

A first-principle study of the effect of Fe/Al impurity defects on the surface wettability of dolomite

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Abstract: The presence of Fe and Al atoms in large quantities in phosphate ores can significantly affect the surface properties of the minerals during flotation. In this study, the effects of Fe/Al impurities on the adsorption of H₂O molecules on dolomite, including the density of states (DOS), Mulliken bond group values, and charge groups, were investigated and the adsorption energy was analyzed using density functional theory. The results show that the adsorption of H₂O molecules on perfect and Fe/Al-substituted dolomites is weak chemisorption, and the Fe and Al impurities weaken and enhance the adsorption capacity of H₂O molecules, respectively. Therefore, the hydrophilicity of the dolomite surface increases in the following order: Fe-substituted dolomite < perfect dolomite < Al-substituted dolomite. The Mulliken charge and bond group analysis shows that the adsorption of H₂O molecules on dolomite is primarily through the interaction between O_w and Ca atoms, where the d orbitals of Ca atoms provide charges for O_w atoms to form ionic bonds, which related to the poor electronegativity of Ca atoms and their weak valence electron binding ability. The DOS analysis shows that, during the adsorption of H₂O molecules on dolomite, Mg and Al atoms have less influence on the dolomite surface, whereas Fe and Ca atoms undergo competitive adsorption, which inhibits the interaction between Ca atoms and H₂O molecules on the dolomite surface.

Keywords: density functional theory, phosphate rock flotation, dolomite, surface wettability, density of states

1. Introduction

Phosphate ore is an essential mineral resource; in China's phosphate ore resource reserves, the low grade phosphate ore reserves of >85% needs to be enriched via flotation before use. Apatite and dolomite are the target mineral and main associated vein mineral of phosphate ore, respectively. These minerals belong to the same microsoluble calcium salt minerals because they contain the same cation, Ca²⁺; thus, they exhibit similar physical and chemical properties, thereby making their separation process difficult.

Flotation is based on the differences in physicochemical properties of mineral surfaces, and the mineral structure determines the mineral surface properties (Liu et al., 2018). Phosphate ore is rich in Fe and Al atoms, which largely impact the surface properties of the target mineral apatite and vein mineral dolomite during phosphate ore flotation, causing differences in the surface wettability of the two minerals and thus affecting phosphate ore flotation. Fe and Al atoms are partly present on the dolomite surface, and the other part will enter the dolomite lattice through homogeneity and lattice substitution, which will cause impurity defects in the dolomite crystal structure. The influence of metal atoms present on the dolomite surface on its surface properties has been studied extensively by numerous authors using the zeta potential analysis, surface morphology analysis, energy spectroscopy, and determination of adsorption (Chen et al., 2022; Huang et al., 2021; Ruan et al., 2018; Wang et al., 2019). However, the influence of impurity defects on the surface properties of dolomite due to the presence of metal atoms inside the dolomite lattice is difficult to study by experimental means.

Recently, molecular simulations have been rapidly developed and widely applied to studies related to mineral surface properties, and the effects of lattice defects on crystal structure and surface properties

can be studied at the atomic level; particularly, the interaction between H₂O molecules and various mineral surfaces has been studied extensively (Lardge et al., 2009; Gao et al., 2012; Zhao et al., 2014; Long et al., 2016). Lardge et al. investigated the adsorption mechanism of H₂O molecules with a calcite (104) surface using a combination of density functional theory (DFT) and ab initio algorithm simulations to reveal the adsorption characteristics of H₂O molecules onto calcite surfaces at different coverages (Lardge et al., 2009). Gao et al. employed DFT to model the structural and electronic properties of the adsorption of Si-terminated, O-intermediate, and O-rich termini on the (001) surface of quartz with H₂O molecules (Gao et al., 2012). Zhao et al. used DFT to study the adsorption of H₂O molecules on sulfide minerals and the changes in their surface wettability (Zhao et al., 2014). When mineral surfaces containing different impurities contact H₂O molecules, the adsorption and dissociation processes of H₂O can change the mineral surface structure, and changes in a mineral's structure and composition can affect its reactivity. Therefore, mineral surfaces with different impurities can exhibit different properties (Lan et al., 2016).

In this study, the effect of different microscopic defects on the surface wettability of dolomite is investigated by introducing Fe and Al to create impurity defects in the dolomite lattice based on the plane wave (PW) super soft pseudopotential method of the first nature principle of density generalized theory, and the influence of Fe and Al atoms on the surface properties of dolomite is discussed theoretically.

2. Computational method and model

2.1. Computational method

Calculations have been done using Cambridge Serial Total Energy Package (CASTEP), which is a first-principle pseudopotential method based on density-functional theory (DFT) (Wang et al., 2014). DFT calculations employ plane wave (PW) basis sets and ultrasoft pseudopotentials. The exchange correlation functional used is the generalized gradient approximation (GGA) developed by Perdew-Wang generalized-gradient approximation (PW91) (Chen et al., 2014). The kinetic energy cutoff (400eV) of the plane wave basis is used throughout and the Brillouin zone is sampled by MONKHORST and PACK special k-point of a 3×3×3 grid for all structure calculations, which shows that the cutoff energy and the K-points meshes are sufficient for the system. The convergence tolerances for geometry optimization calculations are set to the maximum displacement of 0.005 Å, the maximum force of 0.05 eV·Å⁻¹, the maximum energy change of 5.0×10⁻⁶ eV·atom⁻¹ and the maximum stress of 0.02 Gpa, and the SCF convergence tolerance is set to be 5.0×10⁻⁷ eV·atom⁻¹. The valence electron configurations considered in the work are H 1s, C 2s²2p², O 2s²2p⁴, Mg 2p⁶3s², Al 3s²3p¹, Ca 3p⁶4s², Fe 3d⁶4s². Before adsorption, the H₂O is placed inside a 10Å×10Å×10Å cubic cell for optimization calculation. In addition, a vacuum thickness of 10 Å is placed between the surface slabs.

2.2. Computational model

The chemical formula of dolomite is CaCO₃·MgCO₃ or CaMg(CO₃)₂. It is a trigonal crystal system with space group $C_{3i}^2 - R\bar{3}$, which comprises prismatic cells and hexagonal cells. The hexagonal cells are hexagonal lattices with double body centers, which are cubic and closely packed, and the solution surface is (104). Ca and Mg in the dolomite crystal structure are arranged alternately along three axes, forming a cation-ordered superstructure. Unlike calcite, with space group R-3c in the tripartite crystal system, dolomite lacks a c-slip surface. The dolomite cell model used for the calculations was obtained from the American Mineralogist Crystal Structure Database. By testing the number of atomic layers and the vacuum layer thickness, the surface energy of (104) dolomite was taken to be the most stable when the surface was treated as five layers and the vacuum layer thickness was taken to be 18 Å. The side and top views of the (2×1×1) ideal dolomite (104) surface are shown in Fig. 1. The molecular formula is Ca₁₀C₁₀O₂₉·Mg₁₀C₁₀O₂₉ when the 2×1×1 supercell model is used, and the Fe and Al impurities in nature mainly replace the Mg atoms on the dolomite surface through analogous homogeneity, which is due to similarity of the atomic radii of Al (1.43 Å) and Fe (1.27 Å) to the atomic radius of Mg (1.60 Å), which is much smaller than that of calcium (1.97 Å). The dolomite cell parameters before and after substitution are basically the same, so either Fe or Al atom is substituted for one Mg atom to construct a dolomite (104) surface model with different defect types (see Fig. 2).

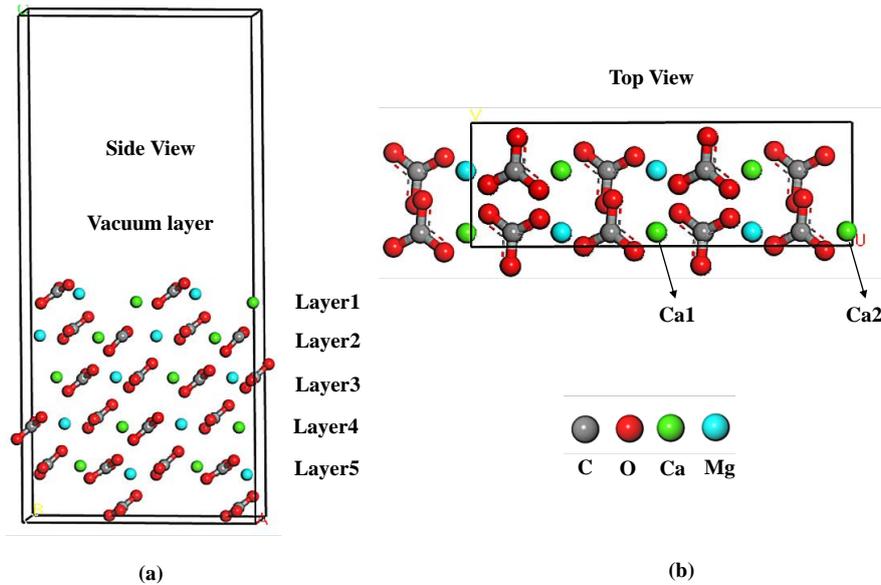


Fig. 1. The slab model of a (2×1×1) dolomite (104) surface: (a) Side view; (b) Top view

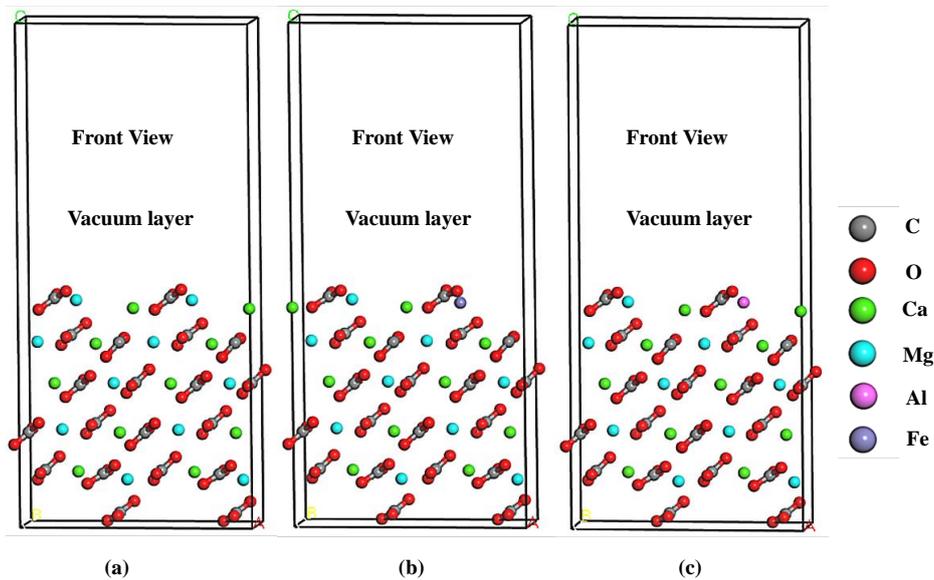


Fig. 2. The slab of various (2×1×1) dolomite surface: (a) Perfect dolomite; (b) Fe-substituted dolomite; (c) Al-substituted dolomite

2.3. Calculation of adsorption energy and heat

The adsorption process is accompanied by an energy transformation because molecules in the adsorption process slow down and eventually stop on the surface of the adsorption medium. This reduction in speed is released as part of the total adsorption energy, which indicates the stability of H₂O molecules on the (104) surface of dolomite. The adsorption energy of the H₂O molecules on dolomite can be calculated as follows:

$$E_{\text{ads}} = E_{X/\text{surface}} - E_X - E_{\text{surface}} \quad (1)$$

where E_{ads} is the adsorption energy of H₂O molecules on dolomite after adsorption, E_X is the energy of a single H₂O molecule, $E_{X/\text{surface}}$ is the energy of the entire system after adsorption, and E_{surface} is the energy of the dolomite surface. Lower adsorption energy indicates higher adsorption stability, vice versa. The adsorption process is accompanied by an energy transformation because molecules in the adsorption process slow down and eventually stop on the surface of the adsorption medium. This

reduction in speed is released as part of the total adsorption energy, which indicates the stability of H₂O molecules on the (104) surface of dolomite. The adsorption energy of the H₂O molecules on dolomite can be calculated as follows:

3. Results and discussion

3.1. Adsorption model of H₂O molecules on dolomite surface

In the flotation process, H atoms in H₂O molecules tend to form H bonds with O atoms on the dolomite surface, whereas O atoms in H₂O (O_w atoms) tend to form Ca–O_w chemical bonds with Ca atoms (Luo et al., 2020). Fig. 1 shows the top view of the (2×1×1) perfect dolomite (104) surface, wherein Ca1 and Ca2 on the dolomite surface are in the same environment and H₂O molecules are initially oriented parallel or perpendicular to the substrate. Fig. 3 shows the most stable adsorption configuration of H₂O molecules on the dolomite (104) surface. From Fig. 3, the O_w end always faces downward to form a chemical bond with Ca (Ca–O_w) on the dolomite surface, indicating that the system has the strongest adsorption tendency when the O_w end is oriented downward.

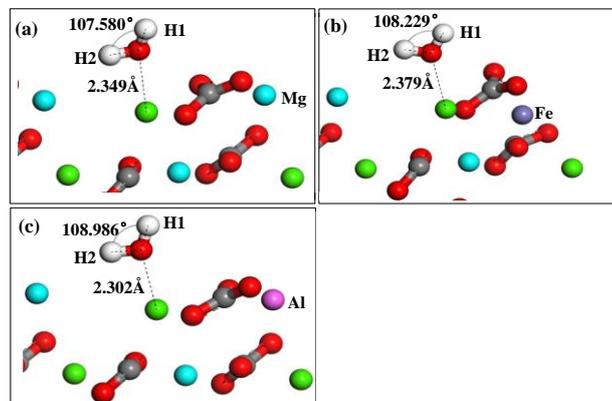


Fig. 3. Adsorption models of H₂O molecule on various (2×1×1) dolomite surface: (a) Perfect dolomite; (b) Fe-substituted dolomite; (c) Al-substituted dolomite

3.2. Effect of Fe/Al impurities on the adsorption of H₂O molecules on the surface of dolomite

Table 1 shows the distances between the O_w atoms of H₂O molecules and the Ca atoms on the dolomite surface after adsorption. The adsorption distance d_{ads} (2.349 Å) of Ca–O_w after the adsorption of H₂O molecules is smaller than the sum of the radii of Ca–O_w atoms of perfect dolomite d_0 (2.630 Å); the distance between the O_w of H₂O molecules and Ca atoms on the dolomite surface is significantly reduced (–0.281 Å), indicating that the interaction between H₂O molecules and dolomite surface is strong. The dolomite doping with Al atoms significantly decreased the Δd value (–0.328 Å) and enhanced bonding strength, indicating that Al atoms make the surface more hydrophilic than Fe atoms. Meanwhile, the Δd value (–0.251 Å) is slightly larger than that of the perfect dolomite (–0.281 Å) when Fe atoms are doped, and the interaction between H₂O molecules and Ca atoms on the dolomite surface is weakened, indicating that Fe atoms increase the repulsive force of H₂O on Ca atoms on the dolomite surface and enhance hydrophobicity.

To ensure the strength of interaction between the H₂O molecules and dolomite surface, the changes in H–O_w–H bond angle and H–O_w bond length of H₂O molecules before and after adsorption on dolomite were calculated; the results are shown in Table 2. The changes in H–O_w–H bond angle and H–O_w bond length of H₂O adsorbed on Al-substituted dolomite were large, and the bond angle and bond length increased from 104.200° and 0.977 Å to 108.986° and 1.011 Å, respectively, whereas the H–O_w bond length and H–O_w–H bond angle of H₂O adsorbed on Fe-substituted dolomite varied slightly, with the bond angle and bond length increasing from 104.200° and 0.977 Å to 108.229° and 0.987 Å, respectively. These results confirm the strong interaction of H₂O with the Al-substituted dolomite surface and the weak interaction of H₂O with the Fe-substituted dolomite surface.

Table 1. Variation of the distance between O_w atoms and Ca atoms on the dolomite surface after adsorption of H_2O molecules on the dolomite surface

Defect type	Adsorption site	$d_0=(r_0+r_1)/\text{\AA}$	$d_{ads}/\text{\AA}$	$\Delta d=(d_{ads}-d_0)/\text{\AA}$
Perfect	Ca	2.630	2.349	-0.281
Al	Ca	2.630	2.302	-0.328
Fe	Ca	2.630	2.379	-0.251

r_0 is the atomic radius of O_w in H_2O ; r_1 is the radius of Ca atoms on the surface of dolomite; d_{ads} is the distance between O_w atom of H_2O and Ca atom on the surface of dolomite after adsorption

Table 2. Variations of H- O_w -H angle and H- O_w bond length of H_2O molecule on dolomite surfaces before and after adsorption

Defect type	Before adsorption		After adsorption	
	H- O_w -H angle/(°)	H- O_w bond length/ \AA	H- O_w -H angle/(°)	H- O_w bond length/ \AA
Perfect	104.200	0.977	107.580	1.015
Al	104.200	0.977	108.986	1.011
Fe	104.200	0.977	108.229	0.987

Table 3 shows the adsorption energies of H_2O molecules on perfect dolomite and Fe/Al-substituted dolomite. In general, it is physical adsorption when the adsorption energy is $-51.61 \text{ kJ/mol} < E_{ads} < 0 \text{ kJ/mol}$ and chemisorption when the adsorption energy is $-946.12 \text{ kJ/mol} < E_{ads} < -51.61 \text{ kJ/mol}$. The adsorption energies of H_2O molecules on the surfaces of perfect dolomite, Al-substituted, and Fe-substituted dolomites are -87.50 , -94.23 , and -78.65 kJ/mol , respectively, indicating that the respective adsorption mode is weak chemisorption. The Fe impurity defect increases the adsorption energy of H_2O molecules on dolomite compared with the perfect dolomite, whereas the Al impurity defect decreases it. In other words, H_2O molecules prefer reacting with Al-substituted dolomite to reacting with Fe-substituted dolomite.

Interactions occur between H_2O molecules, which also affect their adsorption on minerals. When the cohesive energy between H_2O molecules is greater than the adsorption energy of H_2O molecules on the mineral surface ($\Delta E < 0$), the mineral surface are easily wetted by the H_2O molecules and the mineral surface is hydrophilic; when that energy is less than the adsorption energy of H_2O molecules on the mineral ($\Delta E > 0$), the mineral surface are not easily wetted by the H_2O molecules and the mineral surface is hydrophobic. From Table 3, the adsorption energy of H_2O molecules on the perfect dolomite and Fe/Al-substituted dolomite is greater than the cohesion energy between H_2O molecules ($\Delta E = E_{H_2O-surface} - E_{H_2O-H_2O} < 0$), indicating that, in these cases, H_2O molecules are more inclined to become adsorbed on the dolomite. Thus, to a certain extent, Fe atoms enhance the hydrophobicity of H_2O molecules on the dolomite surface.

3.3. Influence of Fe and Al impurities on dolomite surface density of States before and after adsorption of H_2O molecule

The ability of mineral to adsorb H_2O depends on its surface electronic structure, and the presence of lattice defects changes the electronic structure of the atoms around the impurity (Chen et al., 2014). Mulliken was used to obtain the charge distribution of each atomic orbital by equally distributing the charge of the overlapping region to the relevant electron orbitals and comparing the relative sizes of the Mulliken charged atoms under the same basis group condition. Tables 4–6 show the Mulliken charge population of O_w , H atoms, and other dolomite surface atoms. After H_2O molecules adsorption, the 2p orbital of O_w became a charge acceptor and lost some electrons, the 3d orbital of Ca obtained some electrons, and charges were transferred from the Ca 3d orbital to the O 2p orbital, which coincides with the poor electronegativity and weak valence electron binding ability of Ca atoms. The H2 atoms gained electrons for chemisorption, and the H1 atoms hardly underwent electron transfer, thus, physisorption dominated. In addition, the s orbital of Mg, the 3d orbital of Fe, and the p orbital of Al obtained some

electrons. Therefore, the reaction between the H₂O molecules and dolomite surface mainly comprises O_w atom's 2p orbitals and Ca atom's 3d orbitals the adsorption reaction, and charges are transferred from the Ca atom's 3d orbitals to the O_w atom's 2p orbitals. Therefore, the formed Ca-O_w chemical bond is the main reason for the adsorption of H₂O molecules on the surface of dolomite (104).

The Ca atoms on the dolomite surface are electron donors, and the charge increases with the loss of electrons. The charge of Ca atoms on the surface of perfect dolomite (+0.13 unit charge) and Al-substituted dolomite (+0.12 unit charge) changes more than that of Fe-substituted dolomite (+0.05 unit charge). Compared with the perfect dolomite, the Al atoms did not significantly influence the adsorption of H₂O on dolomite, whereas Fe atoms decrease the adsorption of H₂O on dolomite significantly.

Table 3. Adsorption energies of H₂O molecules on the perfect dolomite and Fe/Al-substituted dolomite surfaces (Negative sign represents exothermic reaction)

Defect type	Adsorption Energy/(kJ·mol ⁻¹)		
	E _{H₂O-surface}	E _{H₂O-H₂O}	ΔE = E _{H₂O-surface} - E _{H₂O-H₂O}
Perfect	-87.50	-22.11	-65.39
Al	-94.23	-22.11	-72.12
Fe	-78.65	-22.11	-56.54

E_{H₂O-surface} is the adsorption energy of water molecules on the surface of dolomite; E_{H₂O-H₂O} is the cohesive energy between water molecules.

Table 4. Mulliken charge population of O_w, H atoms of H₂O molecule and perfect dolomite surface atoms

Atomic label	Adsorption model	s	p	d	Total	Charge/e
H1/H2	Before adsorption	0.47/0.48	0.00	0.00	0.47/0.48	0.53/0.52
	After adsorption	0.48/0.56	0.00	0.00	0.48/0.56	0.52/0.44
O _w	Before adsorption	1.89	5.16	0.00	7.05	-1.05
	After adsorption	1.86	5.11	0.00	6.97	-0.97
Ca	Before adsorption	2.37	6.00	0.50	8.87	1.13
	After adsorption	2.22	6.00	0.52	8.74	1.26
Mg	Before adsorption	0.69	6.48	0.00	7.17	0.83
	After adsorption	0.79	6.57	0.00	7.36	0.64

Table 5. Mulliken charge population of O_w, H atoms of H₂O molecule and Fe-substituted dolomite surface atoms

Atomic label	Adsorption model	s	p	d	Total	Charge/e
H1/H2	Before adsorption	0.47/0.48	0.00	0.00	0.47/0.48	0.53/0.52
	After adsorption	0.47/0.55	0.00	0.00	0.47/0.55	0.53/0.45
O _w	Before adsorption	1.89	5.16	0.00	7.05	-1.05
	After adsorption	1.86	5.11	0.00	6.97	-0.97
Ca	Before adsorption	2.36	6.00	0.50	8.87	1.13
	After adsorption	2.22	6.00	0.60	8.82	1.18
Fe	Before adsorption	0.39	0.29	6.81	7.50	0.50
	After adsorption	0.34	0.16	6.86	7.37	0.63

DOS is an essential parameter for describing the state of electron motion in solid-state physics (Wang et al., 2018; Chen et al., 2013). Typically, for solids, the most important electronic transition processes occur near the Fermi energy level. Thus, we made the effect of water molecule adsorption on the electronic density of the states near the Fermi energy level. Therefore, we focused on the effect of water molecule adsorption on the electronic density of the states near the Fermi energy level (Qiu et al., 2017). Figs. 4–6 show the DOS of perfect and Fe/Al-substituted dolomite (104) surfaces before and after H₂O molecule adsorption. The H₂O molecule adsorption mainly occurs through the Ca-O_w chemical bond formation between O_w atoms in H₂O and Ca atoms on the dolomite surface. Charges

are mainly transferred from the 3d orbitals of Ca to the 2p orbitals of O_w , forming $d \rightarrow p$ feedback bonds (Chen and Chen, 2010). After the adsorption of H_2O molecules, the DOS of H and O_w atoms change significantly and the three DOS peaks of O_w 2p orbital decrease significantly and shift toward low energy levels, indicating that the O_w 2p orbital gains charge. The peak and shape of the DOS of Ca atoms changed before and after adsorption, indicating that the Ca atoms on the dolomite surface interacted with the O_w atoms of H_2O molecules. The Al DOS was basically unchanged before and after adsorption, whereas Mg 2p DOS changed from a double peak to a single peak. Fe 3d DOS was divided into two peaks, with higher peaks at the Fermi energy level. The Fe 3d DOS became wider, and the Fe atoms became more active and lost charges more easily in the 3d orbitals, indicating that Fe and Mg atoms interact with H_2O molecules. The competitive adsorption of Fe, Mg, and Ca atoms on the dolomite surface occurred, which inhibited the interaction between the Ca atoms and H_2O molecules on the dolomite surface, wherein the inhibition effect of the Fe atoms was more significant.

The differential charge density map clearly shows the electron gain and loss centers between atoms, the type of bonding between atoms, and the bonding strength, which can visualize the bonding properties between atoms. Fig. 7 shows the difference in electron density for dolomite supercells with different atomic substitutions. Only H_2O molecules and Ca, Mg, Al, and Fe atoms are considered. The red and blue contours indicate an increase and a decrease in electron density, respectively (Xian et al., 2012). The Ca- O_w bond formed between the O_w atoms in the H_2O molecules and the Ca atoms on the dolomite surface does not change the charge density around the Ca atoms; the charge changes around the H and O_w atoms in the H_2O molecules. Therefore, the Ca- O_w bond formed is an ionic bond. The charge around the Mg and Al atoms does not change while the Fe atoms are blue, indicating that the Fe atoms lose electrons while the charge increases, which agree with the results of the Mulliken charge population analysis.

Table 6. Mulliken charge population of O_w , H atoms of H_2O molecule and Al-substituted dolomite surface atoms

Atomic label	Adsorption model	s	p	d	Total	Charge/e
H1/H2	Before adsorption	0.47/0.48	0.00	0.00	0.47/0.48	0.53/0.52
	After adsorption	0.47/0.61	0.00	0.00	0.47/0.61	0.53/0.39
O_w	Before adsorption	1.89	5.16	0.00	7.05	-1.05
	After adsorption	1.85	5.11	0.00	6.96	-0.96
Ca	Before adsorption	2.41	6.00	0.48	8.89	1.11
	After adsorption	2.26	6.01	0.50	8.77	1.23
Al	Before adsorption	1.34	0.94	0.00	2.28	0.72
	After adsorption	1.29	0.98	0.00	2.27	0.73

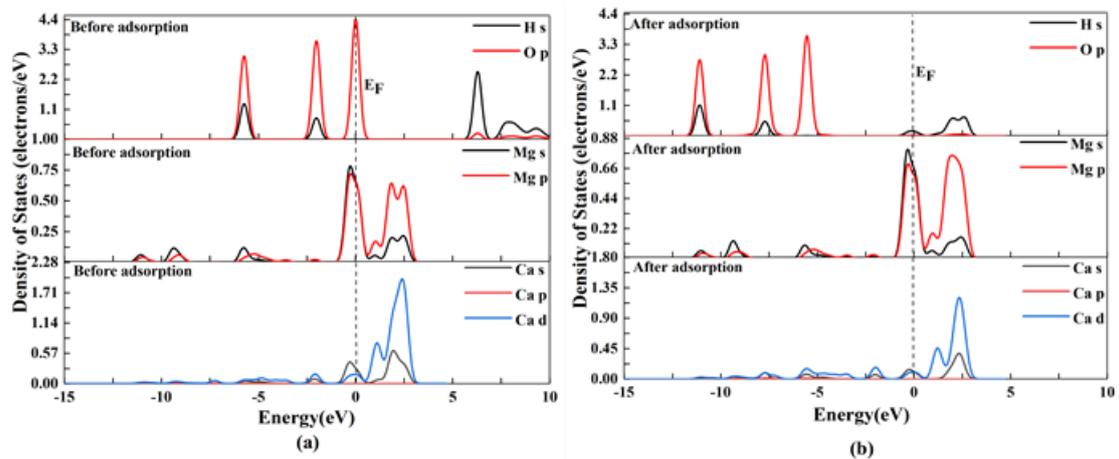


Fig. 4. DOS of Perfect dolomite (104) surfaces before and after H_2O molecule adsorption: (a) Before the adsorption; (b) After the adsorption

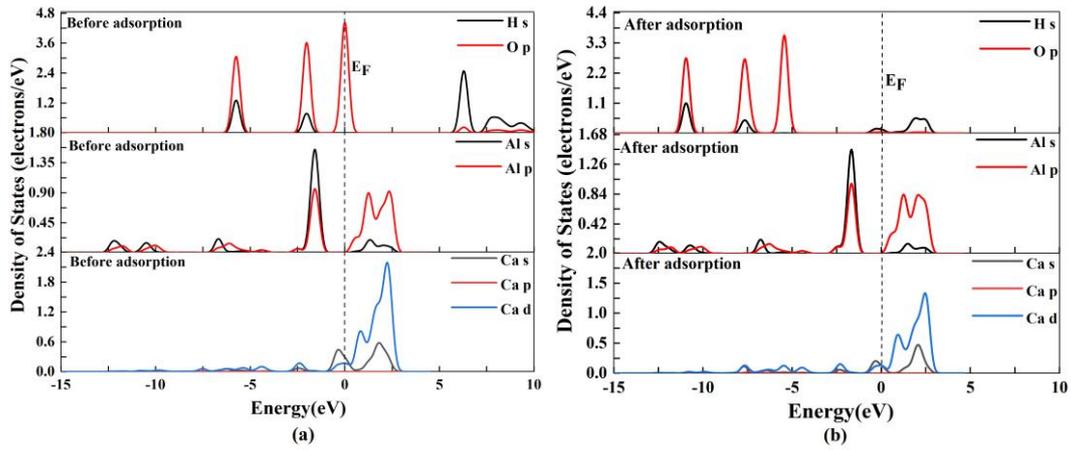


Fig. 5. DOS of Al-substituted dolomite (104) surfaces before and after H₂O molecule adsorption: (a) Before the adsorption; (b) After the adsorption

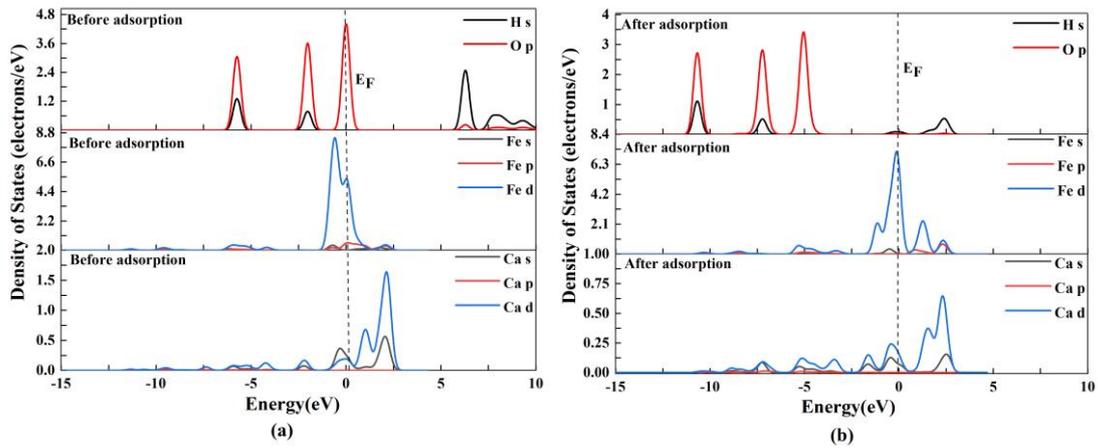


Fig. 6. DOS of Fe-substituted dolomite (104) surfaces before and after H₂O molecule adsorption: (a) Before the adsorption; (b) After the adsorption

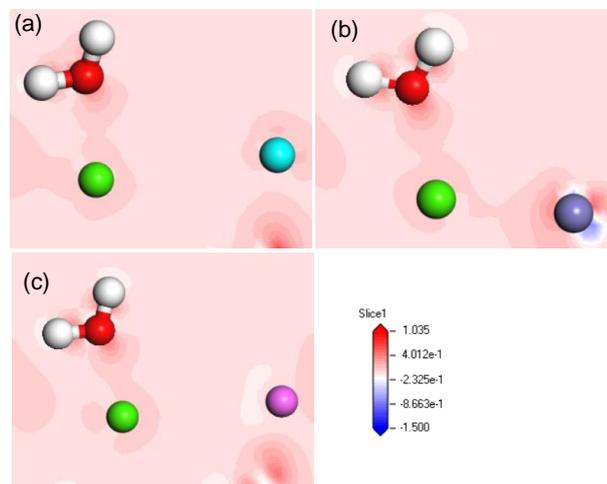


Fig. 7. Electron density difference of different replace dolomite supercell: (a) Perfect dolomite; (b) Fe-substituted dolomite; (c) Al-substituted dolomite

4. Conclusions

- (1) The adsorption energies of H₂O molecules on the perfect, Al-substituted, and Fe-substituted dolomite surfaces are -87.50, -94.23, and -78.65 kJ/mol, respectively, indicating that the adsorption mode of each is weak chemisorption. The Fe impurity defect increases the adsorption energy of H₂O molecules on dolomite compared with the perfect dolomite, whereas the Al impurity defect decreases it. Alternatively, H₂O molecules prefer to react with Al-substituted dolomite surface Ca atoms rather than Fe-substituted dolomite.
- (2) Mulliken charge population and electron density difference show that s orbitals of H atoms and p orbitals of O_w atoms are enriched with additional electrons and the charge is reduced. The d orbitals of Ca atoms lose charge and transfer to O_w atoms, which agrees with the poor electronegativity of Ca atoms and their weak valence electron binding ability. The adsorption mode of H₂O molecules on dolomite was mainly via O_w atoms interacting with Ca atoms, where the d orbitals of Ca atoms provide charge to O_w atoms to form ionic bonds.
- (3) DOS analysis shows that, during the adsorption of H₂O molecules on dolomite, Mg and Al atoms have less influence on the dolomite surface, whereas Fe and Ca atoms undergo competitive adsorption, which inhibits the interaction between Ca atoms and H₂O molecules on the dolomite surface.

Acknowledgements

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