



Interstratification of trioctahedral and dioctahedral smectites through delamination and costacking

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ABSTRACT

Trioctahedral and dioctahedral organosmectites delaminate in 1-octanol to give stable monolayer colloidal dispersions. Addition of acetone to a mixture of these colloidal dispersions yields a composite of the two clays. Layers of the two smectites are interstratified in the composite. Due to random costacking of layers the thermal decomposition behavior of the composite is different from that of the parent smectites and their physical mixture.

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1. Introduction

There have been a large number of reports in recent times on the design and synthesis of composites with novel properties. The composite preparation allows one to fine-tune the properties of the individual components for a desired application. Nanocomposites of layered solids are of importance due to their structural anisotropy [1,2]. There are reports on the preparation of a number of nanocomposites of layered solids with a variety of guest species which include polymers [3,4], biopolymer [5] and carbon nanotubes [6]. Delamination, a process unique to layered solids [7,8], has much to offer in the preparation of nanocomposites as this process gives monolayer colloidal dispersion of layered solids which has the potential to blend layered solids with almost any type of guest species. We have recently shown the use of this method in the preparation of a number of composites such as layered solid-nanoparticle [9], MgAl LDH-CoAl LDH [10] and α -nickel hydroxide- α -cobalt hydroxide [11] composites.

Among layered solids, smectites, also known as cationic clays, are one of the most abundant mineral deposits found in nature and hence have been utilized in a variety of applications since ancient times. The easy availability and variable composition of the smectites made them useful in applications such as adsorption, ion-exchange and molecular sieve catalysis [12–14]. The layered structure of smectites with unique structural anisotropy has been exploited in preparing many composites with different guest species like nanoparticles [15], fullerenes [16] and silica [17]. Smectites

are two-dimensional aluminosilicates or magnesiosilicates consisting of edge sharing layers of $M(O,OH)_6$ octahedra ($M = Al^{3+}$, Fe^{3+} , Mg^{2+} , Li^+ , etc.), sandwiched between two corner sharing layers of SiO_4 or $(Si,Al)O_4$ tetrahedra [14]. Since one octahedral sheet is flanked on either side by two tetrahedral sheets in smectites, they are also called 2:1 clays. Based on the number of octahedral sites occupied per unit cell $[O_{10}(OH)_2]$ the smectites are further classified as trioctahedral and dioctahedral, which derive their structures through lower valent metal ion substitution from their neutral counterparts talc, $Mg_6Si_8O_{20}(OH)_4$ and pyrophyllite, $Al_4Si_8O_{20}(OH)_4$, respectively. In smectites the metal ions of the octahedral sheets or Si^{4+} of the tetrahedral sheets are substituted by lower valent metal ions leading to a net negative charge on the layers. The layer charge is compensated by intercalation of cations such as Na^+ , Ca^{2+} in the interlayer region. The interlayer cations are loosely held and hence are amenable for exchange.

Due to their hydrophilic nature smectites form colloidal dispersions comprising monolayers of clay on soaking in water [18,19]. The delaminated clay possesses no long-range order along the stacking direction. Delamination of smectites has also been studied in organic media [8,20]. Recently we have shown that the delamination of organosmectite in nitrobenzene can be used as a technique for the separation of organosmectite from other mineral impurities [21]. Even though delamination process has been used as a tool to prepare layered nanocomposites till now there is no report on the preparation of composites of two different types of smectites through this route. In this article we report the preparation of composites of trioctahedral and dioctahedral smectites, in which the layers from these smectites are interstratified, through delamination of the individual smectites in 1-octanol followed by costacking the layers. The composites are also blends of natural

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and synthetic clays as the trioctahedral clay used here is synthetic while the dioctahedral clay is a natural mineral.

2. Materials and methods

In this study we have used saponite and montmorillonite as representative trioctahedral and dioctahedral clay minerals, respectively. Saponite with the composition of $\text{Na}[\text{Mg}_6](\text{Si}_7\text{Al})\text{O}_{20}(\text{OH})_4$ (Sap-Na) was prepared following the method due to Kawi et al. [22]. Montmorillonite having the composition $\text{Na}_{0.76}[\text{Al}_{3.1}\text{Fe}_{0.18}^{\text{III}}\text{Fe}_{0.16}^{\text{II}}\text{Mg}_{0.56}](\text{Si}_{7.96}\text{Al}_{0.04})\text{O}_{20}(\text{OH})_4$ (Mont-Na) was procured from Ashapura Group, Bangalore, India. The magnetic impurities present in montmorillonite clay mineral sample were removed by repeatedly stirring the aqueous dispersion of clay in a magnetic stirrer and removing the magnetic particles sticking to the pellet. Both the smectites were subjected to cation-exchange reaction to replace the interlayer ion with a cationic surfactant, cetyl trimethylammonium (CTA) ion, by stirring 1 g of the smectite with 60 ml of aqueous solution containing 6 mmol (~6 times excess the cation exchange capacity of the smectites) of the surfactant cetyl trimethylammonium bromide, CTAB, for 8 days at room temperature. The CTA-exchanged saponite and montmorillonite, referred to as Sap-CTA and Mont-CTA hereafter, were washed free of ions repeatedly with distilled water followed by acetone and dried in air at 65 °C to constant mass.

In separate experiments 1 g each of Sap-CTA and Mont-CTA were dispersed in 1 l of 1-octanol by sonication at 70 °C for 2 h. Both the colloidal dispersions were mixed, sonicated for another hour, and to the resultant mixture an equal volume of acetone was added. After standing overnight the settled solid was filtered, washed with acetone and dried in air at 65 °C to constant mass. The composite obtained at this stage is referred to as Sap/Mont-CTA.

The surfactant ions from the composite were exchanged for Na^+ ions by stirring Sap/Mont-CTA with a 0.5 M solution of NaNO_3 in equal volume mixture of ethanol and water for 8 days with changing the supernatant with fresh NaNO_3 solution each day. The final sodium-exchanged composite (Sap/Mont-Na) was washed with hot water and acetone and dried at 65 °C to constant mass. As a control sample a physical mixture of Sap-Na and Mont-Na (Sap-Na/Mont-Na) was obtained by grinding together the two pristine smectites in equal mass ratio.

All the samples were characterized by powder X-ray diffraction (PXRD) technique using a Philips X'Pert Pro diffractometer fitted with secondary graphite monochromator using $\text{CuK}\alpha$ radiation. Data were collected at the rate of 2° per minute over the 2θ range of 2–65°. The infrared (IR) spectra of the samples were collected using a Nicolet IR200 FTIR spectrometer by KBr pellet method at 4 cm^{-1} resolution. To see the conformational changes of the surfactant in the interlayer of clays the FTIR data of the relevant samples were collected at 2 cm^{-1} resolution. Thermogravimetric (TG) analysis of the materials was carried out using a Mettler Toledo STAR^e SW 7.01 system under continuous nitrogen flow with the heating rate of 5 °C per minute. The scanning electron microscopic (SEM) analysis of the samples was carried out using a JEOL JSM 840A microscope by mounting the samples on conducting carbon tape and sputter coating them with gold to improve the conductivity. Transmission electron microscopic (TEM) investigations were carried out using a JEOL 200CX instrument operated at 160 kV.

3. Results and discussion

The shift of the 001 reflections of the surfactant-exchanged smectites towards higher basal spacing compared to that of pristine smectites indicate that the interlayer sodium ions have been

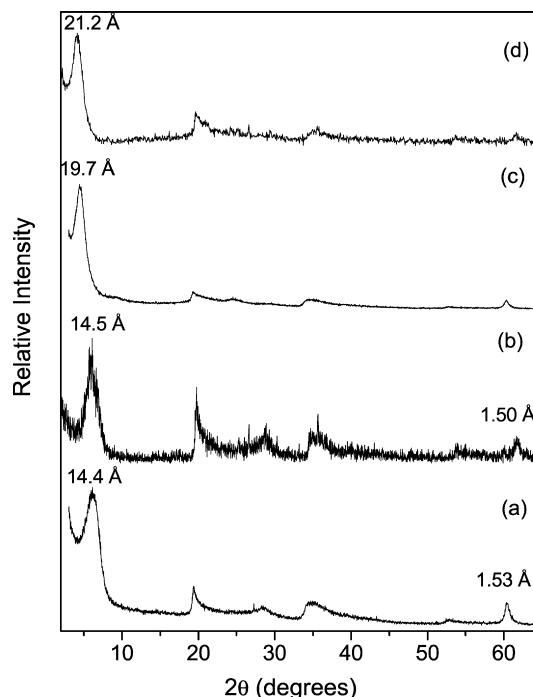


Fig. 1. PXRD patterns of Sap-Na (a), Mont-Na (b), Sap-CTA (c) and Mont-CTA (d).

exchanged for surfactant ions as seen from the corresponding PXRD patterns displayed in Fig. 1. The intense 001 reflection of Sap-Na (Fig. 1a) corresponding to the basal spacing of 14.4 Å along with all other characteristic peaks matches well with that of literature report [22]. The formation of trioctahedral saponite is further confirmed by the presence of the 060 reflection peak with the d spacing of 1.53 Å. The characteristic 060 reflection peak at around 1.5 Å can be used for distinguishing between the trioctahedral and dioctahedral clays, the d spacing for trioctahedral clays being >1.5 Å [23,24]. The PXRD pattern of Mont-Na (Fig. 1b) with the basal spacing of 14.5 Å is almost similar to that of Sap-Na (Fig. 1a) except that the d spacing of the 060 reflection is 1.50 Å indicating that the clay belongs to the dioctahedral group. The increase of the basal spacing of Sap-CTA (Fig. 1c) to 19.7 Å suggests that the CTA^+ ions accommodate a paraffin-type monolayer arrangement in the interlayer space of the clay in line with other literature reports [25,26]. Similarly in the case of Mont-CTA (Fig. 1d) the paraffin-type monolayer arrangement of CTA^+ ions is evident from the increase of the basal spacing to 21.2 Å [25,26]. In both Sap-CTA and Mont-CTA the unaltered d spacing of 060 reflections compared to that of corresponding pristine clays suggest that the layer composition of the surfactant-exchanged clays are not affected during the exchange reaction.

The PXRD patterns of the composites Sap/Mont-CTA, Sap/Mont-Na and the physical mixture Sap-Na/Mont-Na are shown in Fig. 2. The composite (Sap/Mont-CTA, Fig. 2a) with CTA^+ ions in the interlayer shows a reduced d spacing of 17.6 Å compared to both Sap-CTA (19.7 Å) and Mont-CTA (21.2 Å). The possible reorganization of the free end of the alkyl chains of CTA^+ during costacking process could be the reason for this reduced interlayer spacing. The layer structure of smectites is not destroyed during composite preparation process as can be seen from the fact that the 2D reflections are retained. The presence of both the clay components in the composite is confirmed by the presence of the corresponding 060 reflections of both the clays. The sodium-exchanged composite (Sap/Mont-Na, Fig. 2b) shows a reduced interlayer spacing of 13.8 Å compared to Sap-Na (14.4 Å) and Mont-Na (14.5 Å). This could be due to the reduced hydration state of the inter-

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