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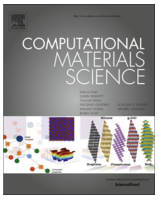

Simulation study of intercalation complexes of kaolinite with simple amides as primary intercalation reagents

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ABSTRACT

Delamination/exfoliation of book-like kaolinite particles is one of the most promising ways to produce aluminosilicate nanoscrolls. For the delamination of the kaolinite layers, multi-step intercalation/deintercalation procedures are used. In the first, direct intercalation step, the intercalation reagents are typically small organic molecules possessing high dipole moment. We modeled, evaluated and compared the incorporation features of formamide, urea and N-methylformamide molecules into the interlayer space of kaolinite by classical molecular simulations using realistic CHARMM-based atomic force fields. Besides the determination of characteristic basal spacings of the intercalation complexes, we compared the density and orientation distributions of the guest molecules, as well as atomic pair correlation functions. From the simulations we also calculated the typical intermolecular interaction energies and estimated the translational mobility of the different substances. Our results show that urea has some preference over the other substances in multi-step, heat-treating intercalation/deintercalation procedures with kaolinite.

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1. Introduction

Kaolinite ($Al_2Si_2O_5(OH)_4$) is a layered aluminosilicate with a 1:1 layer structure. An individual layer consists of an octahedral aluminum hydroxide sheet and a tetrahedral silica sheet, sharing a common plane of apical oxygen atoms. Layers are held together by hydrogen bonds between surface hydroxyl groups of the aluminum hydroxide sheet and the basal oxygen atoms of the silica sheet, forming a distinct space between the layers. The equilibrium basal spacing of natural kaolinite is around 0.72 nm. Kaolinite is often used for the preparation of intercalated materials, as it can readily intercalate a few selected molecules. Highly polar organic molecules such as urea (U), formamide (FA), or dimethyl sulfoxide (DMSO), and alkali salts such as alkali acetates can expand the interlayer space of pure kaolinite by spontaneously replacing the hydrogen bonds between the layers [1]. The expansion caused by such primary intercalation reagents have been studied in several works [2–11]. Multiple intercalation/deintercalation procedures using longer chain molecules as secondary or tertiary reagents (which can replace the already intercalated reagents) [12–16] are applied to increase the layer spacing, even to the extent that the attraction of the layers is overcome. This delamination process enables the formation of kaolinite nanoscrolls. Delamination/exfoliation of the book-like kaolinite particles is one of the most favorable ways to produce aluminosilicate nanoscrolls, which have numerous applications in nanocomposite materials (e. g. as catalyst carrier) [17].

In the present work, we focus on the intercalations of kaolinite with FA and its relative compounds, U and N-methyl-formamide (NMF). U has one of the earliest practical applications in preparation of kaolinite organocomplexes [16], but the kaolinite-FA and kaolinite-NMF intercalation complexes have also been widely studied in experiments [3,4,9,13]. Recent findings [18] highlighted the significance of utilizing U as primary reagent in multiple intercalation/deintercalation procedures, and here application of other small amide molecules is also worth considering. To compare the properties of these complexes in detail, we used classical molecular simulation. Adsorption and intercalation of molecules in clays are effectively studied by means of such techniques [19–24], uncovering material features that are currently not available from experiments. In our earlier studies we provided predictions by molecular simulations for intercalation complexes with potassium and ammonium acetates [25–27], methanol [28], and cetyltrimethylammonium chloride [29], using the standard all-atom force field, CHARMM [30], and its highly realistic extension for kaolinite, INTERFACE [31].

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2. Material and methods

Classical Molecular Dynamics (MD) simulations were carried out with constant number of molecules N, at constant pressure p (mostly 1.013 bar) and at constant temperature T (mostly 298 K). The leap-frog integrator was used with the integral time step of 1 fs. The temperature and pressure controls were realized by using the Nosé-Hoover [32] and Parrinello-Rahman [33,34] schemes, respectively. The pressure coupling was semi-isotropic: isotropic in the x- and y-directions, but different in the z-direction, which latter is perpendicular to the kaolinite layers. Periodic boundary conditions were applied in all three spatial directions. The van der Waals interactions were truncated at 1.2 nm and the periodic electrostatic interactions were calculated by the particle mesh Ewald (PME) [35] algorithm with 1.2 nm cutoff. All the simulations were performed using the GROMACS [36,37] program package.

The lattice parameters of the kaolinite unit cell, $Al_2Si_2O_5(OH)_4$, are $a = 0.5154$ nm, $b = 0.8942$ nm, $c = 0.7391$ nm, $\alpha = 91.93°$, $\beta = 105.05°$, $\gamma = 89.80°$ (the space group symmetry is $C1$) [38]. We constructed a simulation box that consisted of four clay layers built from 96 double unit cells that are arranged in a 6 × 4 × 4 composition resulting in 816 atoms (96 Al atoms, 96 Si atoms, 432 O atoms, and 192 H atoms) per kaolinite layers. The layers are stacked upon each other forming four interlayer regions. The initial atomic positions were set according to the experimental crystal structure of kaolinite [38]. This initial arrangement of the simulation cell is shown in Fig. 1.

The framework of a standard fully flexible all-atom force field, CHARMM [30] was used for handling the atomic interactions. Only the bond vibrations including hydrogen atoms (which are generally beyond the classical limits of molecular simulations based on force fields) were constrained with the LINCS algorithm [39]. The energy expression of the CHARMM force field contains quadratic bond stretching, angle bending, torsion and out-of-plane potential terms (bonded interactions), as well as standard Coulombic and 12-6 Lennard-Jones potential terms (nonbonded interactions). The van der Waals nonbonded interactions were treated with the Lorentz-Berthelot combination rule. The parameters for kaolinite were taken from the INTERFACE v1.5 force field [40]. For the investigated guest molecules (FA, U, NMF and, for comparison, DMSO) the CHARMM27 force field variant implemented in GROMACS [41] were applied. For U, charges were taken from the work of Caflisch and Karplus [42]. For NMF and DMSO, all the parameters are from CGenFF v. 2b8 [43] and the molecular models were adapted from the work of Fisher et al. [44].

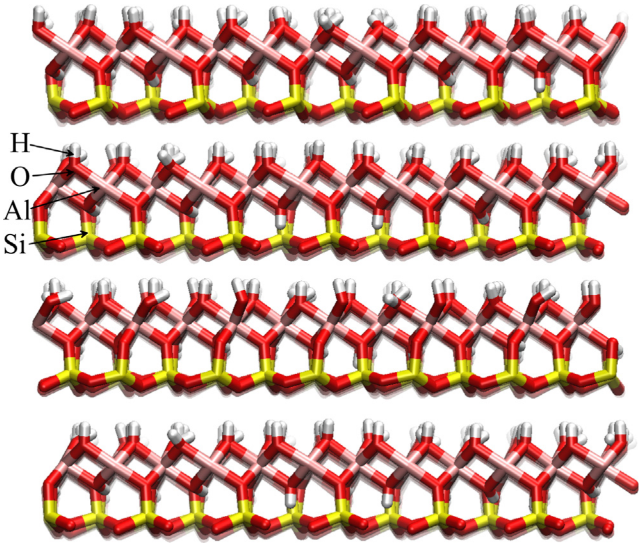

Fig. 1. Snapshot of the simulation cell with the initial configuration of the non-intercalated kaolinite.

Due to moderate convergence of the simulations with such flexible guest molecules, the starting configurations for the production runs were made with special care. Initially, the guest molecules were created with random positions and orientations within artificially enlarged interlayer spaces of the clay, generating four different guest molecule arrangements in the four interlayer spaces. Then, after a short energy minimization of the system, an equilibration period using the more robust Berendsen thermostat and barostat [45,46] were applied with 10 times the final compressibility (material 'softness') parameter in the z-direction. The total production runs using the Nosé-Hoover and Parrinello-Rahman schemes were 20 ns long.

3. Results and discussion

3.1. Identification of stable complexes

We performed a series of NpT MD simulations with various guest molecule loadings of kaolinite at $p = 1.013$ bar and $T = 298$ K and calculated the resulting basal spacings as simulation averages (adsorption on the outer surface of the kaolinite particles was not considered). Following the usual method [47,23], we identified stable regions in the basal spacing vs. loading plane, where the calculated basal spacing does not change substantially with the guest molecule content. Due to its simplicity, this approach is a straightforward choice for simulation analyses, even if it requires a series of simulation runs and the selection of the lower and upper limits for the composition of the stable complexes is somewhat arbitrary. The approach is upheld by our recent work using stability analysis with chemical potential calculations [48]. An inflexion point that can always be found within the selected region (typically a middle point or a point that falls near the middle point at a slightly higher guest molecule content) can serve as a representative point of the region. Generally, this point can be assigned to the experimentally detected complex, taking into account the similarity between the width of the X-ray peak in experiments and the narrow range of basal spacing identified from simulations (at least a part of the usual X-ray peak broadening can be associated with the small change of basal spacing, for a rather large change of loading, within the stability region in simulations).

As a demonstrative example, Fig. 2 shows the loading of kaolinite with DMSO as a function of the calculated basal spacing, together with the first derivative of the loading. The shape of the curve of loading and the intense peak of the curve of first derivative of the loading suggest a stable intercalation complex at 1.12 nm,

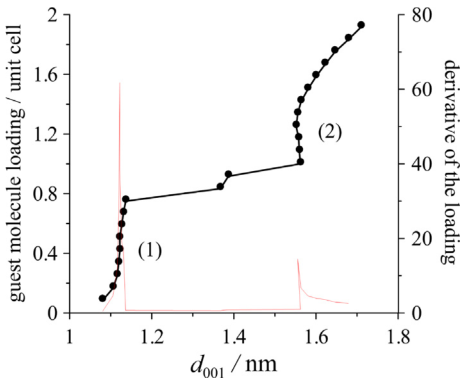

Fig. 2. Loading of kaolinite with DMSO as a function of the calculated basal spacing from NpT MD simulations at 298 K and 1.013 bar.

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