Journal of Colloid and Interface Science 432 (2014) 278–284

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis

Formation of intercalation compound of kaolinite–glycine via displacing guest water by glycine

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ARTICLE INFO

Article history:
Received 15 April 2014
Accepted 6 June 2014
Available online 22 June 2014

Keywords:
Kaolinite–glycine
Formation
Mechanism
Hydrated kaolinite
Intercalation
Guest displacement

ABSTRACT

The kaolinite–glycine intercalation compound was successfully formed by displacing intercalated guest water molecules in kaolinite hydrate as a precursor. The microstructure of the compound was characterized by X-ray diffraction, Fourier Transform Infrared Spectroscopy and Scanning Electron Microscope. Results show that glycine can only be intercalated into hydrated kaolinite to form glycine–kaolinite by utilizing water molecules as a transition phase. The intercalated glycine molecules were squeezed partially into the ditrigonal holes in the silicate layer, resulting in the interlayer distance of kaolinite reaching 1.03 nm. The proper intercalation temperature range was between 20 °C and 80 °C. An intercalation time of 24 h or above was necessary to ensure the complete formation of kaolinite–glycine. The highest intercalation degree of about 84% appeared when the system was reacted at the temperature of 80 °C for 48 h. There were two activation energies for the intercalation of glycine into kaolinite, one being 21 kJ/mol within the temperature range of 20–65 °C and the other 5.8 kJ/mol between 65 °C and 80 °C. The intercalation degree (N) and intercalation velocity (v) of as a function of intercalation time (t) can be empirically expressed as $N = -79.35e^{-t/14.8} + 80.1$ and $v = 5.37e^{-t/14.8}$, respectively.

1. Introduction

Kaolinite is a common nonmetallic mineral material and plays an important role in papermaking, ceramics, cosmetics, environmental protection, pharmaceutical industries, etc. [1–4]. It is a typical 1:1 layer-structured phyllosilicate with the chemical composition being $Al_2Si_2O_5\,(OH)_4$. The individual layers of kaolinite link with each other through hydrogen bonds. In the recent years, functional molecule-clay nanohybrid materials [5–7] have gained considerable interest in a lot of fields, such as electrochemistry [8], pharmaceutical [9], polymer–clay nanocompounds [10], catalyst [11], especially in pharmaceutical field, such as homeostasis, drug delivery, and antibiotic. What are of interest when they are used in pharmaceutical field [6,12,13] are their chemical inertness, good biocompatibility and non-toxicity for the patients as well as high specific area and adsorptive capacity.

It is known that besides constituting protein, amino [14] has special biological function, such as antibiotic, anticancer, antibiosis, anti-tuberculosis of liver and lowering blood pressure, and it is normally used for synthesizing hormone [15]. However, amino acids, as a drug, have complex structure, unstable chemical properties, short biological half life, high clearance ratio in vivo, and high pharmacological activity. They will be destroyed easily by gastrointestinal acids, flora and enzyme system before reaching target organs. Kaolinite, a potential drug carrier with preferable biocompatibility and non-toxicity, is thus important for preventing drugs from speedy decomposition, if the amino molecules are intercalated into its interlayer and then controlled to be released softly.

Nonetheless, the hydrogen bonding force between kaolinite layers is so strong that only a few small-sized molecules with high polarity can be intercalated into kaolinite directly. Most of other molecules are generally intercalated indirectly through the displacement of previously intercalated molecules. Furthermore, small molecules that can be directly inserted into kaolinite interlayer generally exhibit high toxicity, which limits the application of kaolinite intercalation compound.

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http://dx.doi.org/10.1016/j.jcis.2014.06.016
0021-9797/

It has been reported that hydrated kaolinite has non-toxicity and high intercalation ability, and can be used as an environment-friendly precursor [16]. Hence, it is hopeful to be used as a precursor to prepare kaolinite–amino. In fact, kaolinite–glycine can be successfully formed by intercalating glycine into the interlayer of hydrated kaolinite with the layer distance $d_{(001)} = 0.84$ nm [17]. In this case, the hydrated kaolinite was prepared by using kaolinite–dimethylsulfoxide as precursor, and the reaction time was usually as long as several days to even tens of days [17,18]. Recently, hydrated kaolinite with $d_{(001)} = 0.84$ nm was prepared by using kaolinite–hydrazine [16] and kaolinite–urea [19] as transition precursors, which spent only a few hours on preparation. Therefore, it is attractive to find a more effective way to prepare kaolinite–amino, which is of great importance for its commercialization.

As a matter of fact, hydrated kaolinite prepared by different methods possesses different properties even if they have identical layer configuration and layer distance. Take nano-silver-kaolinite for example [20], it can only be formed via hydrated kaolinite by using kaolinite–hydrazine [16] as precursor, but cannot with the precursor of kaolinite–urea. Therefore, it is vitally important to investigate the formation of kaolinite–glycine based on hydrated kaolinite with $d_{(001)} = 0.84$ nm by utilizing kaolinite–hydrazine as a transition precursor.

In this paper, we propose a more effective way to prepare kaolinite–glycine, in which hydrated kaolinite synthesized from kaolinite–hydrazine. The formation of the kaolinite–glycine prepared from the hydrated kaolinite via displacing guest water molecules by glycine molecules was investigated systematically. The mechanisms of the displacement and intercalation of guest molecules were analyzed in detail. And it is believed that this work is beneficial for us to understand the formation mechanism and improve the properties of the kaolinite–glycine for wider applications.

2. Experimental

The raw kaolinite was mined from the Yangshan mining district of Suzhou, China, by China Kaolin Company, named 'Water-Washed Kaolin Clay', T5–1 (1–2 μm). The hydrazine hydrate A (85% weight ratio), ethanol, and glycine (AR, 99.5–100.5%) were from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).

The hydrated kaolinite was prepared by the method described in previous work [14]. Approximately 3 g kaolinite–hydrazine was synthesized by mixing 3 g kaolinite with 60 mL hydrazine hydrate solution with continuous stirring for 24 h at room temperature. Then kaolinite–hydrazine was separated from the liquid by centrifugation. Finally, the hydrated kaolinite was obtained by heating wet kaolinite–hydrate powder for 8 h at 60 °C.

Kaolinite–glycine was prepared by mixing hydrated kaolinite per 5 g with 50 mL of 2 M glycine solution (mass:volume = 1:10) in a beaker. The 2 M glycine solution was prepared by dissolving glycine per 15 g in 100 mL water. Then the mixtures were continuously stirred at temperature between 20 °C and 90 °C for different times. The kaolinite–glycine was ultimately separated from the liquid by centrifugation at a speed of 2220g, washed twice with water and separated by centrifugation several more times, removing the adsorpted glycine from the surface of kaolinite.

The microstructure of kaolinite and its intercalation compounds was characterized by X-ray diffraction using an X'Pert PRO X-ray diffractometer (Cu Kα radiation = 1.5418 Å operating at 40 kV and 40 mA) and Fourier-Transform Infrared Spectroscopy using the KBr pellets method and Scanning Electron Microscope S-4800 with a magnification of 30,000× and a working distance of 7900 μm.

3. Results and discussion

3.1. Formation of kaolinite–glycine intercalation compound

Fig. 1 shows the XRD patterns of kaolinite and its intercalation compounds, in which pattern (a) shows the typical peaks of kaolinite with $d_{(001)} = 0.72$ nm; pattern (b) shows the diffraction peaks of the kaolinite hydrate [16,19,21] with $d_{(001)} = 0.84$ nm; and pattern (c) shows the peaks of kaolinite–glycine, formed at the temperature of 65 °C for 48 h. As can be seen from Fig. 1(c), the intensity of the diffraction peak of $d_{(001)} = 0.84$ nm decreased significantly and a new strong diffraction peak of $d_{(001)} = 1.03$ nm appeared.

Fig. 2(a–d) illustrate the FTIR spectra [17,22] of kaolinite, hydrated kaolinite, kaolinite–glycine, and single-phased glycine, respectively. As is known for kaolinite, the typical absorption bands at 3695, 3669, 3653 cm^{-1} and 3620 cm^{-1} are attributed to OH stretching vibrations. The bands at 1032 and 1010 cm^{-1} are associated with the in-plane Si–O–Si anti-symmetric stretching vibrations, while the band at 1115 cm^{-1} can be assigned to the perpendicular Si–O vibrations. As for the hydrated kaolinite, the bands at 3599 and 3545 cm^{-1} are attributed to the OH stretching vibrations [23] of the interlayer water molecules. Fig. 2(d) reveals the typical absorption bands of glycine. The bands at 3167, 1612, 1595, 1133 and 893 cm^{-1} are ascribed to NH_3^+ asymmetric stretching vibrations, NH_3^+ asymmetric deformation vibrations, COO^- asymmetric stretching vibrations, NH_3^+ rock vibrations and COO^- scissor vibrations, respectively. Fig. 2(c) exhibits the FTIR spectra of the kaolinite–glycine. It is seen that the intensity of the Al–OH stretching vibrations bands at 3695, 3669, 3653 and 3620 cm^{-1} decreased greatly. The band related to NH_3^+ asymmetric deformation at 1612 cm^{-1} blue-shifted to 1663 cm^{-1} after the glycine interacted with hydrated kaolinite. And the band ascribed to COO^- asymmetric stretching blueshifted from 1595 to 1612 cm^{-1}. The bands of the in-plane Si–O–Si anti-symmetric stretching vibrations at 1032 cm^{-1} and 1010 cm^{-1} blue-shifted slightly to 1040 and 1020 cm^{-1}, and that of the perpendicular Si–O vibrations at 1115 cm^{-1}, red-shifted to 1096 cm^{-1}, respectively [24].

It is documented that the band at 940 cm^{-1} corresponds to the bending vibrations of the hydroxyl groups in the inner-surface of the kaolinite, whereas the band at 913 cm^{-1} can be assigned to the bending vibrations of the inner hydroxyls (inaccessible for guest molecules) in the kaolinite [22]. Compared with that of kaolinite or hydrated kaolinite, the band at 940 cm^{-1} disappeared in the kaolinite–glycine, and the band at 913 cm^{-1} remained stable after the process. Moreover, compared with the typical absorption bands of monophasic glycine as shown in Fig. 2(d), the absorption bands of glycine still existed in the kaolinite–glycine except for the

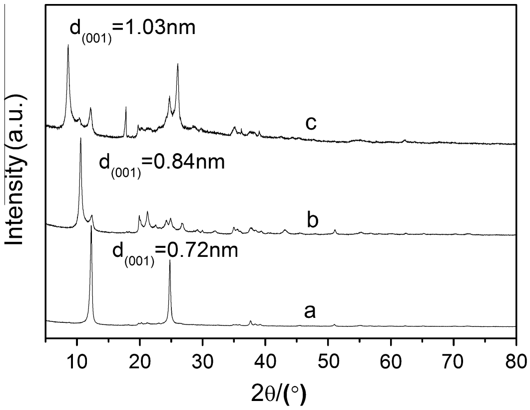

Fig. 1. XRD patterns of (a) raw kaolinite, (b) hydrated kaolinite and (c) kaolinite–glycine.