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Interfacial Structure and Interaction of Kaolinite Intercalated with N-methylformamide Insight from Molecular Dynamics Modeling

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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 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.

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Keywords

Kaolinite; Intercalation; Interfacial structure; Interfacial interaction; Molecular dynamics simulation

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.

1. Models and Simulation Method

The kaolinite unit cell with the structure formula of $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ 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 $41.2 \text{ \AA} \times 44.67 \text{ \AA}$ 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 Figure 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 $41.2 \text{ \AA}$, $44.67 \text{ \AA}$, and $29 \sim 49 \text{ \AA}$ in the x , y , and z dimensions, 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.

Analysis of the MD results

The two kaolinite layers and lower NMF slab inserted in the lower kaolinite interlayer (Figure 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 orientation angles were defined as the angles of the vector of C=O bond ($\varphi_{C=O}$), C-N bond (φ_{C-N}), N-H bond (φ_{N-H}), and N-C (CH₃) bond ($\varphi_{N-C(CH_3)}$), and the normal vector of molecular plane of NMF ($\varphi_{normal\ vector\ of\ plane}$) with respect to the z -axis (perpendicular to the interlayer surface), which have been used to describe the arrangement of small organic molecules in kaolinite interlayer (Fang et al., 2005; Rutkai and Kristóf, 2008).

The interfacial interaction of kaolinite-NMF complex was investigated by means of radial distribution function (RDF) and the corresponding running coordination number (RCN), H-bond statistics, lateral atomic density contour map, and interaction energies (E). RDF is the commonly used correlation function to evaluate the interactions between atoms, which provides the probability of finding the atom j surrounding the atom i at a given distance, relative to the probability expected for a random distribution of atoms at the same density. The RCN was obtained by integrating the corresponding RDF peak, which was used to estimate the coordination number of atom j surrounding the atom i . For the H-bond statistics, the geometric criterion was used to estimate the existence of the H-bond if the distance between H...Y is less than 3.2 Å and simultaneously the angle of X-H...Y is more than 90° (Jeffrey, 1997; Michalková and Tunega, 2007), where the X and Y represent the

proton-donor and proton-acceptor, respectively. The number and bond length of H-bonds were calculated by averaging over the recorded trajectories during the MD production runs. The lateral atomic density contour maps were plotted based on the recorded atomic coordinate during the MD production runs. Here the distribution of NMF atoms on the x, y plane of kaolinite interlayer surface (octahedral surface and tetrahedral surface) were considered. The E for each system was calculated as the difference between the potential energy of the kaolinite-NMF complex and the sum of potential energies of both kaolinite and NMF subsystems. The E was also averaged over the accumulated frames during the production runs. In order to clarify the affinity of the two types of kaolinite interlayer surfaces toward the NMF, the E of NMF with each interlayer surface was also calculated using the same method described in our previous study (Zhang et al., 2017). Because the forcefield-based E is composed of electrostatic and van der Waals energies (Heinz et al., 2006; Wang et al., 2014), the electrostatic and van der Waals interaction energies were also calculated separately to clarify their contributions to the total interaction energies.

2. Results and Discussion

The calculated basal spacings of kaolinite-NMF complexes increase with the increasing NMF content in the kaolinite interlayer as expected (Figure 2). It shows that the basal spacing can be readily expanded to 11 Å at low NMF content, and stabilized at 11 Å with the continuous increase of NMF content from 10 to 70 molecules. The computed E corresponding to this stage are more negative, indicating the substantial preference for the formation of kaolinite-NMF complex with basal spacing of 11 Å, which agrees well with the experimentally obtained one (10.8 Å) (Olejnik et al., 1970; Xie and Hayashi, 1999). The molecular ratio of guest NMF to host unit $\text{Al}_4\text{Si}_4\text{O}_{10}(\text{OH})_8$ of kaolinite-NMF complex models that produced the basal spacing of 11 Å is less than 0.9, agreeing well with that (1.0) revealed by the thermogravimetric and NMR results (Xie and Hayashi, 1999). Although the E are more negative compared to the whole range, they increase slowly with the increase of NMF content. This suggests that the kaolinite interlayer can be readily expanded by NMF at the beginning of intercalation process, the continuous filling of NMF in the interlayer space, however, needs to overcome the energy barrier. With further increase of NMF content from 75 to 125 molecules, the basal spacings experience two rapid increase stages without distinct plateau observed. In addition, the E also increase rapidly without distinct energy minima observed and experience the energy jump with the sharp increase of basal spacing at molecule number of 75 and 105 (Figure 2). This indicates that the kaolinite-NMF complexes with the basal spacings of more than 11 Å are unstable, and thus these kinds of complexes were rarely reported in the experimental studies. The evolution of basal spacing is caused by the evolution of conformation of NMF in the interlayer space during the intercalation process. The computed basal spacings and E of complexes can give the inspiration that the basal spacing of kaolinite may be considerably enlarged by the intercalation of small molecules through overcoming the energy barrier to change the conformation of small molecules in the interlayer space. It should be noted that the entropic energy is not involved in the computation of forcefield-based E , and thus the E is the internal energy rather than the Gibbs free energy, which cannot be directly applied to the prediction of chemical equilibria (Szczerba et al., 2014).

Interfacial structure

Atom density and distribution of orientation angle of NMF are very effective to visualize the conformation change of NMF in the kaolinite interlayer with the increase of NMF content. Here the kaolinite-NMF complex models with the basal spacings of 11 Å, 12.2 Å, and 14.6 Å were chosen to investigate the conformation change of NMF. The unimodal distribution of N atom in the geometric center of NMF molecule in Figure 3a and b suggests the monolayer arrangement of NMF in the kaolinite interlayer with the basal spacings of 11 Å and 12.2 Å. With the increase of basal spacing to 14.6 Å, the NMF develop to bilayer structure reflected by the two peaks in the N atom density profile (Figure 3c). Figure 3a shows that the two narrow C atom peaks in HC=O and CH₃ groups overlap at the middle plane of the interlayer space with a short distance to the N atom peak, indicating the molecular plane of NMF orients at small angles with respect to the interlayer surface. This is confirmed by the distribution of $\varphi_{normal\ vector\ of\ plane}$ (Figure 4a). Because the orientation angle $\varphi_{normal\ vector\ of\ plane}$ is defined as the angle between the normal vector of NMF molecular plane and the z-axis (perpendicular to the interlayer surface), it is actually the same as the angle between the NMF molecular plane and the interlayer surface. However, the conformation of NMF in the kaolinite interlayer calculated in present study differs from that in dickite interlayer predicted experimentally (Adams, 1979), where the molecular plane of NMF was proposed perpendicular to the interlayer surface with the C=O groups and NH groups pointing to the octahedral and tetrahedral surfaces, respectively. The narrow peak of O atom density profile in the region close to the OH groups on the octahedral surface suggests a fairly strong interaction between them. The OH groups function as proton donor driving the O atom of NMF toward them through hydrogen bonding interaction. This is also reflected by the distribution of orientation angle $\varphi_{C=O}$ that shows a significantly wider peak with the peak maximum located more than 90° (Figure 4a), indicating the C=O groups point favorably to the octahedral surface. While the distribution of φ_{N-H} is less than 90°, indicating the N-H bonds orient preferably toward the opposing tetrahedral surface. The H atoms of NH groups distribute scattered close to the basal oxygens on the tetrahedral surface as reflected by the significantly wider peak in the atom density profile in Figure 3a, suggesting the relatively weak hydrogen bonding interaction between them. The stable conformations of NMF in the kaolinite interlayer with the basal spacing of 11 Å are shown in the representative snapshot in Figure 5.

When the basal spacing is increased to 12.2 Å, the two C atom peaks in the HC=O and CH₃ groups are apparently separated, and the C atom peak in CH₃ group is shifted closer to the tetrahedral surface (Figure 3b). The N atom peak remains almost unchanged at the middle plane of interlayer space. In addition, the peak maxima of $\varphi_{normal\ vector\ of\ plane}$ and φ_{C-N} are shifted to higher angle of 70° and lower angle of 35°, respectively, as shown in Figure 4b. This indicates that the NMF molecules are rearranged as a pillar with the molecular planes orienting at higher angles with respect to the interlayer surface with the increase of basal spacings (Figure 5). During the rearrangement of NMF in the interlayer space, the C=O groups still interact with the OH groups on the octahedral surface as reflected by the O atom peak in the atom density profile, which is still in the region close to the OH groups on the octahedral surface (Figure 3b). However, the interaction of NMF with the tetrahedral surface changes during this process. The wider H atom peak in the NH group is shifted to almost the

same level as the N atom peak at the middle plane of interlayer space, and the C atom peak in the CH₃ group is shifted closer to the tetrahedral surface as mentioned above. This suggests that the hydrogen bonding interaction of NH groups with basal oxygens on the tetrahedral surface is weakened, and the CH₃ groups bond to the tetrahedral surface through reasonable hydrophobic interaction since the tetrahedral surface is hydrophobic (Šolc et al., 2011). This is also reflected by the distribution of φ_{N-H} and $\varphi_{N-C(CH_3)}$ in Figure 4b, which are shifted to the higher angle and lower angle, respectively, compared to that in the complex with basal spacing of 11 Å. With the further increase of basal spacing to 14.6 Å, the peaks of $\varphi_{normal\ vector\ of\ plane\ C=O}$, φ_{N-H} and $\varphi_{N-C(CH_3)}$ are widened, especially for the $\varphi_{normal\ vector\ of\ plane\ C=O}$ and φ_{N-H} which show no well-defined peaks (Figure 4c). This suggests that the NMF develop to relatively disordered bilayer structure in the kaolinite interlayer due to the considerably expanded interlayer space as shown in the representative snapshot in Figure 5.

Interfacial interaction

The kaolinite-NMF complex model with the basal spacing of 11 Å that has been experimentally determined was selected for the computation of interfacial interactions by means of RDF, RCN, H-bonds statistics, and interaction energies. Figure 6 shows the time averaged RDF and RCN calculated for the pairs of functional groups of NMF and kaolinite interlayer surfaces. For the correlation between O atom in the HC=O groups of NMF and H atom in the OH groups on the octahedral surface, a pronounced peak occurs at 2.0 Å. At the position of 3.2 Å that is the right boundary of this peak, the corresponding RCN is 3. It suggests that each O atom of NMF is coordinated by three hydrogen atoms. This indicates the NMF tightly bonds to the octahedral surface through H-bonds formed between the O atom of HC=O groups and H atom of OH groups. While the H atoms in HC=O groups and NH groups of NMF show small pair correlation with basal oxygens on the tetrahedral surface, indicating their relatively weak interactions. The direct H-bonds computation confirms the hydrogen bonding interactions between different functional groups of NMF and kaolinite interlayer surfaces. Each O atom of HC=O groups acting as proton acceptor can simultaneously form H-bonds with two or three hydroxyl groups on the octahedral surface with an average bond length of 2.5 Å. While the H atom of NH groups forms 1 H-bond on average with basal oxygens on the tetrahedral surface with an average bond length of 2.7 Å. Better agreement is observed for the H-bond scheme in terms of the numbers of H-bonds calculated in present study with quantum chemistry calculation for NMF intercalated in dickite (Michalková et al., 2002; Scholtzová et al., 2008). However, the results are not fully in agreement with the experimental studies of NMF intercalated in dickite and kaolinite, where the NH groups of NMF did not participate in the formation of H-bonds with basal oxygens on the tetrahedral surface (Adams, 1979; Xie and Hayashi, 1999). The H-bonds computation in present study also shows that some H atoms in the NH groups and HC=O groups of NMF can also form weak H-bonds with O atom of OH groups on the octahedral surface and basal oxygens on the tetrahedral surface, respectively.

Additional information regarding the interfacial interaction of kaolinite-NMF complex can be obtained from the lateral atomic density contour maps as shown in Figure 7. It shows that the O atoms of HC=O groups are preferentially located at the triangular area surrounded by

three surface OH groups (Figure 7a), where the O atoms of NMF acting as proton acceptor can simultaneously form two or three H-bonds with the OH groups as demonstrated by the H-bonds statistics. Because the H atoms of HC=O and NH groups mainly interact with the tetrahedral surface, their distribution on the tetrahedral surface were focused. Figure 7b shows that the H atoms of HC=O groups have no preferred adsorption sites on the tetrahedral surface, indicating their weak interactions. In contrast to the H atoms of HC=O groups, the H atoms of NH groups preferentially occupy the ditrigonal cavity on the tetrahedral surface. The ditrigonal cavity is formed by the Si-bridging basal oxygens that relax outward slightly with respect to the Si atoms, where the H atoms of NH groups can readily form H-bonds with the basal oxygens.

The interaction energies per NMF with kaolinite octahedral and tetrahedral surfaces were calculated to investigate the binding affinity of the two types of kaolinite interlayer surfaces toward NMF in terms of energetics as shown in Table 1. The interaction energies calculated based on the forcefield represent the intermolecular energies consisting of electrostatic and van der Waals energies. Their contributions to the total interaction energies were also calculated separately and listed in Table 1. The results show that the octahedral surface displays stronger binding affinity to the NMF with lower interaction energy of -3.41 kcal/mol compared to the tetrahedral surface (-1.63 kcal/mol). The electrostatic energy dominates the interaction of NMF with the octahedral surface, accounting for around 70% of the total interaction energy. In case of the tetrahedral surface, the van der Waals energy plays the dominant role with a proportion of 77% to the total interaction energy. This indicates that the hydrophobic interaction is reasonable for the binding affinity of tetrahedral surface to the NMF, which is not surprising since the tetrahedral surface possesses hydrophobic property documented by the MD simulations of the microscopic contact angle between water nanodroplet and kaolinite tetrahedral surface (Šolc et al., 2011). The binding affinity of both kaolinite interlayer surfaces toward the NMF can facilitate the intercalation of NMF in kaolinite interlayer.

3. Conclusions

In present study, the basal spacings and interfacial structure of kaolinite-NMF complexes with various numbers of NMF molecules in the interlayer space were investigated using the MD simulations. In addition, the interfacial interactions were also calculated in the case of the complex with the basal spacing of $11 \text{ \AA}$. The basal spacing of kaolinite can be enlarged considerably to larger values with the prerequisite of overcoming the energy barrier with the continuous intercalation of NMF. The increase of basal spacing was caused by the conformation evolution of NMF in the interlayer space during the intercalation process. At the basal spacing of $11 \text{ \AA}$, the molecular plane of NMF oriented at small angles with respect to the interlayer surface with the C=O groups pointing favorably to the octahedral surface and N-H bonds orienting preferably toward the opposing tetrahedral surface due to the hydrogen bonding interactions. With the increase of basal spacing, the NMF molecules were rearranged as a pillar with the molecular plane orienting at higher angles with respect to the interlayer surface. During this process, the C=O groups still interacted with the OH groups on the octahedral surface through H-bonds. While the hydrogen bonding interaction between the NH groups and basal oxygens on the tetrahedral surface was weakened, and the CH_3

groups of NMF bonded to the tetrahedral surface through hydrophobic interaction. With the further increase of basal spacing, the NMF developed to relatively disordered bilayer structure in the kaolinite interlayer. For the interfacial interactions of kaolinite-NMF complex, both kaolinite interlayer surfaces showed binding affinity to the NMF. The octahedral surface displayed stronger affinity to the NMF compared to the tetrahedral surface in terms of both H-bonds and energetics. For the interaction energy of NMF with the octahedral surface, the electrostatic energy made a great contribution to the total interaction energy. While the van der Waals energy prevailed in the interaction of NMF with the tetrahedral surface due to the hydrophobic property of tetrahedral surface. These insights are helpful to further efforts on the selection and molecular tailoring of new chemicals, and experimental strategies for the intercalation of kaolinite and the associated applications.

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References

- Adams JM. The crystal structure of a dickite: N-methylformamide intercalate $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4 \cdot \text{HCONHCH}_3]$. *Acta Crystallogr.* 1979; 35:1084–1088.
- Bhattacharyya KG, Gupta SS. Adsorption of a few heavy metals on natural and modified kaolinite and montmorillonite: A review. *Adv Colloid Interface Sci.* 2008; 140:114–131. [PubMed: 18319190]
- Bish DL. Rietveld refinement of the kaolinite structure at 1.5 K. *Clay Clay Miner.* 1993; 41:738–744.
- Cheng H, Zhou Y, Feng Y, Geng W, Liu Q, Guo W, Jiang L. Electrokinetic energy conversion in self-assembled 2D nanofluidic channels with janus nanobuilding blocks. *Adv Mater.* 2017; 29:1700177.
- Cygan RT, Greathouse JA, Heinz H, Kalinichev AG. Molecular models and simulations of layered materials. *J Mater Chem.* 2009; 19:2470–2481.
- de Faria EH, Lima OJ, Ciuffi KJ, Nassar EJ, Vicente MA, Trujillano R, Calefi PS. Hybrid materials prepared by interlayer functionalization of kaolinite with pyridine-carboxylic acids. *J Colloid Interface Sci.* 2009; 335:210–215. [PubMed: 19433329]
- de Faria EH, Nassar EJ, Ciuffi KJ, Vicente MA, Trujillano R, Rives V, Calefi PS. New highly luminescent hybrid materials: Terbium pyridine–picolinate covalently grafted on kaolinite. *ACS Appl Mater Interfaces.* 2011; 3:1311–1318. [PubMed: 21446749]
- Dedzo GK, Detellier C. Functional nanohybrid materials derived from kaolinite. *Appl Clay Sci.* 2016; 130:33–39.
- Ewald PP. Die berechnung optischer und elektrostatischer gitterpotentiale. *Ann Phys.* 1921; 369:253–287.
- Fang Q, Huang S, Wang W. Intercalation of dimethyl sulphoxide in kaolinite: Molecular dynamics simulation study. *Chem Phys Lett.* 2005; 411:233–237.
- Ható Z, Makó É, Kristóf T. Water-mediated potassium acetate intercalation in kaolinite as revealed by molecular simulation. *J Mol Model.* 2014; 20:2140. [PubMed: 24549796]
- He H, Ma L, Zhu J, Frost RL, Theng BKG, Bergaya F. Synthesis of organoclays: A critical review and some unresolved issues. *Appl Clay Sci.* 2014; 100:22–28.
- Heinz H, Lin TJ, Kishore Mishra R, Emami FS. Thermodynamically consistent force fields for the assembly of inorganic, organic, and biological nanostructures: The interface force field. *Langmuir.* 2013; 29:1754–1765. [PubMed: 23276161]

- Heinz H, Ramezani-Dakhel H. Simulations of inorganic-bioorganic interfaces to discover new materials: Insights, comparisons to experiment, challenges, and opportunities. *Chem Soc Rev*. 2016; 45:412–448. [PubMed: 26750724]
- Heinz H, Vaia RA, Farmer BL. Interaction energy and surface reconstruction between sheets of layered silicates. *J Chem Phys*. 2006; 124:224713. [PubMed: 16784307]
- Hirsemann D, Köster TKJ, Wack J, van Wüllen L, Breu J, Senker J. Covalent grafting to μ -hydroxy-capped surfaces? A kaolinite case study. *Chem Mater*. 2011; 23:3152–3158.
- Jeffrey GA. An introduction to hydrogen bonding. Oxford University press; Oxford: 1997.
- Komori Y, Sugahara Y, Kuroda K. A kaolinite-NMF-methanol intercalation compound as a versatile intermediate for further intercalation reaction of kaolinite. *J Mater Res*. 1998; 13:930–934.
- Kotal M, Bhowmick AK. Polymer nanocomposites from modified clays: Recent advances and challenges. *Prog Polym Sci*. 2015; 51:127–187.
- Ledoux RL, White JL. Infrared studies of hydrogen bonding interaction between kaolinite surfaces and intercalated potassium acetate, hydrazine, formamide, and urea. *J Colloid Interface Sci*. 1966; 21:127–152.
- Liu C, Gu C, Yu K, Li H, Teppen BJ, Johnston CT, Boyd SA, Zhou D. Integrating structural and thermodynamic mechanisms for sorption of PCBs by montmorillonite. *Environ Sci Technol*. 2015; 49:2796–2805. [PubMed: 25629399]
- Liu X, Lu X, Wang R, Meijer EJ, Zhou H, He H. Atomic scale structures of interfaces between kaolinite edges and water. *Geochim Cosmochim Acta*. 2012; 92:233–242.
- Makó É, Kovács A, Ható Z, Zsirka B, Kristóf T. Characterization of kaolinite–ammonium acetate complexes prepared by one-step homogenization method. *J Colloid Interface Sci*. 2014; 431:125–131. [PubMed: 24996021]
- Michalková A, Tunega D. Kaolinite:Dimethylsulfoxide intercalate - a theoretical study. *J Phys Chem C*. 2007; 111:11259–11266.
- Michalková A, Tunega D, Nagy LT. Theoretical study of interactions of dickite and kaolinite with small organic molecules. *J Mol Struct THEOCHEM*. 2002; 581:37–49.
- Olejnik S, Posner AM, Quirk JP. The intercalation of polar organic compounds into kaolinite. *Clay Miner*. 1970; 8:421–434.
- Olejnik S, Posner AM, Quirk JP. The IR Spectra of interlamellar kaolinite-amide complexes—I. The complexes of formamide, N-methyl-formamide and dimethylformamide. *Clay Clay Miner*. 1971; 19:83–94.
- Plimpton S. Fast parallel algorithms for short-range molecular dynamics. *J Comput Phys*. 1995; 117:1–19.
- Rutkai G, Kristóf T. Molecular simulation study of intercalation of small molecules in kaolinite. *Chem Phys Lett*. 2008; 462:269–274.
- Scholtzová E, Benco L, Tunega D. A model study of dickite intercalated with formamide and N-methylformamide. *Phys Chem Miner*. 2008; 35:299–309.
- Sena MM, Morrow CP, Kirkpatrick RJ, Krishnan M. Supercritical carbon dioxide at smectite mineral–water interfaces: Molecular dynamics and adaptive biasing force investigation of CO₂/H₂O mixtures nanoconfined in Na-montmorillonite. *Chem Mater*. 2015; 27:6946–6959.
- Šolc R, Gerzabek MH, Lischka H, Tunega D. Wettability of kaolinite (001) surfaces — molecular dynamic study. *Geoderma*. 2011; 169:47–54.
- Sugahara Y, Satokawa S, Kuroda K, Kato C. Evidence for the formation of interlayer polyacrylonitrile in kaolinite. *Clay Clay Miner*. 1988; 36:343–348.
- Szczerba M, Kłapyta Z, Kalinichev A. Ethylene glycol intercalation in smectites. Molecular dynamics simulation studies. *Appl Clay Sci*. 2014; 91–92:87–97.
- Wang Y, Wohler J, Berglund LA, Tu Y, Ågren H. Molecular dynamics simulation of strong interaction mechanisms at wet interfaces in clay–polysaccharide nanocomposites. *J Mater Chem*. 2014; 2:9541–9547.
- Xie X, Hayashi S. NMR study of kaolinite intercalation compounds with formamide and its derivatives. I Structure and orientation of guest molecules. *J Phys Chem B*. 1999; 103:5949–5955.

- Zeng QH, Yu AB, Lu GQ, Standish RK. Molecular dynamics simulation of organic–inorganic nanocomposites: Layering behavior and interlayer structure of organoclays. *Chem Mater.* 2003; 15:4732–4738.
- Zhang S, Liu Q, Cheng H, Gao F, Liu C, Teppen BJ. Thermodynamic mechanism and interfacial structure of kaolinite intercalation and surface modification by alkane surfactants with neutral and ionic head groups. *J Phys Chem C.* 2017; 121:8824–8831.
- Zhou CH. An overview on strategies towards clay-based designer catalysts for green and sustainable catalysis. *Appl Clay Sci.* 2011; 53:87–96.
- Zhou Q, Shen W, Zhu J, Zhu R, He H, Zhou J, Yuan P. Structure and dynamic properties of water saturated CTMA-montmorillonite: Molecular dynamics simulations. *Appl Clay Sci.* 2014; 97–98:62–71.

Highlights

- Basal spacing of kaolinite can be considerably expanded by small molecules.
- Interfacial structure of kaolinite-NMF complex was visualized by MD simulations.
- Kaolinite octahedral surface displays relatively strong binding affinity to NMF.

Figure 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 (red), Si (orange), Al (purple), H (white), N (blue), and C (gray).

Figure 2. Evolution of basal spacing and E per NMF of kaolinite-NMF complexes as a function of the number of NMF molecules in the kaolinite interlayer calculated by MD simulations.

Figure 3.

Atom density profiles of NMF in the interlayer of kaolinite-NMF complexes with the basal spacings of (a) 11 Å, (b) 12.2 Å, and (c) 14.6 Å. The origin was set at the middle plane of the interlayer space. H-Kao and O-Kao refer to the hydrogen atom on the octahedral surface of lower kaolinite layer and basal oxygens on the tetrahedral surface of upper kaolinite layer in Figure 1, respectively.

Figure 4.

Distribution frequencies of orientation angles $\phi_{C=O}$, ϕ_{C-N} , ϕ_{N-H} , $\phi_{N-C(CH_3)}$, and $\phi_{normal\ vector\ of\ plane}$ of NMF in the kaolinite-NMF complexes with the basal spacings of (a) 11 Å, (b) 12.2 Å, and (c) 14.6 Å.

Figure 5.

Representative snapshots of kaolinite-NMF complexes with the basal spacings of 11 Å, 12.2 Å, and 14.6 Å produced by the MD simulations. Atoms are colored as in Figure 1.

Figure 6.

Radial distribution function (RDF) and running coordination number (RCN) calculated for pairs between the O atom in the HC=O groups of NMF and H atom in the OH groups on the octahedral surface; H atom in the HC=O groups and basal oxygens on the tetrahedral surface; H atom in the NH groups and basal oxygens on the tetrahedral surface.

Figure 7. Lateral atomic density contour maps for (a) O atom in the HC=O group on the alumina octahedral surface, (b) H atom in the HC=O group and (c) H atom in the NH group of NMF on the silica tetrahedral surface.

Table 1

E per NMF with kaolinite octahedral and tetrahedral surfaces averaged over the production runs.

	E_{total} (kcal/mol)	E_{elec} (kcal/mol)	E_{vdw} (kcal/mol)
Octahedral surface-NMF	−3.41	−2.36	−1.05
Tetrahedral surface-NMF	−1.63	−0.37	−1.26