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Theoretical characterization of formamide on the inner surface of montmorillonite

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ABSTRACT

Density functional theory calculations were performed to characterize the low-lying structures of formamide (FA) and protonated formamide (FAH) in the interlayer space of montmorillonite (MMT). The interactions among FA/FAH, H_2O, Na^+, and the inner surface of MMT were systematically analyzed. The carbonyl-O of FA/FAH has strong coulomb interaction with Na^+, while its amide-H forms hydrogen bonds (HBs) with water and MMT surface. The adsorption of FA is promoted by H_2O, which exhibits a cooperative adsorption effect by enhancing the FA–Na^+ coulomb interaction and by forming HBs with FA. Our study reveals the structural basis of FA/FAH as an intercalator for MMT splitting.

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1. Introduction

Formamide (FA) is widely used in the manufacture of pharmaceuticals, herbicides, pesticides and polymers. With their applications in our daily life, considerable amount of FA and its derivatives enter into waste water and eventually seep into soil where they could have harmful effect on our environment. Clay minerals are main components of soil. Due to their high surface area and high swelling capacity, clays have a major role as accumulation phase of many organic and inorganic matter [1,2]. FA is also used as an intercalation agent to split clays into sheets of nano-thickness, which are natural additives for the preparation of polymer nano-composites. In these polymer composites, the nano-sized clays were used to reinforce polymers by increasing their heat durability and mechanical strength [3–7]. The intercalation of guest organic molecules into the interlayer space of clay minerals is an important process to obtain new nanostructure (hybrid organic–inorganic materials) composites with desired properties. The guests, such as FA, can be adsorbed to the internal surfaces of clay minerals, and occur a variety of interactions. These interactions control the mobility, transport and distribution of organics in the soil matrix [8,9]. Although such interactions are important for understanding water and soil pollution caused by harmful organics, as well as for the design of new polymer nano-composites, it remains a challenge to address the details occurring on the inner surfaces of clays. In addition to the organic molecules, water and counterions may also enter into the clay and interact with the internal surfaces and with each other, making the interactions extremely complicated.

Much effort has been devoted to the study of FA-clay interaction. Saladino et al. [10] have studied FA's reactivity with montmorillonites (MMT), finding that MMT has great effect on the reactions of FA as a precursor of nucleic acid synthesis. The experiments [11–13] of IR and Raman spectroscopy of FA-intercalated kaolinites have revealed that the C═O group of FA forms hydrogen bonds (HB) with the inner surface hydroxyls. Weak HBs were also detected [14] between the siloxane layer of kaolinite and the amide group of FA. Several theoretical investigations have focused on the interaction of FA with clays. The intercalates and adsorbates of kaolinite and dickite with FA and its derivatives were investigated by Michalkova et al. [15] using a representative cluster model at B3LYP/3-21G(d) level. Intercalation energies were found significantly larger than adsorption ones. The local geometry and orientation of FA dickite was also studied by Scholtzova et al. [16] with DFT calculations. Rutkai and Kristof [17] conducted Monte-Carlo simulations on the intercalation of FA in kaolinite and found that more than one stable state exists in an intercalated system. At PM3 and PBE/6-31G levels, Campos et al. [18] computed part of the IR spectrum of formamide–kaolinite intercalation compound based on a 110-atom cluster of kaolinite with one formamide molecule. Recently, Dawley et al. [19] and Scott et al. [20] conducted a combined infrared experimental and theoretical study on the adsorption of FA on kaolinite surfaces, as well

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as on the roles of water and sodium ion on the adsorption. Calculations with a cluster model confirm the observed infrared spectra and the measured binding energies of FA-kaolinite systems.

MMT is a 2:1 clay with a laminar structure in which an octahedral sheet is sandwiched by two tetrahedral sheets. In our previous studies, we studied the structures of dry montmorillonite (MMT) [21] and the hydration of ammonia ions inside MMT [22] by using periodic boundary condition (PBC) DFT calculations. Attributed to the binding effect of inner surface, the confined NH_4^+ and water molecules exhibit distinctly different behaviors from in free status. In this work, we further studied the interaction of FA and protonated formamide (FAH) with the inner surface of MMT, in the presence of water and counterions (Na^+) by means of DFT calculations. Because of their complexity, the FA–H_2O–Na^+–MMT systems have not yet been theoretically investigated. Our study would be helpful for understanding the diffusion, accumulation, and degradation of FA in clay, as well as for the preparation of MMT-based nano-composites.

2. Methods

A typical MMT layer consists of one octahedral alumina sheet and two tetrahedral silica sheets. The inner surfaces are mainly occupied by the O atoms of silica sheets. In nature, some of Si^{4+} and Al^{3+} in the layer are replaced by low-valence cations, for example, Al^{3+} and Mg^{2+}, making the layer negatively charged and inclined to trap positively charged ions. In our calculations, the MMT structure was extracted from the experimental crystal structure of Viani et al. [23]. A $2 \times 1 \times 1$ supercell with one Al^{3+}/Mg^{2+} isomorphic substitution in the middle alumina sheet was used.

First, Monte-Carlo (MC) simulations with CLAYFF force field [24] were performed to locate the optimal adsorption sites of the FA/FAH, Na^+ and H_2O. The CLAYFF parameters have been found reliable for clay systems [25–28]. The MC simulations were carried out in the canonical (NVT) ensemble of $T = 300$ K. The initial configurations were generated by putting randomly the adsorbate into the interlayer space. The MMT structure was fixed, and only the adsorbates were allowed to move. At least 500,000 steps were completed for each MC simulation. At least three independent MC runs for each configuration were carried out to generate a number of candidate structures among which the structures whose energies were within 0.10 eV with respect to the lowest structure were sent to further identification.

Next, the MC-predicted structures were relaxed at DFT level. Since the adsorption behaviors of guest molecules are affected by the interlayer space, the lattice parameters of a, b, α, β, and γ were fixed, while the optimal interlayer space was obtained by scanning a series of parameters along the c-direction. Usually the energy-spacing curves are V-shaped for a given configuration, and their bottoms correspond to the stationary structures. Since the middle alumina sheet has little influence on the reactivity of inner surface, all atoms in the middle sheet were fixed during relaxation. The generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) parameterization [29], as implemented in the SIESTA program [30,31], was used in all DFT calculations. The non-local norm-conserving pseudopotentials in the Troullier–Martins form [32] were used to describe the core electrons, while the valence wave functions are expanded on (pseudo) atomic orbitals including multiple-ζ and polarization functions. 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 [33] 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. Such computational settings have predicted reasonable results for organic-clay systems in many studies [34–40].

3. Results and discussion

First, we optimized the structure of FA and MMT separately. The PBE predicted FA structure is in good agreement with experiments [41,42] and other calculations [43–45]. The largest deviation in bond length is less than 0.02 Å from the experiment [40] and 0.01 Å from B3LYP/aug-cc-pVTZ calculation [45]. Since Viani's model [23] gives only a general atomic arrangement in MMT, and the MMT structures vary greatly with intercalated guest molecules and in-layer isomorphic substitution, we validated our computational strategy by comparing the predicted structure of dry and substitution-free MMT with other theoretical [46–50] and experimental [51,52] studies. Our computed lattice parameters are 5.18, 8.98, and 9.51 Å for a, b and c, respectively, in good agreement with the measurements, 5.16, 8.96/8.97, and 9.35 Å [51,52]. In other calculations, similar a and b values were predicted, but c varied from 8.99 to 10.98 Å [46–50].

3.1. FA–MMT and FAH–MMT

Because of Al^{3+}/Mg^{2+} isomorphic substitution, the supercell has an extra electron. Counterions have great tendency to enter into the interlay space to balance the negative charge. Therefore, we study the structures of both FA and protonated FA (FAH) in MMT. The latter possesses $+1e$ net charge. Fig. 1(a) and (b) present the most stable structures of FA–MMT and FAH–MMT.

The upper and lower inner surfaces are occupied by O atoms of tetrahedral silica. Every six O atoms constitute a six-oxygen ring (SOR) that protrudes outward. The adsorbed FA and FAH have rather small change (less than 0.02 Å) in geometry upon adsorption. Moreover, FA and FAH have similar conformation in MMT. The formyl-H of FA and FAH adsorbs to the SOR on the upper surface, while amide-H adsorbs to the SOR on the lower and upper surfaces. The formyl-H of FA and FAH is about 2.07–3.20 Å from the six O atoms of SOR, two of which form HBs with formyl-H (about 2.07–2.36 Å in bond-length). Meanwhile, the amide-H atoms form HBs with upper and lower surfaces simultaneously. The HB bond-lengths are listed in Table 1. Similar HB interaction between FA and siloxane layer has been reported in previous DFT studies [15,20] for FA-kaolinite systems.

The adsorption energy (E_{ad}) of FAH is much larger than that of FA, implying that FA under acid condition has great tendency to intercalate into MMT. The positively charged FAH definitely has strong electrostatic interaction with the negatively charged MMT surface. In addition, the HB strength in FAH–MMT is greater than that in FA–MMT, as indicated by their bond-lengths. Three strong HBs are formed between the amide-H of FAH and MMT, whose O…H distances are about 1.69–1.83 Å.

3.2. FA–MMT–Na

Naturally, MMT exists with metal counterions such as Li^+, Na^+, K^+, Mg^{2+} and Ca^{2+}, etc., which enter into the interlayer space to balance the extra negative charge caused by Si^{4+}/Al^{3+} or Al^{3+}/Mg^{2+} isomorphic substitution in the layers. Now we focus on the FA–MMT interaction in presence of Na^+. The structure of dry MMT-Na has been studied in our previous study [21]. In the lowest-energy structure, Na^+ is positioned above the SOR near to Al^{3+}/Mg^{2+} substitution.

Fig. 2 displays two low-lying conformers, FS_A and FS_B, of FA in MMT–Na, where S denotes the sodium ion. FS_A is 0.12 eV more stable than FS_B. These two conformers were found much more stable than the others. In both structures, Na^+ basically retains its position when FA intercalates, but the distances of Na from SOR are slightly lengthened from 2.35 Å in MMT–Na to 2.40 Å, as shown in Table 2. While the carbonyl-O in FS_A binds with Na^+, its two amide-H atoms form two HBs with the upper surface of MMT. The O…H distances of the two HBs are 2.27 and 2.36 Å, respectively. Such orientation of FA in MMT–Na is similar with measurements [53] in which FA bridges the upper

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