Computational Materials Science 96 (2015) 134–139

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

An interlayer expansion model for counterion-intercalated montmorillonite from first-principles calculations

Jing Shi [a], Zhaoyang Lou [a], Mingli Yang [a,*], Yao Zhang [b], Houbin Liu [b], Yingfeng Meng [b,*]

[a] *Institute of Atomic and Molecular Physics, Sichuan University, Chengdu 610065, China*
[b] *School of Petroleum Engineering, Southwest Petroleum University, Chengdu 610500, China*

ARTICLE INFO

Article history:
Received 3 April 2014
Received in revised form 5 September 2014
Accepted 13 September 2014

Keywords:
DFT calculations
Intercalation
Montmorillonite
Adsorption
Interlayer expansion

ABSTRACT

From density functional theory calculations on dry and hydrated MMT, Na-MMT, NH_4^+-MMT, and formamide-MMT structures at various interlayer spacings, we proposed an interlayer expansion model for the counterion-intercalated MMT systems. Complex interactions exist among the counterions, lower and upper MMT surfaces, including ionic bonding, hydrogen bonding, electrostatic attraction/repulsion, and van der Waals forces. These interactions vary with different counterions and different interlayer spacings, playing a crucial role in the energy landscape of interlayer expansion. The equilibrium spacings are related to counterion volume, and the competition between interlayer electrostatic attraction and repulsion. The expansion energy potential near the equilibrium spacings can be approximately described with a quadratic function of spacing increase. At large spacings, however, the counterions have a tendency to form relatively strong interaction with either surface, making their energy potential in MMT approach to constant values.

1. Introduction

Montmorillonites (MMT) are one of the most widespread chemical compounds on the earth. A typical MMT structure consists of separated layers in which tetrahedral silica and octahedral alumina sheets are arranged alternatively. The interlayer spacings are about 0.5 nm in width, making MMT a natural additive in the preparation of nano-composites [1–3]. The dispersion of nano-sized MMT into polymers often leads to composite materials with enhanced mechanical and thermodynamic properties [4–8]. In addition, the destabilization of MMT caused by water intercalation has been highly concerned in geological science and petroleum development [9,10]. The interaction of MMT surface with intercalators is key to all these processes.

The interlayer spacings in MMT are wide enough for small molecules and ions to enter, occupy and diffuse. On the other hand, the intercalation of guests makes the interlayer spacing even wider, resulting in lattice expansion along the direction perpendicular to the layers. The guests are known as intercalators [11–19]. Understanding to how intercalators hold the adjacent layers apart would be helpful to adjust lattice expansion, so as to control the yield of MMT nano-additives, as well as the destabilization of MMT formation.

A number of studies have focused on the interaction of guest molecules with clays including MMT [20–35]. Tunega et al. [22] studied the adsorption of molecular water and acetic acid on kaolinite by using the B3LYP density-functional method with a cluster model. It was found that the adsorbates are binded to the surface through weak hydrogen bonds. Using a similar cluster model, Michalková et al. [23–25] computed the interaction of dimethylsulfoxide (DMSO), methyltert-butyl ether (MTBE), formamide (FA) and FA derivatives with clay surface at B3LYP and MP2 levels. Both hydrogen bonds between the sulfonyl oxygen atom and surface hydroxyl groups, and those between the methyl groups and the surface oxygen atoms, play an important role in the final localization and stabilization of the DMSO molecule on the clays. Dawley et al. [26] and Scott et al. [27] conducted a combined infrared experimental and theoretical study on the adsorption of FA on kaolinite surfaces. Guégan [28] has studied the mobility of nonionic surfactant ($C_{10}E_3$) in MMT clay by small-angle X-ray scattering in conjunction with Fourier transform infrared spectroscopy. Geatches et al. [29] used DFT to compute the adsorption of selected organic monomers on kaolinite, showing that the adsorption is predominantly electrostatic for charged monomers and H-bonding for the noncharged ones. Berghout et al. [35] studied the hydration and mechanical properties of MMT systems with mono-(Na^+) and

---

* Corresponding authors. Tel.: +86 28 85405515 (M. Yang), +86 28 83032901 (Y. Meng).

E-mail addresses: myang@scu.edu.cn (M. Yang), cwctmyf@swpu.edu.cn (Y. Meng).

http://dx.doi.org/10.1016/j.commatsci.2014.09.013

di-valent (Mg^{2+}, Ca^{2+}, Sr^{2+}, and Ba^{2+}) cations intercalated using first-principles calculations.

In addition, Molecular Dynamics (MD) and Monte Carlo (MC) simulations have been used to study interactions of various molecules with the clays [36–40]. Tunega et al. [36] investigated the sorption of the anionic form of the pesticide 2,4-D (2,4-dichlorophenoxyacetic acid) on the surface of the montmorillonite with a short-time ab initio molecular dynamics (MD) method. Liu et al. [37] investigated the benzene adsorption to montmorillonite using molecular dynamic simulations. Yu et al. [38] found that organic compounds adsorb to mineral surfaces with a maximized contact area in absence of water using an empirical force field-based MD approach. Although many first-principles calculations have been conducted to study the guest-clay interactions, most of them used a so-called cluster model or a periodic slab model. In the former, a small piece of clay structure was extracted to represent the bulk clay and its surface. In the latter, the surface is constructed by applying a periodic vacuum layer along the normal to the surface. Such simplifications provide meaningful information on the adsorbate–surface interaction, however, they do not show the realistic situation of guest-clay interaction in which the guest molecules sit between opposite inner surfaces and interact with both sides. On one hand, the guest molecules reduce the interlayer repulsion and bind the adjacent layers together. On the other hand, the guest molecules enlarge the interlayer spacing and make the adjacent layers apart. These two effects make the guest-clay interaction complicated.

Using a simplified model, we have studied the guest-MMT interaction at fixed interlayer spacings [41–44]. Complicated electrostatic, ionic and hydrogen bonding, and van der Waals interactions have been revealed for the guest-MMT systems. However, the interlayer spacing effect, which is important for the adsorption and desorption of guest molecules, has not yet been investigated. In this work, we focus on the physical model of lattice expansion of MMT upon the intercalation of guest ions or molecules, sodium ion (Na^+), ammonia (NH_4^+), protonated formamide (FAH) and their hydrates. These three guests are representatives of various intercalators. One of the most important characteristics of MMT is its isomorphic substitution by lower-charge cations in either the alumina or the silica layer, making the layer negatively charged. Counterions, like Na^+, NH_4^+, or FAH, then move into the interlayer space to balance the negative layer. The intercalation of Na^+ forms Na^+-MMT, which is one of the main components of clay. Ammonium is one of the main components of drilling fluid, effective in filtration reduction, swelling inhibition, and well-bore stabilization [45,46]. Meanwhile, ammonium exists in waste water, depositing in beneath stratum together with other wastes [45,47–50]. The study of NH_4^+ intercalation in MMT has particular importance in petroleum engineering, environment protection, and material research. FAH and its derivatives are often used to split MMT into separate sheets in nano size. In addition, the MMT-supported FAH has particular reactivity that can be used as a precursor for nucleic acid synthesis [51,52]. Our study started with the characterization of lowest-energy structures of guest-MMT systems. After an analysis on the guest-MMT interaction, we established the energy landscape of guest-MMT by scanning the systems at various interlayer spacings. Finally, the lattice expansion model is proposed for the Na^+, NH_4^+ and FAH intercalated MMT systems.

2. Computational methodology

The MMT model was derived from the experimental crystal structure reported by Viani et al. [53]. In our calculations, a $2 \times 1 \times 1$ supercell with one Al^{3+}/Mg^{2+} isomorphic substitution in the tetrahedral alumina sheet was constructed. The measured lattice parameters of $a = 10.36$ Å, $b = 8.98$ Å and $\alpha = \beta = \gamma = 90°$ were used, while c, which corresponds to interlayer spacing, was scanned for different guest molecules set free. Fig. 1a illustrates the computational model of MMT.

The inner surfaces of MMT are covered by oxygen atoms, as shown in Fig. 1b. The guest cations thus have various adsorbing sites. To locate the optimal adsorbing sites, we used a two-step screening approach. First, Monte-Carlo (MC) simulations were performed with CLAYFF force field [54], which has been used extensively for clay systems [55–57], to locate the optimal adsorption sites of the three counterions Na^+, NH_4^+, FAH and water molecules. The MC simulations proceeded in a supercell with fixed lattice parameters at 300 K. At least three independent MC runs, each has 500,000 steps, were performed for every counterion. The best three structures were collected for further studies at DFT level.

Density functional theory calculations were performed using the numerical atomic orbital (NAO) methodology implemented in the SIESTA [58,59] program. It uses the standard Kohn–Sham self-consistent density functional method in generalized gradient (GGA) approximations and uses norm-conserving pseudopotentials in the Troullier–Martins form [60] to describe the core electrons, while the valence wave functions are expanded on (pseudo) atomic orbitals including multiple-ζ and polarization functions. The Perdew–Burke–Ernzerhof (PBE) parameterization [61] of the exchange–correlation functional, the standard DZP basis set with orbital-confining cutoff radii of 0.02 Ry, and a real-space integration grid with a plane wave cutoff of 220 Ry were used. Calculations were restricted to the Γ-point in the Brillouin zone. A dispersion potential of the Grimme type [62] was used to deal with the weak interaction in the systems. The conjugated gradient minimization method was used to relax the atomic positions until the maximum atomic force is less than 0.01 eV/Å.

3. Results and discussion

On the inner surface of MMT are full of oxygen atoms of tetrahedral silica. The negatively charged surface has great tendency to adsorb atoms or molecules with positively charged domains. The Al^{3+}/Mg^{2+} isomorphic substitution in the middle alumina layer makes the inner surface more negative, about 0.06 e for a $2 \times 1 \times 1$ supercell [41]. Strong electrostatic repulsion thus exists between adjacent surfaces and pushes them apart. The intercalation of counterions not only compensates the negative charge caused by Al^{3+}/Mg^{2+} substitution, but reduces the interlayer repulsion as well. The counterions then have two opposite effects on the lattice structures, narrowing the interlayer spacing by attracting both surfaces together and widening the spacing by occupying the interlayer space. The lattice variation should be an outcome of both effects.

Since all the surface atoms are negatively charged, the counterions may adsorb onto any of them and form various adsorbing conformations. Among a number of low-lying conformations screened from MC and DFT calculations we focus on the lowest-energy structures, which are displayed in Fig. 2. Studies on the other low-lying structures come to similar results and are thus omitted for concision. For Na^+, it does not adsorb directly onto any O atoms. Instead, it sits at about the center of six oxygen atoms which forms a six-oxygen-ring (SOR) cation trap. The shortest three Na–O distances are about 2.42–2.50 Å, a distance of typical Na–O ionic bond. Similar situations were found for NH_4^+ and FAH in which one of their H atoms is trapped by SOR. The shortest three O–H distances are about 2.31, 2.33, 2.54 Å for NH_4^+, 2.13, 2.36, 2.39 Å for FAH. They are typical distances of hydrogen bond. NH_4^+ and FAH have more than one H atoms that may further interact with the surface atoms. Different from Na^+ which is trapped by