

Supercritical CO₂ Phase Intercalation of n-Dodecylamine with Cation Exchanged Expandable Micaceous

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(Received December 25, 2001; CL-011298)

A series of cation exchanged expandable fluorine micaceous exhibiting various swelling properties have been intercalated by neutral n-dodecylamine via supercritical CO₂.

Clay intercalation compounds belong to the large family of layered intercalation compounds which are of interest from various research domains.¹ The first practice of making organo-clay was accomplished by Jordan in 1949² and became a standard procedure which has been studied profoundly with wide exploitation of the organic guest species. Since the basal spacings of expandable clays are around 1 nm, the organo-clay is naturally a nanostructured inorganic-organic hybrid.³ Some guest species could be directly intercalated into expandable clays and form pillars for further immobilization of desired functional molecules, with alkylammonium ions as the representative. The common preparation procedure of organo-clay is the use of aqueous solution of ammonium salts to disperse the clay and then followed by filtration and drying processes. Meanwhile, except the small molecular compound such as methanol and ethanol, bringing neutral molecules into the charged interlayers of clay which are usually hydrophilic, is critical and has not been reported so far.⁴ Considering the extensive applications of the inorganic-organic supramolecular assemblies beyond the traditional clay intercalation compounds,⁵ it is worthy of trying to establish a novel routine for direct intercalation of neutral guest species into inorganic layered solids.

In this communication we present a direct intercalation method using supercritical CO₂, which might lead to a novel route to prepare some organic-inorganic hybrids that are infeasible under traditional conditions. Among the attractive characteristics of supercritical fluids,⁶ the enhanced transport properties that will help for some critical conditions where mass transfer constitutes the bottleneck aroused our interest. Free migration of CO₂ molecules under supercritical conditions within the relatively weakly-charged nanoscale galleries seems to be successful, since Ishii et al. has reported an intercalation of 4-phenylazoaniline with montmorillonite pillared by tetramethylammonium ions using supercritical CO₂.⁷ While CO₂ molecule can migrate within the charged interlayer of the clay or not is still under doubt, though CO₂ favors the solubility of some non-polar or less polar candidate organic guest species. Fortunately the evidence has been found in our experiment. Generally water molecules are easily absorbed to expandable mica and reside either in the interlayer space (manifested by the 1.20 nm basal spacing in Figure 1a) or on the surface of mica, while supercritical CO₂ can bring out a portion of the water molecules from within the interlayers and thus changes the ratio of the relative strength of 2 characteristic peaks in Figure 1a. This phenomenon is seemingly similar to the traditional supercritical fluid drying process⁸ and

also indicates that CO₂ molecule can migrate within the charged interlayers of expandable mica. Compared to water, there is a natural disadvantage of CO₂ as the transport media for its non-polarity to accommodate itself within the charged layers and the inability to delaminate expandable clay as water does.

The sodium type expandable fluorine mica (abbreviated as EM) is commercially available from CO-OP Chemicals, Tokyo, Japan. Several types of cations have been exchanged to the EM, including monovalent and bivalent cations, etc. K⁺, Cs⁺, Mg²⁺, and Ca²⁺. The EM was dispersed in the 0.3–0.5 M aqueous nitrate solution under stirring at room temperature for 24 h and then was filtrated and dried to get the cation-exchanged EMs. n-Dodecylamine, whose carbon number lies intermediately in the number of carbons of the alkyl chain of alkylamines involved in the clay intercalation compounds,⁴ was chosen as the guest species in this study. n-Dodecylamine itself is unable to be intercalated with EM in aqueous solution or in 1 : 1 (v/v) water/ethanol solutions. Intercalation of n-dodecylamine with EM was carried out in a small tube pressure reactor with volume of ca. 10 ml. After a mild mixing, EM, or cation exchanged EM, and 5 folds CEC (cation exchange capacity) of n-dodecylamine were charged into the vessel. The vessel was then flushed with CO₂ and was pressured to 25 MPa. The reaction was maintained at 25 MPa and 60 °C for 24 h followed by filtration and drying procedures which are identical to the traditional methods for preparation of clay-ammonium hybrids.⁴ One significant difference to traditional organo-clay preparation method is that there is no stirring during the reaction, since stirring under high pressure is not so convenient as that under ambient conditions. Generally, lack of stirring is unfavourable to the mass exchange of the system and thus affects the rate of the intercalation.

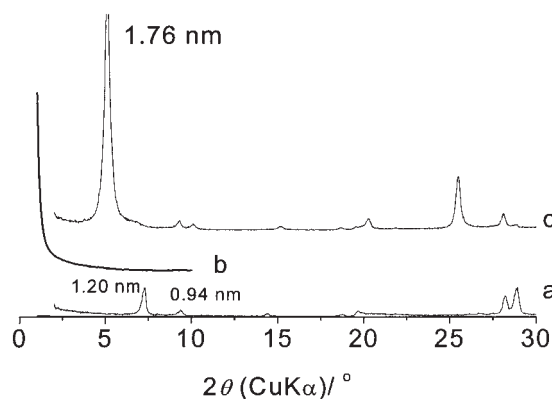


Figure 1. XRD patterns of sodium-type EMs, EM (a), EM in aqueous solution (b), and n-dodecylamine-EM intercalation compound (c).

Figure 1a shows the powder X-ray diffraction patterns

(Philips X'pert-MPD, $\text{CuK}\alpha = 0.15406 \text{ nm}$) of sodium-type EM. XRD pattern of the 0.5%w/w aqueous dispersion of sodium type EM with sufficient stirring and residence time were taken on a Philips X'pert-MPD using an indirect method depicted by Tateyama et al.^{9,10} and was shown in Figure 1b. The comparison indicates that the original EM could be completely delaminated in water and forms 2D platelets. Powder XRD patterns of n-dodecylamine-EM intercalation compound in Figure 1c shows that there is a basal spacing of 1.76 nm, a 0.82 nm increase to the original EM. Carbon content of EM intercalation compound was determined on a Perkin-Elmer CHNS/O 2400 Analyzer to be 8.68%(w/w) and could be converted to 66.0 mequiv per 100 g mica. Therefore the amount of intercalated dodecylamine is about 77% of the CEC of the sodium type EM, which is 84.9 meq/100 g EM.

The calcium and magnesium type EMs exhibit the similar swelling behaviours with sodium type EM, while the cesium and potassium type EMs have very limited swellability in aqueous solutions and were unable to be completely delaminated. Powder X-ray diffraction patterns of the cation-exchanged EMs and their corresponding supercritical CO_2 treated n-dodecylamine-EM reactants are plotted in Figure 2. Alike the intercalation in aqueous solutions under ambient conditions, the swelling properties also seem to be the most important factor to the

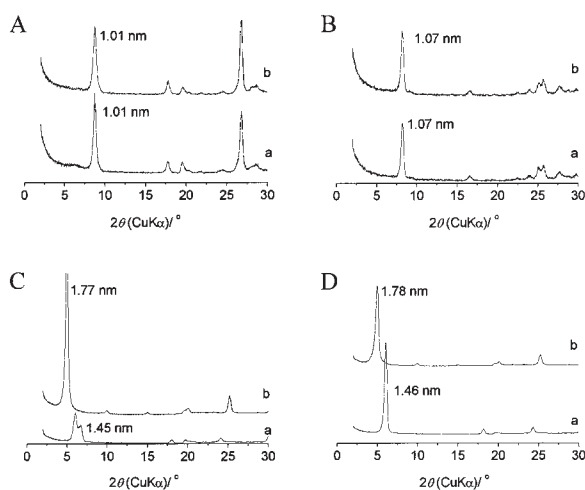


Figure 2. Powder XRD patterns of K^+ (A), Cs^+ (B), Ca^{2+} (C), and Mg^{2+} (D) type EMs (a) and supercritical CO_2 treated n-dodecylamine-EM (b).

feasibility of the intercalation reaction in the presence of supercritical CO_2 . K^+ and Cs^+ type EM could not be intercalated under such conditions while the other types of EM could be intercalated with variation of increase of basal spacing between the silicate layers. The bivalent Mg^{2+} and Ca^{2+} intercalation compounds have close basal spacing of around 1.78 nm, which is almost the same for the sodium type EM although the unintercalated EM has different basal spacings.

In conclusion, we report the first direct intercalation of neutral alkylamine with expandable fluorine micas using supercritical CO_2 . Cation exchanged fluorine micas with limited swellability in water also cannot be intercalated by n-dodecylamine in the presence of supercritical CO_2 . Compared to the classical mica-alkylammonium composites, the formation of clay-alkylamine intercalation compounds indicates the possible existence of a different molecular interaction pattern between the amine molecule and the silicate layers. Detailed investigation on the mechanism is currently underway and will be discussed in following papers.

T.-P.S. gratefully acknowledges the STA fellowship from Japan International Science and Technology Exchange Center (JISTEC) and the financial support thereof (No. 299065).

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- 10 The fluorine expandable mica employed in these experiments had a cation exchange capacity of 84.9 meq per 100 g ($\text{Na}_{0.66}\text{Mg}_{2.70}[\text{Si}_{3.95}\text{Al}_{0.02}\text{Mg}_{0.03}]\text{O}_{10.06}\text{F}_{1.88}$). The initial interlayer spacing is 0.94 nm with a 1.20 nm spacing corresponding to the partial adsorption of water.