Short range order at the amorphous TiO$_2$–water interface probed by silicic acid adsorption and interfacial oligomerization: An ATR-IR and $^{29}$Si MAS-NMR study

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**Abstract**

Adsorption and oligomerization of H$_4$SiO$_4$ at the amorphous TiO$_2$–aqueous interface were studied using in situ Attenuated Total Reflectance Infrared (ATR-IR) and ex situ solid state $^{29}$Si nuclear magnetic resonance (NMR). The ATR-IR spectra indicate that a monomeric silicate species is present at low silicate surface concentration ($I_{Si}$). Above a threshold $I_{Si}$, linear silicate oligomers are formed and these oligomers dominate the surface at high $I_{Si}$. Interestingly the ATR-IR spectra of H$_4$SiO$_4$ on the TiO$_2$ surface are very similar to those previously observed on the poorly ordered iron oxide phase ferrihydrite. The $^{29}$Si NMR spectrum of silicate on the TiO$_2$ surface shows the presence of Si in three states with chemical shifts corresponding to isolated monomers ($Q_0$), the ends of linear oligomers ($Q_1$) and the middle of linear oligomers ($Q_2$). The ratio of the area of the $Q_1$ and $Q_2$ peaks was $\approx 2:1$ which is consistent with the proposed formation of linear silicate trimers by insertion of a solution H$_4$SiO$_4$ between adjacent suitably orientated adsorbed silicate monomers. A structural interpretation indicates that the observed interfacial silicate oligomerization behavior is a general phenomenon whereby bidentate silicate monomers on oxide surfaces are disposed towards forming linear oligomers by condensation reactions involving their two terminal Si–OH groups. The high surface curvature of nanometer sized spheres inhibits the formation of interfacial silicates with a higher degree of polymerization. © 2011 Elsevier Inc. All rights reserved.

1. Introduction

Titanium oxides are wide band-gap semiconductors with applications to photocatalysis, photovoltaics, sensors and pigments [1–3]. The electronic and optical properties of TiO$_2$ have a complex dependence on the bulk and surface properties of the material [2,4], and the association of silicon oxides with TiO$_2$ can dramatically alter these properties. For example the catalytically active TiO$_2$ phase anatase converts to rutile at $\approx 700$ °C, which constrains the utility of anatase. However, in mixed TiO$_2$/SiO$_x$ oxides the temperature of the anatase to rutile phase transition increases from $\approx 700$ to 1000 °C as the amount of Si increases from 0 to 5 atom percent [5]. Studies on the chemistry and application of SiO$_x$–TiO$_2$ systems have included titanium deposited on SiO$_2$ [6,7], silicon deposited on TiO$_2$ [1,8] and sol–gel prepared mixed SiO$_x$–TiO$_2$ phases [8]. A key parameter in understanding the sol–gel prepared SiO$_x$–TiO$_2$ materials is the proportion of Ti–O–Si, Ti–O–Ti and Si–O–Si linkages. The Ti–O–Si linkages are indicative of atomic scale homogeneity while the Ti–O–Ti and Si–O–Si linkages are indicative of SiO$_2$ and TiO$_2$ phase segregation [10]. A key parameter for SiO$_2$ films on TiO$_2$ surfaces is film uniformity and this has been achieved by a two step process involving the chemisorption (here-in simply termed sorption) of a siloxane onto the TiO$_2$ surface forming Ti–O–Si linkages, followed by thermal or photocatalytic oxidation forming Si–O–Si linkages between the monomers [1,11].

Silicon oxides can promote the catalytic activity of TiO$_2$ surfaces in numerous reactions [10,12] and several explanations have been proposed for this observation depending on the system under study. For example, the presence of SiO$_2$ modified the electronic structure of a submonolayer of TiO$_2$ deposited on an SiO$_2$ substrate [13] and this contributed to enhanced photocatalytic oxidation of chlorinated organics by mixed TiO$_2$–SiO$_2$ phases [14]. The rate of the photocatalytic oxidation of rhodamine dye by TiO$_2$/SiO$_2$ mixed oxides was increased up to 3-fold by the presence of SiO$_2$ groups on the oxide surface. The rate of oxidation was correlated with the amount of rhodamine sorption by the mixed oxides with both sorption and oxidation increasing to a maximum as the % SiO$_2$ increased from 0 to 70% [9]. The presence of silicates dramatically alters the acid–base properties of the TiO$_2$ surface. At low SiO$_2$ surface coverage adsorption experiments with pyridine have demonstrated that the TiO$_2$ surface drastically changes from Lewis acid
character (electron acceptor) to Bronsted acid character (proton donor). At high SiO₂ surface coverage the surface has neither Lewis or Bronsted acid groups, consistent with the fact that the pH of zero charge of TiO₂ and SiO₂ are ≈ 6 and 2 respectively. At very high surface coverage TiO₂ photocatalytic activity is inhibited. For example the use of the TiO₂ phase rutile as a pigment requires it to be coated with SiO₂ to inhibit the photocatalyzed oxidation of the organic phase [1].

The current work explores the interaction between the inorganic ligand silicic acid, H₄SiO₄, and the TiO₂ surface in an aqueous suspension. There are several motivations for this study including the role of surface silicate groups in several catalytic reactions involving TiO₂ [10,12] and a comparison of H₄SiO₄ surface chemistry on titanium and iron oxides. In addition solid state ²⁹Si NMR spectra, which clearly distinguish silicates with different degrees of polymerization, can be measured for silicates on the TiO₂ surface but not for silicates on iron oxides because of the large number of unpaired electrons in the high spin Fe⁺⁺ ion. The interaction between silicates and TiO₂ involves sorption via Ti–O–Si bonds and the development of Si–O–Si bonds due to silicate polymerization reactions on the TiO₂ surface. Silicic acid is a weak acid with pKₐ 9.8 [15] and the initial sorption reaction involves ligand exchange of surface Ti–OH groups with the H₄SiO₄. Evidence for Ti–O–Si bonding in mixed SiO₂–TiO₂ phases comes from IR and Raman [16], ²⁹Si NMR [1], and X-ray photoelectron spectroscopy (XPS) [17]. There have been no studies of the specific structure of the TiO₂ sorbed H₄SiO₄ surface complex. In the case of many other oxygen anion ligands, such as phosphate [18], arsenate [19,20], formate, and acetate [21] surface complexes with a bidentate and binuclear attachment are formed on TiO₂ surfaces. This means that two oxygen ions of the ligand are coordinated to two adjacent Ti ions on the TiO₂ surface.

Infrared spectroscopy is particularly useful for the in situ study of silicate sorption and polymerization reactions on the TiO₂ surface because the shape of the Si–O stretching modes (ν(Si–O)) for the sorbed silicate provides insight on the symmetry of the surface complex [22] while the position of the Si–O stretching modes provides insight on the degree of silicate polymerization [23,24]. Water is a very strong absorber of IR radiation and the applicability of IR to the study of the metal oxide–water interface has been dramatically improved by the advent of Attenuated Total Reflectance IR (ATR-IR) which provides a sampling method with the required short path length. In this study we have used an amorphous TiO₂ which is an important precursor in the formation of anatase and rutile because it has a large surface area which provides for high concentrations of adsorbed species and ATR-IR spectra with high signal to noise ratios.

Numerous studies have shown that ²⁹Si NMR is a powerful technique to discriminate between Si atoms with different degrees of polymerization in both solution [15,25] and solid phases [26,27]. Silicon in an SiO₂ unit is designated as Q⁰ where n is the number of Si–O–Si linkages and the ²⁹Si chemical shift becomes increasingly negative with respect to (CH₃)₄Si as n increases. In the case of silicate minerals typical ²⁹Si shifts are −70 ± 4 ppm for isolated SiO₄ tetrahedra (Q⁰), ≈ −80 ± 3 ppm for Q¹ such as in Si₂O₆²⁻ dimers or the ends of linear chains, ≈ −97 ± 1 ppm for Q² such as in single silicate chains, ≈ −98 ± 1 ppm for Q³ such as in silicate sheets and lastly ≈ −109 ± 2 ppm for Q⁴ as in three dimensional silicates like quartz [28]. There is little overlap in the ranges of ²⁹Si peak positions for different degrees of polymerization. For mixed TiO₂–SiO₂ phases the high charge density of Ti means that the ²⁹Si NMR peaks are at lower ppm such as −84 ppm for Q¹, −92 to −96 ppm for Q² and −100 to −102 ppm for Q³ [26].

The study of H₄SiO₄ chemistry on the TiO₂ surface follows several steps of Zero Charge (PZC) of TiO₂ lies between 5 and 6 [2] so at a pH of 9 the H₂SiO₄ / H₄SiO₄ ratio is ≈ 7:1 and the TiO₂ surface has a negative surface charge. Spectra are interpreted based on the recently proposed structural model for amorphous TiO₂ of Zhang et al. [4].

2. Materials and methods

2.1. Materials

All solutions were made from 18 MΩ cm resistivity deionized water that had been distilled, acidified to pH 4 and saturated with N₂. Adjustments to pH were made with 0.01 to 1 M isothermally distilled HCl or low carbonated NaOH solutions. Solutions were stored in polycarbonate containers which were kept either sealed or under a stream of N₂. A stock H₄SiO₄ solution was prepared by dissolving amorphous silica (1 g) in 50:50 (w/w) NaOH:H₂O (8 g) followed by dilution to 1 L. The solution was further diluted to 1.66 mM, the pH lowered to 8−12 days (to allow for depolymerization which is slow at pH 4) and then the pH was lowered to pH 4 and the solution saturated with N₂ to produce a stable stock solution of 1.66 mM monomeric silicic acid in 0.01 M NaCl. The rate of color development in the molybdenum yellow method [38] was used to determine that monomeric silicic acid was the only species present within the limits of detection. For the ²⁹Si NMR spectra the H₂SiO₄ solution was prepared in the same way but starting with an enriched SiO₂ with 99% ²⁹Si purchased from Cambridge Isotope Laboratories. Amorphous TiO₂ was prepared in two methods. An oxide termed TiO₂(a) was precipitated by alkaline hydrolysis of a solution of Ti⁴⁺ dissolved in concentrated H₂SO₄ which was achieved by the drop wise addition of the Ti⁴⁺ in H₂SO₄ to water that was maintained at pH 11 ± 1 by simultaneous drop wise addition of a 50:50 NaOH:H₂O solution while the reaction vessel was stirred rapidly in a water bath at 0 °C. An oxide termed TiO₂(b) was precipitated by the hydrolysis of titanium ethoxide in water at 0 °C using the method of Zhang et al. [4]. This involves quickly adding 29 mL water containing four drops of acetic acid to a mixture of 21 mL titanium ethoxide and 25 mL ethanol under
stirring. Based on X-ray absorption spectra (XAS) and wide angle X-ray scattering (WAXS) this TiO$_2$($\alpha$) phase was described by Zhang et al. [4] as being composed of highly distorted 2 nm diameter particles with a strained “anatase-like core”. In both cases the TiO$_2$ formed instantaneously as a white suspension and was then resuspended in water. The particle size of both TiO$_2$ materials was too small to be discernible by transmission electron microscopy indicating particles smaller than \( \approx 3 \) nm as observed by Zhang et al. [4]. The H$_2$SiO$_4$ adsorption isotherms and the ATR-IR spectra of H$_2$SiO$_4$ adsorbed on both materials were indistinguishable. Despite this the TiO$_2$ material has been specified as (a) or (b) for completeness. The Ti content of the suspensions was determined using the H$_2$O$_2$ colorimetric assay after dissolution of the suspension in conc. H$_2$SO$_4$ with 16 g L$^{-1}$ (NH$_4$)$_2$SO$_4$. Powder X-ray diffraction spectra were measured on a Phillips PW 1140 goniometer using a Cu Kα source with a 0.02° 20 step size and 2 s count time.

2.2. Adsorption experiments

For ATR-IR experiments 50 µL of a 1 g L$^{-1}$ TiO$_2$($\alpha$) suspension was deposited onto a single bounce 45° diamond ATR crystal and the water evaporated under a gentle stream of N$_2$. The diamond ATR crystal was placed in a flow cell and the TiO$_2$ film rinsed for 1 h with 0.1 M NaCl at pH 11 to remove adsorbed carbonate and then equilibrated with 0.1 M NaCl at pH 9 for between 2 and 12 h. After this time ATR-IR spectra were collected (Section 2.3) and when a stable background was obtained the solution flow was stopped, silicic acid stock solution was added to the electrolyte, the pH readjusted to 9.0, and this solution was circulated through the cell at \( \approx 1 \) mL min$^{-1}$ for the duration of the experiment. Infrared spectra were collected (with the fluid flowing) over time for up to 48 h after which time there was little change in the collected spectra as a function of time. The solution H$_2$SiO$_4$ concentration did not change appreciably during the course of an experiment because the amount of TiO$_2$ present (0.5 µmol) was small compared to the amount of H$_2$SiO$_4$ in solution (50–700 µmol).

An H$_2$SiO$_4$ adsorption isotherm from 0.1 M NaCl at pH 9 was measured by equilibrating TiO$_2$ suspensions with a known total concentration of H$_2$SiO$_4$ (Si$_t$), on an end-over-end mixer for 48 h. After this time the suspensions were centrifuged and the clear supernatant filtered through a 0.2 µm membrane and the concentration of Si$_t$ in solution, (Si$_{isol}$), measured by the molybdenum blue method. The adsorbed Si (Si$_{ads}$) was determined from the difference between Si$_t$ and Si$_{isol}$. All Si surface concentrations (\( \Gamma_{Si} \)) are given as moles of Si$_{ads}$ per mole of Ti.

2.3. Infrared spectroscopy

A Nicolet$^\text{a}$ 8700 Spectrometer with DTGS detector and Omnic$^\text{b}$ software was used to obtain ATR-IR spectra (resolution of 4 cm$^{-1}$) between 4000 and 500 cm$^{-1}$. The spectra were corrected for changes to the water signal that affected the low wavelength side of the region of interest (between 1250 and 700 cm$^{-1}$) by adding or subtracting water spectra and then taking a horizontal baseline. Spectra were ATR corrected using the Omnic$^\text{b}$ advanced ATR correction algorithm. Negative Savitsky–Golay 2nd derivatives were calculated to assist band identification using an order of three and with the number of points depending on the signal to noise ratio in the original spectra. The matrix of IR spectra contained 49 rows and 261 columns representing 49 measured spectra between \( \approx 1250 \) and 750 cm$^{-1}$. This matrix was analyzed by Principle Component Analysis (PCA) and then Multivariate Curve Resolution with Alternating Least Squares (MCR-ALS) in Matlab (Mathworks$^\text{c}$) using the constraints of non-negative concentration and non-negative spectra [39]. MCR-ALS analysis was used to decompose the data matrix (termed “\( \mathbf{D} \)) into the product of two matrices; the spectra matrix (termed “\( \mathbf{S} \)) with \( x \) rows and 261 columns, representing the spectra of each of the \( x \) pure surface species and the composition matrix (termed “\( \mathbf{C} \)) with \( 49 \) rows and \( x \) columns representing the contribution of each of the \( x \) surface species to each measured spectrum. MCR-ALS was used to optimize \( \mathbf{C} \) and selected rows from \( \mathbf{S} \) to minimize the difference between the \( \mathbf{D} \) and the product \( \mathbf{CS} \). This is illustrated below for \( x = 3 \).

\[
\begin{align*}
\mathbf{D} &= \begin{bmatrix}
\mathbf{d}_{11} & \cdots & \mathbf{d}_{1x} \\
\vdots & \ddots & \vdots \\
\mathbf{d}_{x1} & \cdots & \mathbf{d}_{xx}
\end{bmatrix} \\
\mathbf{C} &= \begin{bmatrix}
\mathbf{c}_{11} & \cdots & \mathbf{c}_{1x} \\
\vdots & \ddots & \vdots \\
\mathbf{c}_{x1} & \cdots & \mathbf{c}_{xx}
\end{bmatrix} \\
\mathbf{S} &= \begin{bmatrix}
\mathbf{s}_{11} & \cdots & \mathbf{s}_{1x} \\
\vdots & \ddots & \vdots \\
\mathbf{s}_{x1} & \cdots & \mathbf{s}_{xx}
\end{bmatrix}
\end{align*}
\]

\[
\mathbf{d}_{i,j} = \mathbf{c}_{i,j} \mathbf{s}_{i,j}
\]

2.4. Solid state $^{29}$Si NMR

Solid-state NMR spectra were measured on a freeze dried TiO$_2$($\alpha$) sample with $^{29}$Si enriched H$_2$SiO$_4$ using a Bruker AVANCE 300 spectrometer operating at 300.13 MHz proton and 59.63 MHz $^{29}$Si frequency. The $^{29}$Si spectrum was obtained using the standard one-pulse-and-collect sequence (Bloch decay) with heteronuclear decoupling during the acquisition interval. The spectral width was 20 kHz. The sample was spun using a 7 mm Bruker double tuned probe with zirconia rotors. The recycle delay was determined from the experiments with recycle delay increased from 50 up to 300 s until the relative peak intensities remained unchanged. The recycle delay for the final experiment was 150 s and the spectrum was obtained using 450 scans. Rotation speed was 7 kHz. Line broadening of 60 Hz was applied before Fourier transform.

3. Results and discussion

3.1. Macroscopic properties

The XRD patterns of freeze dried TiO$_2$ prepared by both methods are shown in Fig. 1. The main feature was a broad, low

![Fig. 1](image-url)
intensity peak which coincides with one of the main brookite lines as was observed by Zhang et al. [4] for TiO$_2$ prepared by titanium ethoxide hydrolysis. The similarity in the XRD patterns between the two TiO$_2$ oxides is consistent with the similarity in the H$_2$SiO$_4$ adsorption isotherms and the ATR-IR spectra of adsorbed H$_2$SiO$_4$ on both materials and the structural model for amorphous TiO$_2$ developed by Zhang et al. [4] was used to interpret the H$_2$SiO$_4$ surface chemistry in the current study.

The isotherm for H$_2$SiO$_4$ adsorption onto a TiO$_2$ film suspension at pH 9 has two distinct regions (Fig. 2). At $\Gamma_9 < 10^{-1.4}$ the log-log isotherm had a slope of unity while the region of the isotherm with $10^{-1.4} < \Gamma_9 < 10^{-0.5}$ had a slope of 0.30 over two orders of magnitude in $S_{\text{sol}}$. This implies that adsorption at $\Gamma_9 < 10^{-1.4}$ involves a single type of reaction occurring at adsorption sites that are energetically equivalent (i.e. Langmuir adsorption) but at $\Gamma_9 > 10^{-1.4}$ more complex surface processes are evident such as site heterogeneity or chemical interactions between adsorbing species. The ATR-IR data discussed in Section 3.2 show that chemical interactions between the sorbed monomers occurs at $\Gamma_9 > 10^{-1.4}$ and this can account for the change in isotherm slope [32]. Experimental data for ferrihydrite under the same conditions is not available but the isotherm modeled for the same conditions using the parameters from Swedlund et al. [32] (shown in Fig. 2) is surprisingly similar in shape and position to the isotherm measured for TiO$_2$.

3.2. ATR-IR spectra of H$_2$SiO$_4$ adsorbed on am-TiO$_2$

3.2.1. General trends

The ν(Si–O) region of IR spectra measured over time as films of TiO$_2$ were exposed to $S_{\text{sol}}$ between 0.097 and 1.34 mM are shown in Fig. 3. Many aspects of the ATR-IR spectra of H$_2$SiO$_4$ on TiO$_2$ were very similar to those observed for H$_2$SiO$_4$ on ferrihydrite [32] and the spectra are discussed only briefly. The area of the ν(Si–O) feature in the IR spectra (termed $A_{\nu(Si-O)}$) increased approximately linearly as a function of the log of time at each $S_{\text{sol}}$ (Fig. 4a). This type of adsorption kinetics has been observed for several systems in which small molecules are adsorbing onto metal oxides and has been attributed to either site heterogeneity and interparticle or intraparticle diffusion [40]. For TiO$_2$ films exposed to $S_{\text{sol}}$ of either 0.097 or 1.34 mM the maximum IR absorbance after $\sim$30 h were 0.006 and 0.054 respectively. This can be compared to the maximum IR absorbance of 0.00016 for a 1.66 mM H$_2$SiO$_4$ solution under the same ATR conditions but without the TiO$_2$ film deposited on the TiO$_2$ crystal [30,41]. A solution with 1.66 mM H$_2$SiO$_4$ is 10% below the solubility product of an amorphous SiO$_2$ precipitate [15] which demonstrates that the H$_2$SiO$_4$ contained in the volume of the TiO$_2$ film that is sampled by the ATR-IR beam is up to 300 times more concentrated than a saturated H$_2$SiO$_4$ solution. Precipitation of SiO$_2$ is not observed because the H$_2$SiO$_4$ is adsorbed on the oxide surface. It is also evident that the solution H$_2$SiO$_4$ does not contribute appreciably to the measured spectra of adsorbed H$_2$SiO$_4$.

In all cases the spectra collected immediately after introduction of H$_2$SiO$_4$ had a maximum IR absorbance at $\sim$960 cm$^{-1}$. At the
lowest Si$_{\text{ads}}$ of 0.097 mM the shape of the spectra did not change over the 27 h of the experiment. For each experiment with Si$_{\text{sol}}$ > 0.097 mM the IR absorption in the region of $\approx$1015 cm$^{-1}$ increased as $\Gamma_{Si}$ increased over time and this feature became more prominent at higher H$_2$SiO$_4$ concentration. For example with 0.21 mM H$_2$SiO$_4$ the feature at $\approx$1015 cm$^{-1}$ developed over time to become the dominant spectral feature after 32 h while with 0.65 mM H$_2$SiO$_4$ the spectral feature at 1015 cm$^{-1}$ dominated the spectra after 0.12 h. Examining the absorbance scales in Fig. 3 it is evident that at each Si$_{\text{sol}}$ the IR absorbance at $\approx$1015 cm$^{-1}$ exceeded the IR absorbance at $\approx$960 cm$^{-1}$ only when the maximum IR absorbance was $>0.01$. Similarly the wavenumber of maximum IR absorbance increased from $\approx$960 to 1015 cm$^{-1}$ when the area of the Si–O stretching feature exceeded $>2.6$ (Fig. 4b). This implies that there is some threshold H$_2$SiO$_4$ surface concentration on the TiO$_2$($am$) where the silicate species that absorbs at 1015 cm$^{-1}$ becomes the dominant surface species.

3.2.2. Spectra at low $\Gamma_{Si}$

When $A_{\text{TiO}_2}$ was $<1$ the IR spectra had the same shape and the average of these spectra is shown in Fig. 5a. The maximum IR absorbance occurred at 960 cm$^{-1}$ and this band had shoulders on either side of it which are particularly evident in the 2nd derivatives. In addition there is a smaller shoulder at 830 cm$^{-1}$ and a broad band at around 1100 cm$^{-1}$. The position and shape of this spectral feature provides insights into the structure of the adsorbed silicate under these conditions. The IR spectrum of H$_2$SiO$_4$ in solution (Fig. 5c) has an asymmetric triply degenerate v(Si–O) mode at 939 cm$^{-1}$ and a broad weak Si–O–H bending mode at $\approx$1090 cm$^{-1}$ while the symmetric Si–O stretch occurs at 787 cm$^{-1}$ in the Raman spectrum [41]. The spectra of H$_2$SiO$_4$ adsorbed on TiO$_2$ at low $\Gamma_{Si}$ are similar, but at slightly higher frequency, to those of for the monomeric adsorbed H$_2$SiO$_4$ on ferrihydrite at low $\Gamma_{Si}$ (Fig. 5b) [30]. The spectra of the monomeric silicate on the ferrihydrite surface did not change with pH between 4 and 10, or with ionic strength between 0.01 and 0.1 M [32,33].

![Fig. 5. The ATR-IR spectra and band fitting of (a) the low $\Gamma_{Si}$ species on amorphous TiO$_2$ (b) the low $\Gamma_{Si}$ species on ferrihydrite (c) H$_4$SiO$_4$ in solution.](image)

The three asymmetric v(Si–O) bands are all clearly resolved in the silicate on TiO$_2$ spectrum compared to the spectrum for ferrihydrite where two v(Si–O) bands at $>946$ cm$^{-1}$ were not resolved [30]. Both the higher frequency and greater splitting of the v(Si–O) bands for H$_2$SiO$_4$ adsorbed on TiO$_2$ are consistent with the higher charge density of the Ti$^{4+}$ cation compared to that of Fe$^{3+}$. The spectra indicate that H$_2$SiO$_4$ adsorbed on TiO$_2$ at low $\Gamma_{Si}$ is present as a monomeric silicate surface complex with asymmetric v(Si–O) bands at 910, 961 and 1011 cm$^{-1}$, the symmetric v(Si–O) band is weakly IR active at 833 cm$^{-1}$ while the broad band at $\approx$1100 cm$^{-1}$ is the Si–O–H bending mode. The IR spectra indicate a bidentate surface similar to the monomeric H$_2$SiO$_4$ surface complex on the iron oxide surface [30,35].

3.2.3. ATR-IR spectra at high $\Gamma_{Si}$

As the $A_{\text{TiO}_2}$ increased from $\approx$1 to 5 the shape of the spectra changes from having a maximum absorbance at $\approx$960 cm$^{-1}$ to a spectrum with a maximum at $\approx$1020 cm$^{-1}$. However, as $A_{\text{TiO}_2}$ increases from 5 to 10 the ATR-IR spectra have a similar shape (Fig. 6), apart from a small decrease in the IR absorbance around 950 cm$^{-1}$ and a small increase in IR absorbance around 1100 cm$^{-1}$. At these high $\Gamma_{Si}$ the IR spectra of H$_2$SiO$_4$ adsorbed on the TiO$_2$($am$) have the same shape as those observed at high $\Gamma_{Si}$ on ferrihydrite [31] but, as observed at low $\Gamma_{Si}$ they are at slightly higher frequency. This implies the same linear oligomers are formed on the surfaces of both oxides. The structural interpretation for the TiO$_2$ surface is presented in Section 3.3.

The last feature in the ATR-IR spectra is the small increase in IR absorbance intensity between 1050 and 1150 cm$^{-1}$ observed at high $\Gamma_{Si}$ in Fig. 6 and this feature can be attributed to the development of an SiO$_2$($am$) on the TiO$_2$($am$) surface [30]. This high $\Gamma_{Si}$ feature made a comparatively small contribution to the measured IR spectra for the TiO$_2$($am$) system even when Si$_{\text{sol}}$ was just 30% below saturation with respect to precipitation of a bulk SiO$_2$($am$) phase. This indicates that the TiO$_2$($am$) Surface promotes the formation of an oligomeric silicate phase but does not strongly promote the formation of three dimensional polymers.

3.2.4. Quantitative analysis of the ATR-IR spectra

The matrix of all 49 measured spectra (each with 261 data points) were analyzed by MCR-ALS. Prior exploratory analysis of the data using PCA gave eigenvalues similar to the values reported for the ferrihydrite data [31] and were consistent with the proposed model of two main surface species and a third minor species. In the MCR-ALS analysis the monomer spectrum was fixed to the average of the spectra at low $\Gamma_{Si}$ (Fig. 5a), the oligomer spectrum
was optimized with the initial estimate being the average of the high \( \Gamma_{\text{Si}} \) spectra (Fig. 6), and the polymer spectrum was optimized from an initial estimate from the data for ferrihydrite [31]. The optimized model fitted the details of the measured ATR-IR spectra very closely and the largest residual for any spectrum was on average 2\% of the largest IR absorbance of that spectrum. The optimized pure spectra for the surface species and typical fits to measured spectra using these spectra are shown for various surface compositions in Fig. SI 1.

The contributions that each surface species made to the area of the measured spectra as \( \text{H}_2\text{SiO}_4 \) adsors onto \( \text{TiO}_2(\text{am}) \) over time were similar to that observed on ferrihydrite and are shown in Fig. SI 2. At each \( \Gamma_{\text{Si(sol)}} \) the monomeric species adsors initially and then the oligomer species starts to form after some lag period. The lag phase before oligomer formation is shorter at higher \( \Gamma_{\text{Si}} \). For example, the lag phase decreased from \( \approx 10 \) to \( 0 \) h as \( \Gamma_{\text{Si(sol)}} \) increased from 0.097 to 0.65 mM. At each \( \Gamma_{\text{Si(sol)}} \) the growth of oligomer was delayed until a certain surface coverage of monomer was obtained corresponding to a component spectral area of \( \approx 1 \). The contributions that each surface species made to the area of the measured spectra as \( \text{H}_2\text{SiO}_4 \) adsors onto \( \text{TiO}_2(\text{am}) \) are shown as a function of \( A_{\text{Si(O–Si)}} \) in Fig. 7. The data for all \( \Gamma_{\text{Si(sol)}} \) from 0.097 to 1.34 mM follow the same trend indicating that the distribution of surface species at a given surface concentration is independent of solution concentration. The quantitative analysis agrees with the qualitative analysis in that as \( \Gamma_{\text{Si}} \) increased the surface changes from being predominantly monomeric when \( A_{\text{Si(O–Si)}} \) \( \ll 2 \) to being predominantly oligomeric at \( A_{\text{Si(O–Si)}} \) \( > 5 \).

### 3.3. \( ^{29}\text{Si} \) solid state NMR of \( \text{H}_2\text{SiO}_4 \) adsorbed on amorphous \( \text{TiO}_2 \)

Approximately 0.3 g of sample was needed for the NMR analysis and this was obtained by equilibrating a suspension of \( \text{TiO}_2(\text{b}) \) (0.06 g L\(^{-1}\)) with 99\% \( ^{29}\text{Si} \) enriched \( \text{H}_2\text{SiO}_4 \) (0.28 mM total concentration) at pH 9 in 0.1 M NaCl. Preliminary experiments with \( \text{TiO}_2 \) suspensions were undertaken with natural abundance \( \text{H}_2\text{SiO}_4 \) (i.e. 5\% \( ^{28}\text{Si} \)) where the equilibrated \( \text{TiO}_2 \) pastes were collected by centrifugation and ATR-IR spectra measured against \( \text{TiO}_2 \) pastes with no \( \text{Si} \). This was done to choose appropriate \( \text{TiO}_2 \) and \( \text{H}_2\text{SiO}_4 \) concentrations that would result in a sample with appreciable amounts of both monomeric and oligomeric adsorbed \( \text{H}_2\text{SiO}_4 \) for the \( ^{29}\text{Si} \) NMR analysis. In addition the sample for NMR analysis was freeze dried and ATR-IR spectra were measured on the freeze-dried paste to assess for changes during drying. The ATR-IR spectra of \( \text{H}_2\text{SiO}_4 \) on the \( \text{TiO}_2 \) paste and the \( \text{TiO}_2 \) after freeze drying (Fig. SI 3) were very similar with slightly less IR absorbance in the dried sample around 940 cm\(^{-1}\) indicating a small amount of silicate condensation upon drying. The MCR-ALS fitting indicated that the monomeric component comprised 50 and 55\% of the area of the ATR-IR spectra for the dried sample and paste sample respectively.

The main peak in the NMR spectrum of this sample (Fig. 8) occurs at \( \approx -87 \) ppm and there are clearly shoulders on either side of this peak, at \(-79.8 \) and \(-95.7 \) ppm. In addition there is a tail extending on the more negative side of the peak at \( \approx -105 \) ppm. The \( ^{29}\text{Si} \) NMR peak position for a \( Q^2 \) Si depends primarily on the value of \( n \) but for \( \text{Si} \) with the same \( Q^2 \) the peak position become more negative for higher charge densities of the cations to which the silicates are coordinated [42,43]. Therefore to assign the peaks in the spectrum it is necessary to refer to materials where silicates are coordinated with Ti\(^{4+} \) cations. The peak at \(-79.8 \) ppm is within the range observed for \( Q^2 \) Si including the orthosilicate mineral tianite CaT\( _2\text{SiO}_5 \) (\(-79.6 \) ppm) [42] and also \( Q^2 \) Si presumed to occupy interstitial sites in a rutile sample (\(-77.3 \) ppm) [42]. Similarly the peak at \(-95.7 \) ppm is within the range for \( Q^4 \) Si in sol–gel prepared mixed \( \text{TiO}_2–\text{SiO}_2 \) oxides (\(-92 \) to \(-96 \) ppm) [8,26] and in the cyclosilicate mineral benitoite (\(-94.2 \) ppm) [42]. Only one reference value for \( Q^2 \) Si was found which was for a mixed \( \text{TiO}_2–\text{SiO}_2 \) oxide (\(-84 \) ppm) [26] and it is clear that the peak at \(-87 \) ppm is \( Q^2 \). The tail at \( \approx -105 \) ppm indicates a small amount of silicate with \( Q^2–Q^4 \) but the peak is too weak to allow for definitive peak fitting.

The NMR spectrum qualitatively agrees with the proposed model for \( \text{H}_2\text{SiO}_4 \) polymerization at an oxide surface. The \( Q^0 \) peak corresponds to the monomeric adsorbed \( \text{H}_2\text{SiO}_4 \) while the \( Q^1 \) and \( Q^2 \) peaks correspond to terminal and middle \( \text{Si} \) in linear silicate oligomers. Other possible surface silicate oligomers can be excluded. For example a cyclic silicate species would have all \( Q^2 \) and a branched silicate would have \( Q^1–Q^3 \) Si present. The percentage of the NMR spectrum due to the monomeric silicate was 30\% compared with 50\% of the ATR-IR spectrum. The conditions of collecting the NMR spectra were chosen so that the NMR signal will be directly quantitative for the different types of silicate [26] whereas the ATR-IR signal is only approximately quantitative. The ratio of \( Q^2 \) and \( Q^2 \) peak areas would be 1:0.5 for a linear trimer whereas the measured value was 1:0.4. Longer linear oligomers would have larger \( Q^2 \) areas (e.g. 1:1 for a tetramer) and a dimeric species would have no \( Q^2 \) peak [25]. In addition the \textit{in situ} ATR-IR spectra experiments on the \( \text{TiO}_2 \) and the ferrihydrite indicate the formation of an oligomer which is predominantly one species which is larger than a dimer and which forms directly from the monomeric silicates. Possible explanations for the slightly higher
measured $Q^1$:$Q^2$ include a small proportion of either a dimeric silicate or a branched tetramer with $Q^3$:$Q^4$ of 1:0.3. The later option would also explain the small $Q^3$:$Q^4$ peak in the NMR spectrum.

3.4. Structural interpretation

The fact that the same silicate oligomerization product is formed on the surface of two different poorly ordered oxides suggest that this is a general phenomenon whereby bidentate silicate monomers on an oxide surface are disposed towards forming linear oligomers by condensation reactions involving their two terminal Si–OH groups. In this section we explore if the formation of short one dimensional oligomers on the TiO$_2$ surface is structurally reasonable based on geometric constraints of silicate polymerization and the structural model for amorphous TiO$_2$ developed by Zhang et al. [4] based on a combination of reverse Monte Carlo and Molecular Dynamics simulations of wide-angle X-ray scattering data and X-ray adsorption spectra. Zhang et al. [4] kindly provided the atomic coordinates for their structural model of TiO$_2$ particles containing 123 Ti atoms, 246 O atoms and having an irregular “potato” shape as shown in Fig. SI 4. The particles had a diameter of $\approx$2 nm with a small strained “anatase-like” core and a highly distorted shell [4]. The TiO$_2$(am) structural model therefore represents a disordered surface and the applicability of this interpretation of silicate oligomerization to other disordered surfaces, such as ferrihydrite, will be considered.

The average Ti coordination number was 5.3 due to the truncation of the many TiO$_6$ octahedra on the particle surface. In an aqueous suspension H$_2$O will complete the coordination sphere of the coordinatively unsaturated surface Ti ions such that, after deprotonation, the surface will have a large number of terminal Ti–OH groups. For an irregular oxide particle there is no rigorous process for defining which Ti ions are on the surface. For this work Ti ions which were clearly beneath other Ti ions were excluded leaving 88 Ti atoms. The average coordination numbers of the outer 88 Ti ions and the inner 35 Ti ions were 5.05 and 6.00 respectively. There were 67 of the 88 outer Ti ions that had a coordination number less than six and these Ti ions were considered to be surface active.

Geometric constraints for surface monomer and oligomer adsorption sites are proposed based on the range of Si–O bond distances and angles observed in silicate minerals. Liebau [44] reports that Si–O distances vary between 1.57 and 1.72 Å, O–Si–O angles vary between 98 and 122° while the Si–O–Si angles vary between 120 and 180°. Adjacent terminal Ti–OH groups that are sufficiently close to be bridged by a H$_2$SiO$_4$ tetrahedra will provide sites that can undergo ligand substitution producing a monomeric silicate surface complex. The average distance between nearest neighbor surface Ti atoms is 3.1 Å ($\sigma = 0.18$ Å). A slightly larger distance of 3.5 Å was taken to be a maximum Ti–Ti distance for monomer H$_4$SiO$_4$ adsorption (d in Fig. 9) based on the edges of SiO$_4$ tetrahedra in minerals which range from 2.4 to 3.0 Å [44] and the possibility of the surface oxygen ions being closer than the underlying Ti atoms. There are 66 surface Ti–Ti pairs at a distance less than 3.5 Å and three isolated Ti ions as shown in Fig. 10 which is explained more fully below.

Sites for oligomerization require adjacent monomers with an appropriate distance and orientation for insertion of a solution H$_4$SiO$_4$. The geometric constraints for oligomers to form between adjacent monomers are based on the position of the Ti cations because of the large number of degrees of freedom to consider in the range of Si–O bond distances and angles. The geometric constraints are based on the length ($d'$) of the line that connects the midpoints of the two Ti–Ti pairs and the angles ($\alpha_1$ and $\alpha_2$) between this line and the lines between each Ti–Ti pair (Fig. 9). Values of $d'$ between 3 and 6.5 Å combined with $\alpha_1$ and $\alpha_2$ values between 60 and 120° (i.e. within 30° of normal) were considered reasonable for oligomerization between adjacent monomers based on empirical tests. For example Fig. 9 shows a trimer on a base with $d' = 6.5$ Å,

![Fig. 9. A linear silicate trimer (light blue tetrahedra) formed between four Ti ions (gray spheres) to illustrate the scheme for structural constraints for H$_4$SiO$_4$ oligomerization on the TiO$_2$(am) surface. The extreme case where $d' = 6.5$ Å and $\alpha_1 = 120°$ is shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)

![Fig. 10. The arrangement of monomer and oligomer sites on the TiO$_2$(am) model of Zhang et al. [4]. (a) All spheres are Ti. Lines between spheres depict monomer sites and lines between midpoints depict oligomer sites. The Ti are from darkest to lightest the oligomerization sites, monomer sites only and isolated Ti ions. The red quadrilaterals depict the sites for the two adjacent trimers depicted in (b). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
\[ z_1 = z_2 = 120^\circ \] and oligomer formation can occur within the range of observed Si–O bond lengths and angles in minerals at this extreme of the constraints even where the Ti–O bonds are constrained to be within 10° of normal to the surface. For values of \( \phi \) close to 3 Å the fact that the minimum Ti–Ti distance is at 2.9 Å further constrains \( z_1 \) and \( z_2 \). For example where \( \phi = 3 \) Å then \( z_1 \) and \( z_2 \) must be such that the two monomer edges of the quadrilateral are within 5° of being parallel. The dihedral angle was not specifically constrained other than its effect on \( z_1 \) and \( z_2 \). With these constraints there are 40 sites for oligomerization on a TiO\(_{2}(am)\) Particle surface. Of the 67 surface Ti ions 54 are part of a potential oligomerization site, 10 are part of monomer sites that are not predisposed to oligomerization while three are not part of monomer or oligomer sites. With these constraints the Si/Ti ratio at maximum surface coverage would be 0.36 compared to largest value measured from the isotherm of 0.29 (Fig. 2).

This model of the surface is depicted in Fig. 10a which shows oligomers can form on most of the particle surface. From this argument it would appear to be reasonable that oligomers can dominate the high curvature of the surface of the small diameter TiO\(_{2}\) particles which keeps adjacent trimers oriented away from each other because of the relationship between adjacent adsorbed trimers. It is clear that some monomer sites would not be predisposed to oligomerization while some are not part of monomer or oligomer sites. With these constraints the Si/Ti ratio maximum surface coverage would be 0.36 compared to largest value measured from the isotherm of 0.29 (Fig. 2).

The similarity in the H\(_2\)SiO\(_4\) oligomerization chemistry on the poorly ordered oxides of both TiO\(_{2}\) and FeO\(_{2}\) suggests the proposed interpretation of silicate oligomerization may be more generally applicable to disordered surfaces, such as 2-line ferrihydrite. From simple geometric arguments nanometer sized oxide particles will have both a high curvature and also a high surface concentration of coordinatively unsaturated cations that will produce surface hydroxyl groups in water. These are the basic features of the proposed silicate oligomerization model. While various structural models for ferrihydrite have been proposed and refuted [45–48] the TiO\(_{2}(am)\) model indicates that nanometer sized particles with crystalline cores will tend to have a highly strained and disordered surface because of the constraints of high surface curvature. The primary particle size of 2-line ferrihydrite is 2–3 nm [45] which is comparable to that of TiO\(_{2}(am)\). In addition the proposed concentration of monomer adsorption sites are comparable on the two oxides i.e. 0.26 per Ti for TiO\(_{2}(am)\) and 0.2 per Fe for ferrihydrite [32]. These structural and morphological similarities may explain the similar silicate surface chemistry on the ferrihydrite and TiO\(_{2}(am)\).

4. Conclusions

Attenuated Total Reflectance IR and \(^{29}\)Si NMR were used to study the adsorption and interfacial condensation reactions of H\(_2\)SiO\(_4\) on the surface of an amorphous TiO\(_{2}\) at pH 9. At low Si surface concentration the IR spectra show that the interfacial silicate is present as monomers with maximum IR absorption at \( \approx 960 \) cm\(^{-1}\). Condensed oligomeric surface species with Si–O–Si linkages and a maximum IR absorbance at \( \approx 1020 \) cm\(^{-1}\) are formed once a threshold surface concentration of silicate monomers was reached. The condensed silicate surface species was considered to be a linear oligomer formed by a solution H\(_2\)SiO\(_4\) bridging adjacent monomers. The data were interpreted using the atomic coordinates for a structural model of amorphous TiO\(_2\) and the geometric constraints of silicate polymerization observed in mineral systems. The surface of the amorphous TiO\(_2\) was conducive to the formation of linear silicate oligomers because it held adjacent monomers in a configuration which allowed for bridging by a solution H\(_2\)SiO\(_4\). Despite the predominance of oligomeric silicate on the TiO\(_2\) surface the formation of three dimensional polymeric silicates was minimal, even close to saturation saturation with respect to a pure SiO\(_2\) phase. This was attributed to the small diameter and high surface curvature of the TiO\(_2\) particles which keeps adjacent oligomers at too large a distance to be bridged by solution H\(_2\)SiO\(_4\).

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Appendix A. Supplementary material


References