



Research paper

Formation of a kaolinite-serine intercalation compound via exchange of the pre-intercalated transition molecules in kaolinite with serine



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ABSTRACT

A kaolinite-serine intercalation compound was synthesized via the guest displacement method. Serine molecules were intercalated into kaolinite to form kaolinite-serine through exchange between serine and the guest molecules ethylene glycol or water, which was inserted into the interlayer space of kaolinite beforehand. The thickness of kaolinite-serine particles decreased to 14 nm from 30 nm of raw kaolinite after intercalation. The interlayer distance of kaolinite reached approximately 1.13 nm after the intercalation of serine molecules. The serine molecules inserted in the interlayer space of kaolinite molecules were arranged in a flattened monolayer configuration and partially compressed into the tetragonal holes in the silicate layer. The activation energy E_a for releasing the pre-intercalated molecule before ultimate exchanging with serine determines the intercalation degree of serine into kaolinite. Higher E_a makes the expansion of kaolinite with pre-intercalated molecules more stable, which will facilitate the final intercalation of serine. The activation energy is 6.95 kJ/mol for ethylene glycol and 21.2 kJ/mol for water, respectively, resulting in serine intercalation degree of 45%, and 85% correspondingly. The kaolinite-serine intercalation compound is expected to be applied in the pharmaceutical and cosmetics fields.

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1. Introduction

Kaolinite is a phyllosilicate that plays an important role in paper-making, ceramics, cosmetics, electrochemistry, environmental protection and pharmaceutical industries (Carretero, 2002; Dedzo and Detellier, 2013; Kutlakova et al., 2015; Tonle et al., 2007). It possesses a typical 1:1 layer structure with the chemical composition of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The individual layers of kaolinite are assembled together through hydrogen bonds. In recent years, clay-functional molecule nanohybrids (Williams et al., 2011) have gained considerable interest in many fields, such as electrochemistry (Tonle et al., 2009), clay-polymer nanocompounds (Krasny et al., 2014), and catalysts (Araujo et al., 2014). Especially, they also attract wide attention in pharmaceutical and cosmetic fields (Carretero and Pozo, 2010), including drug delivery (Oh et al., 2009), pharmaceutical applications and the formation of a functional protective film in cosmetic applications. The chemical inertness, good biocompatibility, the high specific area and good adsorptive

capacity for drug carrying make clay-functional molecule nanohybrids of great interest for application in various fields (Magriotis et al., 2013). Many kaolinite-drug intercalation compounds have been reported, including kaolinite-cyclic imides prepared by displacing previously intercalated dimethyl sulfoxide (DMSO) molecules (Elbokl and Detellier, 2008), kaolinite-glycine formed via the replacement of water (Zheng et al., 2014), kaolinite 5-fluorouracil obtained through displacing methoxy (Tan et al., 2014) and antibacterial kaolinite/urea/chlorhexidine diacetate nanocomposites through displacing urea (Holesova et al., 2014). Apparently, kaolinite has attracted wide interest as a functional nanohybrid in the pharmaceutical field.

As one of the amino acids, by showing special biological function, serine is widely applied in pharmaceutical (Heresco-Levy et al., 2005) and cosmetic (Ishitsuka et al., 2005) industries. An antibiotic drug, cycloserine (Heresco-Levy and Javitt, 2004), is one serine derivative. However, chemical properties of serine and cycloserine are unstable, showing short biological half-lives, and high pharmacological activity and toxicity for humans. They are easily destroyed by gastrointestinal acids, flora and enzyme systems before reaching the target organs. In this case, if the serine molecules can be intercalated to kaolinite to form an intercalation compound, the rapid decomposition of drugs can be prevented and drugs stability will be enhanced, by which gradual release can be achieved (Aguzzi et al., 2007; Viseras et al., 2010).

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However, unlike montmorillonite (Lin et al., 2002) and layered double hydroxide (Cunha et al., 2012; Desigaux et al., 2006), which are relatively easy to get intercalated by serine molecules (Liu et al., 2013; Mallakpour and Dinari, 2013), the hydrogen bonding between kaolinite interlayers is so strong that only a few small-sized molecules with high polarity can be directly intercalated into kaolinite (Li et al., 2009). Most of other molecules are generally intercalated through the displacement of guest molecules, which are intercalated into kaolinite beforehand. It has been reported that many traditional kaolinite intercalation compounds (Elbokl and Detellier, 2008; Sato, 1999) prepared using kaolinite-DMSO as the precursor may require one or two months tedious preparation. Fortunately, an environmental friendly precursor, kaolinite hydrate, with $d_{001} = 0.84$ nm was prepared in only a few hours (Xu et al., 2011; Zhou et al., 2013a, b). Using this kaolinite hydrate as the starting material to prepare intercalation compounds, the preparation time of the intercalation compound has been significantly shortened (Zheng et al., 2014; Zhou et al., 2013a, b). Obviously, it has been proved to be an attractive and predictable method to prepare kaolinite-serine (Ka-Ser) efficiently.

To prepare of kaolinite intercalation compounds, it is important to find a desired pre-intercalated guest molecule to expand the layer distance of kaolinite beforehand. Especially, this pre-intercalated guest molecule should possess a lower stability than the ultimate destination molecules that need to be intercalated into kaolinite. At last, the destination molecule can exchange with the pre-intercalated molecule to form the final kaolinite intercalation compound.

In this work, we propose an effective method to prepare a Ka-Ser intercalation compound using ethylene glycol and water as pre-intercalation molecules based on precursor kaolinite hydrate of $d_{001} = 0.84$ nm. The formation process and mechanism of Ka-Ser have been investigated systematically, and the degree of serine insertion into kaolinite has also been analysed in detail.

2. Experimental

Raw kaolinite (Water Washed Kaolin Clay, T 5-1, China Kaolin Company, Suzhou, China) and the analytically pure chemicals of hydrazine hydrate A (85% weight ratio), ethanol, ethylene glycol (Sinopharm Chemical Reagent Co., Ltd. Shanghai, China) and L-serine (99%, Ser, Aladdin) were used as raw materials.

Kaolinite-hydrazine was initially synthesized by mixing 3 g raw kaolinite powders with 60 mL hydrazine hydrate in an ampoule for 24 h with continuous stirring. The kaolinite-hydrazine was then separated from the liquid by centrifugation. Finally, the $d_{001} = 0.84$ nm kaolinite hydrate was obtained after the wet kaolinite-hydrazine was heated at 60 °C for 8 h. Then, 10 g $d_{001} = 0.84$ nm kaolinite hydrate was mixed with 100 mL of ethylene glycol in a sealed container for 24 h with continuous stirring to form kaolinite-ethylene glycol (Ka-EG). EG is usually used as guest molecules and kaolinite as the host to prepare intercalated compounds to achieve novel properties, which have been experimentally and theoretically verified (Hou et al., 2014; Qiao et al., 2014; Zhou et al., 2013a, b). Finally, around 10 g Ka-EG powder was obtained, which was separated from the liquid by centrifugation.

For Ka-Ser prepared from Ka-EG, Ka-EG powder is mixed with serine solutions of different concentration (from 0 M to 1 M) for 2 h to investigate the effect of serine concentration on formation of Ka-Ser. With serine concentration fixed at 0.6 M, the intercalation process is performed at different temperature from 20 to 90 °C for 1 h and the temperatures effect is also investigated. Similarly, the serine concentration effect on the synthesis of Ka-Ser directly from Kaolinite hydrate is also studied. At last, the Ka-Ser was separated from the liquid by centrifugation at a speed of 2200g. For a better separation of the components, the centrifugation was repeated several times.

The microstructure of the kaolinites was measured by X-ray powder diffraction (XRD) technology using an X'Pert PRO X-ray diffractometer (Almelo, the Netherlands) (CuK α radiation λ of 1.54 Å operating at

40 kV and 40 mA). The samples were softly ground to a uniform powder and poured through a 325 mesh sieve on the XRD sample holder. Fourier transform infrared (FTIR) spectra were performed with a Nexus 670 instrument (Boston, USA) with a resolution 4 cm⁻¹ using the KBr pellet method. The morphology of the kaolinites was observed using a field emission scanning electron microscope (FEI, FESEM, S-4800, Hillsboro, OR, USA) with a magnification of 30,000 \times and a working distance of 7900 μ m.

The intercalation degree N for Ka-Ser is defined as the fraction of Ka-Ser in the entire kaolinite (Elbokl and Detellier, 2008; Tunney and Detellier, 1996). The formula for the intercalation degree (N) of the sum of Ka-Ser and kaolinite hydrate (Ka-Water) is as follows:

$$N = \frac{I_{(001)\text{Ka-Ser}} + I_{(001)\text{Ka-Water}}}{I_{(001)\text{Ka-Ser}} + I_{(001)\text{Ka-Water}} + I_{(001)\text{Kaolinite}}} \times 100\% \quad (1)$$

where $I_{(001)}$ is the intensity of the diffraction peak of (001) planes measured by XRD. Ka-EG is not included in this equation. This is due to the experimental result that after 2 h of reaction, no Ka-EG can be detected in XRD, either becoming kaolinite by releasing ethylene glycol or becoming kaolinite hydrate of $d = 1.0$ nm by exchanging between water and EG in Ka-EG.

3. Results and discussion

3.1. Characteristics of kaolinite and compounds

Fig. 1a–c shows the SEM images of raw kaolinite, Ka-EG (Janek et al., 2007) and Ka-Ser. The main shapes of the kaolinites are platy and tubular structures, and the grain sizes are approximately 1–2 μ m. All of the kaolinites, there are no typical differences in their morphology, except that a small change occurs in particle size or layer thickness. The grain size of kaolinite becomes slightly smaller and the layer thickness of the kaolinite becomes relatively thinner after interacting with ethylene glycol and then interacting with the serine solution.

Fig. 2 shows the XRD patterns of raw kaolinite, Ka-EG and Ka-Ser. It is observed that the layer distance d_{001} of raw kaolinite and Ka-EG is 0.72 nm (Fig. 2a) and 1.08 nm (Fig. 2b), respectively. When the precursor Ka-EG reacted with the serine solution, as shown in Fig. 2c, the inter-layer distance d_{001} increased further to 1.13 nm.

Fig. 3 shows the FTIR spectra of raw kaolinite (Fig. 3a), Ka-EG (Fig. 3b), Ka-Ser (Fig. 3c) and serine (Fig. 3d). As shown in Fig. 3a, the band at 3620 cm⁻¹ is ascribed to the stretching frequency of the inner hydroxyl groups. Only when a number of the molecules are embedded into the ditrigonal holes, the stretching band of the inner hydroxyl will be influenced. The stretching band slightly shifts from 3620 cm⁻¹ to 3621 cm⁻¹ when Ka-EG further reacts with the serine solution. The bands at 3695, 3669 and 3652 cm⁻¹ are attributed to the surface hydroxyl groups of the kaolinite inner layers (accessible for guest molecules) (Elbokl and Detellier, 2008). As shown in Fig. 3b and c, the relative bands shift from 3651, 3670 and 3695 cm⁻¹ in Ka-EG (Janek et al., 2007) to 3650, 3657, 3675 and 3697 cm⁻¹ of Ka-Ser, respectively. The intercalation of serine might probably have changed the frequency of OH3 group a little bit from the previous 3651 to 3657. However, this effect is very minor, resulting in a minor peak in spectra (Tosoni et al., 2006). As has been reported, the band of the perpendicular vibration of Si—O appears at 1115 cm⁻¹ (Zhou et al., 2013a, b). The relative bands shift from 1010, 1030, 1106 cm⁻¹ of Ka-EG to 1012, 1032 and 1110 cm⁻¹ of Ka-Ser, respectively. The serine vibrations can be seen in Fig. 3d between 1800 and 1200 cm⁻¹ within which the bands of NH₃⁺ and COO⁻ groups in serine molecule can be identified. The band at 1601 cm⁻¹ and 1638 cm⁻¹ are associated with the asymmetric stretching vibration of COO⁻ and asymmetric deformation vibration of NH₃⁺ (Jarmelo et al., 2007). Fig. 3c shows the bands of NH₃⁺ and COO⁻ groups in Ka-Ser. Some bands show typical shift or split. The COO⁻ band red shifts slightly from 1601 to 1599 cm⁻¹. The NH₃⁺ band is

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