Short Communication

Combined DFT and IR evidence on metastable-equilibrium adsorption of arsenate on TiO_2 surfaces

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ABSTRACT

Adsorption of arsenate on TiO_2 surfaces under the same total mass and thermodynamic conditions reached to different final equilibrium states when the reaction was conducted through different pathways. The microscopic structure for equilibrium adsorption samples were significantly affected by the way arsenate was added to the TiO_2 suspension (e.g. 1-batch or multi-batch). The As–OTi asymmetric stretching vibration of 3-batch samples shifted to lower wavenumbers by 15 cm^{-1} than that of 1-batch samples. Combined analysis of ATR-FTIR spectroscopy and DFT calculation indicated that the change of reaction pathway altered the ratio of double-corner complex to single-corner complex and, hence, the real equilibrium state that is a mixture of the two surface complexes.

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1. Introduction

The interaction of arsenate with metal (hydr)oxides is important in controlling the mobility and bioavailability of arsenate in the natural environment [1,2]. Infrared (IR) spectra is particular useful to explore protonation of reactants which significantly influence their chemical reactivity and adsorption mechanism at solid/liquid interfaces. Previous studies have indicated that the IR vibrational spectra of arsenate on several minerals (such as goethite, ferrihydrite and anatase) contain abundant coordination information [3–5].

Traditionally, for a given adsorption reaction under same thermodynamic conditions (temperature, pH, etc.), equilibrium constants should not be affected by the kinetic pathways or how initial adsorbate is added in the experiment (e.g. the adding speed of adsorbate or whether the adsorbate is added once or multiple batches). Here, we examined whether a change in reaction pathway could cause a change in final “equilibrium” adsorption microscopic states by attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy. For this purpose, we designed a multi-batch adsorption experiment to manipulate the reaction pathway of arsenate adsorption on TiO_2 surfaces. DFT frequency calculations [6–9] were performed to predict theoretical IR spectra of arsenate onto titanium (hydr)oxide surfaces. The combination of theoretical and experimental analysis was used to identify the

dominant surface complexes and metastable-equilibrium adsorption (MEA) states.

2. Materials and methods

Two adsorption samples for ATR-FTIR analysis were prepared under the same total mass and thermodynamic conditions but through different pathways (the way adsorbate was added). One was conducted by adding the total mass of arsenate (0.42 mmol) once (single batch) into the TiO_2 suspension (1 g TiO_2 , in 30 mL). The other was conducted by dividing the total arsenate into three equal parts and adding them into the reaction vessel in succession at 0, 4, and 8 h (3 batches). Both adsorption experiments were conducted at 25 °C. A constant ionic strength was maintained using 0.01 M NaNO_3 . pH was controlled at 7.0 by 0.1 M NaOH or 0.1 M HNO_3 . After 24 h of equilibration, the wet samples were used for ATR-FTIR measurement. Other materials, experimental details and DFT calculation methods were presented in the [Supplementary material](#).

3. Results and discussion

3.1. DFT calculation of vibrational frequency

The geometries of dissolved H_2AsO_4^- and potential adsorption complexes calculated by DFT theory are presented in Fig. 1. H_2AsO_4^- was calculated because it was the major species of $\text{H}_n\text{AsO}_4^{3-n}$ [10] under the adsorption experiment condition (pH 7.0). EXAFS analysis in another related paper [11] showed that two MEA states of double-corner (DC) and single-corner (SC) link-

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Fig. 1. Optimized structures for dissolved arsenate and arsenate-TiO₂ surface complexes geometries: (a) H₂AsO₄⁻ (12 outer-sphere H₂O molecules were omitted for visual aid); (b) double-corner (DC) complex; (c) and (d) are single-corner arsenate H-bonded to a H₂O and -OH surface group occupying the next-nearest neighbor surface site (SC₁ and SC₂), respectively. Red, big gray, small gray, and purple balls denote O, Ti, H, As atoms, respectively. Distances were shown in angstroms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

age coexisted in the adsorption system of As(V)-TiO₂. Hence, the geometries of DC (Fig. 1b) and SC (Fig. 1c and d) were calculated to analyze the theoretical IR vibrations.

The theoretical IR vibration position and assignment of As-O bonds (Table 1) were obtained by frequency analysis calculation based on the fully optimized geometries in Fig. 1. The theoretical vibrational bands of As-OH, As-OTi and As-O bonds located in the position of 731–824 cm⁻¹, 835–890 cm⁻¹, and 925 cm⁻¹, respectively. SC₁, SC₂ and DC arsenate-TiO₂ complexes exhibited different shifts in As-OX (X = Ti or H) stretching vibrations and degenerate modes split comparing to the dissolved arsenate. The

As-OTi ν_{as} vibration of SC and DC complexes located at 855 and 835 cm⁻¹, respectively.

3.2. Experimental IR spectra

ATR-FTIR results indicated that both dissolved and adsorbed As(V) spectra were dominated by the As-O strong stretching vibration bands at 750–1000 cm⁻¹, and no band was detected in TiO₂ sample at this wavenumber range (Fig. 2). Compared analysis of ATR-FTIR and FTIR method can be found in the [Supplementary material](#). Only two dominant vibrational bands at 903 and 868 cm⁻¹ were observed in the dissolved arsenate spectrum (Fig. 2). Based on the calculated frequency analysis on dissolved arsenate in Table 1, the 903 cm⁻¹ and 868 cm⁻¹ band was assigned as the asymmetric stretching mode and the symmetric stretching mode of As-O bond, respectively.

The IR spectra of adsorbed samples were significantly different from those of dissolved arsenate (Fig. 2), indicating the forming of inner-sphere complexes. The diversity and shifts of IR peaks proved that the symmetry of arsenate was lowered and the degeneration vibration modes split and shifted when arsenate was adsorbed onto TiO₂. The ν_s (As-O) vibration at 868 cm⁻¹ in the dissolved arsenate spectrum split into two bands due to the form of inner-sphere surface complexes, which were at 873 and 849 cm⁻¹ in 1-batch adsorption sample, while 873 and 835 cm⁻¹ in 3-batch adsorption sample (Fig. 2). According to theoretical results on adsorbed arsenate (Table 1), bands at 873 cm⁻¹ was assigned to ν_s (As-OTi) vibration, and bands at 835 and 849 cm⁻¹

Table 1

Theoretical bond length and stretching vibrational frequency for dissolved and adsorbed arsenate.

Species	Bond length (Å)			Stretching vibration (cm ⁻¹)					
	As-OH	As-OTi	As-O	As-OH		As-OTi		As-O	
				ν_s	ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}
Dissolved arsenate									
H ₂ AsO ₄ ⁻	1.78	–	1.66	711	–	–	–	851	895
Adsorbed arsenate									
SC ₁	1.70	1.70	–	750	824	890	855	–	–
SC ₂	1.73	1.73	1.63	731	768	890	–	–	925
DC	1.70	1.70	–	760	811	882	835	–	–

ν_s : Symmetric stretching vibration; ν_{as} : asymmetric stretching vibration.

Fig. 2. ATR-FTIR spectra of adsorbed As(V) of 1-batch and 3-batch adsorption samples, dissolved arsenate, and TiO₂ at pH 7.0.

Fig. 3. Schematic diagram of band split of 868 cm⁻¹ in the dissolved arsenate spectrum after 1-batch and 3-batch adsorption.

were assigned to ν_{as} (As–OTi) vibration. The ν_{as} (As–O) vibration at 903 cm⁻¹ of the deprotonated As–O bond was observed in both dissolved As(V) and complexed As(V) spectra, indicating the existence of SC₂ complex since only SC₂ included deprotonated As–O bond among all (Fig. 1d). Compared with the theoretical frequency (Table 1), the observed wavenumbers below 822 cm⁻¹ were due to the stretching of the As–OH bond of complexed As(V).

3.3. Vibrational frequency evidences of metastable-adsorption

There was an obvious difference around 840 cm⁻¹ band between 1-batch and 3-batch adsorption samples (Fig. 2). The ν_{as} (As–OTi) vibration shifted to lower wave number from 849 cm⁻¹

for 1-batch to 835 cm⁻¹ for 3-batch adsorption sample. In the theoretical IR spectrum, the asymmetric stretching vibration frequency of As–OTi was located at a higher position (855 cm⁻¹) for SC₁ MEA state and a lower position (835 cm⁻¹) for DC MEA state (Table 1). According to the difference between ν_{as} (As–OTi) vibration frequency of DC and SC complex, the shifts around 840 cm⁻¹ band indicated that the dominant configuration for 1-batch and 3-batch samples was significantly different, which was described by the schematic diagram in Fig. 3. The decrease of vibration frequency from 1-batch to 3-batch samples indicated that adsorption under 1-batch pathway preferred to form SC complex, while DC complex was favorable through 3-batch pathway. These results were consistent with our previous finding of EXAFS [11], which can be found in the Supplementary material and more samples will be discussed in Ref. [11]. The real “equilibrium” adsorption constants were therefore fundamentally affected by the kinetics or reactant concentration. This phenomenon contradicts to conventional thermodynamic adsorption theories but proves an inference of MEA theory [11,12].

4. Summary

Both theoretical and experimental IR spectra confirmed that different reaction pathways, such as the adding mode of arsenate, changed the final metastable-equilibrium adsorption states under the same thermodynamic conditions. Adsorption sample obtained through 1-batch pathway preferred to form single-corner linkage surface complex, while double-corner adsorption mode was favorable for multi-batch pathway in As(V)–TiO₂ system.

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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.2009.06.024.

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