



Hydrothermal syntheses and characterization of alkylammonium phyllosilicates containing CSiO_3 and SiO_4 units

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Abstract

Alkylammonium phyllosilicate hybrids were synthesized hydrothermally from mixtures of $\text{Mg}(\text{OH})_2$, LiF and Si-containing reagents without using any layered silicates. Octadecyldimethyl(3-trimethoxysilylpropyl)ammonium chloride, silica sol and tetraethoxysilane (TEOS) were used as silica sources. A formation of a covalent bonding between an inorganic moiety and an organic moiety and a formation of a layered structure took place simultaneously in one pot. The structure of the hybrids was revealed by means of elemental analysis, X-ray diffraction (XRD), transmission electron microscope (TEM), electron diffraction (ED), high-resolution solid-state nuclear magnetic resonance (NMR) and infrared (IR). The inorganic moiety of the hybrids is a magnesium phyllosilicate analogous to Mg-trioctahedral smectites. The organic moiety is analogous to alkylammonium ($\text{C}_{18}\text{H}_{37}\text{N}^+(\text{CH}_3)_2\text{C}_3\text{H}_6^-$) and exists between layers of the inorganic moiety, being combined with the inorganic moiety through Si–C covalent bonds. Furthermore, solid-state ^{29}Si NMR and XRD revealed that there are some defects in the inorganic moiety because of substitution of CSiO_3 for the Si tetrahedral site. The lateral dimension of the inorganic moiety is closer to that of an Mg-trioctahedral sheet in a free state as the organic/inorganic ratio is higher.

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1. Introduction

Layered silicate/organic complexes (e.g., Weiss, 1963; Weiss and Lagaly, 1967; Lagaly, 1976, 1994; Lagaly and Weiss, 1969, 1970; Tamura and Nakazawa, 1996; Fujita et al., 1998; Takagi et al., 1989;

Ogawa et al., 1990) attract much attention because they can be synthesized by intercalation reactions of organic guests into interlayers of layered silicates and also because the organic guests can be arranged regularly in the two-dimensional space. The complexation has potentials for improving properties of the organic guests and the layered silicates and for providing solid-state materials with functions (Fujita et al., 1998). It is also interesting from a viewpoint of

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materials science to synthesize these complexes hydrothermally (Carrado, 2000; Carrado et al., 1991, 2000, 2002). Carrado et al. (2002) reported that magnesium phyllosilicates can be synthesized by using both silica sol and TEOS as silica sources and that a formation of the phyllosilicate phase was faster when TEOS was used rather than when silica sol was used. They described many analytical results. TEM images for “(silica)-hectorites” synthesized with using silica sol showed flexible thin sheets and a 15–30 nm sphere-like phase.

In order to synthesize hybrids, in which the organic moiety bonds covalently with the inorganic moiety, reactions between silanol groups on the surface of an inorganic layer and organic reagents were utilized (Fernandez and Ruiz-Hitzky, 1979; Ruiz-Hitzky and Rojo, 1980; Ruiz-Hitzky et al., 1985; Thiesen et al., 2000, 2002). Kuroda et al. studied silylation of surfaces of clay minerals (Kuroda and Kato, 1977, 1978, 1979; Yanagisawa et al., 1990). However, the former method can be applied only to layered materials with surface silanols and it has also been reported that some clay minerals were decomposed during pretreatments before silylation (Kuroda and Kato, 1977, 1978, 1979). It seems more advantageous to synthesize such hybrids directly by a one-step synthesis without using any layered silicates (Fukushima and Tani, 1995, 1996; Burkett et al., 1997; Whilton et al., 1998; da Fonseca et al., 1999, 2000a,b; Carrado et al., 2001). Fukushima and Tani (1995, 1996) succeeded in synthesizing such layered hybrids by reacting only chemical reagents and Hotta et al. (1997) applied such hybrids to modified electrodes. However, it has also been reported that the hybrids have a well-ordered octahedral sheet and slightly disordered $-C-SiO_3$ tetrahedral sheets (Fukushima and Tani, 1995, 1996), that is, there is no SiO_4 tetrahedron in the inorganic parts. It is speculated that the structure of the hybrids is supported by hydrogen bonds and/or hydrophobic interactions of the organic parts as well as by the octahedral sheets.

The final goal in the present work is a synthesis of a model hybrid described below: The inorganic layer has an Mg-trioctahedral sheet and tetrahedral sheets consisting of both SiO_4 tetrahedrons and $-C-SiO_3$ units. The organic moiety lies between layers of the inorganic moiety and bonds covalently with the inorganic moiety. It is expected that such hybrids

incorporate various kinds of organic moieties even if the organic moieties have functions and/or do not support formation of layered structures because the structures of the hybrids are supported by Si tetrahedral sheets with SiO_4 tetrahedrons as well as by an octahedral sheet. A structure analogous to Mg-trioctahedral smectites is chosen for the model inorganic moiety because of its relatively flexible structure. Alkylammonium with a long alkyl chain is chosen for the model organic moiety because alkylammonium ions are well known to form intercalation compounds easily. First, we try to develop synthesis conditions. Both Si-containing reagents with four Si–O bonds and organotrialkoxysilane are tested as silica sources. The hybrids were synthesized by a one-step hydrothermal synthesis without using any layered silicates. Then, structures of the synthesized hybrids are studied in detail by various analytical methods, e.g., elemental analysis, high-resolution solid-state nuclear magnetic resonance (NMR). The experimental results verify that the hybrids have the desired structure. Furthermore, it is shown that defects are produced in the inorganic moiety when the inorganic moiety is combined with the organic moiety. It is also shown that the organic/inorganic ratio is important to successfully synthesize the hybrids probably because the defects in the inorganic moiety may increase as the ratio increases.

Indeed, it is meaningful to synthesize the inorganic/organic compounds at room temperature in order to protect the environments. It is interesting from the viewpoint of the materials science to synthesize the inorganic/organic compounds by chemical methods, e.g., heat treatments and reactions with catalysts, because those methods are strongly expected to produce a wide variety of inorganic/organic compounds. So the hydrothermal synthesis was applied in this study. The synthesis method can be applied to produce functional hybrids (Fujii and Hayashi, 2001) and it is expected that electrons and charges are transferred easily through the covalent bonds between the inorganic and the organic moieties and that electronic structures are changed from those of elementary substances. It is also expected to control arrangements of the organic moiety by utilizing structural restrictions. The hybrid synthesized in this study has potential applications as fillers, ion exchangers and antimicrobial materials.

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