Research paper

Interfacial structure and interaction of kaolinite intercalated with *N*-methylformamide insight from molecular dynamics modeling

Shuai Zhang[a], Qinfu Liu[a,*], Feng Gao[b], Rujia Ma[a], Zeguang Wu[c], Brian J. Teppen[b]

[a] *College of Geoscience and Surveying Engineering, China University of Mining &Technology (Beijing), Beijing 100083, People's Republic of China*
[b] *Department of Plant, Soil, and Microbial Sciences, Michigan State University, East Lansing, MI 48824, United States*
[c] *School of Chemistry and Chemical Engineering, Hunan University of Science and Technology, Xiangtan, Hunan 411201, People's Republic of China*

ABSTRACT

The evolution of basal spacing and interfacial structure of kaolinite-*N*-methylformamide (NMF) complexes during the intercalation process were difficult to obtain using experimental methods. In present study, a series of kaolinite-NMF complex models with various numbers of NMF molecules in the interlayer space were constructed to mimic the progressive stage of the intercalation process of kaolinite intercalated by NMF. The MD simulations were performed on these models to explore the evolution of basal spacing and interfacial structure of kaolinite-NMF complexes during the intercalation process. It was found that the basal spacing of complex was stabilized at 11 Å during the intercalation process, where the molecular plane of NMF oriented at small angles with respect to the interlayer surface with the C=O groups and N−H bonds pointing toward the octahedral and tetrahedral surfaces, respectively, due to the hydrogen bonding interactions. The basal spacing can be enlarged to larger values with the prerequisite of overcoming the energy barrier. With the increase of basal spacing during the intercalation process, the NMF were rearranged as a pillar with the molecular planes orienting at higher angles with respect to the interlayer surface, and then developed to disordered bilayer structure. For the interfacial interaction of kaolinite-NMF complex, both the octahedral surface and tetrahedral surface showed binding affinity to the NMF, which is the driving force for the intercalation of NMF in kaolinite. The octahedral surface displays stronger binding affinity to the NMF in terms of the the H-bonds and energetics compared to the tetrahedral surface partially due to the highly active surface hydroxyl groups. The present study provides insight into the basal spacing evolution, and interfacial structure and interaction of kaolinite-NMF complexes, which can enhance the understanding of kaolinite intercalated by small molecules.

1. Introduction

Intercalation of clay minerals is defined as inserting molecules or ions into the interlayer space of clay minerals with preservation of the layered structure, which is an important research area in the development of the hybrid materials. Intercalated clay minerals have been widely used as the catalysts, highly efficient sorbents, and fillers for the preparation of clay minerals-based hybrid materials (Bhattacharyya and Gupta, 2008; Cheng et al., 2017; He et al., 2014; Kotal and Bhowmick, 2015; Zhou, 2011). Among the clay minerals, kaolinite is used in large quantities in traditional industries such as paint, paper coating, and ceramics, but is still undeveloped for the high value-added kaolinite products due to its crystal structure (Dedzo and Detellier, 2016). The crystal structure of kaolinite has been well known, which belongs to the aluminosilicate layers of 1:1 type. The unit layer of kaolinite is consisting of an alumina octahedral sheet and a silica tetrahedral sheet connected by the shared plane of oxygens. The unit layers are connected by the H-bonds formed between the hydroxyl groups on the alumina octahedral surface and the basal oxygens on the silica tetrahedral surface to form the bulk kaolinite stacks. The interlayer H-bonds of kaolinite make it difficult to be surface modified and restrain its applications in the fine chemistry. A small group of organic molecules such as hydrazine, urea, dimethyl sulfoxide (DMSO), potassium acetate, formamide, *N*-methylformamide (NMF) can break the interlayer H-bonds of kaolinite and directly penetrate into the interlayer space (Ledoux and White, 1966; Olejnik et al., 1970). The complexes of kaolinite intercalated with small organic molecules can be used as the precursor to achieve the intercalation of compounds that cannot be directly intercalated in kaolinite through the displacement intercalation method (Komori et al., 1998; Sugahara et al., 1988). Once the interlayer space of kaolinite is opened, the highly active surface hydroxyl groups on the interlayer octahedral surface are more readily

accessible, which allows the octahedral surface to be covalently grafted by the compounds to produce the stable inorganic-organic hybrid materials (de Faria et al., 2009; de Faria et al., 2011; Hirsemann et al., 2011). Therefore, the intercalation of kaolinite is a requirement prior to further chemical modification of the interlayer surface. However, the compounds that can be directly intercalated in kaolinite are still limited as mentioned. One could assume that developing new chemicals and experimental strategies to make the intercalation of kaolinite be well controlled can considerably improve its applications. In order to achieve this goal, it is necessary to fully understand the underlying molecular force responsible for the intercalation of kaolinite.

NMF is the commonly used agent to intercalate in kaolinite, and the kaolinite-NMF complex has been experimentally investigated to explore the conformation of NMF in the interlayer space and its interactions with kaolinite interlayer surfaces (Olejnik et al., 1970, 1971; Xie and Hayashi, 1999). The disordered interlayer structure and the difficulty in locating H atoms, however, make the detailed picture be hard to obtain using the experimental diffraction or spectroscopic data. The molecular simulations have been developed to a powerful tool to successfully describe the interfaces of clay minerals-water/organics in terms of structure at atomic scale and energetics (Cygan et al., 2009; Heinz and Ramezani-Dakhel, 2016; Liu et al., 2015; Liu et al., 2012; Sena et al., 2015; Szczerba et al., 2014; Zeng et al., 2003; Zhang et al., 2017; Zhou et al., 2014). The interface of dickite-NMF was investigated using the quantum chemistry method. It was found that the C═O group of NMF acting as proton acceptor forms strong H-bonds with two or three surface hydroxyl groups surrounding the octahedral vacancy on the octahedral surface, and the NH group functioning as proton donor forms weak H-bonds with one basal oxygen surrounding the ditrigonal cavity on the tetrahedral surface (Michalková et al., 2002; Scholtzová et al., 2008). The molecular dynamics (MD) simulations and Monte Carlo (MC) simulations of interface of kaolinite-NMF complex were rarely reported.

In present study, a series of kaolinite-NMF complex models with various numbers of NMF molecules in the interlayer space were constructed to mimic the progressive stage of the intercalation process of kaolinite intercalated by NMF. The MD simulations were performed on these models to explore the evolution of basal spacing and interfacial structure of kaolinite-NMF complexes during the intercalation process. The interfacial interaction was also calculated based on the model produced the experimentally obtained basal spacing. The aim of the present study is to enhance the understanding of kaolinite intercalation by small molecules.

2. Models and simulation method

The kaolinite unit cell with the structure formula of $Al_4Si_4O_{10}(OH)_8$ used as the basis for the simulations was built based on its crystal structure determined by neutron diffraction data (Bish, 1993). The kaolinite supercell was created by expanding the unit cell to a $8 \times 5 \times 1$ supercell with $41.2\,Å \times 44.67\,Å$ in the x and y dimensions. Then the (001) surface terminated with the OH groups on the octahedral surface of kaolinite supercell was constructed by cleaving the bulk crystal structure along the required (001) plane with the octahedral and tetrahedral sheets keeping intact. Amorphous slab of NMF with the same size as the x, y plane of kaolinite supercell was prepared and stacked on the (001) surface to create the kaolinite-NMF complex models. Then two kaolinite-NMF complex models were stacked along the z dimension making the simulation supercell consist of $8 \times 5 \times 2$ unit cells of kaolinite with two interlayer space intercalated by NMF as shown in Fig. 1. The amorphous NMF slab inserted in the kaolinite interlayer was loaded with 5 to 125 NMF molecules to mimic the intercalation process with the aim at exploring the evolution of basal spacing and structure of kaolinite-NMF complexes during the intercalation process. The initial simulation supercell had the dimensions of $41.2\,Å$, $44.67\,Å$, and $29 \sim 49\,Å$ in the x, y, and z dimensions,
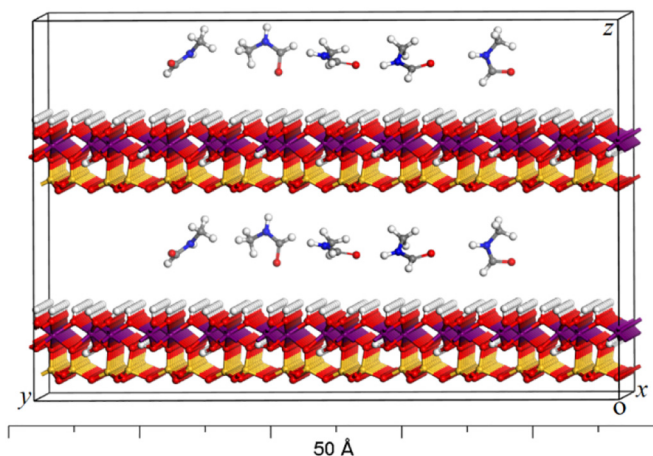

Fig. 1. Simulation supercell of kaolinite-NMF complex model. The kaolinite and NMF are shown in ball and stick style, where the ball color scheme is O (read), Si (orange), Al (purple), H (white), N (blue), and C (gray). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

respectively, depending on the loading numbers of NMF in the kaolinite interlayer.

The CVFF-Interface forcefield (Heinz et al., 2013) was selected to model the kaolinite-NMF complexes in present study, which has been successfully applied to the simulations of clay minerals-organics interfaces (Ható et al., 2014; Heinz et al., 2013; Makó et al., 2014; Zhang et al., 2017). The CVFF-Interface forcefield is the extension of common harmonic forcefields, which was described in detail in the ref. (Heinz et al., 2013). The forcefield parameters for kaolinite and NMF models were directly taken from the CVFF-Interface forcefield. The MD simulations were performed with periodic boundary conditions in all three dimensions using LAMMPS package (Plimpton, 1995). A 10000 steps of energy minimization was firstly performed using the conjugate gradient technique to remove the high energy contact of systems. The optimized structures were then used as the starting configurations for the following MD simulations with the time step of 1 fs. The MD simulations were carried out in the NPT-ensemble for 5 ns to equilibrate the systems. The pressure and temperature were maintained at 300 K and 0.1 MPa using the Nose-Hoover thermostat and barostat (Plimpton, 1995). During the NPT simulations, the pressure was controlled independently in the x, y, and z dimensions, and the dimensions of supercells were allowed to change independently in the three dimensions. After the systems reached equilibrium, the production runs of 1 ns were performed in the NPT-ensemble with the trajectories of systems recorded at the interval of 2000 steps. The long range electrostatic energy was calculated using Ewald summation method (Ewald, 1921), and a real-space cutoff of 10 Å was used for the short range interactions. The van der Waals interactions were truncated using a cutoff of 10 Å with an analytical tail correction.

2.1. Analysis of the MD results

The two kaolinite layers and lower NMF slab inserted in the lower kaolinite interlayer (Fig. 1) were chosen as the research target for the following analysis of the MD results. The interfacial structure of kaolinite-NMF complexes was characterized by atom density and distribution of orientation angle of NMF in kaolinite interlayer. The atom densities of NMF were calculated in the direction perpendicular to the kaolinite interlayer surface by averaging over the recorded frames during the MD production runs for each system. The middle plane of interlayer space of the complex was defined as the origin. In order to track the graphic conformations of NMF in the kaolinite interlayer, the distribution of orientation angles of NMF were also calculated. The