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Theoretical study of interaction of amide molecules with kaolinite

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ABSTRACT

In this paper, we have constructed the cluster models $Si_6O_{18}H_{12}$, $Al_6O_{24}H_{30}$ and $Si_6Al_6O_{42}H_{42}$ for Si—O, Al—O surfaces and isolated kaolinite, respectively. All calculations have been performed at the B3LYP (Becke, three-parameter, Lee–Yang–Parr exchange–correlation functional) level using the 6-31G(d) basis set to investigate the various gas phase properties of interaction of amide (including formamide (FA), acetamide (AA), cis-N-methylformamide (NMFA1), trans-N-methylformamide (NMFA2), cis-N-methylacetamide (NMA1) and trans-N-methylacetamide (NMA2)) with kaolinite, such as optimal structures, structural parameters, interaction energies, charge transfer, vibrational frequencies, electrostatic potential, and so on. Moreover, extra calculations have also been performed at the M052X/6-31G(d) level in order to test the effect of van der Waals interactions on the order of stability of complexes in adsorption or intercalation systems. The results show that hydrogen bonds are formed between amide and the hydroxyl groups of the Al—O surface or the basal oxygen atoms of the Si—O surface in kaolinite. Moreover, the adsorption between amide and Al—O surface of kaolinite is stronger than that of amide and Si—O surface of kaolinite, and the intercalation interaction is more stable than the adsorption interaction. As for the order of the stability of intercalated kaolinite complexes, there is a slight difference between the order (K–NMFA2 > K–FA > K–AA > K–NMA2 > K–NMFA1 > K–NMA1) calculated at the level of M052X/6-31G(d) and the order (K–NMFA2 > K–FA > K–AA > K–NMFA1 > K–NMA2 > K–NMA1) calculated at the level of B3LYP/6-31G(d), in which K denotes kaolinite. The order is different from that of adsorbed systems at the same computational level.

1. Introduction

In recent years, clay minerals have attracted more attention due to the special properties when interacting with small molecules. The organic intercalated kaolinite complexes have been widely used in many aspects such as the catalyst, adsorbent, the environmental pollution remediation material, and so on [1–3].

Kaolinite is a kind of layer aluminosilicate with a variety of physicochemical properties in clay minerals. An individual kaolinite layer consists of two different sheets, one of which is SiO_4 tetrahedral sheet (Si—O layer) and the other one is AlO_6 octahedral sheet (Al—O layer). They are connected by the hydrogen bonds forming between the hydroxyl groups of Al—O layer and oxygen atoms of Si—O layer and the VDW (Van der Waals) interaction [4,5]. Small molecules of high polarity can be inserted into the interlayer space of kaolinite. When kaolinite interacts with small molecules, the original hydrogen bonds break and new hydrogen bonds form between the small molecules and surface hydroxyl groups on the octahedral sheet as well as oxygen atoms on the SiO_4 tetrahedral sheet. The stability of new complex is dependent on the strength of the new hydrogen bonds. The small molecules, such as formamide (FA), acetamide (AA), N-methylformamide (NMFA), N-methylacetamide (NMA), can be easily inserted into the interlayer space of kaolinite. So far, a lot of experimental works have been done to study structural parameters of intercalated clay system, such as the traditional powder diffraction technology, infrared spectroscopy, nuclear magnetic resonance, and so on [6–20]. However, these results cannot fully explain the formation of hydrogen bonds between intercalated molecules and surface hydroxyl groups and/or basal oxygen atoms.

Compared to the experimental methods, the theoretical methods cannot only give interesting insight into the structure of the system but also discuss the mechanism of the formation of hydrogen bonds deeply. The theoretical methods about the solid include periodic model calculation [21–23] and cluster model [24–27]. The former is based on the exploitation of the translational symmetry in the calculation procedure, which may be impractical or over costly for a very large system just like ours. The latter is dependent on the application of standard molecular approach in which the cluster is formed by cutting the periodic structure and the model

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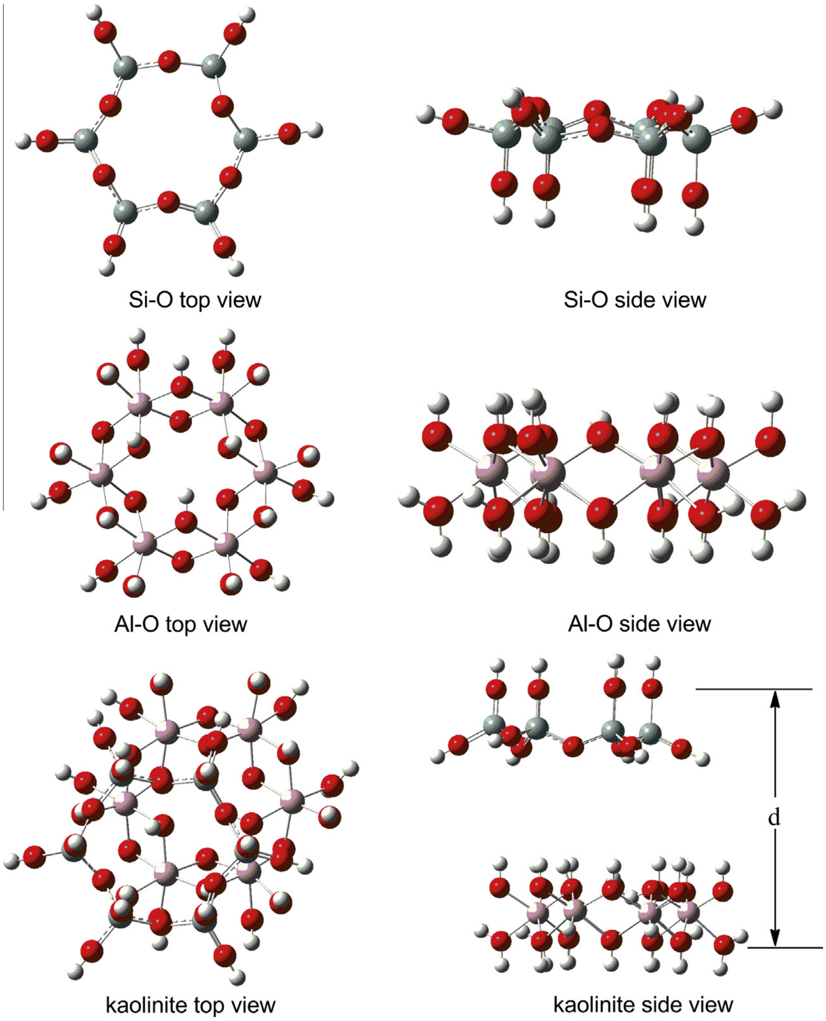


Si-O top view

Si-O side view

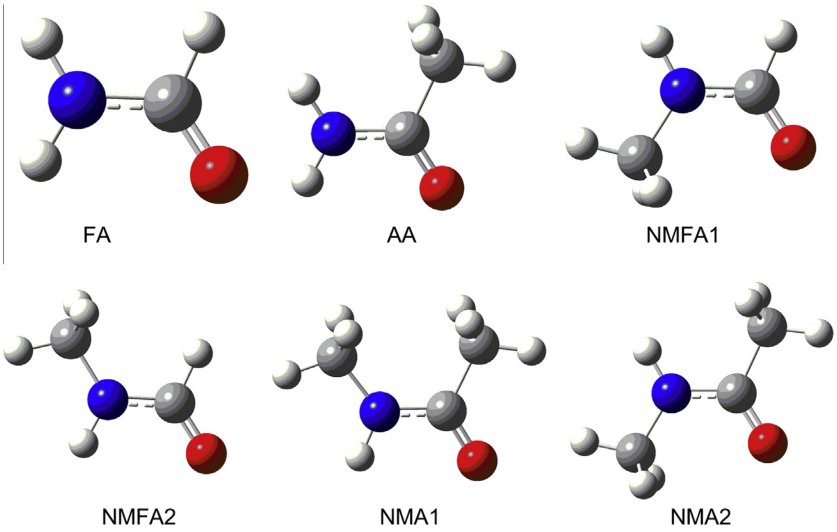
Al-O top view

Al-O side view

kaolinite top view

kaolinite side view

Fig. 1. Different views of cluster models for Si—O surface, Al—O surface and isolated kaolinite, respectively.



FA

AA

NMFA1

NMFA2

NMA1

NMA2

Fig. 2. The optimized structures of various amide molecules.