DFT Study on the Adsorption of Monomeric Hydroxyl Aluminum on Fe(II)/Mg Replacement Kaolinite (001) Surfaces

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ABSTRACT: In the natural environment, Al and Si in the kaolinite crystal structure are likely to form lattice defects or be replaced by low-valence positive ions so that the base surfaces have permanent negatively charged sites. It is therefore very important to investigate the adsorption process and adsorption mechanism of adsorbates on the replaced surfaces. In this paper, two types of surface models formed by replacing Al atoms in the alumina octahedron of kaolinite (001) surface with Fe(II) and Mg were selected as the adsorption surfaces, these being the kaolinite Fe(II)Al-(001) and MgAl-(001) surfaces, respectively. Then, we used density functional theory (DFT) to simulate the adsorption of three monomeric hydroxy aluminum models (i.e., Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-)$ on the two replaced surfaces. Results show that, when compared to the adsorption on the ideal kaolinite (001) surface, the adsorption energies of the three adsorbates adsorbed on the replaced surfaces are lower and the adsorption is more stable. When the three adsorbates are adsorbed on the kaolinite Fe(II)Al-(001) surface, adsorption stability increases with the number of hydroxyl groups, and hydrogen bonding and electrostatic adsorption play a major role. Conversely, when they were adsorbed on the kaolinite MgAl-(001) surface, the stability of the adsorption deteriorated as the number of hydroxyl groups increased. Moreover, the decisive roles are the interaction between the aluminum atoms in the adsorbates and the oxygen atoms on the replaced surface and the electrostatic adsorption.

1. INTRODUCTION

Kaolinite is a clay mineral and its layered structure comprises a layer of −Al− (O, OH) octahedron and a layer of −Si−O tetrahedron. This layered structure is connected via hydrogen bonding. Consequently, when subjected to external forces, kaolinite is more likely to split in a direction parallel to the layer and break into two different types of surfaces with different properties, i.e., base surfaces and edge surfaces. So far, to reduce research challenges that are complex for this topic, theoretical$^{16-19}$ and experimental studies$^{10-15}$ need to be continued on the ideal kaolinite structure without any lattice defects. Yet, the structure of the actual kaolinite crystal in the natural surrounding is different from that of the ideal kaolinite crystal due to the replacement of the aluminum and silicon ions by the lower positive valence ions or the formation of defects, which also leads to changes in the electrical properties of the crystal surfaces.$^{16,17}$ As part of the scientific research process, we need to understand how the structures and characteristics differ between the ideal and actual kaolinite crystal.

When the kaolinite crystal is cleaved, the base surfaces are negatively charged due to lattice defects or isomorphic substitution. For example, Al in the aluminum−oxygen octahedron is replaced by Fe(III), Fe(II), and Mg (which are abbreviated as Fe(III)$_{Al}$, Fe(II)$_{Al}$, and Mg$_{Al}$, respectively), while Si in the silicon−oxygen tetrahedron is replaced by...
Fe(III) and Al. For the base surfaces, the charge properties are independent of the solution’s pH value, but they are related to the defects in the lattice and the substitution position of lower valence positive cations. In 1954, Schofield et al. placed pure kaolinite in a certain concentration of NaCl solution for shaking. The kaolinite washed with distilled water retained exchangeable Na, which indicated that the crystal was negatively charged. When the kaolinite crystals were placed in 0.5 M NaCl solution and resheaken, they would adsorb chloride, which confirmed that parts of the kaolinite crystal’s surfaces (presumably the edge surfaces) were positively charged. Malden et al. confirmed the substitution of aluminum by trivalent iron ions in the aluminum–oxygen octahedron of kaolinite in 1967. Mestdagh et al. and Balan et al. studied the relationship between kaolinite crystallinity and iron content and the substitution sites using electron paramagnetic resonance (EPR).

With the development of quantum chemistry calculations, scholars also began to analyze the lattice defects of the kaolinite crystal from the perspective of theoretical simulation. Chi et al. showed that the permanent negative charge generated by Al substitution of Si in the silicon–oxygen tetrahedral of kaolinite is not significant. In 2009, through the theoretical calculation with density functional theory (DFT), He et al. demonstrated that Fe in the natural environment could be easily substituted for Al atoms in aluminum oxide octahedron, and the substitution of Mg for Al also introduced a negative charge in the kaolinite crystal structure. Then, in 2012, the team further studied the adsorption and penetration of H2O on the kaolinite (001) surface with Mg, Ca, and Fe(II) doping through DFT theoretical calculations. Recently, Liu et al. calculated that the content order of differently coordinated Fe in kaolinite in a certain area and the degree of ease of substitution are six coordination Fe > four coordination Fe > Fe > six coordination Fe > six coordination Fe > six coordination Fe > six coordination Fe. During the replacement process, the resulting crystal charge transfer, and density of states. This research can also provide a theoretical basis for the development and design of aluminum-containing reagents and the optimization of the reagent system.

2. COMPUTATIONAL METHODS AND MODELS

2.1. Computational Methods. The construction of models and all simulation calculations were done using Materials Studio 2017 (Accelrys, Inc.). The optimization and property calculation of the adsorption models are mainly carried out using the CASTEP module based on DFT. With reference to the necessary parameters, the ultrasoft pseudopotential (USPP) was selected, and the energy cutoff for the plane waves was 460 eV. For the convergence tolerance scenario, we chose fine as the self-consistent iterative convergence accuracy. The corresponding relevant parameters were 1.0 × 10−5 eV/atom for total energy, 0.03 eV/Å for maximum atomic force, 0.05 GPa for maximum atomic stress, and 1 × 10−4 nm for maximum atomic displacement. The exchange-correlation function was set to GGA-PBE (abbreviation of Generalized Gradient Approximation with Perdew–Burke–Ernzerhof). For electronic structure calculations, the spin polarization method was used, with the spin parameter set to +4 for the Fe(II) atom. Furthermore, we chose TS (abbreviation for the Tkatchenko–Scheffler method) to correct the dispersion force in the optional parameters. The grid parameters about k-points of the kaolinite supercell models and the surface models were selected as (4 × 2 × 3) and (2 × 2 × 1), respectively. Meanwhile, Al(OH)4, Al(OH)3, and Al(OH)2 were optimized in a 15 Å × 15 Å × 15 Å cubic box and the k-point set was to γ. The other optimization parameters were the same as the kaolinite supercell models. When calculating the adsorption of adsorbate on the kaolinite replaced surfaces, the parameter settings were the same as those in the surface model, except that the k-point was set to γ. All simulation calculations were carried out in the reciprocal space, and the calculation of the pseudopotential of the atoms involved in the calculation selects the valence electrons as Al 3s3p1, Si 3s3p3, Fe 3d84s2, Mg 2p63s2, O 2s2p4, Na 2p63s1, and H 1s1.

2.2. Kaolinite Surface Models. In our work, the supercells of the calculation models were obtained by Fe(II) and Mg atoms replacing the Al atoms in the kaolinite (2 × 1 × 1) supercell models, which were called Fe(II)Al and MgAlK, respectively. During the replacement process, the resulting charge loss was compensated by adding a Na+ ion. To investigate the difficulty of replacing Al with Fe(II) and Mg atoms, we performed lattice substitution energy calculations on the two supercells after replacement, and the calculation formula is as follows:

\[ E_f = E_{\text{total \, impurity}}^{\text{total \, ideal}} - \mu_{\text{impurity}} \]

where \( E_{\text{total \, impurity}} \) is the total energy of kaolinite crystal after replacement, \( E_{\text{total \, ideal}} \) is the total energy of the ideal kaolinite crystal, and \( \mu_{\text{impurity}} \) and \( \mu_{\text{ideal}} \) are the chemical potentials of the replaced atom and impurity atom, respectively. The balance ion (Na+) is not considered here.

The surface models used in the calculations were cut from the Fe(II)Al-K and MgAl-K supercell models along the (001) direction, which were modeled by a slab made up of six atomic layers and with a vacuum thickness of 20 Å. The Fe(II) and Al(OH)2- and Mg and Al(OH)-terminated surfaces were called the kaolinite Fe(II)Al-(001) and MgAl-(001) surfaces and abbreviated as Fe(II)Al-K(001) and MgAl-K(001) surfaces in
the tables below, respectively. During the geometric optimization process, the upper four sublayers were relaxed, and the remaining sublayers at the bottom of the slab were fixed. The optimized parameters of the ideal kaolinite unit were close to the experimental test values with an error within 1.5%, and the calculation results of the parameters were \(a = 5.180 \text{ Å}, b = 8.971 \text{ Å}, c = 7.358 \text{ Å}, \alpha = 92.280^\circ, \beta = 105.593^\circ, \gamma = 90.054^\circ, \) and \(V = 329.063 \text{ Å}^3\).

2.3. Calculation of Adsorption Energy. The lower the adsorption energy, the more stable the adsorption of the corresponding adsorbate. The calculation formula of adsorption energy is written below

\[E_{\text{ads}} = E_{\text{total}} + E_{\text{surface}} - E_{\text{adsorbate}}\]

where \(E_{\text{total}}\) is the energy value of the adsorption configuration after the adsorbate is adsorbed on the replaced kaolinite surface, \(E_{\text{surface}}\) and \(E_{\text{adsorbate}}\) are the energy values of the surface model and adsorbate before adsorption, \(\text{kj/mol}\), respectively. The adsorption energy values of the optimal adsorption configurations for \(\text{Al(OH)}_2^+, \text{Al(OH)}_3^+,\) and \(\text{Al(OH)}_4^-\) on the ideal kaolinite (001), \(\text{Fe(II)}\text{Al}^-\text{(001)},\) and \(\text{MgAl}^-\text{(001)}\) surfaces are shown in Figure 2.

3. RESULTS AND DISCUSSION

3.1. Surface Properties and Adsorption Characteristics. 3.1.1. Unit Cell Characteristics. First, the CASTEP module was used to optimize the unit cells after lattice substitution, and the optimized unit cell parameters are shown in Table 1. Then, we calculated the lattice substitution energies of the unit cells replaced by Fe(II) and Mg atoms, which were 3.572 and 6.021 eV, respectively. Low lattice substitution energy corresponds to easy substitution. This shows that compared with the replacement of Al by Mg atom, Al is more easily replaced by Fe(II) atom.

3.1.2. Frontier Orbital. Up to now, the frontier orbital theory proposed by Fukui has been widely used in the fields of organic/inorganic chemistry, catalytic, quantum biology, and surface adsorption, which can better explain the reaction mechanism between molecules. Generally speaking, the interaction of two substances is more likely to occur between the highest occupied molecular orbital (HOMO) of one substance and the lowest occupied molecular orbital (LUMO) of another substance. Therefore, we can determine the possible initial adsorption sites according to the frontier orbital theory and the structural characteristics of the replaced surface models. The purpose of this is to reduce the number of

![Figure 1. LUMO distributions of the replaced surfaces models ((a, b) Fe(II)\text{Al}^-\text{(001)} surface and (c, d) Mg\text{Al}^-\text{(001)} surface). HOMO distributions of the adsorbates models ((e) Al(OH)$_2^+$, (f) Al(OH)$_3^+$, and (g) Al(OH)$_4^-$). The isovalue is 0.03 electrons/Å$^3$.](https://example.com/figure1)

![Figure 2. Adsorption energies of Al(OH)$_2^+$, Al(OH)$_3^+$, and Al(OH)$_4^-$ on the kaolinite (001) (Fang et al., 2020), Fe(II)\text{Al}^-\text{(001)},\) and \(\text{MgAl}^-\text{(001)}\) surfaces.](https://example.com/figure2)
When Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$ are adsorbed on the kaolinite Fe(II)$_{A(001)}$ and Mg$_{A(001)}$ surfaces, the adsorption energies are lower and the adsorptions are more stable than the adsorption on the ideal kaolinite (001) surface. The adsorption energies are $309.37$, $322.06$, and $312.04$ kJ/mol for Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$, respectively. When they are adsorbed on the kaolinite Mg$_{A(001)}$ surface, the adsorption energies are $300.72$, $335.52$, and $312.04$ kJ/mol for Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$, respectively. The adsorption energies are higher than those on the Fe(II)$_{A(001)}$ surface. The LUMO orbitals of the adsorbates interact with the LUMO orbitals of the replaced surfaces. Figure 1 shows the model structures of adsorbates and replaced surfaces and their corresponding diagrams of HOMO and LUMO orbitals. As shown in Figure 1a,b, the LUMO orbitals of the kaolinite Fe(II)$_{A(001)}$ surface are mainly distributed on the balance ion Na$^+$ and the Fe(II) atom, and the O$_{Sn}$ atoms of the surrounding hydroxyl groups. The LUMO orbitals of the kaolinite Mg$_{A(001)}$ surface are mainly distributed on the O$_{Sn}$ atoms of the hydroxyl group near the substitution atom Mg, and the balance ion Na$^+$ are shown in Figure 1c,d. According to Figure 1e–g, it is found that the HOMO orbitals of the three types of hydroxyl aluminum are mainly located on the end O atoms.

### Table 2. Bonding Analysis of Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$ on the Kaolinite Fe(II)$_{A(001)}$ and Mg$_{A(001)}$ Surfaces

| name | bond | population | length (Å) |
|------|------|------------|------------|
| Al(OH)$_2^+$ on Fe(II)$_{A(001)}$ surface | O$_2$–H$_{S1}$ | 0.02 | 2.3779 |
| | O$_2$–H$_{S2}$ | 0.08 | 1.8498 |
| Al(OH)$_3^-$ on Fe(II)$_{A(001)}$ surface | O$_3$–H$_{S1}$ | 0.03 | 2.5664 |
| | O$_3$–H$_{S2}$ | 0.06 | 1.9916 |
| | O$_3$–H$_{S3}$ | 0.09 | 1.7939 |
| Al(OH)$_4^-$ on Fe(II)$_{A(001)}$ surface | O$_4$–H$_{S1}$ | 0.01 | 2.3546 |
| | O$_4$–H$_{S2}$ | 0.05 | 1.7760 |
| | O$_4$–H$_{S3}$ | 0.03 | 2.2376 |
| | O$_4$–H$_{S4}$ | 0.06 | 2.0287 |
| | O$_4$–H$_{S5}$ | 0.07 | 1.9185 |
| Al(OH)$_2^+$ on Mg$_{A(001)}$ surface | O$_2$–H$_{S1}$ | 0.00 | 2.2469 |
| | O$_2$–H$_{S2}$ | 0.07 | 1.8018 |
| Al(OH)$_3^-$ on Mg$_{A(001)}$ surface | O$_3$–H$_{S1}$ | 0.06 | 1.9988 |
| | O$_3$–H$_{S2}$ | 0.09 | 1.7327 |
| Al(OH)$_4^-$ on Mg$_{A(001)}$ surface | O$_4$–H$_{S1}$ | 0.06 | 1.9044 |
| | O$_4$–H$_{S2}$ | 0.04 | 2.1818 |
| | O$_4$–H$_{S3}$ | 0.08 | 1.8820 |
| | O$_4$–H$_{S4}$ | 0.07 | 1.9447 |
| | O$_4$–H$_{S5}$ | 0.00 | 2.1555 |

Theoretical simulation calculations and to find the optimal adsorption sites more efficiently.

When Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$ are adsorbed on the kaolinite Fe(II)$_{A(001)}$ and Mg$_{A(001)}$ surfaces, the adsorption energies are $309.37$, $322.06$, and $312.04$ kJ/mol for Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$, respectively. When they are adsorbed on the kaolinite Mg$_{A(001)}$ surface, the adsorption energies are $300.72$, $335.52$, and $312.04$ kJ/mol for Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$, respectively. The adsorption energies are higher than those on the Fe(II)$_{A(001)}$ surface. The LUMO orbitals of the adsorbates interact with the LUMO orbitals of the replaced surfaces. Figure 1 shows the model structures of adsorbates and replaced surfaces and their corresponding diagrams of HOMO and LUMO orbitals. As shown in Figure 1a,b, the LUMO orbitals of the kaolinite Fe(II)$_{A(001)}$ surface are mainly distributed on the balance ion Na$^+$ and the Fe(II) atom, and the O$_{Sn}$ atoms of the surrounding hydroxyl groups. The LUMO orbitals of the kaolinite Mg$_{A(001)}$ surface are mainly distributed on the O$_{Sn}$ atoms of the hydroxyl group near the substitution atom Mg, and the balance ion Na$^+$ are shown in Figure 1c,d. According to Figure 1e–g, it is found that the HOMO orbitals of the three types of hydroxyl aluminum are mainly located on the end O atoms.

### 3.1.3. Adsorption Energy

As can be seen from Figure 2, unlike the adsorption on the ideal kaolinite (001) surface, the monomer-hydrolyzed components of aluminum salt have different adsorption stabilities on the kaolinite (001) surface when replaced by Fe(II) and Mg. The adsorption energies of the adsorbates on the kaolinite Fe(II)$_{A(001)}$ surface are $−309.37$, $−321.04$, and $−489.44$ kJ/mol, while the corresponding adsorption stability order is Al(OH)$_4^-$ > Al(OH)$_3^-$ > Al(OH)$_2^+$. When they are adsorbed on the kaolinite Mg$_{A(001)}$ (001) surface, the adsorption energies are $−335.52$, $−300.72$, and $−222.06$ kJ/mol, and the order of adsorption stability is Al(OH)$_2^+$ > Al(OH)$_3^-$ > Al(OH)$_4^-$. It is exactly the opposite in the case of the former. The results show that when the three monomer-hydrolyzed components adsorbed on the kaolinite (001) surfaces are replaced by Fe(II) and Mg, the adsorption energies are lower and the adsorptions are more stable than

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**Figure 3.** Stable adsorption configurations of Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$ on the kaolinite Fe(II)$_{A(001)}$ surface.

**Figure 4.** Stable adsorption configurations of Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$ on the kaolinite Mg$_{A(001)}$ surface.

**Figure 5.** Differences in the electron densities of Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$ adsorbed on the kaolinite Fe(II)$_{A(001)}$ surface. The isovalue is 0.01 electrons/Å$^3$. 

**Table 2.** Bonding Analysis of Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$ on the Kaolinite Fe(II)$_{A(001)}$ and Mg$_{A(001)}$ Surfaces

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that on the ideal kaolinite (001) surface. When the adsorbates are adsorbed on the kaolinite Fe(II)$_{4+}$K(001) surface, the adsorption energy decreases when the number of hydroxyl groups increases. In other words, the stability of adsorption increases with the increasing number of hydroxyl groups. In contrast, when they are adsorbed on the kaolinite Mg$_{4+}$K(001) surface, the stability of the adsorption is weakened as the number of hydroxyl groups is increased.

### 3.2. Analysis of Adsorption Configuration and Bonding

**Figures 3 and 4** show the stable adsorption configurations of Al(OH)$_2^+$, Al(OH)$_3^-$, and Al(OH)$_4^-$ adsorbed on the kaolinite Fe(II)$_{4+}$K(001) and Mg$_{4+}$K(001) surfaces, respectively. The Mulliken bond population and the length of the bonded atoms between the adsorbates and the replaced kaolinite surfaces are shown in **Table 2**. In the figures and tables below, O$_n$ and H$_m$ represent the oxygen atoms and hydrogen atoms, which form a hydrogen bond between the adsorbate and the replaced surface, respectively.

As shown in **Figure 3**, when Al(OH)$_2^+$ is adsorbed on the kaolinite Fe(II)$_{4+}$K(001) surface, two hydrogen bonds are formed between the O$_n$ and the replaced surface H$_m$ atoms. The maximum population value is 0.08 and the hydrogen bond strength is strong (**Figure 3a**). When Al(OH)$_3^-$ is adsorbed, three hydrogen bonds are formed, and the distribution of population value is uniform, with a maximum of 0.09 (**Figure 3b**). Six hydrogen bonds are formed after the adsorption of Al(OH)$_4^-$, and the maximum population value is 0.07 (**Figure 3c**). From the point of view of stable adsorption configurations, all three adsorbates are easy to adsorb above the oxygen atoms in the hydroxyl group parallel to the replaced surface. However, when adsorbed on the oxygen atom near Fe(II) replacement, the adsorption energy is lower and the adsorption is more stable. After adsorption occurs, the oxygen atoms in the three adsorbates form a variety of hydrogen bonds with the hydrogen atoms on the replaced surface, and these hydrogen bonds retain noticeable strength.

**As can be seen from Figure 4**, when Al(OH)$_3^-$ is adsorbed on the kaolinite Mg$_{4+}$K(001) surface, two hydrogen bonds are formed, with the population values of 0 and 0.07 (**Figure 4a**). When Al(OH)$_3^-$ is adsorbed, two hydrogen bonds are formed, with the bond population values of 0.06 and 0.09, confirming the strength of the hydrogen bonds (**Figure 4b**). Five hydrogen bonds are formed after the adsorption of Al(OH)$_4^-$, with the maximum population value of 0.08 (**Figure 4c**). The number of hydrogen bonds formed is the highest, and these hydrogen bonds are strong when Al(OH)$_4^-$ is adsorbed; however, the
adsorption energy is the highest ($E_{\text{ads}} = -222.06$ kJ/mol), indicating that the adsorption is relatively unstable. The number of hydrogen bonds formed by the adsorption of Al(OH)$_3^+$ on the kaolinite Mg$_{Al^-}(001)$ surface is small and with poor strength; however, it has the lowest adsorption energy ($E_{\text{ads}} = -335.52$ kJ/mol) and the most stable adsorption. This shows that during the adsorption process, in addition to hydrogen bonding, there are other nonhydrogen bonding effects for the first two types of adsorption.

### 3.3. Charge Analysis

To expose the nonhydrogen bond effects between the adsorbates and the replaced surface that were analyzed in the previous section and to observe the charge transfer between the adsorbates and the replaced surface, we conducted an electron density difference analysis of the optimal adsorption configurations (Figures 5 and 6). In these figures, blue and yellow areas indicate an increase and decrease in electron density, respectively. Tables 3 and 4 show the bonded atoms' population and charge of Al(OH)$_3^+$, Al(OH)$_4^+$, and Al(OH)$_4^-$ before and after adsorption on the replaced kaolinite surfaces and the changes in the charge of the adsorbates and the replaced surfaces.

According to Tables 3 and 4, the hydrogen atoms participating in the bond formation exhibit electron loss, while the oxygen atoms acquire electrons. As shown in Figures 5 and 6, the electron density around oxygen atoms in the adsorbates involved in bonding increases, and the electron density around hydrogen atoms decreases on the replaced surfaces. These findings correspond to the results documented in the tables.

As shown in Table 3, when Al(OH)$_3^+$ and Al(OH)$_4^+$ are adsorbed on the kaolinite surface, a large amount of electron transfer occurs between the aluminum atoms in the adsorbates and the oxygen atoms on the replaced surface. However, this charge transfer is not obvious after the adsorption of the Al(OH)$_4^-$ ion. These will be analyzed by the density of states in Section 3.4.

### 3.4. Partial Density of States (PDOS)

To further explore the interaction between Al atoms in the adsorbates and O atoms on the surfaces when Al(OH)$_3^+$ and Al(OH)$_4^-$ are adsorbed on the replaced kaolinite surfaces, we analyzed the change in the partial density of states (PDOS) before and after the adsorption of the two types of atoms (Figures 7 and 8). The Fermi level ($E_F$) value was set at 0 eV. Figure 7 shows the change in the PDOS before and after the three adsorbates were adsorbed on the kaolinite surface.

As shown in Table 3, when Al(OH)$_3^+$, Al(OH)$_4^+$, and Al(OH)$_4^-$ adsorbed on the kaolinite Fe(II)$_{Al^-}(001)$ surface, the adsorbed Al(OH)$_3^+$ is adsorbed, the bonding of Al 3p and O 2p is in the $-10.3$ to $-2.5$ eV range, and the antibonding is in the $1.5$–$14.0$ eV range (Figure 7a). When Al(OH)$_4^+$ is adsorbed, the bonding of Al 3p and O 2p occurs in the $-11.2$ to $-3.5$ eV range, and the antibonding is in the $1.3$–$13.3$ eV range (Figure 7b). After the adsorption of Al(OH)$_4^-$, the bonding of Al 3p and O 2p is in the $-9.5$ to $-1.3$ eV range.
and the antibonding is in the 3.5−15.5 eV range. The bonding effect is stronger than the antibonding effect.

As shown in Figure 8, what is significant is the change in the PDOS before and after the three adsorbates were adsorbed on the kaolinite MgAl-(001) surface. When Al(OH)$_2^+$ is adsorbed, Al 3p in the adsorbate has a bonding effect with the replaced surface O$_{S1}$ 2p and O$_{S2}$ 2p in the −11.5 to −4.0 eV range, while the antibonding is in the 0.7−13.0 eV range. After the adsorption of Al(OH)$_3^-$, the bonding of Al 3p and O$_S$ 2p occurs in the −7.5 to 0 eV range, and the antibonding is in the 5.0−16.8 eV range. When Al(OH)$_4^-$ is adsorbed, the bonding of Al 3p and O$_S$ 2p is in the −7.5 eV to 0 eV range, and the antibonding is in the 5.0−17.0 eV range. Compared with the antibonding effect, the bonding effect is stronger.

Combined with the PDOS diagrams, it can be observed that all of the densities of states move to a lower energy level as a whole, and the density of states near the Fermi level declined after the Al−O$_S$ atom interaction, indicating that the surface energy decreases after adsorption. In addition, the bonds between Al and O$_S$ atoms are strong, which means that there is a strong interaction between the aluminum atoms in the adsorbates and the oxygen atoms on the replaced surfaces, and this effect yields a decisive influence on the adsorption results. When Al(OH)$_2^+$ is adsorbed on the kaolinite MgAl-(001) surface, the bonding between the Al atom and the two O$_S$ atoms is very strong. Therefore, when Al(OH)$_2^+$ is adsorbed on the kaolinite MgAl-(001) surface, the adsorption energy is the lowest ($E_{ads} = -335.52$ kJ/mol) and the adsorption is the most stable.
4. CONCLUSIONS

(1) Compared with the replacement of Al by Mg atom, Al is more easily replaced by Fe(II) atom in the kaolinite crystals. When Al(OH)$_3$$^+$, Al(OH)$_3$$^−$ and Al(OH)$_2$$^−$ are adsorbed on the replaced kaolinite (001) surfaces, the adsorption energies are lower and the adsorption is more stable than adsorption on the ideal kaolinite (001) surface. The optimal adsorption sites are all above the oxygen atoms in the hydroxyl groups, which are parallel to the replaced surfaces and adjacent to the replacement sites.

(2) When the three adsorbates are adsorbed on the kaolinite Fe(II)$_{Al}$(001) surface, the adsorption stability increases with the number of hydroxyl groups. In contrast, the stability of the adsorption weakened as the number of hydroxyl groups increased when they are adsorbed on the kaolinite Mg$_{Al}$(001) surface.

(3) For the adsorption of three adsorbates on the kaolinite Fe(II)$_{Al}$(001) surface, hydrogen bonding and electrostatic adsorption play a major role. However, when they are adsorbed on the kaolinite Mg$_{Al}$(001) surface, the decisive roles are the interaction between the aluminum atoms in the adsorbates and the oxygen atoms on the replaced surface and the electrostatic adsorption between the two.

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