Studies on the reaction pathway of arsenate adsorption at water–TiO₂ interfaces using density functional theory

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ABSTRACT

Reaction pathway information of transition states and intermediate species is crucial for understanding the adsorption mechanism of pollutants at mineral–water interfaces. However, it has been difficult to obtain such information using existing experiments. Here, the activation barriers, transition states, intermediate species and surface complexes of arsenate adsorption on TiO₂ surfaces were studied using DFT-based reaction pathway calculations. The results indicated that the bidentate binuclear (BB) adsorption structure was formed through a monodentate mononuclear (MM) metastable–equilibrium adsorption (MEA) state. A two-step adsorption mechanism was proposed on the basis of the detailed picture of bond breaking and bond formation during each reaction step. When the adjacent surface sites were occupied, the transform from MM mode to BB mode was greatly inhibited so that both MM and BB coexisted in the equilibrium adsorption sample. The BB complex was energetically more stable than the MM complex, and so, the adsorption irreversibility was fundamentally related to the ratio BB:MM in the final equilibrium state. This mechanism may also explain the initial concentration effect, where, for the given adsorption experiment of arsenate on TiO₂ under the same thermodynamic conditions, both equilibrium constants and the BB:MM ratio in equilibrium adsorption samples changed with the reaction kinetics.

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1. Introduction

Electronic structure methods such as density functional theory (DFT) were widely used to calculate the adsorption structures of oxyanions on mineral surfaces [1–4]. However, the details of the formation of the surface complexes are little discussed. Because the adsorbate molecules may be generally ended on the surfaces in various adsorption modes [5–8], it is necessary to identify the interrelation of different adsorption structures to enhance our understanding of the adsorption of ions at mineral–water interfaces. Reaction pathway information containing transition states and intermediate species can provide a detailed picture of bond breaking and bond formation during each reaction step. Yet, measuring it precisely through experiments is challenging. First-principle DFT calculations have been used to study the surface reaction processes of gas, water, or organic small molecules [9–12]. To our knowledge, the reaction pathway calculation for the adsorption of oxyanions on mineral surfaces is very limited. The difficulty may be due to the complexity of the potential energy surface (PES) and the high computational cost in search of the transition states for heavy-atom-containing oxyanions (such as the arsenic atom in arsenate) adsorption on metal-(hydr)oxides [13].

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Arsenate dominates the aqueous speciation of arsenic at oxidizing conditions, which is of worldwide serious concern [14,15]. The adsorption processes at solid–water interfaces are believed to govern the toxicity and transport of arsenic in the environment [3,16]. Thus, the reaction pathway calculations have significant advantages in the understanding of arsenic geochemical cycling in natural waters, sediments, and soils. In a related study [8], a clear initial concentration (C₀) effect (i.e., equilibrium adsorption constants change with the reaction kinetics) was observed in As(V)–TiO₂ system by multi-batch adsorption experiments. The initial concentration effect indicated that reactant concentration or reaction kinetics can fundamentally alter real equilibrium adsorption constant by affecting the final metastable–equilibrium adsorption (MEA) states [8,17]. Experimentally measured equilibrium adsorption constants, therefore, bear the property of inconstancy in nature. Although it is now possible to measure the microscopic adsorption structures from samples using spectroscopic methods such as X-ray absorption fine structure (XAFS) [15,18–20], it is extremely difficult to experimentally catch up the reaction pathways and activation barriers for the ion adsorption at mineral–water interfaces. Moreover, little is known about the interrelation of different MEA states.

Here, we identified the dominant surface complexes of arsenate on TiO₂ surfaces using DFT calculations combined with EXAFS measurement. TiO₂ was chosen as the adsorbent because it is a widely used material in many interface-related studies [21,22]

including the treatment for arsenic pollution [15,23]. Activation barriers, transition states, MEA states of the minimum energy reaction pathway, and the correlation between different adsorption states were studied using the DFT-based reaction pathway calculations. The reaction pathway results also provided a dynamic interpretation of the initial concentration effect.

2. Methods and theory

The geometry and energy of MEA states and transition states were computed using gradient-corrected density functional theory with the Becke three-parameter nonlocal exchange functional [24] and the Lee–Yang–Parr correlation functional [25] (i.e., B3LYP). This approach has been widely used to study the adsorption of oxyanions on transition metal oxides [2,8,26,27]. Low spin and unrestricted formula using a fully optimized calculation strategy were employed to optimize the MEA states and search the reaction transition states, because the nature of stationary points on the potential energy surface (PES) needed to be identified by frequency analysis on the fully optimized structures. MEA states possess no imaginary frequency, while transition states possess only one. The geometry and energy were calculated using the 6-31+G(d) basis set for O and H; the 6-311+G(d) basis set for As; and the LANL2DZ relativistic effective core potential (RECP) basis set for Ti transition metal [28,29]. To eliminate boundary effects and reduce charge on the clusters, the dangling bonds of boundary O atoms were saturated with H atoms [2–4,28].

A Ti_4O_{18} cluster model was used to represent the (100) anatase surface in this study. The surfaces of anatase particles consist predominantly of (101), (100) and (001) crystal planes [30,31], with the specific expression of crystal planes (i.e., the crystal habit) depending on the synthesis technique [32,33]. The crystal planes and model cluster were also selected based on the good agreement of calculated As–O and As–Ti distances with our experimental EXAFS results.

There are two different oxygen sites on anatase surface, O(2) and O(3), which are bonded by two and three titanium atoms, respectively [33,34]. The 16 boundary oxygens in the Ti_4O_{18} model cluster were saturated with 24 H atoms to assure the coordination

numbers of O(2) and O(3) were the same as those of anatase surface structure. This method avoided the over-relaxation of model clusters [3,28] (discussed in the Supporting information). This cluster was verified to be reliable to describe the typical adsorption sites of arsenate [3,4] (discussed in the Supporting information).

According to the optimized geometries of the adsorbed intermediate species, reactant and product, the tentative geometry of transition state was prepared by gradually adjusting the cluster structures along the minimum energy path on the PES [35]. The initial guess structure is crucial to making the subsequent optimization of transition states be successfully converged. Then, the saddle point marking the transition state for each reaction step was located using the Newton–Raphson algorithm [36].

To improve the estimation of reaction energies, single-point energy calculations were subsequently performed on each optimized geometry using the 6-311++G(2df,p) basis set for O, H, and As and the LANL2DZ relativistic effective core potential (RECP) basis set for Ti atoms. The integral equation formalism polarized continuum model (IEFPCM) was used to consider the solvent effects [2,37]. The total free energies in solution for each optimized species were calculated at 298.15 K using Universal Force Field (UFF) atom radii. The DFT calculations were performed using Gaussian03 [36]. The detailed discussion on cluster charge and cluster size effects is described in the Supporting information.

3. Results and discussion

3.1. Surface adsorption complexes

Calculated structures for corner-sharing and edge-sharing arsenate with the TiO_2 surfaces are shown in Fig. 1. Comparison between DFT calculated and EXAFS measured structural parameters is presented in Table 1. The EXAFS results were taken from a related study [8]. The calculated As–O distances for the four surface complexes (1.70–1.71 Å) agreed well with the EXAFS analysis values (1.69 Å). The two experimentally measured As–Ti distances (3.20 ± 0.05 and 3.60 ± 0.02 Å) were close to the DFT calculated values of bidentate binuclear (3.26 Å) and monodentate mononuclear (3.50 Å) complexes (Table 1). The bidentate mononuclear (BM)

Fig. 1. Calculated Ti-AsO_4 surface complexes using density functional theory: (a) monodentate mononuclear (MM); (b) bidentate binuclear (BB); (c) bidentate mononuclear-A (BM-A); (d) bidentate mononuclear-B (BM-B). Purple, red, big gray, and small gray circles denote As, O, Ti, and H atoms, respectively. Distances are shown in angstroms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

Summary of DFT calculated and EXAFS measured structural parameters of arsenate adsorption on Ti(hydr)-oxides.

Calculated values	As–O		As–Ti	
	CN	<i>R</i> (Å)	CN	<i>R</i> (Å)
BB	4.0	1.70	2.0	3.26
MM	4.0	1.70	1.0	3.50
BM-A	4.0	1.71	2.0	2.75
BM-B	4.0	1.70	2.0	2.88

EXAFS values	As–O			As–Ti		
	CN	<i>R</i> (Å)	CN ₁	<i>R</i> ₁ (Å)	CN ₂	<i>R</i> ₂ (Å)
Adsorption samples	4.1	1.69	2.0 ± 0.4	3.20 ± 0.05	1.0 ± 0.4	3.60 ± 0.02

CN: coordination number; R: atomic distance. EXAFS results were taken from a related study [8], which was purposely designed for As(V)–TiO₂ system. Detailed description of the EXAFS data collection and analysis were presented in it.

edge-sharing modes would yield an As–Ti distance near 2.80 Å (Fig. 1), much smaller than the distance obtained from EXAFS analysis (Table 1). This phenomenon was also observed in the adsorption of arsenate on Fe-(hydr)oxides [3]. Therefore, the BM adsorption modes were excluded in the theoretical analysis and calculations we described below.

3.2. Surface reactivities

3.2.1. Reactivity of arsenate

H₂AsO₄[−] is one of the most important species of H_nAsO₄^{3−n} and dominates under weak acidic conditions (pK_{a1} = 2.2, pK_{a2} = 7.0) [3,38]. Frontier orbital analysis showed that the HOMO of H₂AsO₄[−] was mostly localized on the two unprotonated oxygen atoms (Fig. 2a). NBO population analysis indicated that the negative charge density of unprotonated oxygen atoms (−1.17) was higher than that of protonated oxygen atoms (−1.08) (Fig. 2b, twelve outer-sphere H₂O molecules were omitted for visual aid). These electronic structures of H₂AsO₄[−] showed that the two unprotonated oxygen atoms have much higher reactivity than the other two protonated oxygen atoms to bond with the positively charged metal centers of mineral surfaces and form the inner-sphere adsorption complex.

3.2.2. Reactivity of hydrated TiO₂ surfaces

Frontier orbital analysis showed that the LUMO of TiO₂ surfaces (pK_{a1} = 3.8, pK_{a2} = 7.8) [15] was mostly localized on the Ti atoms (Fig. 3a). Such electronic structures indicated that the Ti atoms were the surface reactive sites to bond with water molecules and form the surface functional groups (i.e., hydrated surfaces) in aqueous solutions [11,31,39]. For the hydrated TiO₂ surfaces, the

Fig. 2. (a) HOMO orbitals of H₂AsO₄[−] species; (b) NBO charge population of H₂AsO₄[−] species. Purple, red, and small gray circles denote As, O, and H atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

calculated surface Ti–O distances were 2.06 Å (Fig. 3b). NBO analysis showed that the hydrated surface structures were stabilized by the electron donation from O1 (O2) lone pair to σ_{Ti1–O3}^{*} (σ_{Ti2–O4}^{*}) antibond NBO. The stabilization energy was 16.04 kcal/mol, indicating that the hydration processes were thermodynamically favorable. The hydrated TiO₂ surfaces may subsequently dissociate to form hydroxyl groups through a deprotonation process at sufficiently high pH (Fig. 3c) [2,8].

3.2.3. Surface complexation mechanism

The chemical reactivity suggested that the inner-sphere arsenate complexation may occur via a ligand exchange of the unprotonated oxygen atoms on arsenate with the surface functional groups (−H₂O and −HO) on TiO₂ surfaces. A simplified view of the ligand exchange mechanism was that, at low pH, reactive surface groups were primarily protonated and arsenate exchanged

Fig. 3. (a) LUMO orbitals of hydrated TiO₂ surfaces; (b) hydrated TiO₂ surfaces; (c) schematic diagram for the surface protonation–deprotonation processes. Red, big gray, and small gray circles denote O, Ti, and H atoms, respectively. Distances are shown in angstroms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

with two H₂O. At intermediate pH, a mixture of reactive surface groups (–H₂O and –HO) coexisted, and arsenate exchanged with one HO[–] and one H₂O. At high pH, arsenate exchanged only with surface HO[–]. Similar mechanism was also proposed for analogous oxyanions adsorption on metal-(hydr)oxides in the literature [2,40]. Detailed reaction processes of arsenate adsorption on diprotonated TiO₂ surfaces (i.e., low pH conditions) were further computed by DFT-based reaction pathway calculations.

3.3. Reaction pathway calculation

Reaction pathway calculation results indicated that the monodentate mononuclear (MM) adsorption state and the bidentate binuclear (BB) adsorption state coexisted in the reaction coordinate of the potential energy surface (PES) (Fig. 4). When arsenate molecule approached to the Ti-(hydr)oxide surfaces, it would firstly exchange with one –H₂O/–OH functional group and form a MM metastable-equilibrium adsorption (MEA) state. Then, the –AsO₄ group may continue to react with an adjacent surface group and release the H₂O/OH[–] to form a BB MEA state. The whole two-step reaction process from MM to BB complex was described below as two half-reactions.

3.3.1. The first half-reaction: Forming of MM MEA state

The transition state (TS₁) of the first half-reaction was shown in Fig. 5a and b. When arsenate approached to Ti₁, the Ti₁ and O₃ began to interact with each other due to the donation of charge from the O₃ lone pair to the empty levels of Ti₁. Meanwhile, the cluster surfaces released one –H₂O group and reached a metastable-equilibrium adsorption state (i.e., MM MEA state).

In the first transition state, the Ti₁–O₁ distance was increased to 2.09 Å, which was much longer than that in the initial reactant (1.87 Å), whereas the Ti₁–O₃ distance was shortened to 2.68 Å. Like the binding of –H₂O/–OH to surface –Ti species described in Section 3.2.2, this adsorption process involved a Lewis acid/base interaction between Ti₁ and O₃. Frontier orbital analysis indicated that there was an injection of electron from the HOMO on O₃ into the LUMO on Ti₁ (Fig. 5a), which led to the donation of occupancy from the O₃ lone pair to the Ti₁ antibond orbital. As a result, Ti₁ and O₃ showed strong Lewis acid/base interaction, which decreased the Ti₁–O₃ distance to 1.86 Å when this half-reaction ended at MM MEA state. The NBO analysis of MM MEA state (Fig. 1a) indicated that a two-center $\sigma_{\text{Ti-O}}$ was formed with significant contribution from O₃ (91%). The first half-reaction was exothermic by 9.2 kcal/mol with an activation barrier of 24.5 kcal/mol (Fig. 4).

3.3.2. The second half-reaction: Forming of BB MEA state

The MM arsenate may continue to attack the unreacted adjacent –H₂O/–OH species and form a BB MEA state (Fig. 4). In the second transition state (TS₂), the interaction between the unprotonated oxygen atom of adsorbed arsenate and the surface Ti atom site led to the delocalization from the O₄ lone pair to the unfilled Ti₂ antibond orbital (Fig. 5c and d). Frontier orbital analysis (Fig. 5c) indicated that there was an injection of electron from the HOMO on O₄ into the LUMO on Ti₂. As a result, the Ti₂–O₄ distance decreased to 2.62 Å, showing that a two-center $\sigma_{\text{Ti-O}}$ was partially formed and the Ti₂–O₂ bond was partially broken at a distance of 2.16 Å (Fig. 5d).

Due to the increased overlap between the O₄ p orbitals and the Ti₂ d orbitals, Ti₂ and O₄ bonded with each other. As a result, the BB MEA state was formed at the Ti₂–O₄ distance of 1.91 Å (Fig. 1b). The NBO analysis of BB complex indicated that a two-center $\sigma_{\text{Ti-O}}$ was formed with significant contribution from O₄ (93%). The second half-reaction was exothermic by 16.7 kcal/mol with an activation barrier of 22.4 kcal/mol (Fig. 4).

Fig. 4. Zero point energy (ZPE)-corrected PES for the two-step reaction process of arsenate on Ti-(hydr) oxide surfaces. RC: reactant complex. TS₁: the first transition state. MM: monodentate mononuclear metastable complex. TS₂: the second transition state. BB: bidentate binuclear metastable complex.

For actual adsorption experiments, another reaction is also possible. When the adjacent surface sites have been occupied by adsorbed arsenate, an unreacted arsenate molecule would react with the surface –H₂O/–OH species via a process similar to the first half-reaction forming an adjacent MM MEA state (see Eq. (c) in Fig. 6). Thus, the interaction between arsenate molecules and two surface –H₂O/–OH groups was able to generate either a BB complex or two MM complexes. This consecutive process was controlled by the surface conditions. When the adjacent surface sites were occupied, the transform from MM mode to BB mode was inhibited and the adsorbed arsenate had to stabilize at sterically favorable MM MEA state.

3.4. Dynamic explanation of C₀ effect

A clear initial concentration (C₀) effect was observed in As(V)–TiO₂ adsorption system, where under the same thermodynamic conditions, when a series of fixed total mass of arsenate was added by multi-batch, adsorption isotherms and actual equilibrium adsorption constant declined as the number of batch increased [8]. Here, the two-step adsorption mechanism provided a qualitative interpretation on the C₀ effect at molecular level.

The initially formed MM MEA state could either keep stable temporarily or transfer to BB MEA state in the second step depending on the surface conditions (Fig. 6). In multi-batch experiment (low initial concentration and low surface coverage conditions), more MM adsorbed arsenate may transfer to BB adsorption mode than that in 1-batch experiment, making the adsorption density decreased as the number of batch increased because BB mode occupied more surface area than MM mode. Although the repulsion between the adsorbed arsenate and neighbor adsorption sites would be serious for such a small ideal cluster used in the DFT calculation (Fig. 1), in the actual infinite surfaces, the average occupied sites of one MM complex (more than one, but less than two) is expected to remain less than that of BB complex (which occupies two active surface sites). The MM adsorption mode is still sterically more favorable than BB adsorption mode.

In this study, we primarily identified the interrelation of different MEA states using DFT-based reaction pathway calculation with a small model cluster. However, the activation barriers of the two-step adsorption process would be dependent on the interactions between the adsorbates, the intermediate species, and the surface

Fig. 5. Frontier orbitals and geometries of transition states. (a and b): The first transition state; (c and d): the second transition state. Blue mesh represents HOMO orbitals, while green mesh represents LUMO orbitals. Purple, red, big gray, and small gray circles denote As, O, Ti, and H atoms, respectively. Distances are shown in angstroms. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Fig. 6. Schematic diagram for the reaction mechanism of arsenate adsorption onto Ti-(hydr)oxides.

functional groups (e.g., $\text{-H}_2\text{O}$, -OH) in the actual system. The evaluation of the interaction between intermediate species and adsorbates and the solvation of outer-sphere water molecules are anticipated with the development of larger-scale *ab initio* molecular dynamics simulations or periodic boundary calculations (PBC) for the reaction pathway study of oxyanions adsorption at mineral–water interfaces.

4. Conclusion

The interrelation between different metastable-equilibrium adsorption (MEA) states of arsenate on TiO_2 surfaces was studied by DFT-based reaction pathway calculations. The results indicated that the bidentate binuclear (BB) adsorption structure evolved from a monodentate mononuclear (MM) MEA state. For actual

adsorption experiments, MM cannot be totally transferred to BB because of the kinetic limitations. The transform between BB and MM adsorption states would be controlled by adsorption kinetics and surface coverage. The two-step adsorption mechanism also provided a molecular-level interpretation on the initial concentration (C_0) effect.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jcis.2011.08.040](https://doi.org/10.1016/j.jcis.2011.08.040).

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