



Research paper

New insights into the molecular structure of kaolinite–methanol intercalation complexes

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ABSTRACT

A series of kaolinite–methanol complexes with different basal spacings were synthesized using guest displacement reactions of the intercalation precursors kaolinite–*N*-methyformamide (Kaol–NMF), kaolinite–urea (Kaol–U), or kaolinite–dimethylsulfoxide (Kaol–DMSO), with methanol (Me). The interaction of methanol with kaolinite was examined using X-ray diffraction (XRD), infrared spectroscopy (IR), and nuclear magnetic resonance (NMR). Kaolinite (Kaol) initially intercalated with *N*-methyformamide (NMF), urea (U), or dimethylsulfoxide (DMSO) before subsequent reaction with Me formed final kaolinite–methanol (Kaol–Me) complexes characterized by basal spacing ranging between 8.6 Å and 9.6 Å, depending on the pre-intercalated reagent. Based on a comparative analysis of the three Kaol–Me displacement intercalation complexes, three types of Me intercalation products were suggested to have been present in the interlayer space of Kaol: (1) molecules grafted onto a kaolinite octahedral sheet in the form of a methoxy group (Al–O–C bond); (2) mobile Me and/or water molecules kept in the interlayer space via hydrogen bonds that could be partially removed during drying; and (3) a mixture of types 1 and 2, with the methoxy group (Al–O–C bond) grafted onto the Kaol sheet and mobile Me and/or water molecules coexisted in the system after the displacement reaction by Me. Various structural models that reflected four possible complexes of Kaol–Me were constructed for use in a complimentary computational study. Results from the calculation of the methanol kaolinite interaction indicate that the hydroxyl oxygen atom of methanol plays the dominant role in the stabilization and localization of the molecule intercalated in the interlayer space, and that water existing in the intercalated Kaol layer is inevitable.

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1. Introduction

Intercalation is a well-known means of forming inorganic-organic nanocomposites under mild conditions, with clay minerals commonly utilized as host materials for this process (Li et al., 2009). Kaolinite (Kaol) intercalation and its applications for polymer-based functional composites have attracted great interest, both in industry and in academia, because these materials frequently exhibit remarkable improvements in desired properties as compared to the virgin polymer or conventional micro and macro-composites (Frost et al., 2003, 2004; Gardolinski and Lagaly, 2005; Jia et al., 2008; Detellier and Letaief, 2013). A variety of inorganic and organic species can be used for the intercalation of the interlayer spaces of Kaol, including formamide

(Churchman et al., 1984; Joussein et al., 2007), dimethylsulfoxide (DMSO) (Costanzo and Giese, 1986), methanol (Me) (Komori et al., 1999; Kuroda et al., 2011; Caglar et al., 2013), urea (U) (Nicolini et al., 2009), potassium acetate (Frost et al., 2000a; Cheng et al., 2010, 2011, 2012a), aniline (Luca and Thomson, 2000), and hydrazine (Horváth et al., 2003). The intercalation of the small molecules into the interlayer spaces of Kaol causes an increase in the basal spacing from 7.2 Å to 14.2 Å and can be used as a preliminary expansion step permitting insertion of large-sized, non-reactive molecules by displacement intercalation methods. For example, based on previous reports, a Kaol–Me complex can be an effective intermediate for further intercalation reactions. Through utilizing a Kaol–Me complex as the second intermediate, further intercalation reactions of ethylene glycol (Hirseman et al., 2011), hexylamine (Matusik et al., 2012a), quaternary ammonium salts (Kuroda et al., 2011; Yuan et al., 2013), and *n*-alkylamines (Gardolinski and Lagaly, 2005) have also been reported.

More recently, several studies were conducted using molecular simulation studies to assess the intercalation of simple molecules in Kaol (Fang et al., 2005; Vasconcelos et al., 2007; Rutkai et al., 2009;

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Benazzouz and Zaoui, 2012). Molecular simulations are useful because they allow a more detailed interpretation of experimental results, as well as provide findings that cannot easily be derived from strictly experimental data. In most cases, experimental observations alone cannot provide a clear picture of the mechanism of the molecular intercalation process, or the influences of intercalation on the clay structure. On the other hand, molecular simulations can contribute information about intercalation phenomena at the microscopic level. Despite previous research, the exact structure of Kaol–Me complex remains largely unknown. However, detailed and accurate molecular simulations can be used to furnish evidence about the structure of Kaol–Me complex. Therefore, it is necessary that research be completed to study the exact structure of Kaol–Me complex.

In the present study, the desired intercalation product was made by displacing pre-intercalation guest molecules from the intermediate intercalate complex. Data obtained using X-ray diffraction (XRD), infrared spectroscopy (IR), and nuclear magnetic resonance (NMR) were combined in order to elucidate the molecular arrangement of Kaol–Me complexes from different pre-intercalated guest molecules. In addition, molecular simulation studies were completed to provide valuable insights into the structural arrangement of the complexes. The purpose of the present study was to make clear the intercalation interaction mechanism for Kaol–Me complex as well as to provide novel structural insight regarding the structural model of the intercalation complex.

2. Experimental

2.1. Materials

Natural, pure Kaol with an average size of 20 μm was obtained from Hebei Zhangjiakou in China for use in this study. The chemical composition of the obtained Kaol by percent mass was SiO_2 44.64%, Al_2O_3 38.05%, Fe_2O_3 0.22%, MgO 0.06%, CaO 0.11%, Na_2O 0.27%, K_2O 0.08%, TiO_2 1.13%, P_2O_5 0.13%, and MnO 0.002%, with a loss on ignition of 15.06%. The major mineral constituent is well-ordered Kaol (95 % by mass) with a Hinckley index of 1.31. The DMSO, *N*-methylformamide (NMF), U, and Me used in this study were purchased from Beijing Chemical Reagents Company, China.

2.2. Intercalation reaction

Intercalation complexes of Kaol with DMSO and NMF were prepared using the method described by Tunney and Detellier (1993, 1996). Kaol–DMSO intercalation complex as the precursor was prepared by adding 50 g Kaol into a closed container that contained 90 ml DMSO and 10 ml deionized water, and Kaol–NMF intercalation complex was prepared by adding 50 g Kaol into a closed container that contained 90 ml NMF and 10 ml deionized water. The mixture was stirred with the magnetic stirrer at 60 °C for 12 h, and then the suspension was separated by centrifugation with ethyl alcohol. The intercalation complex of Kaol with urea was prepared using the method by Frost et al. (2000a,b,c). The Kaol–U intercalation complex as the intermediate was prepared by adding 50 g Kaol into a closed container that 100 ml urea saturated solution. The mixture was stirred with the magnetic stirrer at 60 °C for 12 h, and then the suspension was separated by centrifugation with ethyl alcohol. The Kaol–DMSO, Kaol–NMF, and Kaol–U intercalates were used as precursors for further intercalation with Me. Me was added to the pre-intercalation complexes (Kaol–DMSO, Kaol–NMF, and Kaol–U), and the reaction mixtures were stirred for 10 days replacing the Me with fresh Me each day. The resulting materials are noted Kaol–DMSO–Me, Kaol–NMF–Me, and Kaol–U–Me derived, respectively, from the Kaol–DMSO, Kaol–NMF, and Kaol–U pre-intercalation complexes reacted with Me. Following these steps, the reaction products were centrifuged and then allowed to dry at room temperature before subsequent XRD, FTIR, and NMR analysis.

2.3. Characterization

X-ray diffraction (XRD)

The XRD patterns of the prepared samples were collected using a Rigaku D/max 2500 PC powder X-ray diffraction meter with Cu Ka radiation of 1.540596 Å and a scanning rate of 2°/min in the 2 θ range of 1.0°–45°, while operating at 40 kV and 150 mA.

Infrared spectroscopy

Fourier-transform infrared spectroscopy (FTIR) was performed using a Thermofisher Nicolet 6700 spectrometer. The samples were prepared as potassium bromide (KBr) pellets (ca. 2% by mass in KBr). The FTIR spectra of prepared samples were recorded between 400 and 4000 cm^{-1} .

Solid-state magic-angle spinning (MAS) nuclear magnetic resonance (NMR) measurement

Solid-state ^1H NMR spectra were recorded using a Bruker MSL400 spectrometer with a Larmor frequency of 61.42 MHz. A quadrupole echo pulse sequence was used, with a 90° pulse width of 2.5 μs and a 15 μs pulse interval between the two pulses. Solid-state ^{13}C CP (cross-polarization)/MAS (magic-angle-spinning) NMR measurements were performed using Bruker ASX400 (magnetic field of 9.4 T) and ASX200 (4.7 T) spectrometers with Larmor frequencies of 100.63 and 50.33 MHz, respectively. The sample spin rate was 5 kHz. A total of 2000 data points were recorded over a spectral width of 500 ppm. Transients were acquired using a recycle delay of 1 s until a sufficient signal-to-noise ratio had been achieved (ranging from –250 to 250 ppm).

2.4. Computational details

The primitive unit cell of Kaol was optimized using the generalized gradient approximation (GGA) for the exchange–correlation potential (PW91) (Perdew et al., 1996). This approach is appropriate for the relatively weak interactions present in the models studied (Martorell et al., 2010). The resulting primitive unit cell is characterized by the parameters $a = 10.384\text{Å}$, $b = 18.013\text{Å}$, $c = 7.434\text{Å}$, and $\alpha = 91.7^\circ$, $\beta = 105.3^\circ$, $\gamma = 89.8^\circ$. Based on this primitive unit cell, a series of (2 × 2 × 1) supercells were built with the basal spacing of layers set to 8.6 Å, 8.8 Å, or 9.6 Å.

Four structural models that reflect four possible models of Kaol–Me complexes were constructed for use in the computational study. The first model represents Kaol intercalated by one Me molecule (Kaol–Me). The second model represents Kaol intercalated by one Me and one water molecule simultaneously (Kaol–Me–W). The third model represents Kaol with one grafted methoxy group (Kaol–gMeO). The fourth model represents Kaol with one grafted methoxy group as well as one intercalated water (Kaol–gMeO–W). In order to investigate the intercalation mechanism of Me into a pure Kaol layer, a simulated annealing algorithm was used to perform canonical Monte Carlo (MC) simulations with one Me and one water molecule as adsorbates on the layer of pure Kaol. The $d_{(001)}$ values were 8.6 Å, 8.8 Å, and 9.6 Å. For Kaol–gMeO and Kaol–Me–W, MC simulation was firstly performed with one Me or both one Me and one water molecule as adsorbate. The adsorption behavior was modeled using the Universal force field (Rappe et al., 1992). The number of cycles was 3, and the step of one cycle was 10^6 , a representative piece of the interface devoid of any arbitrary boundary effects. Based on the preferential adsorption models of Me and water in the layer of Kaol predicted by the MC calculation, GGA-PW91 was used to further optimize the structure and predict the interaction energy between the Me and the Kaol complex with greater accuracy. Results from an earlier DFT study suggested that the Al surface of Kaol exhibits two types of hydroxyl groups: one with the –OH group oriented perpendicular to the surface (–OH_v) and the other with the –OH group oriented parallel to the surface (OH_i). In the model of

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