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Preparation of inorganic–organic pillared montmorillonite using ultrasonic treatment

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Abstract Montmorillonite (Mt) is a clay mineral with expandable layer structure. Mesoporous pillared montmorillonite can be prepared by introducing gallery templates, such as simple metal cations, quaternary ammonium cations, long chain amines, and hydroxyed inorganic metal ions. In this paper, inorganic–organic pillared montmorillonite intercalated by aluminium and alkyl ammonium chloridize (HDTMA–Cl) was successfully prepared by ultrasonic treatment, and the physicochemical properties of the materials were systematically characterized by XRD, FT-IR, SEM and TEM techniques. The d_{001} basal spacings and microstructures of Mt–Al–HDTMA were characterized by XRD. The function group, crystal surface morphology, structural and chemical analysis of Mt–Al–HDTMA were measured by FT-IR, SEM, TEM and EDX. The results indicated that ultrasonic method might accelerate the diffusion of the intercalating species, which enhanced the textural properties and the morphologies. The results also suggested that aluminium and HDTMA–Cl reagent entered the interlayer of Mt, and that the crystal structure of the final Mt was preserved.

Introduction

Montmorillonites are cationic clays, which consist of negatively charged layers, composed of octahedral sandwiched sheets between two tetrahedral sheets. Al^{3+} cations are located in octahedral positions, while Si^{4+} ions occupy tetrahedral sites. The negative charge of the layers results from a partial replacement of Al^{3+} ions by Mg^{2+} ions in the octahedral positions. This charge is compensated by common cations (e.g. Na^+, Ca^{2+}), which together with water molecules are localized in the interlayer spaces. These cations can be easily replaced by large polynuclear cations or organic cations during thermal treatment process, which form stable metal oxide pillars that link permanently the silicate layers. Such modifications of natural clays produce thermally stable microporous solids, which are very attractive materials for catalytic and adsorbent applications [1–6].

Pillared interlayered montmorillonites (PILMs) or cross-linked montmorillonites make up a family of microporous materials developed by molecular engineering. They are typically synthesized by exchanging the interlayered cations of layered clays with bulky inorganic polyoxocations followed by calcination. The intercalation of montmorillonites with aluminium oligomers has been widely studied. The synthesis of alumina-pillared clays is now well-established and usually carried out using the so-called Al_{13} polycation $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ as the pillaring agent. The resulting pillared materials generally present high surface areas, large interlayer spacings and high thermal stability.

The intercalated polycations increase the basal spacing of the clays and, upon heating, they are converted to metal oxide clusters by dehydration and dehydroxylation processes. These metal oxide clusters, named pillars, are inserted between the clay layers yielding temperature-stable oxide pillars that permanently keep apart the layers preventing their collapse and generating an interlayer space of molecular dimensions. Modification by alkyl ammonium chloridize or bromize (e.g. HDPY–Cl, TMA–Br, HDTMA–Cl) can greatly increase the basal spacing, textural properties and surface areas of pillared montmorillonite [6–9].

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On the basis of the above analysis, we propose a facile and efficient process to prepare a novel pillared montmorillonite modified by Al^{3+} and alkyl ammonium chloridize (HDTMA–Cl) through ultrasonics. The properties of the samples were characterized by means of XRD, FT-IR, SEM and TEM. This novel modified montmorillonite was expected to be used in the fields of catalysis and absorbents for their enhanced textural properties.

Experimental

Starting materials and experimental apparatus

The starting material of Na–montmorillonite was from Zhejiang province, China. The cation exchange capacity (CEC) of the material was found to be 90–95 meq 100 g^{-1}. The CEC is the main physical property of Na–montmorillonite and is determined using a method of ammonium chloridize—50% ethanol.

Ultrasonic treatment uses high frequency energy to cause vibration in liquids to produce physical or chemical effects. Ultrasound, part of the sonic spectrum that ranges from 20 to 10 MHz, is generated by a transducer that converts mechanical or electrical energy into high frequency acoustical (sound) energy. The sound energy is then fed to a horn that transmits the energy as high frequency vibrations to the liquid being processed. The role of ultrasound is to accelerate the Al_{13} polycation and HDTMA diffusion within the clay layers. The type of sonicator using in the preparation of Al pillared montmorillonite and Mt–Al–HDTMA is SK3200H.

Preparation of Al pillared montmorillonite

In a typical procedure, the Al_{13} polycation solution was prepared by slow titration of $AlCl_3 \cdot 6H_2O$ solution with NaOH solution (OH^-/Al^{3+} mole ratio of 2.4) under power ultrasonic treatment for 30 min, then aged at room temperature for 96 h [10]. After this, the intercalating solution was added to previously prepared suspensions containing 1 wt% of the clays under power ultrasonic treatment for 30 min, using an Al/clay ratio of 10 mmol/g. The new suspensions were aged at room temperature for 24 h, washed by centrifugation and dialysis until absence of chloride (tested by $AgNO_3$), dried at 80 °C for 12 h, and calcined at 400 °C for 4 h.

Preparation Mt–Al–HDTMA

The $HDTMA^+$–Cl solution was put into the suspension of the as-made Al-pillared montmorillonite, using an $HDTMA^+$–Cl/clay ratio of 0.6 mmol/g, followed by 30 min ultrasonic treatment. The suspension was then centrifuged, washed, dried at 80 °C, pulverized to pass through a 200 mesh sieve, and stored in the desiccator.

Characterization

X-ray diffraction (XRD) patterns were recorded on Rigaku D/max-IIIB diffractometer with CuKα radiation (λ = 1.5406 Å). Scans were made using a 0.1° step size at 1s/step.

FT-IR spectra were obtained on a FTS-135 Fourier transform infrared spectrometer using a KBr pressed disk technique. The spectra were collected for each measurement over the spectral range of 400–4,000 cm^{-1}.

The surface morphology of the as-made inorganic–organic pillared montmorillonite was examined on a Philips FEI Sirion 200 scanning electron microscope (SEM) at 20 kV. Prior to SEM observation, small drops of dilute suspension of 0.1 g of the sample in 50 mL of ethanol and mixed with Au. The chemical analysis of Mt–Al–HDTMA were measured by the energy-dispersive X-ray spectrometry (EDX). And I use 'ZAF standardless' method to calculate the element ratios which are highly useful for intercalation studies.

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed on a Philips CM200 transmission electron microscope operated at an accelerating voltage of 200 kV. Prior to TEM observation, small drops of dilute suspension of 0.1 g of the sample in 50 mL of ethanol, and small amounts of the suspension were dried on copper mesh grids coated with a carbon film.

Results and discussion

Structure of montmorillonites

It is known that the easiest way to determine whether pillar intercalation is successful is to record the X-ray diffraction pattern of an oriented film of the product. Figure 1 depicts XRD patterns of Mt–Na, Mt–Al and Mt–Al–HDTMA, respectively. It can be seen that the characteristic diffraction peak (001) of montmorillonite shifts to lower 2 <theta> values. The d_{001} basal spacings for the Mt–Na, Mt–Al and Mt–Al–HDTMA samples, which indicate the extent of propping apart of clay layers, are 15.4, 19.6 and 23.1 Å, respectively. The calculated interlayer distance of Mt–Al and Mt–Al–HDTMA increased 4.2 and 7.7 Å. The increase in $d_{(001)}$ spacing plane to 19.6 Å is indicative of the presence of Al_{13} polycations. This polymer with structural formula, $[Al_{13}O_4(OH)_{24}(H_2O)_{12}]^{7+}$ is a tri-decamer composed of one aluminium tetrahedra surrounded by 12

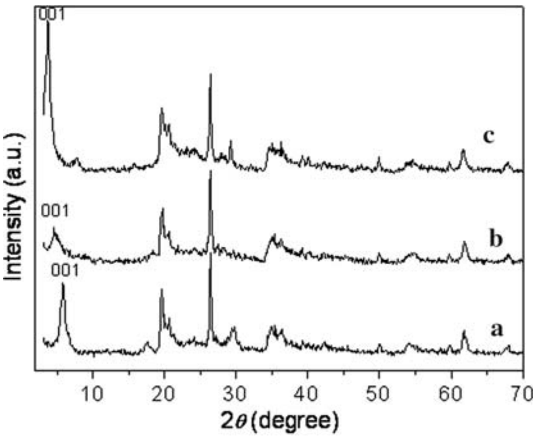


Fig. 1 d (001) X-ray diffraction patterns of (*a*) Mt–Na, (*b*) Mt–Al and (*c*) Mt–Al–HDPMA

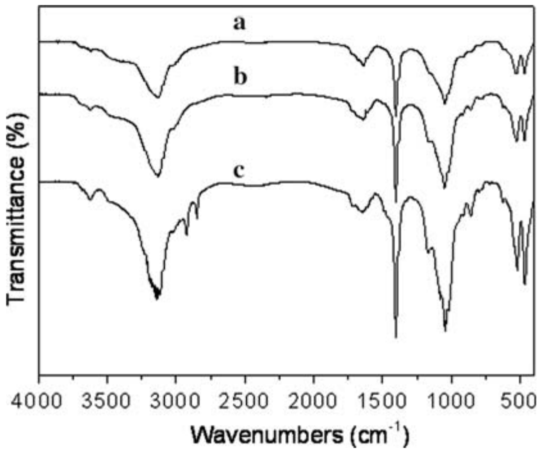


Fig. 2 FT-IR spectra of (*a*) Mt–Na, (*b*) Mt–Al and (*c*) Mt–Al–HDTMA

aluminium octahedra [11]. It contains four layers of superimposed oxygen atoms needed for expanding clay basal spacings to 19.6 Å. As observed in Fig. 1c, the XRD patterns were exactly identical to that of montmorillonite [12]. Thus, it can be concluded that intercalation of Al_{13} polycations and HDTMA$^+$ to the pillared materials does not affect the basic porous microstructure of montmorillonite. Additional peaks corresponding to the exchanged organic compound were not observed. This may be due to the diminutive amounts of the exchanged organic compound in these samples.

FT-IR study

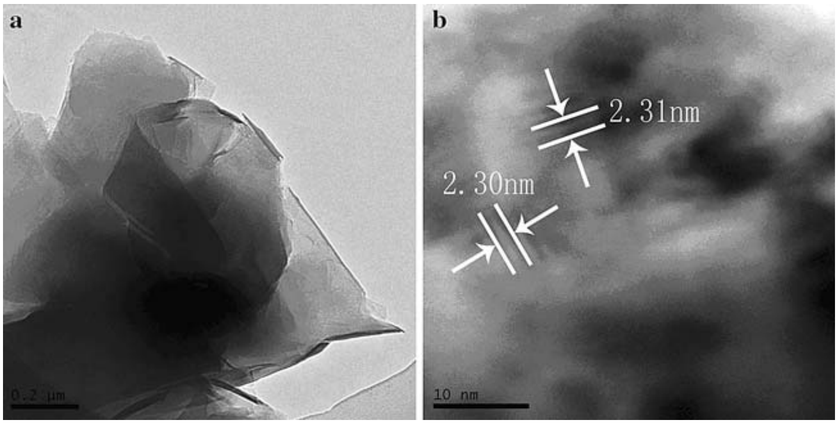
Figure 2 shows the IR spectra that were obtained for Mt–Na, Mt–Al and Mt–Al–HDTMA, respectively. The spectral regions of interest are the H–O–H bending region and OH-stretching region of H_2O. The H–O–H bending region (1,600–1,700 cm^{-1}) and the O–H stretching region (3,100–3,700 cm^{-1}) are attributed to the physical adsorbed water.

FT-IR spectra of the Mt–Na (Fig. 2a) which showed the characteristic bands in the –OH stretching region may correspond to Al–O–H group (3,631 cm^{-1}) and H–O–H group (3,444 cm^{-1}). Bending vibrations of water molecules may contribute to –OH peaks (1,630 cm^{-1}). The band at about 1,040 cm^{-1} in the stretching mode region are due to Si–O–Si, and bands centered at about 471 and 525 cm^{-1} in the stretching mode are due to Si–O–Al and Si–O–Mg, respectively [10].

FT-IR spectra of the Mt–Al (Fig. 2b) show the changes of the absorption band related to the *v*2 (H–O–H) bending vibrations of water molecules adsorbed on montmorillonite. The position of this band gradually shifts from 1,630 to 1,637 cm^{-1}. This could be explained by the decrease of the H_2O content with the replacement of the intercalated Al_{13} polycations.

FT-IR spectra of the Mt–Al–HDTMA (Fig. 2c) show that the characteristic bands of the initial montmorillonite remain unaffected. Both the characteristic bands are due to vibrations of tetrahedral and octahedral sheets and the bands located at 3,700–3,100 cm^{-1}and 1,630 cm^{-1} are related with water molecules. The other bands at 2,917, 2,849 cm^{-1} and 1,463, 723 cm^{-1} are consistent with those observed for HDTMA alone [10]. The bands at 2,917 and

Fig. 3 TEM and HRTEM micrographs of Mt–Al–HDTMA with intercalated layers



2,849 cm^{-1} correspond to the antisymmetric and symmetric CH_2 stretching modes of amine, respectively. Meanwhile, the symmetric and antisymmetric C–H stretching of the terminal $–CH_3$ groups appears at 2,867 and 2,952 cm^{-1}. The FTIR spectra of organic-clays at 1,440–1,480 cm^{-1} and 700–750 cm^{-1} correspond to the CH_2 scissoring and the rocking modes, respectively [10, 13, 14]. The FT-IR results are in accordance with XRD results (see Fig. 1).

TEM and SEM results

TEM complemented with SEM is the best technique to investigate the morphology of clay minerals. Representative TEM morphology of Mt–Al–HDTMA is shown in Fig. 3. Figure 3b demonstrates the laminar structure of a single grain of Al–HDTMA-pillared montmorillonite, and the layer-to-layer distance of Mt–Al–HDTMA is calculated about 2.30 nm, corresponding to the XRD result of 2.31 nm.

The SEM micrographs in Fig. 4 show surface morphology of the samples. It can be seen that the original Mt–Na (Fig. 4a) consists of massive and curved plates. However, the clay introduced by Al polycations and organic surfactant (Fig. 4b, c) shows significant changes in the morphology. Different from the morphology of the Mt–Na, the samples show many relatively small particles and the plates become relatively flat.

SEM together with energy-dispersive X-ray spectrometry (EDX) has allowed chemical analysis of large areas down to about 1 μm. This combination of structural and chemical analysis in the SEM is a powerful tool for studying complex, fine-grained clay minerals, and in particular pillared clays. EDX spectra from the Mt–Na, Mt–Al and Mt–Al–HDTMA are depicted in Fig. 5. Both atomic ratios to silicon and concentrations of the elements were calculated from the spectra. The ratio to Si was used since Si is a relatively constant element within the structure and is not affected by the pillaring process [9, 10]. From the spectra, the mean atomic ratio of Al–Si was 0.5172, 0.6905 and 0.6655 for the Mt–Na, Mt–Al and Mt–Al–HDTMA, respectively. The increase of Al–Si is indicative of the presence of Al_{13} polycation in the Mt–Al and Mt–Al–HDTMA. The mean atomic ratio of C–Si was 1.0235, 1.0371 and 2.8341 for the Na–Mt, Mt–Al and Mt–Al–HDTMA, respectively. The evident increase of C–Si suggests that $HDTMA^+$ is incorporated into the structure of Mt–Na and Mt–Al.

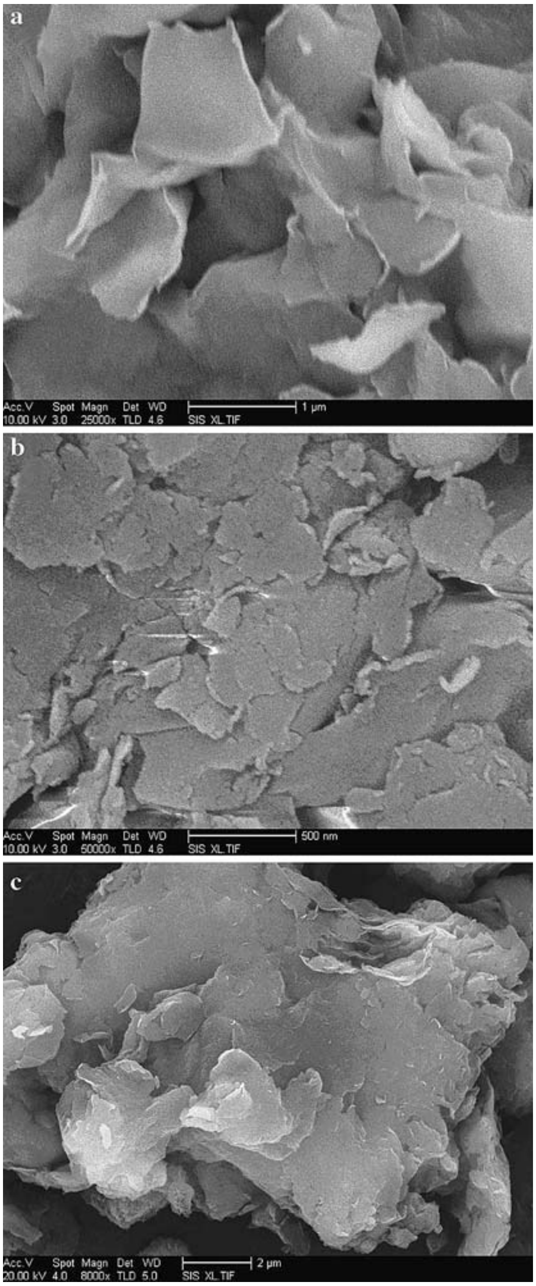


Fig. 4 SEM micrographs of (**a**) Mt–Na, (**b**) Mt–Al and (**c**) Mt–Al–HDTMA

Conclusions

Montmorillonite interlayer compounds are a new family of functional materials, and can be used widely as catalysts carriers, and selective adsorbents potentially, as well as in the fields of nanocomposite materials. In this paper, we use Na–montmorillonite as material, after modifying it with aluminium and alkyl ammonium chloridize, rapid and efficient synthesizing inorganic–organic pillared montmorillonite using ultrasonic agitation treat. The d_{001} basal spacings for the Na–Mt, Mt–Al and Mt–Al–HDTMA samples are 15.4, 19.6 and 23.1 Å, as determined by XRD. The clean pattern of the intercalated clay indicated that the intercalation process was completed. FT-IR spectroscopy

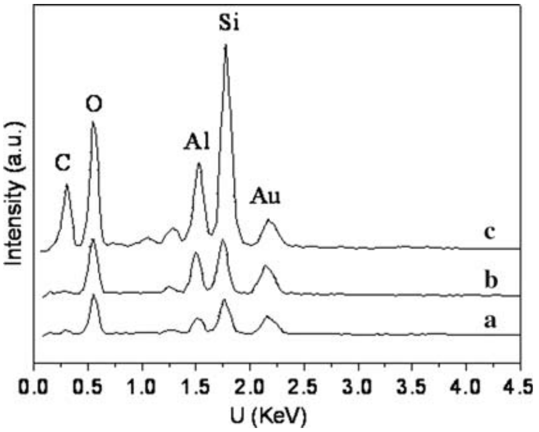


Fig. 5 EDX spectra from analyses in the SEM of small grains of (**a**) Mt–Na; (**b**) Mt–Al and (**c**) Mt–Al–HDTMA. The Au peaks derive from the SEM sample

using KBr pressed disk techniques has been used to characterize water and HDTMA in the Mt–Al and Mt–Al–HDTMA, respectively. The characteristic bands of the Na–Mt, Mt–Al and Mt–Al–HDTMA suggested that the Al_{13} polycations have entered the Mt–Al, the Al_{13} polycations and HDTMA have entered the Mt–Al–HDTMA. The basal layer spacings from TEM micrographs are the same to the values expected from XRD measurements. The SEM and EDX show that the morphology and the chemical analysis of Na–Mt, Mt–Al and Mt–Al–HDTMA samples. SEM, EDX and TEM in conjunction with XRD and FT-IR techniques have been used to investigate and characterize the interlayer structure and morphology of Mt–Al–HDTMA organic-clays. The study showed that aluminium and $HDTMA^+$–Cl reagent have entered the interlayer of montmorillonite and the intercalation step is strongly accelerated when ultrasound treatment is employed.

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