



Interfacial structures and acidity of edge surfaces of ferruginous smectites

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Abstract

We report an FPMD (first-principles molecular dynamics) study of the interfacial structures and acidity constants of the edge surfaces of ferruginous smectites. To understand the effects of Fe oxidation states on the interfacial properties, we investigated both the oxidized and reduced states of the (010)-type edges of two clay models with different Fe contents. The coordination states of edge Fe atoms are determined from the free energy curves for the desorption of the H₂O ligands. The results of both clay models show that for Fe(III), only the 6-coordinate states are stable, whereas for Fe(II), both the 6- and 5-coordinate states are stable. Using the FPMD-based vertical energy gap technique, the pK_a values of the edge sites are evaluated for both oxidation states. The results indicate that for both clay models, both the octahedral and tetrahedral sites become much less acidic upon Fe reduction. Therefore, the comparison reveals that the interfacial structures and protonation states are strongly dependent on the Fe oxidation states. Using the calculated results, we have derived the pH-dependent surface complexing mechanisms of ferruginous smectites.

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1. INTRODUCTION

Fe-containing smectites are distributed commonly in soils and sediments, and they are greatly interesting to both fundamental research and practical applications (Stucki, 2006). These layered silicates form an important Fe pool in nature, and due to the high chemical reactivity, they play active roles in the global Fe cycle. Fe-smectites take part in numerous natural processes, and thus, they closely connect with other organic and inorganic Fe pools (Murad and Fischer, 1988; Alimova et al., 2009). Due to the reducing capacity, Fe-bearing clay minerals can reduce and

immobilize many pollutants including nitroaromatic compounds and toxic metal cations (e.g., Tc(VII), UO₂²⁺), and therefore, they are potential environmentally friendly materials and have attracted significant attentions. (Cervini-Silva et al., 2000; Favre et al., 2006; Hofstetter et al., 2006; Jaisi et al., 2008; Peretyazhko et al., 2008; Bishop et al., 2011; Gorski et al., 2012a,b, 2013; Neumann et al., 2013).

The surfaces of smectites are usually grouped into basal surfaces and edge surfaces (Schoonheydt and Johnston, 2006). Basal surfaces are terminated with Si–O rings and their interfacial properties are normally pH-independent. On edge surfaces, the presence of amphoteric sites (e.g., SiOH, AlOH, FeOH and MgOH) leads to apparent pH-dependence. The effects of the Fe oxidation state on interfacial properties have attracted numerous studies, and it has been found that the oxidation/reduction of

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structural Fe significantly alters the properties of clays, such as hydration, swelling capability and catalytic activity (Stucki, 2006). However, most previous studies are based on macroscopic experiments, but the microscopic information is still scarce, for example, the identities of active edge sites and their hydration structures are unclear.

As is well known, acid-base chemistry is essential for the interfacial properties of minerals, e.g., surface charging, adsorption, catalysis and dissolution. At present, it is very hard to derive the pristine acidity of surface sites by using experimental techniques. With titration experiments, surface deprotonation constants can be derived by fitting proton adsorption curves with empirical models. However, the results are very sensitive to the assumed models, and the link between the assumed and real surface sites is unclear, e.g., (Bourg et al., 2007; Tourmassat et al., 2013). For ferruginous clays, proton transfer events may couple with electron transfer processes, which make their surface chemistry more complicated than non-Fe clays. To the best of our knowledge, there is still no experimental study on surface acidity of ferruginous clay minerals.

The first-principles molecular dynamics (FPMD) method is a powerful complement to experiment in interface chemistry because it treats the solvent effects explicitly and at the same quantum mechanical level as the solid surface. FPMD has been widely employed to investigate clay systems and proven to be an effective tool, e.g., (Tunega et al., 2002, 2004; Boek and Sprik, 2003; Churakov, 2007; Larentzos et al., 2007; Suter et al., 2008; Ockwig et al., 2009; Churakov and Kosakowski, 2010; Liu et al., 2010). We have investigated the structures of edge surfaces of kaolinite and montmorillonite using FPMD simulations (Liu et al., 2012a,b).

By integrating FPMD and the free energy perturbation technique, our group developed the FPMD-based vertical energy gap method for evaluating pK_a . This technique has been applied on mineral surfaces, e.g., rutile (Cheng and Sprik, 2010), quartz (Sulpizi et al., 2012) and pyrophyllite (Tazi et al., 2012). Extensive tests on molecules indicate an accuracy of 2 pK_a units (Sulpizi and Sprik, 2008; Cheng et al., 2009; Costanzo et al., 2011). The previous studies on molybdic acid (Liu et al., 2013a) and rutile (Cheng et al., 2012) show that the GGA (generalized gradient approximation) functionals generally give satisfactory estimates of acidity constants of transition metal systems. With this method, we have calculated the pK_a values of the edge sites of a 2:1 type dioctahedral clay minerals and revealed the effects of the most common substitutions (i.e., Al for Si in T-sheets and Mg for Al in O-sheets) on the surface pK_a (Liu et al., 2014). The results show that $\equiv\text{Al}(\text{OH})$ sites in T-sheets (i.e., Al-sub) and $\equiv\text{Mg}(\text{OH}_2)$ sites (i.e., Mg-sub) have extremely high pK_a values, and they always remain protonated in normal pH. It was also found that both substitutions increase the pK_a values of the apical O sites on (110) surfaces and that Mg substitution increases the pK_a 's of neighboring silanol sites.

In this study, to obtain a microscopic understanding of the effects of Fe oxidation state, we employ the FPMD technique to investigate the acid chemistry of ferruginous smectites by taking the (010)-type edge as the model

surface. The stable coordination states of edge Fe atoms have been determined by the constrained FPMD method. The FPMD-based vertical energy gap method is applied to evaluate the acidity constants of edge surface sites. We have made detailed comparisons between the oxidized and reduced states and revealed the effects of the Fe oxidation state. Based on the computed results, we further discussed the surface complexing mechanisms of ferruginous smectites.

2. METHODOLOGY

2.1. Systems

The chemical formula of the used nontronite model is $\text{Si}_8(\text{Fe}_3\text{Al}_1)\text{O}_{20}(\text{OH})_4$, which has a similar Fe content in octahedral sheets to NG-1 nontronite $\text{Na}_{0.70}(\text{Si}_{7.29}\text{Fe}_{0.63}^{3+}\text{Al}_{0.08})(\text{Fe}_{3.08}^{3+}\text{Fe}_{0.01}^{2+}\text{Al}_{0.88}\text{Mg}_{0.06})\text{O}_{20}(\text{OH})_4$ (Gates et al., 2002). The initial lattice parameter is taken from the experimental measurement: $a = 5.277 \text{ \AA}$, $b = 9.140 \text{ \AA}$, $c = 9.780 \text{ \AA}$, $\alpha = \beta = 90^\circ$ and $\gamma = 101^\circ$ (Manceau et al., 1998). Using cell optimization with a fixed box shape, the lattice is well reproduced: $a = 5.351 \text{ \AA}$, $b = 9.216 \text{ \AA}$, $c = 10.601 \text{ \AA}$. It has been shown that the overestimate of the c axis is due to the poor description of dispersion interaction by GGA functional (Tunega et al., 2012). For the reduced state, the predicted lattice is $a = 5.3790 \text{ \AA}$, $b = 9.265 \text{ \AA}$ and $c = 11.835 \text{ \AA}$, but there are no available experimental data. The calculated a and b lengths are used to build the models. For the c -axis, one can expect that the dispersion interaction does not influence the pK_a result, so the basal spacings are fixed at 9.78 \AA in all simulations.

The Fe-containing montmorillonite model has a chemical formula of $\text{Si}_8(\text{Al}_3\text{Fe}_{0.5})\text{O}_{20}(\text{OH})_4$. It is built by substituting one outermost Al with one Fe in the model we built in a previous work (Liu et al., 2012a).

The edge surface models are cut from the unit cell and repeated along the a axis. Therefore, each model contains two unit cells. Nontronite and montmorillonite edge models are denoted as Non and Mon, respectively. The chemical compositions of Non and Mon frameworks are $\text{Si}_{16}\text{Al}_6\text{Fe}_1\text{O}_{48}\text{H}_8$ and $\text{Si}_{16}\text{Fe}_6\text{Al}_2\text{O}_{48}\text{H}_8$, respectively. For the initial models, the dangling $\equiv\text{Si}-\text{O}$, $\equiv\text{Al}-\text{O}$ and $\equiv\text{Fe}-\text{O}$ bonds are all saturated by protons. The edge surface model is placed in a 3D periodically repeated cell, which has a solution space of approximately 12 \AA in the horizontal direction (Fig. 1). The solution region contains 36 water molecules, which approximately reproduce the density of bulk water at ambient conditions.

2.2. First principles molecular dynamics

All simulations were performed using the CP2K/QUICKSTEP package (VandeVondele et al., 2005a), which implements density functional theory with a hybrid Gaussian plane wave approach (Lippert et al., 1997). BLYP functional was used for the exchange–correlation (Becke, 1988; Lee et al., 1988). Goedecker–Teter–Hutter type pseudopotentials were employed to represent

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