

Article

Description of Si and Al Release from Aluminosilicate in the Acidic Condition Using Density Functional Theory: Protonated Terminal Oxygen

Chen-Yang Zhang ^{1,2} , Ya-Ling Yu ¹, Huan Yang ¹ , Li-Ming Wang ³, Ming-Feng Zhong ³, Shao-Min Lin ^{1,4,*}, Zhi-Jie Zhang ^{3,*}, Yun-Ying Wu ², Yang Liu ⁵ and Wei Xu ³

¹ School of Materials Science and Engineering, Hanshan Normal University, Chaozhou 521041, China

² Guangdong Chaoshan Institute of Higher Education and Technology, Chaozhou 521041, China

³ School of Materials Science and Engineering, South China University of Technology, Guangzhou 510641, China

⁴ Chaozhou Branch of Chemistry and Chemical Engineering Guangdong Laboratory, Chaozhou 521000, China

⁵ Chaozhou Three-Circle (Group) Co., Ltd., Chaozhou 515646, China

* Correspondence: lsm678@hstc.edu.cn (S.-M.L.); imzhang@scut.edu.cn (Z.-J.Z.)

Abstract: The molecular clusters $(\text{HO})_3\text{Si-O-Si}(\text{OH})_3$ and $(\text{HO})_3\text{Al-O-Si}(\text{OH})_3$ representative of aluminosilicate mineral surface were employed to study the dissolution of aluminosilicate in acidic condition via density functional theory (DFT) with the M06-2X+G(d,p) methodology. The surface termination sites (Si and Al) were both tetra-coordinated and the terminal oxygen was protonated in an acidic condition. In the dissolution reaction, the calculated barrier height of the six-membered ring transition state complex containing two water molecules was predicted to be 76.13 kJ/mol, lower than that of the four-membered ring transition state complex containing one water molecule. The barrier height of the reaction decreased to 6.17 kJ/mol and was 91.90% lower than that for the $\text{Si}_{\text{ter}}\text{-O-Si}$ without protonation. In addition, the calculated barrier heights for Al-terminated sites were predicted to be 22.23 kJ/mol, lower than those for the Si-terminated sites, suggesting that breaking the Al-O bond is easier than the Si-O bond in the aluminosilicate mineral surface. With the fracture of Si-O and Al-O bonds, the Si and Al release from the aluminosilicate. The results indicate that the acidic condition facilitates the release of Si and Al from the aluminosilicate, and the concentration of Al leaching from the aluminosilicate is higher than the Si.

Keywords: aluminosilicate mineral; dissolution; protonated terminal oxygen; DFT



Citation: Zhang, C.-Y.; Yu, Y.-L.; Yang, H.; Wang, L.-M.; Zhong, M.-F.; Lin, S.-M.; Zhang, Z.-J.; Wu, Y.-Y.; Liu, Y.; Xu, W. Description of Si and Al Release from Aluminosilicate in the Acidic Condition Using Density Functional Theory: Protonated Terminal Oxygen. *Sustainability* **2022**, *14*, 14390. <https://doi.org/10.3390/su142114390>

Academic Editor: Changhyun Roh

Received: 30 August 2022

Accepted: 2 November 2022

Published: 3 November 2022

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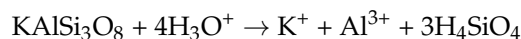


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1. Introduction

The dissolution of aluminosilicate minerals in an aqueous solution occurs nearly everywhere on Earth and has an effect on a number of processes such as soil chemistry, water contaminants, and the global CO_2 cycle. Furthermore, investigating the dissolution mechanisms in an acidic condition will provide some implication for the acid activation of aluminosilicate minerals and energy saving. High sintering temperature is required in the porcelain industry as the destruction of Si-O and Al-O bonds of aluminosilicate minerals in the raw material needs high activation energy [1], which results in high energy consumption. In order to decrease the energy consumption, methods for reducing sintering temperature are investigated. Activating the raw material can destroy the Si-O and Al-O bonds in the mineral and then reduce the sintering temperature [2]. Acid activation is a common activation method [3–5] since the dissolution rate of the mineral increases in an acid aqueous solution. Aluminosilicate minerals (such as kaolin and feldspar) account for a large proportion in the raw ceramic material. It is therefore worth investigating the dissolution mechanism of aluminosilicate minerals. A. Steudel [6] has reported that under acidic conditions, the dissolution rate of Si and Al from kaolin and feldspar increased significantly and a large number of Si-O and Al-O bonds in mineral are destructed.

The dissolution of minerals in aqueous solutions has been studied for nearly a century. Most authors have investigated the dissolution rate law of minerals based on the concentration of Si and Al released from minerals [7–9]. However, the hydrolysis of minerals generally occurs in a number of steps rather than as written stoichiometrically. For example, orthoclase dissolution can be described thermodynamically by



However, the probability of an orthoclase formula unit reacting with $4\text{H}_3\text{O}^+$ molecules in one step is vanishingly small. Instead, the reaction occurs in a number of elementary steps, such as ion exchange of K^+ , the hydrolysis of individual Al-O-Si and Si-O-Si linkages, the formation of K^+ and Al^{3+} species. Among these elementary steps, close attention has been paid to the breakage mechanisms of Al-O and Si-O bonds in the mineral surfaces. To investigate the reaction pathways, some scholars have simulated the Si-O and Al-O bond cleavage at the molecular level using quantum mechanical calculations in recent decades [10,11].

Theoretical studies have been carried out on the effect of different molecules on the clusters of $(\text{SiO})_n$, $(\text{AlO}_4)_n$ or $(\text{Al/Si-O-Si})_n$ [12–14]. C. Zhang [15] explored the stability of the Al-O/water system and Si-O/water system, using the Si-O layer ($\text{Si}_6\text{O}_{18}\text{H}_{12}$) or Al-O layer ($\text{Al}_6\text{O}_{24}\text{H}_{30}$) cluster model of kaolinite at the B3LYP. A. Rimola [16] studied the ring opening reactions of $(\text{SiO})_n$ ring motifs at silica surfaces by their interaction with H_2O and HCOOH by means of quantum chemical methods, adopting the B3LYP-D2/6-311++G(d,p) level of calculations for computing the energetics of the reaction; the calculation shows that the energy barriers of the ring opening reactions with H_2O is significantly lowered by the presence of an additional H_2O molecule acting through the proton relay mechanism. However, the basic structure unit of aluminosilicate minerals was not presented and the effect of the proton was also not discussed in detail.

Two typical molecular clusters (Figure 1) on aluminosilicate mineral surface were chosen for calculation. The dotted line in Figure 1 represents the surface of the mineral, and each tetra-coordinated Si or Al is terminated with hydroxyl groups. Both the Si and Al terminal sites (Si_{ter} and Al_{ter}) are connected to the bulk of mineral by a bridge oxygen atom (O_{bri}). Si sites on the surface is depicted by the $\text{Si}_{\text{ter}}\text{-O-Si}$ to simulate the breakage of $\text{Si}_{\text{ter}}\text{-O}$ bond and the release of Si. Similarly, the Al terminated sites is depicted with $\text{Al}_{\text{ter}}\text{-O-Si}$ to indicate the breakage of $\text{Al}_{\text{ter}}\text{-O}$ bond and the release of Al. The oxygen in the hydroxyl group attached to the Si_{ter} and Al_{te} on the surface is called terminal oxygen.

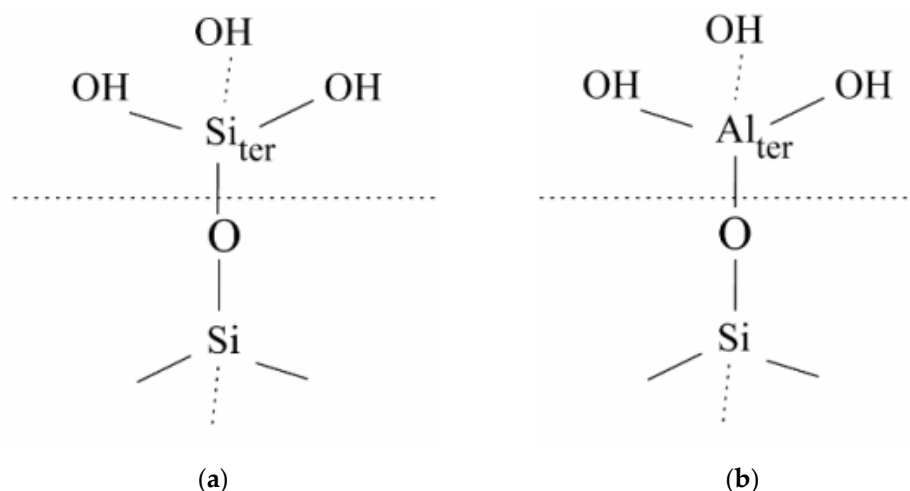


Figure 1. Schematic of hydroxylated aluminosilicate mineral surface showing (a) Si and (b) Al terminal.

In the presence of an acidic aqueous solution, the H^+ is easily captured by the terminal oxygen on the hydroxylated aluminosilicate mineral surface for the weak space steric effect. This study focuses on the reaction pathway for hydrolyzing $Si_{ter}-O-Si$ and $Al_{ter}-O-Si$, and the effect of the proton on the breakage of $Si_{ter}-O$ and $Al_{ter}-O$ bonds. The reaction rate constants were calculated by the Arrhenius equation via the barrier height computed by data in the output file. Before the investigation of the barrier height for the $Si_{ter}-O-Si$ and $Al_{ter}-O-Si$ surface sites, the effect of the configuration of transition state complexes containing four- and six-membered rings (Figure 2) on the activation energy is discussed.

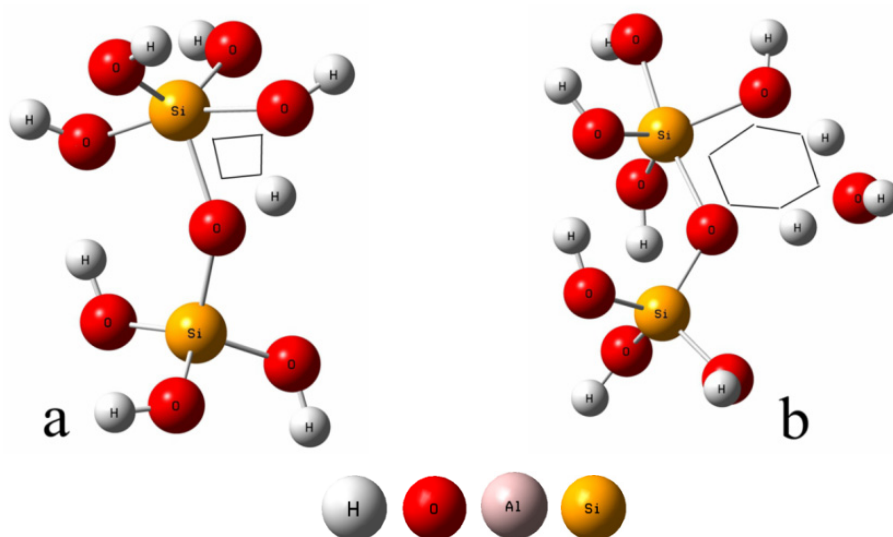


Figure 2. Transition state complexes of $Si_{ter}-O-Si$ reacting with H_2O containing (a) four-membered and (b) six-membered ring.

2. Materials and Methods

2.1. Reaction Models

The most important aspect of a reaction pathway is determining the transition state complex, which has no stability in time and has no real finite concentration, by definition. Recent descriptions of quartz and aluminosilicate mineral dissolution included different transition state complexes during the hydrolysis of $Al-O-Si$ and $Si-O-Si$ linkage on the mineral surface [17,18]. However, the configurations of the transition state complexes for the hydrolysis reaction of aluminosilicate are presented. The four-membered ring configuration contained an Si and O atom in the reaction center of $Si_{ter}-O$, and H and O from a water molecule (Figure 2a), whereas the addition of H and O from in the six-membered ring configuration (Figure 2b) came from another water molecule.

In the beginning of the hydrolysis reaction, the water molecule approached the reaction center and the coordination of Si and Al was changed from four to five. Then the $Si_{ter}-O$ and $Al_{ter}-O$ bonds lengthened and the coordination of Si_{ter} and Al_{ter} converted into four. Finally, the Si and Al species left away from the mineral surface and migrated to the liquid phase.

To model dissolution process for the surface reaction sites above, the following six reactions were studied. Equations (1) and (2) represent the $Si_{ter}-O-Si$ (Figure 3a) and $Al_{ter}-O-Si$ (Figure 3b) sites without protonated terminal oxygen, respectively. With the breakage of the $Si_{ter}-O$ or $Al_{ter}-O$ bond, the Si and Al species are extracted from the reaction sites as H_4SiO_4 and $[Al(OH)_4]^-$, respectively. Equations (3) and (4) represent the $Si_{ter}-O-Si$ (Figure 4a), and $Al_{ter}-O-Si$ (Figure 4b) sites with protonated terminal oxygen, respectively (Figure 3). After the hydrolysis reaction, the protonated monosilicic acid molecule releases from the $Si_{ter}-O-Si$, and the $[Al(OH)_3 \cdot H_2O]$ forms from the $Al_{ter}-O-Si$ site. The bridge

oxygen in the surface sites becomes the terminal oxygen after reaction. The charge of the molecular cluster in the Equations (1)–(4) is retained during calculation.

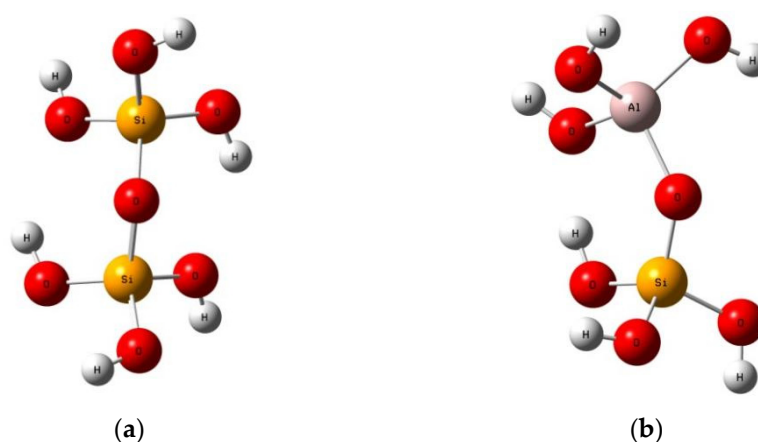
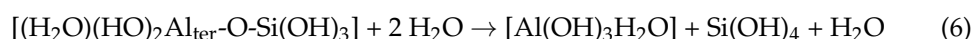
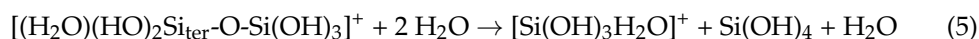
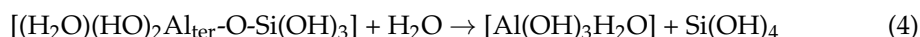
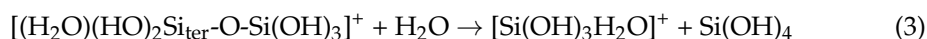
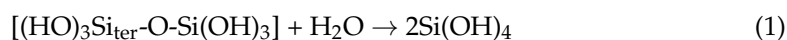


Figure 3. The molecular clusters of (a) $\text{Si}_{\text{ter}}-\text{O}-\text{Si}$ and (b) $\text{Al}_{\text{ter}}-\text{O}-\text{Si}$.

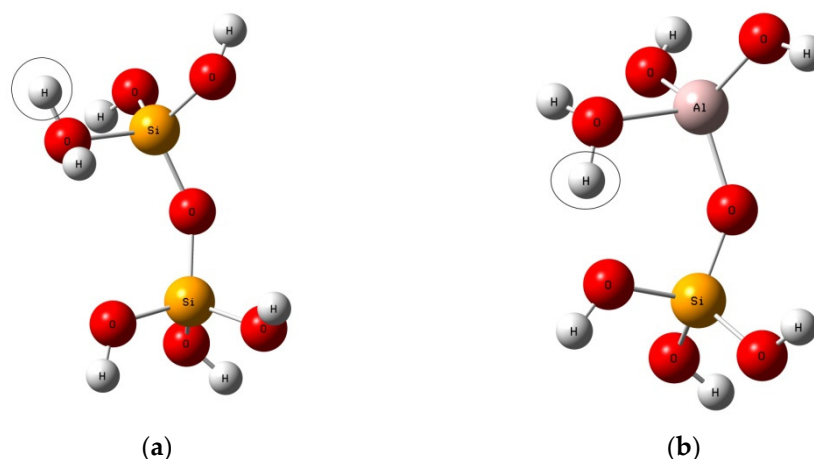


Figure 4. The terminal oxygen in (a) $\text{Si}_{\text{ter}}-\text{O}-\text{Si}$ and (b) $\text{Al}_{\text{ter}}-\text{O}-\text{Si}$ before and after protonation.

2.2. Reaction Rate

Once the reactant and transition state has been optimized in the gas-phase (1 atm, 298 K) for each reaction, the frequency in output files is used to calculate the rate constant via the Arrhenius equation:

$$k = Ae^{\frac{-\Delta E}{RT}}$$

where A is referred to as the pre-exponential factor, ΔE is the activation energy, R is the gas constant and T is the temperature in degrees Kelvin.

3. Computational Methods

Some articles have successfully applied the DFT method to explain the hydrolysis reaction of the silicate mineral surface [10,19–21]. Thus, the application of the M06-2X functional method [22] here to model the hydrolysis of aluminosilicate is reasonable. In the dissolution process, the coordination number of the Si atom and the Al atom with d orbitals and p orbitals is altered; the H atom is important and calculated. Thus, the 6-311+G(d,p) basis set is employed in this study. All calculations were performed on the reactants, products and transition state complexes given in Equations (1)–(6) with the Gaussian 09 package [23] without any constraints. The transition state was obtained by requiring that there was one and only one imaginary frequency for the configuration of the constructed cluster; otherwise, we readjusted or even redesigned the configuration to find the correct transition state configuration.

4. Results

The configurations of transition state complexes were firstly discussed. Then the hydrolysis mechanisms of $\text{Si}_{\text{ter}}\text{-O-Si}$ and $\text{Al}_{\text{ter}}\text{-O-Si}$ sites in an acidic condition were investigated.

4.1. The Configuration of Transition State

The hydrolysis process of $\text{Si}_{\text{ter}}\text{-O-Si}$ with H_2O is shown in Figures 5 and 6, distinguished by the configuration of transition state complexes (Table 1). When the $\text{Si}_{\text{ter}}\text{-O-Si}$ surface site reacted with a H_2O molecule (Figure 5), the transition state complex contained a four-membered ring. Along the reaction path, the H in the water molecule was absorbed by the bridge O and the rest of water molecule (OH) was captured by the Si_{ter} , while simultaneously, the $\text{Si}_{\text{ter}}\text{-O}$ bond fractured. The barrier height of this reaction (labelled as R_f) was 121.11 kJ/mol. When the $\text{Si}_{\text{ter}}\text{-O-Si}$ surface site reacted with two H_2O molecules (Figure 6), six-membered ring complexes of transition state formed. Along this reaction path, the H in the H_2O beside the bridge O side bonded with the bridge O and the OH in the other H_2O near the Si_{ter} was captured by the Si_{ter} . In addition, a new water molecule formed with the rest of H and OH from different H_2O molecules. The barrier height of this reaction (labelled as R_s) was 76.13 kJ/mol.

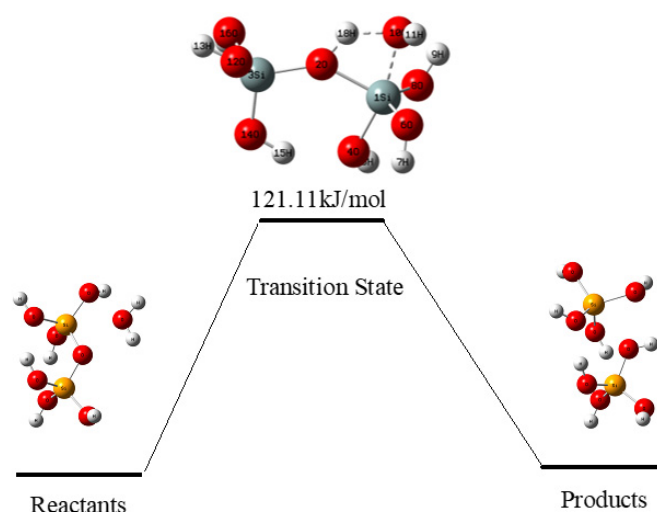


Figure 5. Reaction mechanism for the hydrolysis of the $\text{Si}_{\text{ter}}\text{-O-Si}$ site in the presence of a H_2O molecule. The transition state complex contains a four-membered ring (TS4).

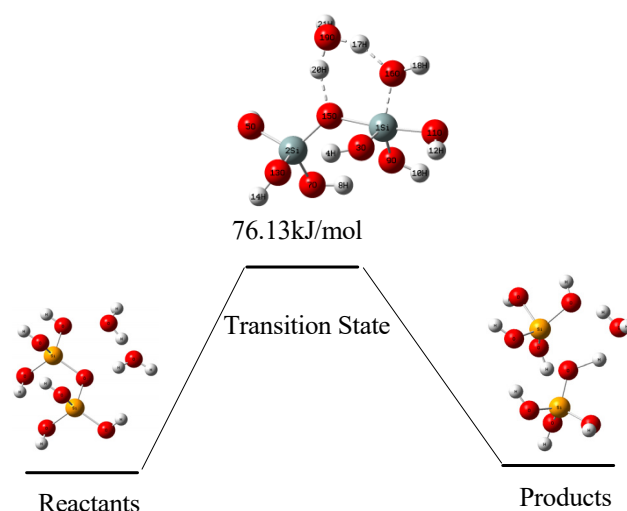


Figure 6. Reaction mechanism for the hydrolysis of the $\text{Si}_{\text{ter}}\text{-O-Si}$ site in the presence of two H_2O molecules. The transition state complex contains a six-membered ring (TS6).

Table 1. Selected geometry parameters of the transition state complex containing a four-membered ring (TS4) and a six-membered ring (TS6). Bond Lengths in Å, Bond Angles in Degrees.

Model	Si-O _{bri}	Si _{ter} -O _{bri}	O _{bri} -H	1Si-10O	1Si-16O	Si _{ter} -O _{bri} -Si
TS4	1.68016	1.80964	1.11736	1.84944	–	141.62679
TS6	1.62984	1.84868	1.49800	–	1.72330	127.61374

According to the Arrhenius equation, the rate constant of R_s was 7.60×10^7 times of the R_f . The addition of the H_2O insignificantly affects the activation energies. The lower activation energy and larger rate constant of R_f is possibly attributed to the weaker bond strength of $\text{Si}_{\text{ter}}\text{-O}$ in the reaction of the six-membered ring. Compared with the experimental data for the hydrolysis activation energy of quartz, only containing Si-O-Si site, which was 67–89 kJ/mol [24–26], the barrier height of six-membered ring transition state was reasonable. Thus, the six-membered ring configuration of the transition state was appropriate and is used in the following text.

4.2. Hydrolysis Reaction at $\text{Si}_{\text{ter}}\text{-O-Si}$ Site

The energy profiles of $\text{Si}_{\text{ter}}\text{-O-Si}$ with protonated terminal oxygen reacting with two H_2O molecules are shown in Figure 7 and Table 2. After the breakage of the $\text{Si}_{\text{ter}}\text{-O}$ bond on the mineral surface, the Si species was left as $[\text{Si}(\text{OH})_3(\text{H}_2\text{O})]$. The barrier height of the reaction decreased to 6.17 kJ/mol and was 91.90% lower than that for the $\text{Si}_{\text{ter}}\text{-O-Si}$ without protonation. The rate constant of this hydrolysis reaction was 1.81×10^{12} times of that of the $\text{Si}_{\text{ter}}\text{-O-Si}$ without protonated terminal oxygen. The proton significantly affected the electron cloud of the terminal oxygen and the bond strength of Si-O , resulting in the lower barrier height. This indicated that the proton facilitates the fracture of the $\text{Si}_{\text{ter}}\text{-O}$ bond on the mineral surface, corresponding to the experimental data that the dissolution rate of Si release from quartz and feldspar increased in the acidic condition [27,28].

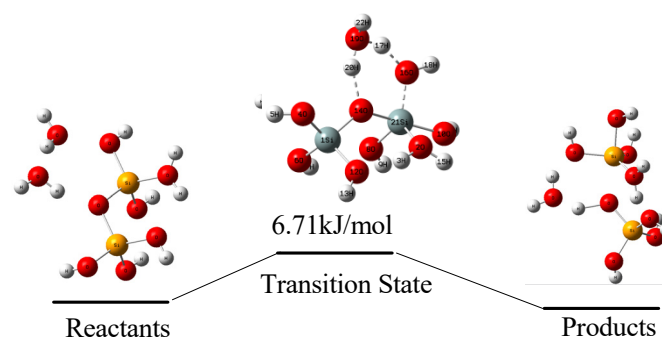


Figure 7. The reaction path of a protonated $\text{Si}_{\text{ter}}\text{-O-Si}$ site.

Table 2. Selected geometry parameters of the transition state of $\text{Si}_{\text{ter}}\text{-O-Si}$ with protonated terminal oxygen reacting with two H_2O molecules (TS6-1). Bond Lengths in Å, Bond Angles in Degrees.

Model	Si-O_{bri}	$\text{Si}_{\text{ter}}\text{-O}_{\text{bri}}$	$\text{O}_{\text{bri}}\text{-H}$	21Si-16O	$\text{Si}_{\text{ter}}\text{-O}_{\text{bri}}\text{-Si}$
TS6-1	1.65078	1.75820	1.52743	1.71474	129.06299

4.3. Hydrolysis Reaction at $\text{Al}_{\text{ter}}\text{-O-Si}$ Site

The energy profiles of hydrolysis reaction at $\text{Al}_{\text{ter}}\text{-O-Si}$ site are shown in Figure 8 and Table 3. The barrier height for the $\text{Al}_{\text{ter}}\text{-O-Si}$ without protonation was 22.23 kJ/mol. The results suggest that the $\text{Al}_{\text{ter}}\text{-O-Si}$ site was easier to hydrolyze than the $\text{Si}_{\text{ter}}\text{-O-Si}$ site. This may be attributed to the higher bond energy and symmetry of $\text{Si}_{\text{ter}}\text{-O-Si}$, which needed higher energy to break.

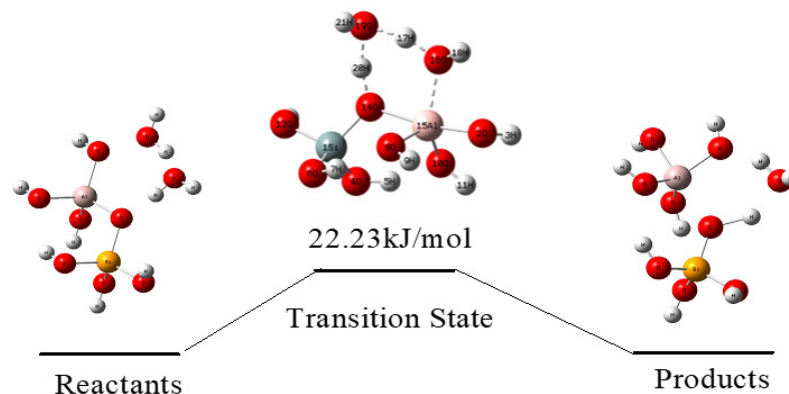


Figure 8. The reaction path of $\text{Al}_{\text{ter}}\text{-O-Si}$ site without protonated terminal oxygen.

Table 3. Selected geometry parameters of the transition state of $\text{Al}_{\text{ter}}\text{-O-Si}$ site (TS6-2) and $\text{Al}_{\text{ter}}\text{-O-Si}$ site with protonated terminal oxygen reacting (TS6-3) with two H_2O molecules. Bond Lengths in Å, Bond Angles in Degrees.

Model	Si-O_{bri}	$\text{Al}_{\text{ter}}\text{-O}_{\text{bri}}$	$\text{O}_{\text{bri}}\text{-H}$	$\text{Al}_{\text{ter}}\text{-16O}$	$\text{Al}_{\text{ter}}\text{-15O}$	$\text{Al}_{\text{ter}}\text{-O}_{\text{bri}}\text{-Si}$
TS6-2	1.64804	1.97997	1.16485	1.89625	–	120.14675
TS6-3	1.63210	1.94006	1.25021	–	1.83037	123.71870

Figure 9 and Table 3 show the energy profile and hydrolysis mechanism of $\text{Al}_{\text{ter}}\text{-O-Si}$ with protonated terminal oxygen. The barrier height was -0.86 kJ/mol. The negative activation energy suggested that the intermediate existed with a lower energy than the transition state [29]. The two reactants formed an intermediate with lower energy, due to the strong hydrogen bond before the transition state formed. These results led to the same conclusion, that the protonated site was easier to hydrolyze than the unprotonated site.

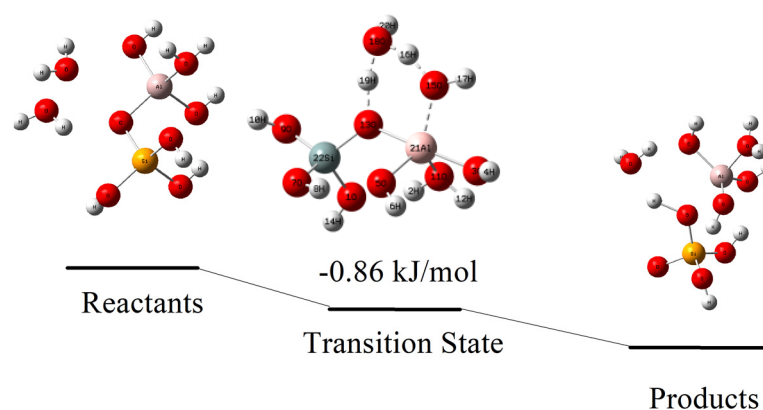


Figure 9. The reaction path of $\text{Al}_{\text{ter}}\text{-O-Si}$ site with protonated terminal oxygen.

Compared to barrier height for the hydrolysis of $\text{Si}_{\text{ter}}\text{-O-Si}$ clusters, the barrier height for the hydrolysis of $\text{Al}_{\text{ter}}\text{-O-Si}$ clusters was lower, due to the longer chemical bond of $\text{Al}_{\text{ter}}\text{-O}_{\text{bri}}$, and the chemical bond strength was weakened. This implies that the $\text{Al}_{\text{ter}}\text{-O-Si}$ site reacted more easily with H_2O , which indicates the hydrolysis reaction may take place preferentially at the $\text{Al}_{\text{ter}}\text{-O-Si}$ site on the aluminosilicate mineral.

5. Conclusions

The $\text{Si}_{\text{ter}}\text{-O-Si}$ and $\text{Al}_{\text{ter}}\text{-O-Si}$ clusters representative of aluminosilicate mineral surface were employed to study hydrolysis reactions in an acidic condition via density functional theory with the M06-2X+G(d,p) methodology. The transition state complex containing a six-membered ring for $\text{Si}_{\text{ter}}\text{-O-Si}$ linkage yielded barrier heights of 76.13 kJ/mol, which was lower than 121.11 kJ/mol for the complex containing a four-membered ring and was closer to the experimental data of 67–89 kJ/mol for the hydrolysis activation energy of quartz.

In the hydrolysis reaction, the calculated barrier heights of $\text{Si}_{\text{ter}}\text{-O-Si}$ and $\text{Al}_{\text{ter}}\text{-O-Si}$ clusters without protonated terminal oxygen molecule were 76.13 and 22.23 kJ/mol, respectively; the calculated barrier heights of $\text{Si}_{\text{ter}}\text{-O-Si}$, and $\text{Al}_{\text{ter}}\text{-O-Si}$ clusters with protonated terminal oxygen molecule were 6.71 and -0.86 kJ/mol, respectively. It was obvious that the barrier height decreased as the terminal oxygen was protonated and the hydrolysis activation energy of $\text{Al}_{\text{ter}}\text{-O}$ was lower than that of $\text{Si}_{\text{ter}}\text{-O}$ before and after protonation. The barrier height of the three surface sites was ranged as: $\text{Al}_{\text{ter}}\text{-O-Si} < \text{Si}_{\text{ter}}\text{-O-Si}$. With the fracture of the $\text{Si}_{\text{ter}}\text{-O}$ and $\text{Al}_{\text{ter}}\text{-O}$ bonds, the Si and Al were released from the aluminosilicate. These results confirm that the proton facilitates the release of Si and Al, and the dissolution of Al was easier than Si in the aluminosilicate mineral surface.

Author Contributions: Conceptualization, C.-Y.Z.; methodology, H.Y.; software, L.-M.W.; validation, Y.-L.Y.; formal analysis, M.-F.Z.; investigation, Y.-L.Y.; resources, H.Y. and W.X.; data curation, Y.-Y.W.; writing—original draft preparation, C.-Y.Z., S.-M.L.; writing—review and editing, Y.L., C.-Y.Z. and L.-M.W.; visualization, Z.-J.Z.; supervision, S.-M.L.; project administration, S.-M.L. and; funding acquisition, Y.-L.Y. and Z.-J.Z. 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. 21207027 and 51372090), the Science and Technology Planning Project of Guangdong Province (No. 2017B090921002), the Scientific Research Project of the Department of Education of Guangdong Province (2022KQNCX046) and the Science and Technology Planning Project of Chaozhou (2021ZC29).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: The innovative research team of advanced ceramic materials at Hanshan Normal University, the Chaozhou Branch of Chemistry and Chemical Engineering Guangdong Laboratory and the Guangdong Chaoshan Institute of Higher Education and Technology are all acknowledged.

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

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