to indicate chlorite structure with a new hydroxide sheet between 2:1 type layers of fluoromica (Figure 3b). The basal spacings of fluoromica and chlorite are very consistent with the results from XRD analysis. It is worth noting here that there are no significant changes in the crystal shape in comparison with the pristine fluoromica. On the other hand, the resulting brucite also shows its well-known lattice image (HRTEM image in Figure 3c). The brucite structure can be clearly confirmed by its electron diffraction pattern (the inset in the HRTEM image). Its crystal shape is also comparable to the original platelike one of fluoromica, although the size significantly decreases (SEM image in Figure 3c). Such a significant decrease in the crystal size dose not result from disintegration of the inherent sheet but from the well-reported lattice default of Mg sheets in phyllosilicate clay.[7,8] All of the above results clearly reveal that the topochemical transformation of phyllosilicate clay can be precisely controlled at a crystal lattice level over the whole crystal domain by the dry gel method.

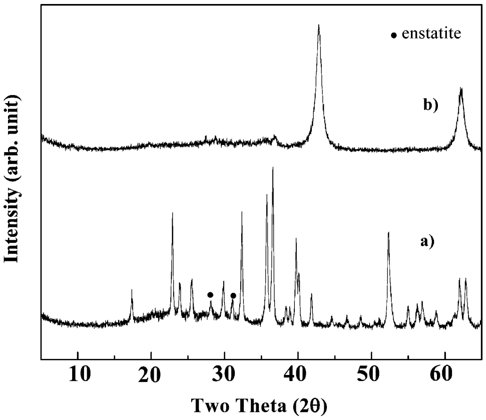

Figure 4. Powder X-ray diffraction patterns of (a) forsterite and (b) periclase obtained from chlorite and brucite at 850 °C for 1 h, respectively. The trace of enstatite ($MgSiO_3$) was co-crystallized as is well-known.[11]

The resultant chlorite and brucite were found to be excellent precursors for the synthesis of related useful materials such as forsterite and periclase. We have also found that chlorite could be transformed into forsterite (Mg_2SiO_4) with high quality under the reaction conditions of 850 °C and 1 h (Figure 4a). As is well-known,[11] forsterite has been typically prepared from the mixture of MgO and SiO_2 by a solid-state reaction at a high temperature above 1000 °C. Such a low synthetic temperature does result most likely from chemical homogeneity of the resultant chlorite, that is, interstratified structure consisting of two types of layer. Such new molecular level homogeneity could not be achievable from any physical mixing of MgO and SiO_2. In addition, brucite obtained by selective leaching is also considered as a potentially useful resource for a new and inexpensive method to produce periclase (MgO) (Figure 4b).[12]

In conclusion, this selective leaching of a specific silicate sheet could be applicable to the various 2:1 type layered clays consisting of an alkaline-resistant octahedral sheet between tetrahedral silicate sheets. The manipulation of intralayer structure in magnesia silicate clays could be readily accomplished without any significant changes in the original integrity of the sublattice as well as layer morphology. Therefore, the sheet-by-sheet manipulation developed here leads to a novel chemical route to smart extraction of silicates as well as to advanced materials from natural clays.

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Supporting Information Available: Experimental details and additional figures (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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