

Article

Mechanism of Selective Chlorination of Fe from Fe_2SiO_4 and FeV_2O_4 Based on Density Functional Theory

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Abstract: Vanadium slag is an important resource containing valuable elements such as Fe, V, Ti, and so on. A novel selective chlorination method for extracting these valuable elements from vanadium slag has been proposed recently. The proposed methods could recover valuable elements with a high recovery ratio and less of an environmental burden, while the study on the chlorination mechanism at the atom level was still insufficient. Fe_2SiO_4 and FeV_2O_4 are the two main phases of vanadium slag, and the iron element can be selectively extracted via the chlorination of NH_4Cl . The NH_4Cl decomposes into NH_3 gas and HCl gas, which was the true chlorination agent. As a result, the chlorination reactions of Fe_2SiO_4 and FeV_2O_4 with HCl were firstly calculated using FactSage 8.0. Then, this paper studied the characteristics of HCl adsorption on the $\text{Fe}_2\text{SiO}_4(010)$ surface and the $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface mechanism of the selective chlorination of Fe from Fe_2SiO_4 and FeV_2O_4 via DFT calculations. The processes of chlorination of Fe_2SiO_4 and FeV_2O_4 involved the processes of removing O atoms from them with HCl gas. The iron in Fe_2SiO_4 was selectively chlorinated because HCl could adsorb on the iron site but could not adsorb on the silicon site. The iron in FeV_2O_4 was selectively chlorinated because the electronegativity gap between V and O was more significant than that between the Fe and O elements.

Keywords: DFT; vanadium slag; selective chlorination

Citation: Du, J.; Xiao, Y.; Liu, S.; Wang, L.; Chou, K.-C. Mechanism of Selective Chlorination of Fe from Fe_2SiO_4 and FeV_2O_4 Based on Density Functional Theory. *Metals* **2023**, *13*, 139. <https://doi.org/10.3390/met13010139>

Academic Editor: Mark E. Schlesinger

Received: 1 December 2022

Revised: 31 December 2022

Accepted: 2 January 2023

Published: 10 January 2023



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1. Introduction

Vanadium is an important element for alloying and is indispensable for manufacturing micro-alloyed steel [1,2]. Vanadium titanomagnetite ore is scattered in Australia, China, Russia, and South Africa as the main resource of vanadium element [3–5]. The vanadium slag produced after pyrometallurgical processes of vanadium titanomagnetite ore still contained many valuable elements with the composition of approximately 30–40 mass% total Fe, 13.52–19.03 mass% V_2O_3 , 6.92–14.32 mass% TiO_2 , 7.44–10.67 mass% MnO , and 0.93–4.59 mass% Cr_2O_3 [6]. Additionally, it produced about 1.4 million tons each year. The vanadium slag was mainly composed of encompassed structures, such as fayalite, manganoan ($(\text{Fe}, \text{Mn})_2\text{SiO}_4$), titanomagnetite ($\text{Fe}_{2.5}\text{Ti}_{0.5}\text{O}_4$), and vuorelainenite ($(\text{Mn}, \text{Fe})(\text{V}, \text{Cr})_2\text{O}_4$) [7]. The main difficulty of extracting valuable elements from vanadium slag was the destruction of its encompassed structure [8].

The traditional method used to extract vanadium from the vanadium slag used the oxidation method, direct vanadium alloying, and ferrovanadium production with the vanadium slag [9–11]. The direct vanadium alloying with the vanadium slag demonstrated the shortcomings of low vanadium recovery, complex steelmaking operation, the introduction of impurities in steel, and high energy consumption which were disadvantages to the efficient utilization of resources [12,13]. Therefore, this made the oxidation technologies key to vanadium extraction from vanadium slag. Oxidation technologies included salt roasting, direct leaching, etc. [14]. The salt roasting of vanadium slag was widely used in

the industry. The salt roasting of vanadium slag included the following steps in order: salt roasting of vanadium slag under an oxidation atmosphere, water leaching of the produced roasting product, separation of vanadium from the leachate and vanadium precipitation, calcination precipitation, and, finally, the reduction of V_2O_5 [15,16]. During this process, the Cr(III) was also oxidized to Cr(VI) which was one of the main carcinogen contaminants. The insoluble vanadium(III) in vanadium slag was converted into water-soluble vanadate(V) which was highly toxic [17]. The disposal of leaching lixivium and roasting tailings containing hazardous vanadium(V) and chromium(VI) became a great burden to environmental protection.

To alleviate the shortcomings of salt roasting technology and efficient resource utilization, our team proposed a new process to comprehensively extract the valuable elements with a high recovery ratio and less of an environmental burden from vanadium slag [8,12,18–21]. The vanadium slag was selectively chlorinated using a chlorination agent to accomplish the separation of valuable elements. For example, NH_4Cl was used as the chlorination agent to selectively extract iron and manganese from vanadium slag. The manganese and iron chlorination ratio can be reached at 95% and 72%, respectively [8]. During the chlorination process, the Cr and V were not oxidized to high valence toxic oxidation but remained at the original valence which was inspiring for tailing disposal and environmental protection. Our team also proposed other chlorination agents to selectively chlorinate V and Cr elements in vanadium slag and produced valuable products via extracted resources. In previous work, the optimal chlorination agent ratio and maximum chlorination rate were determined. Additionally, the thermodynamic mechanism of selective chlorination of the valuable element Fe in vanadium slag was clarified. However, the investigation of the selective chlorination mechanism of Fe in vanadium slag from the atomic level was necessary for a deep understanding of the mechanisms. The first principles calculation is applied more and more frequently to investigate the mechanism of chemical reactions and material properties due to the progress of computational algorithms and the rapid development of computer technologies.

2. Computational Methods

2.1. Computational Theory

All the calculations were performed using the CASTEP module in Material Studio 2017 (Accelrys, San Diego, CA, USA) software with the projector augmented wave (PAW) basis sets and periodic boundary conditions [22,23]. The electron–ion core interaction of Fe, Si, V, and O atoms was described using the ultrasoft potential in CASTEP. The generalized gradient approximation (GGA) defined by Perdew–Burke–Ernzerhof (PBE) was applied to describe the exchange–correlation energy [24]. The irreducible Brillouin zone (IBZ) was integrated using meshes generated via the Monkhorst–Pack method for self-consistent field calculation [25]. The total energy and atomic displacement convergence criteria were set to 1.5×10^{-5} eV/atom and 1×10^{-4} nm, respectively. The stress deviation criterion was set to be smaller than 0.05 GPa. The structure optimization was treated within the Fletcher–Goldfarb–Shanno algorithm (BFGS), and all the energy calculations were performed in reciprocal space [26].

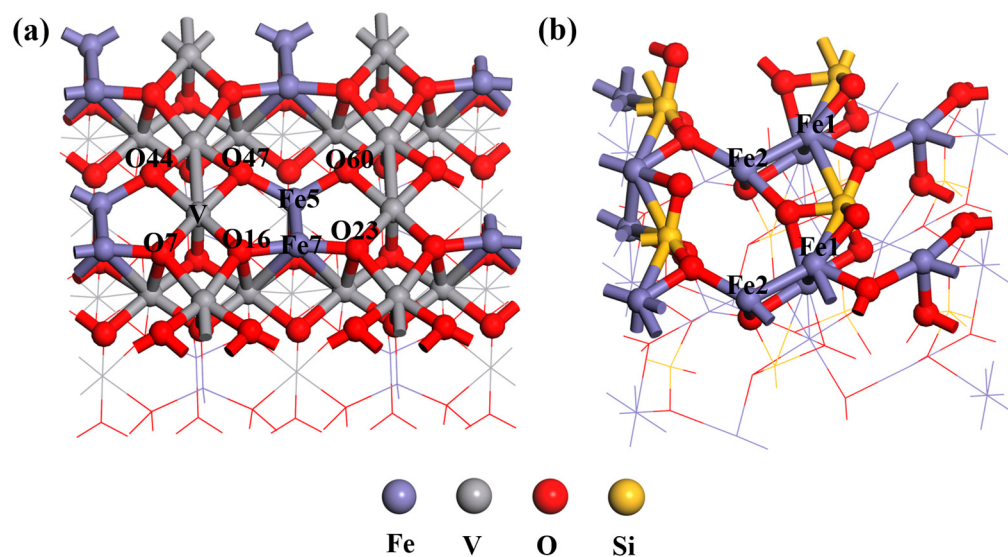
2.2. Computational Details

In this paper, the geometry optimization of bulk FeV_2O_4 , bulk Fe_2SiO_4 , and their surfaces was applied to obtain the corresponding minimum energy structure that was the stable structure for further exploration of the chlorination mechanisms of FeV_2O_4 and Fe_2SiO_4 . The bulk FeV_2O_4 was cubic while the bulk Fe_2SiO_4 was a face-centered orthorhombic lattice in terms of crystallography. For the geometry optimization of bulk FeV_2O_4 and bulk Fe_2SiO_4 , the Monkhorst–Pack k-point mesh of $2 \times 2 \times 2$ and $1 \times 3 \times 4$ was adopted. The Kohn–Sham wave functions were expanded using an optimized kinetic energy cutoff of 700 eV for all calculations. The optimized lattice parameters of Fe_2SiO_4 and FeV_2O_4 exhibited in Table 1 are consistent with the reference data.

Table 1. Lattice parameters of Fe_2SiO_4 and FeV_2O_4 .

	Calculated Results	Reference
Fe_2SiO_4	$a = 10.647$, $b = 6.188$, $c = 5.014$	$a = 10.485$, $b = 6.093$, $c = 4.820$ [27]
FeV_2O_4	$a = b = c = 8.535$	$a = b = c = 8.439$ [28]

The (001) surface of FeV_2O_4 was the most stable one. There were two classes of terminated surface for FeV_2O_4 defined as Fe-terminated surface and VO-terminated surface, which were similar to spinel FeCr_2O_4 [29]. However, the exposure of iron atoms was necessary to unravel the mechanism of the selective chlorination of iron in FeV_2O_4 . As a result, in this paper, the Fe-terminated (001) surface of FeV_2O_4 was chosen to investigate the iron selective mechanism of FeV_2O_4 , despite the existence of the Fe-terminated surface and VO-terminated surface. To eliminate the size effect, the calculated Fe-terminated (001) surface was a $2 \times 2 \times 1$ slab with 13 layers of atoms and 112 atoms as shown in Figure 1a. A vacuum layer of 15 Å was inserted between adjacent slabs. For the geometry optimization of the FeV_2O_4 (001) Fe-terminated surface, the Monkhorst–Pack k-point mesh of $1 \times 1 \times 1$ was adopted. The three bottom layers of atoms were fixed during the DFT calculation of the FeV_2O_4 (001) Fe-terminated surface. There were two classes of Fe site on the FeV_2O_4 (001) Fe-terminated surface which were defined as Fe5 and Fe7 in this paper. Both the Fe–O bonds and V–O bonds on the FeV_2O_4 (001) Fe-terminated surface were classified into two classes according to their Mulliken bond order. The corresponding Mulliken bond order from the DFT calculation is exhibited in Table 2. O7, O16, O17, O23, O44, O47, and O60 represent different oxygen atoms as denoted in Figure 1a.

**Figure 1.** (a) FeV_2O_4 (001) Fe-terminated surface, (b) Fe_2SiO_4 (010) surface.**Table 2.** Bond order of Fe–O bond and V–O bond in FeV_2O_4 (001) Fe-terminated surface.

Bond	Bond Order
V–O44, V–O47	0.28
V–O7, V–O16	0.32
Fe5–O47, Fe5–O60	0.40
Fe7–O16, Fe7–O23	0.47

As for Fe_2SiO_4 , the (010) index surface was chosen for its lowest surface energy according to the calculations. Additionally, the chosen Fe_2SiO_4 (010) surface as shown in Figure 1b. was the lowest energy-terminated surface. A $2 \times 1 \times 1$ slab with 84 atoms of Fe_2SiO_4 was applied for further calculations to eliminate the size effect. For the geometry optimiza-

tion of the $\text{Fe}_2\text{SiO}_4(010)$ surface slab, the Monkhorst–Pack k-point mesh of $1 \times 1 \times 1$ was adopted. The three bottom layers of the atom were fixed during the DFT calculations on the $\text{Fe}_2\text{SiO}_4(010)$ surface. A vacuum layer of 15 Å was inserted between adjacent slabs. Figure 1b shows the optimized structure of the clean $\text{Fe}_2\text{SiO}_4(010)$ surface. There were two crystallographically inequivalent Fe sites defined as the Fe1 site and the Fe2 site, as shown in Figure 1b. The Fe1 site atom was surrounded by two O atoms and one Fe atom, while the Fe2 site atom was surrounded by three O atoms and one Fe atom. The discrimination of the ambient chemical environment led to different atom charges of the Fe1 site and Fe2 site atom. The Mulliken charge of the iron atom in the Fe1 site and Fe2 site was 1.09 and 1.22, respectively.

3. Results and Discussion

3.1. Thermodynamic Calculations

The standard Gibbs free energies of Reactions (1) and (2) at different temperatures were calculated via the FactSage 8.0 program, using the pure substance database and the oxide database. The results are shown in Figure 2 and demonstrate that the reactions could occur in the temperature range of 0 to 600 °C and the standard Gibbs free energy of both reactions increased with an increase in temperature. Increasing the temperature was not conducive to Reactions (1) and (2). Meanwhile, it was found that Fe in Fe_2SiO_4 was easier to be chlorinated than Fe in FeV_2O_4 . However, since the amount at each temperature in the chlorination process was not known, the following calculation was performed.

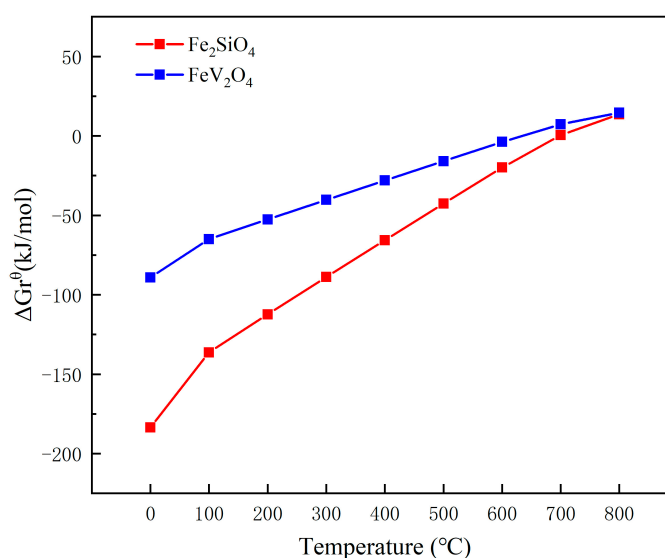
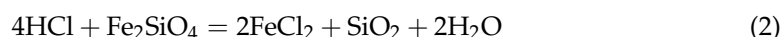
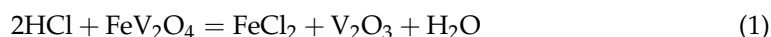


Figure 2. Gibbs free energy variation for Reactions (1) and (2) with different temperatures.

It can be seen in Figure 3 that as the temperature increased, Fe could be chlorinated in the form of FeCl_2 . Si was present in the form of SiO_2 . The amounts of Fe_2SiO_4 and HCl increased with increasing temperature, and the total amount of FeCl_2 , SiO_2 , and H_2O decreased with increasing temperature. This means that only iron could be selectively chlorinated to produce FeCl_2 . It can be seen in Figure 4 that as the temperature increased, vanadium in FeV_2O_4 could not be chlorinated and the iron could be chlorinated to form FeCl_2 . The amounts of V_2O_3 and H_2O increased with increasing temperature, and the total amount of FeCl_2 and FeV_2O_4 decreased with increasing temperature. In summary, the selective chlorination of Fe_2SiO_4 and FeV_2O_4 to form ferric chloride was found to be thermodynamically achievable using calculations with FactSage 8.0.

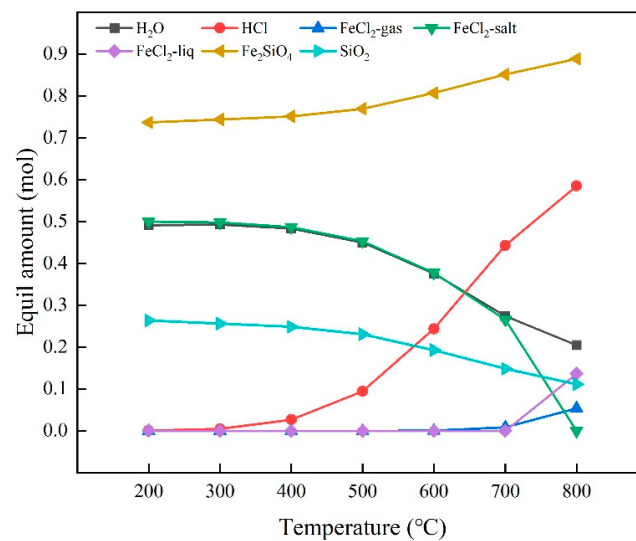


Figure 3. Changes in the content of each substance in the reaction of Fe_2SiO_4 with HCl at different temperatures.

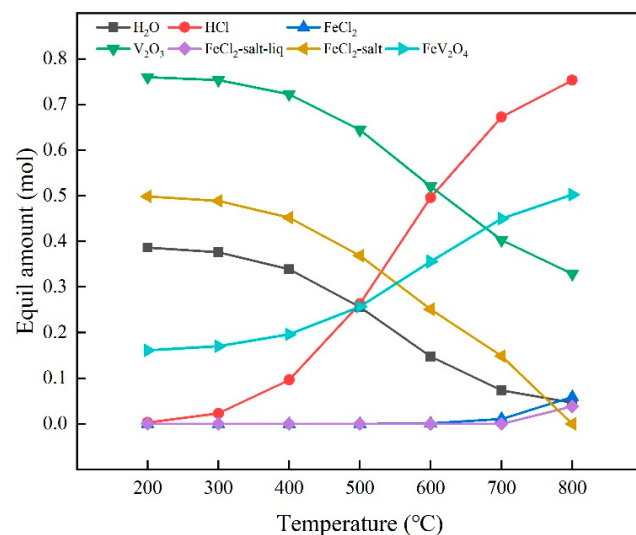


Figure 4. Changes in the content of each substance in the reaction of FeV_2O_4 with HCl with increasing temperature.

3.2. HCl Adsorption on Fe_2SiO_4

The adsorption of the HCl molecule on the Fe_2SiO_4 surface is no doubt an important step for the chlorination of Fe_2SiO_4 . As a result, it is necessary to explore the characteristics of HCl adsorption on the Fe_2SiO_4 surface. As previously discussed, the (010) surface is the most stable surface, implied by it having the lowest surface energy. As a result, the Fe_2SiO_4 (010) surface is believed to be the most likely exposed surface during chlorination. When we consider the chlorination of Fe_2SiO_4 via HCl gas, it is natural to think that the H atom bonds with the O atom while the Fe atom bonds with the Cl atom. However, it is unclear whether the HCl dissociated adsorption on the surface is either mainly led by the interaction between the adsorbed O and H atoms or between the adsorbed Fe atom and Cl atom. Moreover, it is also unclear in what manner the HCl would adsorb on the Fe_2SiO_4 (010) surface. To clarify these questions, adsorption configurations were designed as shown in Figure 5. In Figure 5a, the HCl molecule was vertically put on the surface with a H atom near one O atom, while in Figure 5b, the HCl molecule was vertically put on the surface with a Cl atom near one Fe atom. The results showed that when the H atom was put near the O atom, the H atom and Cl atom in the HCl molecule were still bonded.

Moreover, the HCl molecule was pushed away from the surface. The most significant change was that the vertical HCl molecule rotated until it was horizontal to the surface. This suggested that it was preferable for the HCl molecule to horizontally adsorb on the $\text{Fe}_2\text{SiO}_4(010)$ surface. When the Cl atom was put near the Fe atom, the HCl molecule was dissociated and adsorbed on the $\text{Fe}_2\text{SiO}_4(010)$ surface. The distance between the adsorbed iron atom and the O atom was extended from 1.946 Å to 3.061 Å. This result indicates that the dominant force to break the H-Cl bond is the interaction between the Cl atom and the iron atom instead of the interaction between the H atom and O atom. In addition, it is preferable for the HCl molecule to adsorb on the $\text{Fe}_2\text{SiO}_4(010)$ surface horizontally.

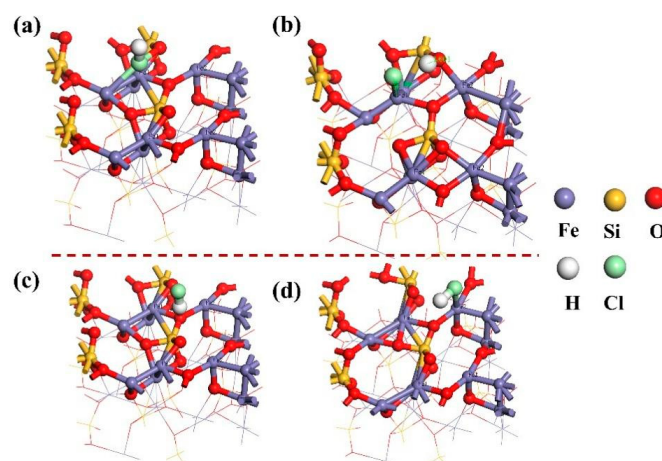


Figure 5. HCl adsorption on Fe_2SiO_4 : (a) Configuration of HCl vertical adsorption with H atom near one O atom before optimization and (b) after optimization. (c) Configuration of HCl vertical adsorption with Cl atom near one Fe atom before optimization and (d) after optimization.

Therefore, the HCl molecule was put on the Fe_2SiO_4 surface horizontally to the Fe-O bond with the H atom above one O atom and the Cl atom above one Fe atom, as shown in Figure 6a,c. The two classes of iron sites were taken into consideration by putting the HCl molecule on the Fe1 site and Fe2 site, respectively. Therefore, two adsorption configurations were considered for the HCl adsorption on the iron site. Additionally, the adsorption results were interpreted for further understanding of the chlorination mechanism of Fe_2SiO_4 via HCl.

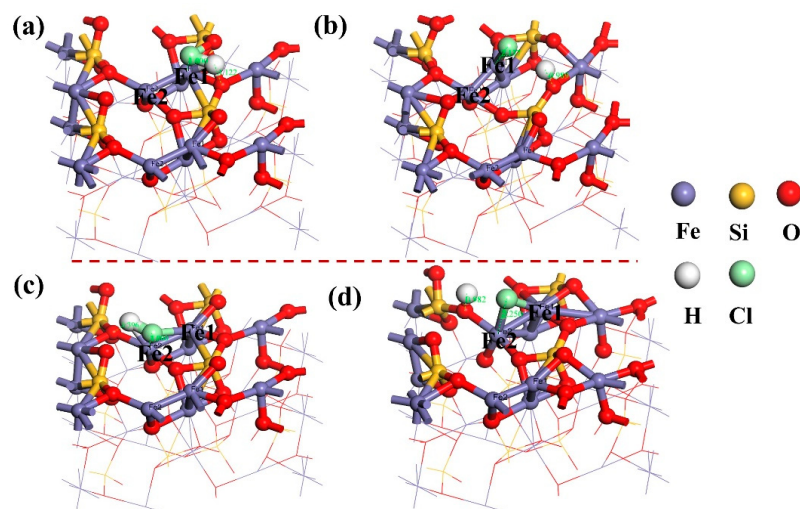


Figure 6. HCl adsorption on Fe_2SiO_4 : (a) Configuration of HCl adsorption on Fe1 site before optimization. (b) Configuration of HCl adsorption on Fe1 site after optimization. (c) Configuration of HCl adsorption on Fe2 site before optimization. (d) Configuration of HCl adsorption on Fe1 site after optimization.

When the HCl molecule was put on the Fe1 site, the HCl molecule was dissociated and adsorbed on the $\text{Fe}_2\text{SiO}_4(010)$ surface, as shown in Figure 6b. The H atom bonded with the O atom and the Cl atom bonded with the Fe atom in the Fe1 site after geometry optimization. The adsorption energy was -0.84 eV, as exhibited in Table 3. The adsorbed Fe atom and O atom were dragged away from each other by the attraction of the Cl atom and H atom, respectively. The distance of the adsorbed Fe1-O before and after adsorption was 1.922 Å and 3.174 Å, respectively. The distance of adsorbed Fe1-Cl changed from 2.289 Å to 1.985 Å. It can be concluded that the adsorbed Fe1 and O atoms were dragged away from the $\text{Fe}_2\text{SiO}_4(010)$ surface by the Cl and O atoms. When the HCl molecule was put above the Fe2 site of the iron atom, similarly, the HCl molecule was dissociated and adsorbed on the Fe_2SiO_4 surface, as shown in Figure 6d. The dissociated H atom was adsorbed on the O atom and the Cl atom was adsorbed on the Fe2 atom, while the Cl atom was also attracted by the neighboring Fe1 site of the iron atom. The adsorption energy was -0.51 eV which indicates weaker adsorption than the previously discussed HCl adsorption on the Fe1 site. However, unlike the HCl adsorption on the Fe1 site of the iron atom, the adsorbed Fe atom and O atom were pulled closer to each other with a distance shortened from 2.047 Å to 1.985 Å. This may have resulted from the weaker attraction between the adsorbed Fe2 atom and the Cl atom than that between the Fe1 atom and Cl atom. The distances of Fe1-Cl and Fe2-Cl when the HCl molecule was initially put above the Fe2 site of the iron atom were 2.272 Å and 2.251 Å, respectively. In other words, the adsorbed Cl atom was in the bridge site of the Fe1 atom and Fe2 atom, as shown in Figure 5d. This phenomenon indicates that the attraction between the Fe1 site of the iron atom and Cl atom is stronger than that between the Fe2 site of the iron atom and Cl atom. From the previous analysis we gain the Mulliken charge of the Fe1 site of the iron atom and Fe2 site of the iron atom: 1.09 and 1.22 , respectively. The lower charge of the Fe1 site of the iron atoms means that it is easier to lose electrons here than in the Fe2 site of the iron atoms. As a result, the Fe1 site is a preferable site to the Fe2 site for HCl adsorption. The Mulliken charge of the Fe1 site and Fe2 site atoms after adsorption was 0.35 and 0.52 , respectively. It can be concluded that during the HCl adsorption process, the Cl captures an electron from the adsorbed Fe atoms and leads to a weakened adsorbed Fe-O bond. Additionally, the weakened Fe-O bond results in electron capture for the adsorbed Fe atom and electron loss for the adsorbed O atom. Therefore, both the adsorbed Fe atom and Cl atoms seize electrons while the adsorbed O atom loses electrons in total. The Fe1 site of the atom seizes more electrons from the O atom than the Fe2 site of the atom, indicating more serious destruction of the Fe-O bond. During the HCl adsorption process, the Cl captures electrons from adsorbed Fe atoms leading to a weakened adsorbed Fe-O bond.

Table 3. HCl adsorption energy on Fe_2SiO_4 .

Adsorption Site	Adsorption Energy (eV)
Fe1	-0.84
Fe2	-0.51

The Si atom is also a possible adsorption site for the HCl molecule; as a result, we conducted the geometry optimization of structure where HCl is horizontally above the surface with a Cl atom right above one Si atom, while a H atom is right above one neighboring O atom. The structure before and after geometry optimization is shown in Figure 7a,b, respectively. The result shows that the HCl molecule adsorbed on the surface in a dissociated way after geometry adsorption. Unlike the HCl adsorption on the iron sites, the Cl atom was not bonded with the nearest Si atom but bonded with neighboring iron atoms. As a result, we can conclude that the Cl atom is inclined to interact with the iron atom instead of the Si atom. This is consistent with the experiment result of Liu et al. that found that Si element cannot be chlorinated by HCl gas which leads to the selective chlorination of Fe element [8].

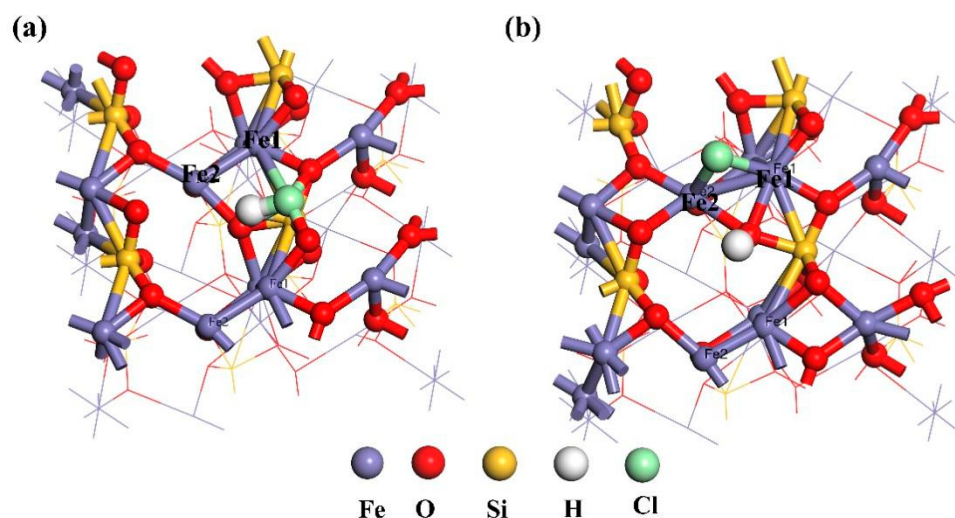


Figure 7. HCl adsorption on Fe_2SiO_4 : (a) HCl adsorption on Si site before optimization. (b) HCl adsorption on Si site after optimization.

3.3. HCl Adsorption on FeV_2O_4

To unravel the HCl adsorption characteristics on the $\text{FeV}_2\text{O}_4(010)$ surface and the mechanism of selective chlorination of Fe in FeV_2O_4 , we conducted a series of DFT calculations as discussed henceforth. The chlorination of FeV_2O_4 via HCl means that the Cl atom bonds with the Fe atom or V atom while the H atom bonds with the O atom. As a result, we focus on the difference between the Fe atom, V atom, and their neighboring O atoms. We obtained the bond order of Fe-O and V-O bonds; we found that there are two classes of V-O bond and two classes of Fe-O bond, as well. The obtained bond order is exhibited in Table 2. As a result, we first conducted a calculation of HCl adsorption on these four sites. The HCl adsorption energy on these sites is exhibited in Table 4.

Table 4. HCl adsorption energy on FeV_2O_4 .

Adsorption Site	Adsorption Energy (eV)
Fe7	−2.84
Fe5	−2.72
V-O47	−3.20
V-O16	−0.27

We first conducted HCl adsorption on the $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface with the H atom above the O23 atom while the Cl atom was right above the Fe7 atom. The H atom bonds with the O23 atom while the Cl atom bonds with the Fe7 atom. The distance between the Fe7 atom and the O23 atom changed from 1.834 Å to 2.758 Å, while the distance between the Fe5 atom and the O60 atom changed from 1.862 Å to 2.994 Å. The Fe5 atom was attracted by the neighboring O47 atom. This means that the adsorption of HCl on Fe7-O23 results in a significant change in the neighboring Fe-O bond but not the adsorbed Fe7-O23 bond. Figure 8a,b show the structures before and after the geometric optimization of HCl adsorption at the Fe7 site, respectively. The more significant change related to Fe5-O60 over Fe7-O23 may have resulted from the smaller bond order of Fe5-O40, that is, the weaker bond strength of Fe5-O40. The geometry optimization of configuration was where HCl was parallel to the Fe5-O60 bond with the H atom being right above the O60 atom and the Cl atom being right above the Fe5 atom. It can be seen that HCl was dissociated and adsorbed on the $\text{FeV}_2\text{O}_4(010)$ surface with the H atom bonding with the O60 atom and the Cl atom bonding with the Fe5 atom. The distance of Fe5-O60 changed from 1.862 Å to 2.254 Å, while the distance of Fe7-O23 remain unchanged. The adsorption energy of HCl adsorption on the Fe7-O23 and Fe5-O60 sites was −2.84 eV and −2.72 eV,

respectively. The distance change for Fe-O was consistent with the adsorption energy. The minor restructure corresponds to smaller adsorption energy in the absent value. Figure 8c,d show the structures before and after the geometric optimization of HCl adsorption at the Fe5 site, respectively. From the previous result, it can be concluded that it is preferable for HCl to adsorb on the Fe7-O23 site which leads to a more significant configuration restructure. As a result, during the chlorination process of FeV_2O_4 , the HCl molecule would adsorb on the Fe7-O23 site first, while the Fe5-O60 bond would break off first.

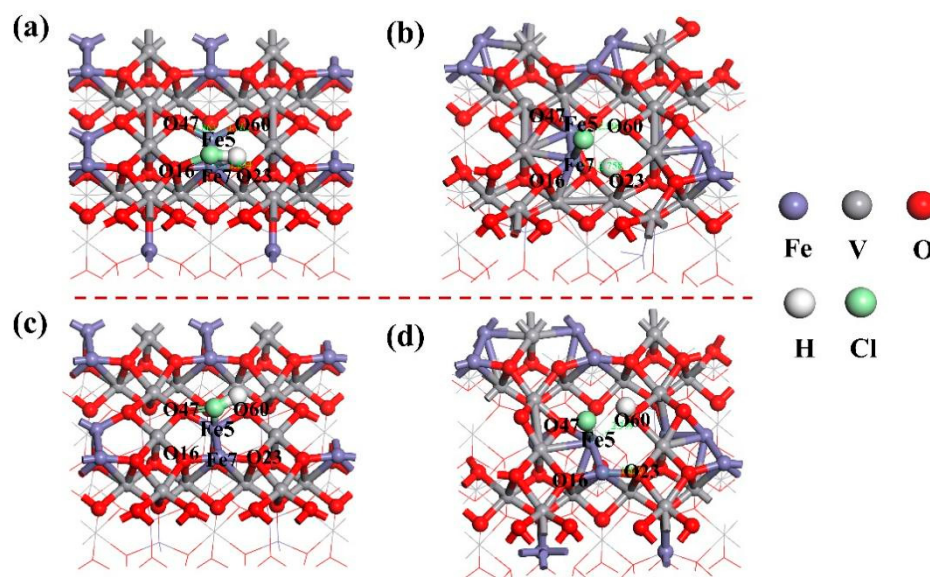


Figure 8. HCl adsorption on FeV_2O_4 : (a) HCl adsorption on Fe7 site before optimization. (b) HCl adsorption on Fe7 site after optimization. (c) HCl adsorption on Fe5 site before optimization. (d) HCl adsorption on Fe5 site after optimization.

The HCl adsorption on the V-O site was conducted to explore the possibility of chlorination of the V element by HCl gas. There were also two classes of V-O bonds on the $\text{FeV}_2\text{O}_4(010)$ surface. Therefore, the calculation of HCl adsorption on these two classes of sites was conducted. The HCl adsorption on the V-O47 site was first conducted. The result shows that the HCl molecule was broken off with the H atom adsorbed on the V atom and the Cl atom adsorbed on the O47 atom. The distance of V-O47 changed from 1.963 Å to 2.176 Å, while the distance of Fe5-O47 changed from 1.863 Å to 2.576 Å. In other words, the HCl adsorption on the V-O site leads to a more significant change in the neighboring Fe5-O47 bond, which roots from the weaker bond strength of Fe5-O47. Figure 9a,b show the structures before and after the geometric optimization of HCl adsorption at the V-O47 site, respectively. Similarly, the result of HCl adsorption on the V-O16 shows that the HCl molecule was also dissociated and adsorbed on the $\text{FeV}_2\text{O}_4(010)$ surface. The most significant configuration restructure other than the dissociation of the HCl molecule is that the distance of V-O16 extended from 2.042 Å to 2.674 Å. Figure 9c,d show the structures before and after the geometric optimization of HCl adsorption at the V-O16 site, respectively. The adsorption energy of HCl adsorption on V-O47 and V-O16 was -3.20 eV and -0.27 eV, respectively. The difference in adsorption energy results from the different configuration restructures. When HCl was adsorbed on the V-O47 site, the most significant change in surface was the breakoff of the Fe5-O47 bond; when the HCl was adsorbed on the V-O16 site, the most significant change in surface was the elongation of the V-O16 bond. This phenomenon implies that the V-O bond's breakoff needs more energy than the Fe-O bond's breakoff, with HCl as the chlorination agent. This is consistent with the experiment result that the Fe element is selectively chlorinated from FeV_2O_4 via HCl gas.

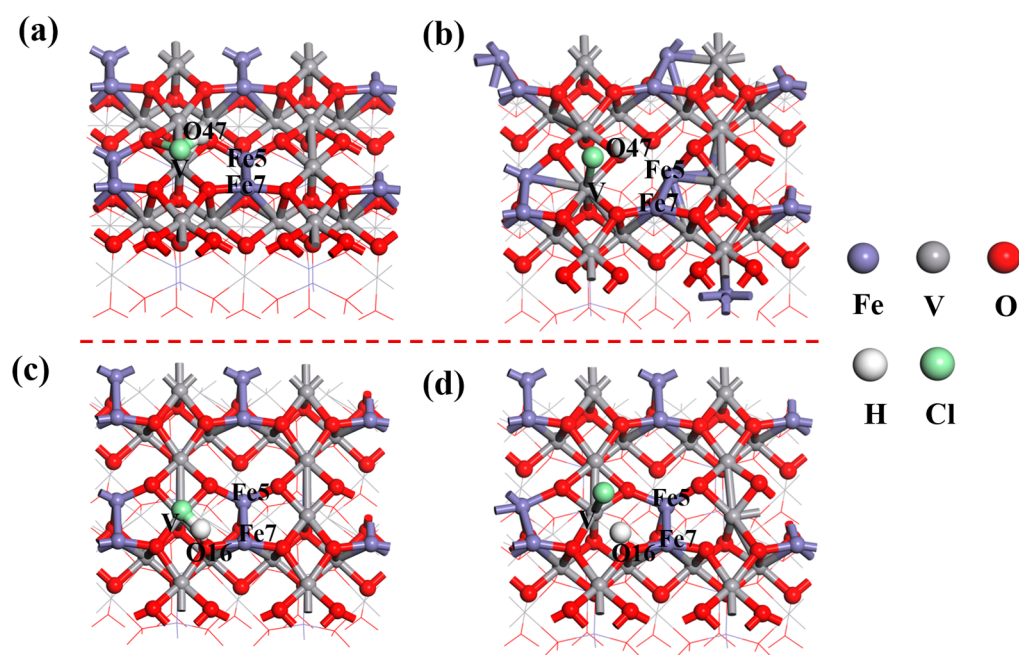


Figure 9. HCl adsorption on FeV_2O_4 : (a) HCl adsorption on V-O47 site before optimization. (b) HCl adsorption on V-O47 site after optimization. (c) HCl adsorption on V-O16 site before optimization. (d) HCl adsorption on V-O16 site after optimization.

3.4. Selective Chlorination Mechanism of Fe_2SiO_4 and FeV_2O_4

The essence of chlorination of Fe_2SiO_4 and FeV_2O_4 is, as a matter of fact, the process of removing the O atom in the form of water while the remaining metal atom bonds with the Cl atom to form chloride. The formation of one water molecule needs two H atoms, that is, two HCl molecules. From the previous discussion, we can conclude that the adsorption of one HCl molecule leads to the formation of one OH^- on the surface. There are two possible pathways for water formation during chlorination, as follows: (1) one HCl molecule is adsorbed on the surface while the H atom bonds with one previous OH^- to form a water molecule; (2) the H atom in the formed OH^- moves to its formed neighbor OH^- to form a water molecule. However, when we optimized the structure using the first pathway, it was found that the H atom in the HCl could not bond with the formed OH^- but was attracted by the neighboring O atom to form another OH^- . Therefore, the formation of a water molecule may be a process whereby one adsorbed H atom moves into its neighboring OH^- forming one water molecule, and then the water molecule departs from the surface. The optimized structure with H drifting to neighboring OH^- formed a cluster of H_2O^- on the surface, as shown in Figure 10. Figure 10a,b show the optimized structure with H_2O^- on the $\text{Fe}_2\text{SiO}_4(010)$ surface and the $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface, respectively. The angle of H-O-H and length of the H-O bond in the H_2O^- cluster are exhibited in Table 5. The angle of the H-O-H angle and the H-O bond length on both the $\text{Fe}_2\text{SiO}_4(010)$ surface and the $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface are close to those of the water molecule which are about 104.45° and $0.96 \text{ \AA}$ [30]. Therefore, the oxides in vanadium can be chlorinated by two HCl molecules with one O atom removed from the oxide. In other words, the metal atom is the active site for Cl atom adsorption while the O atom is the active site for H atom adsorption. Although the chlorination process can be considered a reduction process, the O atom in the olivine or spinel FeV_2O_4 acts as a catalyzer, just as Xiaolu Xiong et al. proposed that O adsorption is conducive to the chlorination of Cu_2S by NH_4Cl [31]. As a result, it is reasonable to conjecture that the pre-oxidation of vanadium before chlorination is a good way to enhance the chlorination rate.

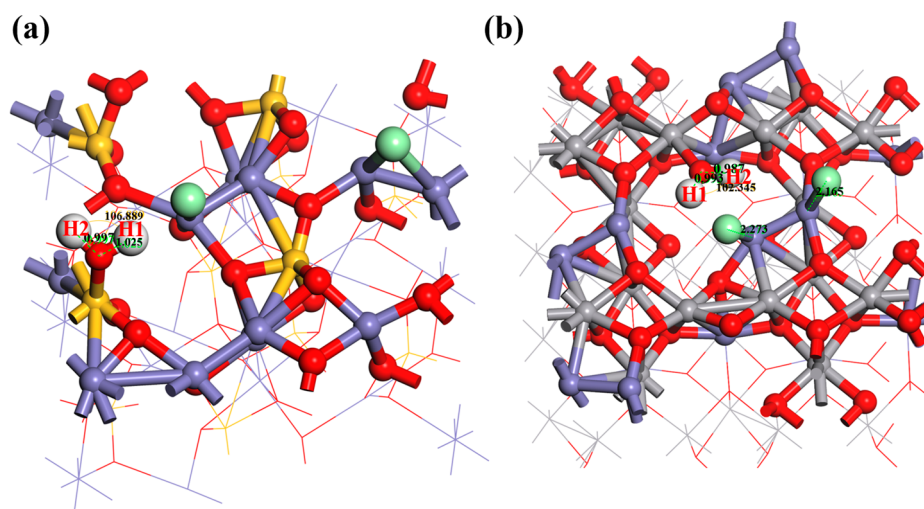


Figure 10. Optimized (a) $\text{Fe}_2\text{SiO}_4(010)$ and (b) $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface with H_2O^- .

Table 5. Structure parameter of formed H_2O^- .

	Angle of H-O-H (Degree)	Bond Length of H1-O, H2-O (Å)
Fe_2SiO_4	106.889	1.025, 0.997
FeV_2O_4	102.345	0.993, 0.987

We conducted a transition state search of the process of a H atom moving to combine with neighboring OH^- on the $\text{Fe}_2\text{SiO}_4(010)$ surface and the FeV_2O_4 Fe-terminated surface. The results show that the energy barrier of the two processes is 1.80 eV and 0.76 eV, respectively, as shown in Figure 10a,b. Figure 11a,b show the energy path of the chlorination process of Fe_2SiO_4 and FeV_2O_4 , respectively. It can be concluded that the HCl adsorption on the $\text{Fe}_2\text{SiO}_4(010)$ surface and the $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface is thermodynamically favorable while the formation of water is an endothermic process. The energy barrier of H moving on the $\text{Fe}_2\text{SiO}_4(010)$ surface is greater than that on the $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface which results from the stronger H-O bond on the $\text{Fe}_2\text{SiO}_4(010)$ surface. However, it is preferable for the chlorination of Fe_2SiO_4 to happen according to the thermodynamic calculations [8]. The HCl adsorption on the Fe site of the $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface is thermodynamically preferable according to previous calculations. During the adsorption process, the breaking bond is the Fe-O bond; while during the water departure process, the breaking bond is the Si-O bond or the V-O bond on the $\text{Fe}_2\text{SiO}_4(010)$ and $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface, respectively. Additionally, the electronegativity difference between Si and O was smaller than that between the V and O bond, implying a stronger Si-O bond than the V-O bond. As a result, the conclusion can be made that the rate-determining step in the chlorination of vanadium can be water departure from the surface instead of H moving to neighboring OH^- to form water or HCl adsorption.

It can be concluded that the Cl atom cannot adsorb on the Si atom of Fe_2SiO_4 according to the previous calculation. Additionally, the adsorption of HCl on the Fe site results in the breakoff of the Fe-O bond and the weakening of the corresponding Si-O bond. Additionally, the H_2O^- formation on the surface would weaken the Si-O bond further, eventually resulting in water departure under high-temperature conditions. The difference in the chlorination of FeV_2O_4 with Fe_2SiO_4 is that both the Fe atom and V atom are possible adsorption sites for HCl, while only the Fe atom is the adsorption site on the $\text{Fe}_2\text{SiO}_4(010)$ surface. Additionally, the HCl adsorption on V-O47 is preferable with a relatively large adsorption energy of 3.20 eV. However, the neighboring Fe-O bond breaks off instead of the adsorbed V-O bond, as described in Section 3.2. The chlorination process is the process of the H atom in the HCl molecule fighting for the O atom with the Fe atom and V atom on the $\text{FeV}_2\text{O}_4(001)$ surface. As a result, the selective chlorination of the Fe element or

selective chlorination of the V element depends on the difference in attraction between V-O and Fe-O. Additionally, the electronegativity gap between V and O is more significant than that between Fe and O atoms [32,33]. The more significant the electronegativity gap between elements, the stronger the interaction between them. In other words, after the O atom was removed as a water molecule, it was preferable for the Cl atom to combine with the Fe atom instead of the V atom. Therefore, the Fe element can be selectively chlorinated by HCl gas from FeV_2O_4 .

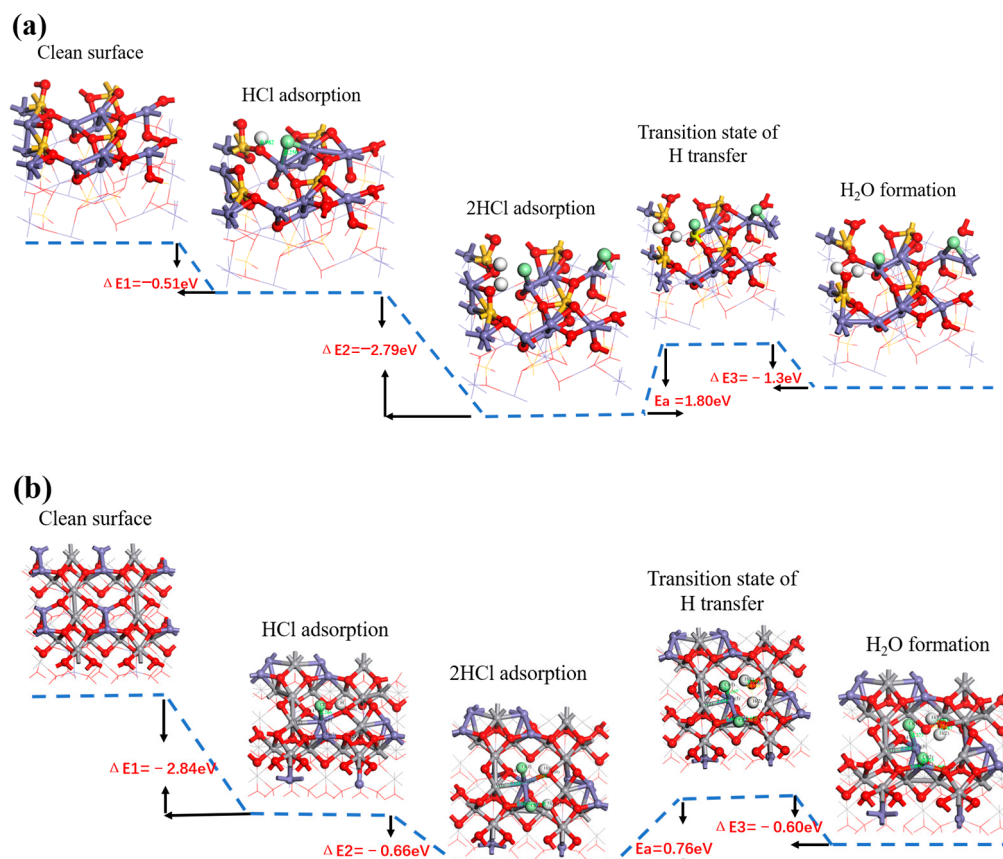


Figure 11. Energy path of chlorination of (a) Fe_2SiO_4 and (b) FeV_2O_4 by HCl.

4. Conclusions

In summary, the feasibility was calculated using FactSage 8.0 and it was found to be thermodynamically possible to achieve selective chlorination of Fe_2SiO_4 and FeV_2O_4 to form iron chloride. However, FactSage 8.0 could not further explain the microscopic chlorination process, so a first principles calculation was performed. The adsorption and chlorination mechanisms of Fe_2SiO_4 and FeV_2O_4 via HCl gas were studied using DFT calculations. The HCl molecule could be dissociated and adsorbed on both the $\text{Fe}_2\text{SiO}_4(010)$ surface and the $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface. However, the HCl could not adsorb on the silicon site of the $\text{Fe}_2\text{SiO}_4(010)$ surface which implies that the silicon element cannot be chlorinated by HCl gas. As a result, the iron element in Fe_2SiO_4 could be selectively chlorinated by HCl gas. It was preferable for the HCl molecule to adsorb on the Fe1 site compared to the Fe2 site, which indicated that the Fe1 iron atom may be chlorinated first. Moreover, the DFT calculation showed that the dissociation adsorption of HCl was mainly caused by the attraction between the Fe atom and the Cl atom. The HCl could be adsorbed on both the Fe site and the V site on the $\text{FeV}_2\text{O}_4(001)$ Fe-terminated surface. However, the electronegativity gap between V and O was more significant than that between Fe and O elements, which implied a stronger attraction between V and O elements. Therefore, the iron element in FeV_2O_4 could be selectively chlorinated by HCl gas. The HCl adsorption in Fe_2SiO_4 and FeV_2O_4 led to the formation of OH^- on their surface. The neighboring

adsorbed H atom could be attracted by OH^- to form a water molecule. Thus, Fe_2SiO_4 and FeV_2O_4 could be chlorinated by removing the O atom through water formation. The chlorination mechanism of Fe_2SiO_4 and FeV_2O_4 investigated may provide possible ideas for the chlorination of other oxides.

Author Contributions: Conceptualization, J.D. and Y.X.; methodology, J.D. and Y.X.; validation, J.D.; formal analysis, Y.X.; investigation, Y.X., S.L. and L.W.; resources, S.L. and L.W.; writing—original draft preparation, J.D. and Y.X.; writing—review and editing, S.L. and L.W.; visualization, S.L. and L.W.; supervision, S.L., L.W. and K.-C.C.; funding acquisition, S.L., K.-C.C. and L.W. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Nos. 52274406, 51922003, 51904286) and Interdisciplinary Research Project for Young Teachers of USTB (Fundamental Research Funds for the Central Universities) (FRF-IDRY-21-015).

Data Availability Statement: The data presented in this study are available from the corresponding author, upon reasonable request.

Acknowledgments: The authors are grateful for the financial support of this work from the National Natural Science Foundation of China (Nos. 52274406, 51922003, 51904286) and Interdisciplinary Research Project for Young Teachers of USTB (Fundamental Research Funds for the Central Universities) (FRF-IDRY-21-015).

Conflicts of Interest: The authors declare no conflict of interest.

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