Density Functional Theory Study of Water Molecule Adsorption on the \( \alpha \)-Quartz (001) Surface with and without the Presence of \( \text{Na}^+ \), \( \text{Mg}^{2+} \), and \( \text{Ca}^{2+} \)

Chunfu Liu, Fanfei Min, Lingyun Liu, and Jun Chen

School of Materials Science and Engineering, Anhui University of Science and Technology, Huainan 232001, China

Supporting Information

ABSTRACT: Adsorption of the single water molecule on the \( \alpha \)-quartz (001) surface with and without the presence of \( \text{Na}^+ \), \( \text{Mg}^{2+} \) and \( \text{Ca}^{2+} \) was analyzed utilizing the density functional theory method. Our results demonstrate that the optimal adsorption configuration of the single water molecule on the \( \alpha \)-quartz (001) surface lies in the bridge being configured with two formed hydrogen bonds. These were Os–\( \text{Hw} \) and Hs–\( \text{Ow} \) (s and w represent, respectively, surface and water molecules), while the main hydrogen bond is Hw–Os. Furthermore, the corresponding adsorption energy was \( \sim -72.60 \text{ kJ/mol} \). In this study, the presence of metal ions helped to deflect the spatial position of the water molecule, and the distance between \( \text{Ow} \) and Hs was altered significantly. Furthermore, the charge transfer between the interacting atoms increased in the presence of metal ions, wherein the effects of \( \text{Ca}^{2+} \) and \( \text{Na}^+ \) proved to be significant compared to \( \text{Mg}^{2+} \). Finally, it emerged that metal ions interacted with the water molecule and were subsequently adsorbed on the \( \alpha \)-quartz (001) surface. This occurred due to the electrostatic attraction, consequently impacting the hydration characteristics of the quartz surface.

INTRODUCTION

Water molecules are adsorbed on the hydrophilic mineral’s surface (e.g., quartz and clay minerals) and arranged in a certain order which is referred to as mineral hydration. This process plays an important role in colloidal chemistry, wastewater treatment, and mineral processing. For instance, with highly muddied coal slurry containing a large amount of hydrophilic quartz and clay mineral particles, slurry’s sedimentation and dewatering becomes more difficult owing to mineral hydration. The reason for this is the strong hydration repulsion and stereohindrance effect being produced and making the dispersion system stable. For this reason, the mineral surface hydration characteristics have emerged as the critical aspect of solving problems dealing with how to treat coal slurry.

Mineral hydration in aqueous solution has been extensively studied using SFA, X-ray diffraction, transmission electron microscopy, NMR, atomic force microscopy (AFM), and other experimental methods. Referring to the hydration model, Manciu et al. proposed a polarization strategy, wherein an “ice-like” hydration layer structure appeared on the quartz surface in aqueous solution. The mineral’s hydration layer is characterized by its elasticity and strength, and the water molecules in this region have larger density and viscosity when compared to bulk water. The thickness of the hydration layer on the silica surface was measured using two methods, namely, viscosity and AFM.

It was reported that the hydration layer thickness of the clay mineral varied in the \( \sim 0–50 \text{ nm} \) range. Density functional theory (DFT) is an effective theoretical tool for calculating the mineral structure and its surface adsorption, and the first-principles calculation method based on DFT can analyze the interaction mechanism of the mineral surfactant and mineral water at the molecular/atomic level. For example, Liu et al. reported that the hydration layer of a mineral can prevent direct adsorption of ether amine, dodecylamine ethoxylate (AC1201) ether and DDA on the mineral surface. Peng et al. have employed the periodic DFT method to document the adsorption mechanism of water on sodium-montmorillonite (001) basal and (010) edge surfaces. The atomic structure, preferred adsorption sites, adsorption energies, and vibrational frequencies for water adsorption on the \( \alpha \)-quartz (101) surface have been investigated by Bandura et al. They noted that the structure of water adsorption on the \( \alpha \)-quartz (101) surface was defined by the comprehensive effect of the interactions involving water–water, water–silanol, and silanol-silanol hydrogen bonds. The hydroxylated surfaces were stabilized by weak hydrogen bonds that were evident between the silanol groups and surface-bridging oxygens.

Received: May 28, 2019
Accepted: July 12, 2019
Published: July 26, 2019
Generally, metal ions are commonly found in flotation pulp and coal slurry. With that, the activation mechanism of quartz by Ca(II) was revealed in the atomic level using the DFT method. It was reported that the Ca(OH)+ ions can repulse the hydration shell and consequently adsorb on the quartz surface; the Ca(OH)+ ion acts as a bridge between the α-quartz (001) surface and α-Bromolauric acid (CH₃(CH₂)₉CHBrCOOH, a-BLA). Despite the fact that water molecules’ adsorption on the minerals’ surface is generally understood, the effects of various metallic ions (e.g., Na⁺, Mg²⁺, Ca²⁺, etc.) on the quartz surface remain largely unexplored. This requires further investigation and consequently, in this paper, we have undertaken a systematic theoretical study on the adsorption characteristics of a single water molecule on the α-quartz (001) surface with and without the presence of Na⁺, Mg²⁺, and Ca²⁺. It has been done employing the periodic DFT method. The frontier orbital analysis, adsorption configurations, adsorption energies, Mulliken atomic charges, the partial densities of states (PDOSs), and the electron transfer are presented and discussed in this research study.

RESULTS AND DISCUSSION

Frontier Orbital Analysis. The frontier orbital theory asserts that the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the most reactive. In Table 1 mentioned below, the orbital energy and HOMO–LUMO gap (ΔE, calculated by eq 1) of the reactants are summarized.

\[
\begin{align*}
\Delta E_1 &= |E_{\text{HOMO}}^{\text{H}_{2}\text{O}} - E_{\text{LUMO}}^{\alpha\text{-quartz}(001)}| \\
\Delta E_2 &= |E_{\text{HOMO}}^{\alpha\text{-quartz}(001)} - E_{\text{LUMO}}^{\text{H}_{2}\text{O}}| \\
\end{align*}
\]

where \(E_{\text{HOMO}}^{\text{H}_{2}\text{O}}\) and \(E_{\text{LUMO}}^{\text{H}_{2}\text{O}}\) represent the orbital energy of the water molecule. Similarly, \(E_{\text{HOMO}}^{\alpha\text{-quartz}(001)}\) and \(E_{\text{LUMO}}^{\alpha\text{-quartz}(001)}\) are the orbital energy of the α-quartz surface.

According to the frontier orbital theory, the smaller the ΔE is, the stronger is the interaction. \(\Delta E_1 < \Delta E_2\) indicates that the electrons of the HOMO orbital of the water molecule were transferred to the empty LUMO orbital of the α-quartz (001) surface. It can therefore be predicted that the adsorption of the water molecule on the quartz surface is due to the interaction between the hydrogen atoms of the water molecule and the oxygen atoms of the α-quartz (001) surface. The frontier orbital properties of the water molecule and the α-quartz (001) surface are shown in Figure 1a,b, respectively. It is evident that the HOMO orbital of the water molecule appears on the oxygen atom, while the LUMO orbital of the α-quartz (001) appears on both hydrogen and oxygen atoms located on the surface.

Table 1. Frontier Orbital Energy and HOMO–LUMO Gap (ΔE) between the Water Molecule and α-Quartz (001) Surface

| Frontier orbital energy/a.u | HOMO  | LUMO  | ΔE₁    | ΔE₂ |
|-----------------------------|-------|-------|--------|-----|
| H₂O                         | -0.238205 | -0.010765 | 0.16575 | 0.27248 |
| α-quartz (001)              | -0.28325   | -0.07246     |         |      |

Adsorption Energies and Configuration. Using the following formula below, the adsorption energies (\(E_{\text{ads}}\)) of the water molecule on the α-quartz (001) surface were calculated

\[
E_{\text{ads}} = E_T - (E_Q - E_W)
\]

where \(E_T\) is the total energy of the water and the α-quartz (001) surface. \(E_W\) is the energy of an isolated water molecule. \(E_Q\) is the energy of the α-quartz (001) surface.

The adsorption energies (\(E_{\text{ads}}\)) of the water molecule on the α-quartz (001) surface at different initial positions were calculated using eq 2 and plotted as a function of different positions as illustrated in Figure 3. It can be seen that the \(E_{\text{ads}}\) of the water molecule on the α-quartz (001) surface range from -16.46 to -72.60 kJ/mol; a similar amount of adsorption...
energy \((-75.8\ kJ/mol)\) was documented by de Leeuw et al.\(^{43}\) The strong interaction between the water molecule and the quartz surface is indicated here.

The optimal adsorption configuration of the single water molecule on the quartz surface is illustrated in Figure 4. In this present study, the interacted atoms of the water molecule and quartz surface were Hw, Ow, and Hs, Os, respectively. It was observed that the water molecule was vertically adsorbed on the \(\alpha\)-quartz (001) surface. The optimal adsorption site (i.e., the hydrogen atom, Hw and oxygen atom, Ow of the water molecule interacting with the adjacent oxygen atom, Os and hydrogen atom, and Hs on the nearby quartz surface, respectively) of the water molecule on the \(\alpha\)-quartz (001) surface was found at initial position B 6.

**Charge Analysis.** The electron density difference and Mulliken charge populations were investigated to discover the adsorption mechanism of the single water molecule on the \(\alpha\)-quartz (001) surface. Figure 5 depicts the electron density difference of the adsorption system of the water molecule on the \(\alpha\)-quartz (001) surface. In the plot of electron density difference, the blue and yellow regions between two atoms represented the accumulation and depletion of electrons, respectively. It appears that a significant charge was transferred between the water molecule and adjacent atoms of the \(\alpha\)-quartz (001) surface. The electrons were transferred from the hydrogen atoms of the water molecule to the \(\alpha\)-quartz (001) surface.

The Mulliken charge analysis was conducted on the atoms directly involved in the adsorption of the water molecule on the \(\alpha\)-quartz (001) surface, and results are summarized in Table 2. From Table 2, it can be observed that the 1s state of the hydrogen atom (Hw) of the water molecule lost 0.03\(e\) while interacting with the oxygen atoms (Os) on the \(\alpha\)-quartz (001) surface. In contrast, the hydrogen atom (Hs) of the \(\alpha\)-quartz (001) surface lost 0.04\(e\) during the interaction with oxygen atoms (Ow) of the water molecule. Meanwhile, the oxygen atom (Os) of the \(\alpha\)-quartz (001) surface and the oxygen atom (Ow) of the water molecule obtained the corresponding electrons. Based on this observation, it can be concluded that the hydrogen bond is responsible for adsorbing the water molecule on the \(\alpha\)-quartz (001) surface.

**Partial Density of States Analysis.** Figures 6 and 7 illustrate the PDOS of the interaction atoms between the water molecule and the \(\alpha\)-quartz (001) surface in the optimal equilibrium configuration. The zero point denoted Fermi level \(E_F\). It can be seen in Figure 6 that the energy of Os 2p has a negative shifting tendency during the water molecule adsorption process. Bonding effects were evident in the region of \(-10 \leq \text{energy/eV} \leq -5\) (Figure 6) and \(-8 \leq \text{energy/eV} \leq -5\) (Figure 7) for Hw 1s and Os 2p, and Hs 1s and OW 2p, respectively. Hence, the existence of the hydrogen bond (Ow–Hs) and (Os–Hw) between the water molecule and the –OH group of the \(\alpha\)-quartz (001) surface was observed (see the insets of Figures 6 and 7). The peak intensity ratio of Hw 1s (Figure 6) was found to be larger when compared to the Hs 1s at \(-6.4\ eV\), which indicates that the Os–Hw hydrogen bond was stronger.

![Figure 3](image1.png) **Figure 3.** Adsorption energies of the single water molecule on the \(\alpha\)-quartz (001) surface at different initial positions.

![Figure 4](image2.png) **Figure 4.** Spatial position diagram of the optimal equilibrium configurations of the single water molecule on the \(\alpha\)-quartz (001) surface; (a) top view; (b) side view.

![Figure 5](image3.png) **Figure 5.** Electron density difference of the optimal equilibrium configurations of single water adsorbed on the \(\alpha\)-quartz (001) surface; (a) top view; (b) side view. The isosurface value is 0.02 electrons/Å\(^3\).

| atomic location | atomic number | adsorption states | s | p | charge/e |
|-----------------|---------------|-------------------|---|---|---------|
| H\(_2\)O        | Hw            | Before            | 0.48 | 0 | 0.52    |
|                 | After          |                   | 0.51 | 0 | 0.49    |
|                 | Ow             | Before            | 1.89 | 5.16 | -1.05   |
|                 | After          |                   | 1.86 | 5.16 | -1.01   |
| \(\alpha\)-quartz (001) | Hs        | Before            | 0.48 | 0 | 0.52    |
|                 | After          |                   | 0.52 | 0 | 0.48    |
|                 | Os             | Before            | 1.85 | 5.24 | -1.09   |
|                 | After          |                   | 1.84 | 5.23 | -1.07   |

**Table 2.** Mulliken Charge Populations of Interacted Atoms before and after Adsorption
Figure 6. PDOS of the interacted atoms (Hw−Os) between water and the α-quartz (001) surface in the optimum adsorption configuration.

Figure 7. PDOS of the interacted atoms (Hs−Ow) between water and the α-quartz (001) surface in the optimum adsorption configuration.

Figure 8. Initial adsorption position (a), adsorption equilibrium position (b), and electron density difference (c) of water molecule adsorption on the α-quartz (001) surface in the presence of Na⁺, Mg²⁺, and Ca²⁺ (the isosurface value is 0.02 electrons/Å³).
Table 3. Mulliken Charge Population of the Atoms in the Presence of Metal Ions

| adsorption system | atomic number | adsorption state | Na⁺ | Mg²⁺ | Ca²⁺ |
|------------------|---------------|-----------------|-----|------|------|
|                  |               |                 | Mulliken charge population | Mulliken charge population | Mulliken charge population |
|                  |               |                 | s   | p   | charge/e | s   | p   | d   | charge/e |
| H₂O              | Hw            | before          | 0.46 | 0   | 0.54     | 0.46 | 0   | 0.54 |
|                  |               | after           | 0.56 | 0   | 0.44     | 0.55 | 0   | 0.45 |
|                  | Ow            | before          | 1.86 | 5.16 | −1.01    | 1.86 | 5.16 | −1.01 |
|                  |               | after           | 1.86 | 5.10 | −0.96    | 1.87 | 5.11 | −0.98 |
| α-quartz (001)   | Hs            | before          | 0.52 | 0   | 0.48     | 0.52 | 0   | 0.48 |
|                  |               | after           | 0.56 | 0   | 0.44     | 0.53 | 0   | 0.47 |
|                  | Os            | before          | 1.84 | 5.23 | −1.07    | 1.84 | 5.23 | −1.07 |
|                  |               | after           | 1.83 | 5.22 | −1.05    | 1.83 | 5.22 | −1.05 |
| M²⁺/M⁴⁺         | M             | before          | 3.00 | 6.00 | 0        | 2.00 | 6.00 | 0   |
|                  |               | after           | 2.60 | 6.00 | 0.40     | 1.72 | 6.08 | 0.20 |

Eₘₑₜ (kJ/mol) −172.56 −131.32 −173.36

**Effect of Na⁺, Mg²⁺, and Ca²⁺ on the Charge Transfer and Adsorption Configurations.** Based on the optimal adsorption configuration of the individual water molecule on the α-quartz (001) surface, metal ions were added to the system. The objective here was to investigate the effects of metal ions on the hydration of quartz. It is noted that the simulation parameters were chosen based on the results of water molecule adsorption on the quartz surface. The electron density difference of the water molecule and α-quartz (001) adsorption systems in the presence of different metal ions, namely, Na⁺, Mg²⁺, and Ca²⁺ are shown in Figure 8.

It can be seen in Figure 8 that the charge transfers and spatial position between the interacted atoms of the water molecule and quartz surface changed in the presence of metal ions. Although no significant electron accumulation or depletion between the Na⁺ and the adjacent atoms occurred, what did occur was the phenomenon of electron transfer between Mg²⁺, Ca²⁺, and oxygen atom of the water molecule. This happened due to the electrostatic interactions. It is worth noting that the distance (1.598 Å) between Ow and Hs (shown in Figure 4) has been significantly increased (~8.39 to 77.78%) in the presence of metal ions, namely, 1.732 Å (Mg²⁺), 1.734 Å (Na⁺), and 2.841 Å (Ca²⁺). In contrast, the distance (1.688 Å) between Hw and Os slightly decreased in the presence of metal ions, specifically 1.629 Å (Na⁺), 1.674 Å (Mg²⁺), and 2.504 Å (Ca²⁺). This changed to 2.504 Å when Ca²⁺ was present.

The spatial position of the water molecule appeared to be deflected. The adsorption energies in the presence of Na⁺, Mg²⁺ and Ca²⁺ became, respectively, −172.56, −131.32, and −173.36 kJ/mol. From this it can be stated conclusively that in the presence of Na⁺ and Ca²⁺, the adsorption system become more stable, and furthermore the interaction of the water molecule with the surface proved to be stronger. This in turn promoted hydration of the quartz surface and demonstrated that the influence of Mg²⁺ is weaker than that of Na⁺ and Ca²⁺.

In the presence of metal ions, the Mulliken charge population of the atoms in the adsorption system is shown in Table 3. The analysis shows that the Hs 1s state interacts with the Ow and lost (0.00−0.04) electron, while the Hw 1s state lost (0.07−0.10) electrons when metal ions were present. In contrast, the Mulliken charge population of the Os revealed no significant changes before and after the adsorption of the water molecule. The water molecule obtained a few electrons, and the Ow 2p state gained (0.01−0.05) electrons. In the presence of metal ions, the charge transfers (0.04−0.07e) between interacted atoms in the adsorption system were found to be larger than that (0.00−0.40e) without metal ions. The electrons were transferred from the water molecule to the α-quartz (001) surface, causing the quartz surface to become negatively charged. The positively charged metal ions and negatively charged quartz surfaces were adsorbed and this was explained by the electrostatic attraction. The adsorption of metal ions on the surface of the quartz enhanced the interaction between the water molecule and the surface, while the adsorbed metal ions connected the water molecule and surface. Subsequently, these actions promoted hydration of the quartz surface.

**CONCLUSIONS**

This study investigated the effects of metal ions, specifically Na⁺, Mg²⁺, and Ca²⁺ on the adsorption of the single water molecule on the α-quartz (001) surface. To do this, the DFT method was employed. The main findings of the present study are summarized below:

1. The DFT calculation results show that the adsorption energies of the single water molecule on different initial positions of the α-quartz (001) surface ranged from −72.60 to −16.46 kJ/mol, and the corresponding adsorption energy of the optimal adsorption configuration was −72.60 kJ/mol. The water molecule spontaneously formed two hydrogen bonds (i.e., Hw–Os and Hs–Ow) with the surface to adsorb on the α-quartz (001) surface.

2. In the presence of metal ions, the spatial position of the water molecule is deflected, revealing a tendency to move away from Hs and closer to Ow. The Ow–Hs lengths change from 1.598 to 1.734, 1.732, and 2.841 Å in the presence of Na⁺, Mg²⁺, and Ca²⁺, respectively. Meanwhile, the Hw–Os lengths (1.688 Å) change to 1.629, 1.674, and 2.504 Å. The main hydrogen bonding effect is Hw–Os. It appeared that the adsorption systems became stronger in the presence of Na⁺ and Ca²⁺, while a relatively weak promotion comes from Mg²⁺.

3. The surface hydration mechanism of the α-quartz (001) surface occurs mainly through the adjacent water molecules which are adsorbed on the quartz surface by forming hydrogen bonds. Metal ions interact with the quartz surface via electrostatic interaction, subsequently influencing the adsorption of the water molecule and surface hydration characteristics.
COMPUTATIONAL METHODS

Models. In quartz, the silica tetrahedra are bonded in the three-dimensional framework. Each tetrahedron is bonded to four other tetrahedra (with an oxygen atom shared at every corner of each tetrahedron). The geometric optimization of the quartz primitive cell was conducted and the results are summarized in Table 4. Compared with the previous simulations44,45 and experimental46 results, the $\alpha$-quartz lattice parameters obtained in this simulation are comparable to the experimental values.

Unlike many brittle crystals, $\alpha$-quartz does not possess perfect crystallographic planes of cleavage, and the (001) surface emerges as the most stable surface as predicted by both interatomic potential48 and DFT methods.43 While the fresh $\alpha$-quartz (001) surface is easily hydroxylated in aqueous solution, the top and side views of the hydroxylated $\alpha$-quartz (001) surface are shown in Figure 9a,b, respectively. The periodic supercell ($2 \times 2 \times 1$) was used with a vacuum thickness of 10 Å to avoid the interaction between the adjacent levels.

Computational Details. DFT calculations were implemented in the CASTEP program (Materials Studio version 8.0 software, Accerly Corporation).49 Electron exchange and correlation were described using the Perdew–Burke–Ernzerhof (PBE) function of the generalized gradient approximation (GGA).50 The interaction between valence electrons and the ionic core was described by the ultrasoft pseudopotential,51 and the valence electron configurations considered in this study were H 1s$^1$, O 2s$^2$2p$^4$, Na 2s$^2$2p$^6$3s$^1$, Mg 2s$^2$2p$^6$3s$^2$, and Ca 3s$^2$3p$^6$4s$^2$.

The Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm52 helped to optimize the atomic positions. The Tkatchenko–Scheffler van der Waals correction method 53 was employed to correct density functional calculations for the missing van der Waals interactions. With computation accuracy and efficiency being taken into account, the kinetic energy cut-off for the plane wave basis was set to 400 eV, and the symmetrized Brillouin zone was obtained with a $2 \times 2 \times 1$ Monkhorst–Pack grid according to a series of convergence tests (see Figure S1 in the Supporting Information). Regarding other calculations, the tolerances of energy, force, stress, and displacement were $1.0 \times 10^{-5}$ eV/atom, 0.05 eV/Å, 0.05 GPa, and 0.001 Å, respectively.

Finally, the Dmol3 module was employed to calculate the frontier orbital of water and quartz. In other words, after optimization in CASTEP, the frontier orbital energy could be obtained by calculating the optimized unit cell with single-point energy and Gamma point (K-point) in DMol3. The parameters selected were shown as follows: exchange correlation function GGA-PBE, effective core potential and DNP basis set, fine precision, and convergence standard of the self-consistent field $1.0 \times 10^{-6}$ eV/atom.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b01570.

Batch convergence tests of bulk $\alpha$-quartz to obtain the reasonable cut-off energy and K-point (PDF)

AUTHOR INFORMATION

Corresponding Author
*E-mail: ffmin@aust.edu.cn.

ORCID
Chunfu Liu: 0000-0003-1506-4712
Fanfei Min: 0000-0001-9161-745X
Lingyun Liu: 0000-0002-8676-097X

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The financial support for this work was provided by the National Natural Science Foundation of China under grant no. 51874011 and the National Natural Science Foundation of China under grant no. 51804009. Both sources are gratefully acknowledged for their contribution to this study.

Table 4. Comparison between the Experimental and Computational Lattice Parameters of Optimized Bulk $\alpha$-Quartz

| computational parameters | $a$/Å | $b$/Å | $c$/Å | $\alpha$/(deg) | $\beta$/(deg) | $\gamma$/(deg) | references |
|--------------------------|-------|-------|-------|----------------|--------------|--------------|------------|
| GGA/700 eV               | 5.05  | 5.05  | 5.54  | 90             | 90           | 120          | 44         |
| GGA/1000 eV              | 5.09  | 5.09  | 5.58  | 90             | 90           | 120          | 47         |
| experimental values     |       |       |       |                |              |              | 46         |
| GGA/400 eV               | 4.93  | 4.93  | 5.44  | 90             | 90           | 120          | this work  |
(44) Goumans, T. P. M.; Wander, A.; Brown, W. A.; Catlow, C. R. A. Structure and stability of the (001) alpha-quartz surface. Phys. Chem. Chem. Phys. 2007, 9, 2146−2152.

(45) Plessow, P. N.; Sánchez-Carrera, R. S.; Li, L.; Rieger, M.; Sauer, S.; Schaefer, A.; Abild-Pedersen, F. Modeling the Interface of Platinum and alpha-Quartz(001): Implications for Sintering. J. Phys. Chem. C 2016, 120, 10340−10350.

(46) Levien, L.; Prewitt, C. T.; Weidner, D. J. Structure and Elastic Properties of Quartz at Pressure. Am. Mineral. 1980, 65, 920−930.

(47) Plessow, P. N.; Sánchez-Carrera, R. S.; Li, L.; Rieger, M.; Sauer, S.; Schaefer, A.; Abild-Pedersen, F. Modeling the Interface of Platinum and α-Quartz (001): Implications for Sintering. J. Phys. Chem. C 2016, 120, 10340−10350.

(48) Rignanese, G.-M.; De Vita, A.; Charlier, J.-C.; Gonze, X.; Car, R. First-principles molecular-dynamics study of the (0001) alpha-quartz surface. Phys. Rev. B 2000, 61, 13250−13255.

(49) Segall, M. D.; Lindan, P. J. D.; Probert, M. J.; Pickard, C. J.; Hasnip, P. J.; Clark, S. J.; Payne, M. C. First-principles simulation: ideas, illustrations and the CASTEP code. J. Phys.: Condens. Matter 2002, 14, 2717−2744.

(50) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. Phys. Rev. Lett. 1996, 77, 3865−3868.

(51) Vanderbilt, D. Soft self-consistent pseudopotentials in a generalized eigenvalue formalism. Phys. Rev. B: Condens. Matter Mater. Phys. 1990, 41, 7892−7895.

(52) Liu, D. C.; Nocedal, J. On the Limited Memory Bfgs Method for Large-Scale Optimization. Math. Program. 1989, 45, 503−528.

(53) Bućko, T.; Lebegue, S.; Hafner, J.; Angyan, J. G. Tkatchenko-Scheffler van der Waals correction method with and without self-consistent screening applied to solids. Phys. Rev. B: Condens. Matter Mater. Phys. 2013, 87, 064110.