Suggested Reference
The influence of surface structure on H₄SiO₄ oligomerization on rutile and amorphous TiO₂ surfaces: An ATR-IR and synchrotron XPS study

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ABSTRACT

Silicic acid (H₄SiO₄) is ubiquitous in natural aquatic systems. Applications of TiO₂ in these systems will be influenced by H₄SiO₄ sorption and oligomerization reactions on the TiO₂ surface and this can affect many aspects of TiO₂ reactivity. The spatial arrangement of sorption sites on a metal oxide surface can promote specific lateral interactions, such as oligomerization, between sorbed species. In this work we explore the relationship between surface structure and interfacial H₄SiO₄ oligomerization by quantifying the extent of H₄SiO₄ sorption and oligomerization on three TiO₂ phases; a rutile phase having well developed (110) faces (R180), a rutile phase with poorly developed (110) faces (R60) and an amorphous TiO₂ (TiO₂(am)). The in situ ATR-IR spectra measured over time as 0.2 mM H₄SiO₄ reacted with TiO₂ were quite different on the 3 TiO₂ phases. The percentage of the surface H₄SiO₄ that was present as oligomers increased over time on all phases but after 20 h almost all H₄SiO₄ on the R180 surface was oligomeric while the H₄SiO₄ on TiO₂(am) was predominantly monomeric. The extent of H₄SiO₄ oligomerization on R60 was intermediate. When the TiO₂ phases reacted with 1.5 mM H₄SiO₄ the ATR-IR spectra showed oligomeric silicates dominating the surface of all three TiO₂ phases, however after 20 h the percentage of the surface H₄SiO₄ present as three dimensional polymers was ≈ 30, 10 and 0 % on R180, R60 and TiO₂(am) respectively. The Si 2s photoelectron peak binding energy (BE) and the H₄SiO₄ surface coverage (Γ_Si) were measured by XPS over a range of Γ_Si. For any given Γ_Si the Si 2s BE’s were in the order R180 > R60 > TiO₂(am). A higher Si 2s BE indicates a greater degree of silicate polymerization. The ATR-IR and XPS results support the existing model for interfacial H₄SiO₄ oligomerization where linear trimeric silicates are formed by insertion of a solution H₄SiO₄ between suitably orientated adjacent bidentate sorbed monomers. The TiO₂(am) has previously been shown to consist of ≈2 nm diameter particles with a highly disordered surface. When compared to the TiO₂(am) surface the regular arrangement of TiO₆ octahedra on the rutile (110) face means that sorbed H₄SiO₄ monomers on adjacent rows of singly coordinated oxygen atoms are oriented so as to favor linear trimer formation. Higher silicate polymers can form between adjacent trimers and this is
favored on the rutile (110) surfaces compared to the TiO$_2$(am). This is also expected based on the arrangement of surface sites on the rutile (110) surface and because the high surface curvature inherent in a \( \approx 2 \) nm spherical TiO$_2$(am) particle would increase the spatial separation of adjacent trimers.

1. Introduction

The TiO$_2$ phases have diverse applications ranging from photocatalysis, photovoltaics, sensors and pigments. Many applications of TiO$_2$ depend on its electronic and optical properties which in turn have a complex dependence on the material’s bulk and surface properties.$^{1-4}$ The association of silicon oxides with TiO$_2$ can dramatically alter bulk properties, such as mineralogy and morphology. For example, in mixed Ti/Si oxides the temperature of the anatase to rutile phase transition increases from 700 to 1000 °C as the amount of Si increases from 0 to 5 atom percent.$^5$ Silicon oxides also alter the surface properties of TiO$_2$ for example the Lewis acid character of pure TiO$_2$ changes to a Bronsted acid character at low SiO$_2$ coverage.$^6$ Silicon oxides have been shown to promote the catalytic activity of TiO$_2$ phases in several reactions$^{7-9}$ either through SiO$_2$ modifying the TiO$_2$ surface electronic structure$^{10}$ or by increasing substrate adsorption affinity.$^{11}$ Because silicates are ubiquitous in natural water systems the study of silicate chemistry on TiO$_2$ surfaces is also relevant to TiO$_2$ use in aqueous systems such as photocatalysis in water treatment. In this work we explore the relationship between the arrangement of TiO$_6$ octahedra on the TiO$_2$ surface and silicate sorption and oligomerization on that surface in aqueous systems. This work contributes to the applications of TiO$_2$ and to the many fundamental studies of chemistry at the TiO$_2$-water interface.$^{12-14}$

The spatial arrangement of sorption sites at the metal oxide/water interface can promote specific lateral interactions, such as condensation reactions, between sorbed species.$^{15}$ For example solid state $^{29}$Si NMR and in situ infrared spectroscopy of silicic acid (H$_4$SiO$_4$) polymerization at the aqueous interface of 2-3 nanometer sized amorphous particles of both Ti$^{IV}$ and Fe$^{III}$ oxides indicated the almost exclusive formation of linear trimeric silicates.$^{16-18}$ In contrast a recent $^{29}$Si NMR correlation spectroscopy study of H$_4$SiO$_4$ polymerization in an aqueous solution detected 48 species with a diverse
range of linear, branched, cyclic and cage structures. A structural model was proposed for interfacial silicate oligomerization that was consistent with all the spectroscopic data. In this model silicate monomers sorb on Ti$^{IV}$ and Fe$^{III}$ oxide surfaces via a bidentate and binuclear surface complex in which SiO$_4$ tetrahedra share two corners with singly coordinate oxygen ions on the corners of the adjacent edge sharing FeO$_6$ or TiO$_6$ octahedra (depicted in Figure 1, panel 2). This type of bidentate, binuclear surface complex has been invoked to describe many, but not all, ligand exchange reactions on oxide surfaces. Each sorbed SiO$_4$ monomer has 2 terminal non-bonding OH groups and linear trimers form on the Ti$^{IV}$ and Fe$^{III}$ oxide surfaces by insertion of a solution H$_4$SiO$_4$ between suitably orientated, adjacent, sorbed silicate monomers.

The work of Zhang et al shows that the amorphous TiO$_2$ (TiO$_2$(am)) consists of ≈ 2 nm diameter particles with a high surface concentration of Ti cations that are coordinatively unsaturated in the absence of H$_2$O. In an aqueous suspension these Ti cations are considered to be the H$_4$SiO$_4$ sorption sites. It has been demonstrated for TiO$_2$(am) that the high surface sorption site concentration means that almost all H$_4$SiO$_4$ monomer sorption sites have an adjacent monomer site with suitable orientation for the formation of linear silicate trimers. The high surface curvature inherent to a ≈ 2 nm sized particle inhibits the condensation reactions between adjacent silicate trimers so these surfaces do not favor the formation of more highly condensed surface silicates. The current work compares H$_4$SiO$_4$ surface chemistry on the disordered, high curvature TiO$_2$(am) surface with H$_4$SiO$_4$ surface chemistry on the ordered, low curvature surfaces of rutile needles.

Bae et al prepared rutile needles with predominantly 110 terminations which provides an interesting surface to explore the relationship between surface structure and surface silicate oligomerization. The enclosing faces for the rutile needles are depicted in Figure 1. The rutile-water interface has been the subject of many theoretical studies. Despite this (or possibly because of this) there is controversy as to whether the singly co-ordinated oxygen atoms depicted in Figure 1 are actually coordinated to the Ti or if the Ti is 5 co-ordinate with a loosely associated H$_2$O. This debate is not directly relevant to our study and we depict the [110] terminations as having rows of singly coordinated oxygen ions on the
corners of the TiO₆ octahedra alternating with rows of doubly coordinate oxygen ions on the TiO₆ edges. Adjacent singly coordinated oxygen ions within a row are spaced at 2.96 Å which lies within the 2.4 - 3.0 Å range for the edges of SiO₄ tetrahedra in silicate minerals.²⁵ This implies that H₄SiO₄ can form bidentate monomeric complexes between adjacent singly coordinated oxygen ions. Figure 1 shows several SiO₄ tetrahedra sorbed on a (110) surface and oriented normal to the surface plane. There is 5.9 Å between the terminal Si-OH groups of adjacent monomers on the same row (i.e. in the [001] direction) which is too large to allow for insertion of a solution H₄SiO₄ to form a trimeric species. In contrast the terminal Si-OH groups of monomers on adjacent rows of single coordinated oxygen atoms (i.e. in the [1̅10] direction) are orientated towards each other at a distance of 3.8 Å and also have freedom to pivot towards each other such that their terminal Si-OH groups become sufficiently close for insertion of a solution H₄SiO₄ to form a linear trimeric species. Comparison of these adjacent monomers with a trimeric section of the linear silicate ferrosilicate (Figure 1) suggests that the rutile (110) face could act as a template for the formation of linear trimeric silicates with further linear polymerization (such as to a pentamer) presumably inhibited by the diminished degrees of freedom of trimers termini.¹⁶ On the (111) face adjacent corner oxygen ions are 5.5 Å apart in both directions which does not allow for H₄SiO₄ adsorption so this face is not considered in this work. The (001) face contains only TiO₆ edges which are alternately on the surface and below the surface. Each TiO₆ edge has 2 corner oxygen atoms which are 3.3 Å from the nearest neighbor, however, because the (001) is a very minor face it is assumed for the purposes of this work that only H₄SiO₄ sorption on (110) is relevant.
Numerous studies have demonstrated that in situ Attenuated Total Reflectance Infrared Spectroscopy (ATR-IR) is a powerful tool in the study of silicate sorption and polymerization reactions on metal oxide surfaces.\textsuperscript{17, 18, 26-29} The shape and position of the (Si-O) stretching modes ($\nu$(Si-O)) of sorbed silicates provide insight into the symmetry of the surface complex and on the degree of silicate polymerization. For example monomeric silicates sorbed on Ti\textsuperscript{IV} and Fe\textsuperscript{III} oxide surfaces at low Si surface concentrations ($\Gamma_{\text{Si}}$) have $\nu$(Si-O) bands centered at $\approx$ 950 cm$^{-1}$ with band splitting\textsuperscript{17, 18} consistent with the bidentate and binuclear surface complex proposed from Extended X-ray Absorption Fine Structure (EXAFS) spectra.\textsuperscript{20} As $\Gamma_{\text{Si}}$ increases silicate condensation produces a species with $\nu$(Si-O) bands centered at $\approx$ 1100 cm$^{-1}$.
1020 cm⁻¹ which is attributed to a linear trimeric silicate based on the IR and solid state ²⁹Si NMR data.¹⁶ A minor IR feature at ≈ 1100 cm⁻¹ at high Γₜₙ indicates the formation of a small amount of a three-dimensional SiO₂ phase. X-ray photoelectron spectroscopy (XPS) is also an effective probe for the degree of silicate polymerization. In silicate minerals the Si 2s binding energy (BE) increases systematically from ≈ 152.8 eV to ≈ 154.4 eV as silicate polymerization increases from isolated (i.e. monomeric) SiO₄⁴⁻ tetrahedra of almandine to the fully polymerized quartz.³⁰ The Si 2s BE for H₄SiO₄ on an iron oxide surface increased from 153.1 to 153.9 eV as the surface H₄SiO₄ species changed from being almost exclusively monomeric to trimeric.³¹ Synchrotron radiation certainly facilitates the XPS measurements but was primarily used so that the Si K edge X-ray adsorption spectra could also be measured. The current paper uses in situ ATR-IR and synchrotron XPS to compare interfacial silicate condensation reactions on the surface of the TiO₂(amide) with two rutile phases with different morphologies. The proposed model of heterogeneous silicate oligomerization predicts that, compared to TiO₂(amide), the arrangement of TiO₂ octahedra on the rutile (110) face would promote linear oligomer formation and possibly the formation of silicates with a higher degree of polymerization. The purpose of this study is to test this model.

2. Materials and Methods

Materials

All solutions and suspensions were made from 18.2 MΩ cm resistivity deionized water that was distilled, acidified to pH ~ 4 and then sparged with N₂. Isothermally distilled HCl and low-carbonate NaOH solutions were used to adjust the pH. The distillation of H₂O and HCl removes ppb level traces of SO₄⁻² which sorb to iron oxides at low pH producing a surprisingly intense band at ≈ 1100 cm⁻¹. A 1.66 mM monomeric silicic acid (H₄SiO₄) stock solution in 0.1 M NaCl at pH 4 was prepared as previously described in detail¹⁷ by dissolving amorphous silica in 50:50 (w/w) NaOH/H₂O followed by dilution, pH adjustment and sparging with N₂. An amorphous TiO₂ (TiO₂(amide)) was prepared by titanium ethoxide hydrolysis in a 0 °C ice-water bath using the method of Zhang et al.³². Two rutile
phases with distinct morphologies were synthesized by the hydrolysis of TiCl₃ at either 60 or 180 °C and are therefore termed R60 and R180 respectively. The R60 rutile was prepared by adjusting the pH of a 0.15 M TiCl₃ solution to 4 under an air atmosphere and then keeping the solution in a closed vessel at 60 °C for 24 h. The R180 rutile was prepared from a 0.15 M TiCl₃ solution prepared by dilution of 20 % TiCl₃ in 3 % HCl without pH adjustment. Hydrolysis was achieved by keeping the 0.15 M TiCl₃ in 5 M NaCl at 180 °C in a sealed Teflon-lined autoclave reactor for 6 h. Each TiO₂ suspension was centrifuged and rinsed repeatedly with water. A portion of the rinsed suspension was dried in a vacuum oven at 70 °C for X-ray diffraction (XRD) and surface area analysis used the Brunauer-Emmer-Teller (BET) N₂ adsorption method at −195 °C with a Micromeritics Tristar 3000 instrument. The TiO₂ used for sorption experiments was not dried. The TiO₂(am) suspensions were used within a week of synthesis because Raman and XRD demonstrated some crystallization occurring when suspensions were stored for several months at room temperature. For example after freeze drying a 6 month old TiO₂(am) suspension the powder XRD contained a small narrow peak corresponding to the main rutile peak and larger but broader peaks corresponding to anatase. The morphology of the TiO₂ particles was examined by transmission electron microscopy (TEM) and selected area electron diffraction (SAED).

Adsorption experiments

The effect of pH on H₄SiO₄ sorption and H₄SiO₄ sorption isotherms were measured using a batch method. Suspensions of TiO₂(am), R60 and R180 were prepared in 0.1 M NaCl and distributed into a number of 50 mL polypropylene centrifuge tubes. Stock H₄SiO₄ solution was added to each tube and the pH adjusted to the desired value. The tubes were capped and equilibrated for 48~60 h on an end-over-end mixer and over this time the small drifts in pH were corrected manually at intervals. After equilibration the pH was remeasured, and the solid phase removed by centrifugation followed by filtration through a 0.2 μm cellulose acetate membrane. Based on reactivity with molybdenum yellow and the thermodynamic database of Felmy et al all solution phase Si is monomeric and this concentration (S_{isol}) was measured with the molybdenum blue method. For the adsorption isotherms
the solid phase Si to Ti amount ratios (on a mole per mole basis) were measured by electron microprobe analysis of polished mounts of the solids set in an epoxy resin. The solids were collected on the filter membrane, rinsed for a few seconds with water to remove solution phase Si and then freeze dried. Microprobe analysis was used because the very low solubility of TiO$_2$ makes quantification of TiO$_2$, and therefore the solid phase Si/Ti ratio, by acid digestion difficult.

**ATR-IR Experiments**

For the ATR-IR experiments $\approx 5$ µL of a 1 g/L suspension of TiO$_2$ (TiO$_2$(am), R60 or R180) was deposited on a Smart Orbit$^\text{®}$ single bounce diamond ATR crystal and the water evaporated at room temperature. After $\approx 1$ h a TiO$_2$ film remained on the diamond surface and this was mounted in a flow cell in a Thermo 8700 FTIR Spectrometer equipped with an MCT detector and controlled using Omnic software. The TiO$_2$ film was rinsed with 0.1 M NaCl at pH 11 for $\approx 1$ h to remove carbonate which desorbs from the TiO$_2$ at high pH and then equilibrated with 0.1M NaCl electrolyte at pH 9 for 2 - 4 h. Background IR spectra were collected over this time and H$_4$SiO$_4$ stock solution was added to the electrolyte once a stable background spectrum was obtained. The pH of this silicic acid solution was kept at 9.0 and the solution was circulated at $\approx$1 mL min$^{-1}$. ATR-IR spectra (resolution of 2 cm$^{-1}$) were collected over time as the H$_4$SiO$_4$ equilibrated with the TiO$_2$ surface until there was little change in the spectra as a function of time (24–48 h). The matrix of ATR-IR spectra were analysed using multivariate curve resolution with alternating least squares (MCR-ALS) in Matlab$^\text{®}$.35

**XPS Analysis**

Samples for XPS analysis were prepared in batches. Silicic acid stock solution was added to TiO$_2$ suspensions to yield a range of Si/Ti ratios as for the adsorption isotherms at I = 0.1 M and pH = 9.0. Suspensions were equilibrated for 48 h and the pH was readjusted to 9.0 at intervals to correct for small drifts in pH. After equilibration suspensions were centrifuged, and the resulting paste was collected on a 0.22 µm cellulose acetate membrane and briefly rinsed with water. Silicate-free TiO$_2$ samples were prepared at the same time following the same procedures. The ATR-IR spectrum of
each paste was measured directly using the appropriate silicate free paste as background and the remaining pastes were freeze dried for further ATR-IR, electron microprobe and XPS analysis. The H$_4$SiO$_4$ concentration of the supernatant was measured with the molybdenum blue method.

XPS spectra were collected at the soft x-ray spectroscopy beamline of the Australian Synchrotron. Samples were mounted on carbon tape and measurements were conducted at excitation energy of 1486.6 eV with a 10 eV pass energy and a 0.10 eV step. A low energy electron flood gun was employed to neutralize the sample charge during spectra collection. A carbon 1s BE of 285 eV for adventitious hydrocarbon was used as an internal reference for BE shifts. Data were analyzed with CasaXPS software. Peak fitting used a Shirley-type background and a Gaussian-Lorentzian (20:80) product peak. The surface Si/Ti mole ratios ($\Gamma_{\text{Si(XPS)}}$) were determined from the areas of the Si 2s and Ti 2p peaks.

3. Results and Discussion

3.1. Characterization of the TiO$_2$ materials

The X-ray diffraction patterns of the three TiO$_2$ powders are shown in Figure SI 1. The rapid hydrolysis of titanium tetraethoxide produces a phase with weak broad humps in the XRD trace that do not correspond to the crystalline TiO$_2$ phases and for this reason the material has been described as amorphous (TiO$_2$(am)).$^3$ The hydrolysis of TiCl$_3$ produced phases with XRD patterns characteristic of a pure rutile in which the main peak at 27.45 2$\theta$° had a FWHM of 2.9 and 0.29 for R60 and R180 respectively. The R180 TEM and SAED (Figure 2) show single crystal needles with widths of $\approx 25$ nm and an aspect ratio of $\approx 10$. Needles are elongated in the 001 direction and the sides of the needles are terminated by [110] crystal faces while the needle ends are predominantly terminated with [111] faces.$^{21}$ The R60 material consists of rod shaped particles with dimensions of $\approx 15 \times 5$ nm. The particles are reported to have [110] faces along the length of the rods with ends terminated by [001] faces.$^{33}$ The TiO$_2$(am) phase had no discernable features in the TEM.
The terminal Ti-O groups on the rutile (110) surface which are involved in silicate sorption (Figure 1) are denoted here as \( \equiv \text{TiOH} \) and have a density of 5.2 nm\(^{-2}\). The measured SSA of R180 was 27 m\(^2\)g\(^{-1}\) and based on the proposed morphology \( \approx 95\% \) of the surface is terminated by [110] faces corresponding to an overall \( \equiv \text{TiOH} \) density of 4.9 nm\(^{-2}\) or 0.018 moles \( \equiv \text{TiOH} \) per mole TiO\(_2\). The measured SSA of R60 was 220 m\(^2\)g\(^{-1}\) and \( \approx 86\% \) of the surface is terminated by [110] faces corresponding to an overall \( \equiv \text{TiOH} \) density of 4.5 nm\(^{-2}\) or 0.13 moles \( \equiv \text{TiOH} \) per mole TiO\(_2\). The surface area calculated using the above morphologies and the rutile density (4.25 g cm\(^{-3}\)) were 41 and 220 m\(^2\)g\(^{-1}\) for R180 and R60 respectively. The lower measured SSA for R180 could be due to the “rafting” of crystals as observed in the TEM while the R60 calculated value is somewhat surprisingly identical to the measured value.

![Figure 2](image)

**Figure 2** TEM images and selected area electron diffraction (SAED as a negative image) of rutile produced from TiCl\(_3\) hydrolysis at 180 °C (TEM part a, and SAED part b) and 60 °C (TEM part c, and SAED part d).
Zhang et al’s structural model for the TiO$_2$(am) particle contains 123 Ti atoms and 246 O atoms (Fig. SI 2). In this model the particle has a diameter of $\approx 2$ nm and the average Ti coordination number for the whole particle is 5.3 due to the truncation of the many TiO$_6$ octahedra on the particle surface. Out of the 123 Ti ions in a particle 67 were on the particle surface with a co-ordination number less than six and these were considered to be surface active giving 0.54 mole $\equiv$TiOH per mole TiO$_2$. The theoretical TiO$_2$(am) SSA would be 800 m$^2$ g$^{-1}$ and with this value the $\equiv$TiOH site density would be 8.9 µmol m$^{-2}$. However, the measured SSA in this work (390 m$^2$ g$^{-1}$) and from Zhang et al $^3$ (433 m$^2$ g$^{-1}$) were considerably lower than the theoretical value because of particle aggregation promoted by the drying of the material prior to the BET analysis. Therefore the SSA that is relevant to the aqueous suspensions of TiO$_2$(am) will lie between the BET value of 390 m$^2$ g$^{-1}$ and the theoretical value of 800 m$^2$ g$^{-1}$ depending on the extent of particle aggregation in suspensions under the experimental conditions of this work. This difference in measured SSA and the SSA based on primary particle size is similar to that observed for the nanometer sized iron oxide phase ferrihydrite where a value of 600 m$^2$g$^{-1}$ is often used for the material in aqueous suspension based on assessments of the oxide’s reactivity.

3.2. H$_4$SiO$_4$ chemistry at the TiO$_2$ surfaces

*Macroscopic properties:* The adsorption of H$_4$SiO$_4$ from solution by the three TiO$_2$ phases is shown as a function of pH in Figure SI3. On all TiO$_2$ phases the maximum H$_4$SiO$_4$ adsorption occurs at pH $\approx 9$, close to the H$_4$SiO$_4$ pK$_{A,1}$. A similar effect of pH has been observed for H$_3$AsO$_3$ adsorbed on TiO$_2$ and also for H$_4$SiO$_4$ adsorbed on several iron oxides and the reasons for this general phenomenon have been discussed. All TiO$_2$ samples for IR and XPS analysis in this work were prepared at pH 9. The H$_4$SiO$_4$ isotherms at pH 9 are plotted as the bulk solid phase Si/Ti mole ratio ($\Gamma_{BK}$) from the microprobe analysis in Figure 3a. The solid vertical line shows the maximum Si$_{sol}$ (2.2 mM) with respect to SiO$_2$(am) precipitation at pH 9 and the Si$_{sol}$ relevant to the ATRIR experiments (0.2 and 1.5 mM) are also indicated. The horizontal line segments show the maximum surface coverage ($\Gamma_{BK,max}$) for each TiO$_2$ calculated from the number of singly coordinated oxygen ions assuming either trimeric
silicate coverage i.e. 3 Si per 4 singly coordinated $\equiv$TiOH groups, or monomeric silicate coverage i.e. 1 Si per 2 singly coordinated $\equiv$TiOH groups. This calculation used the site densities in Section 3.1. The main difference between the three isotherms is the material surface area and in each case $\Gamma_{BK}$ is close to the calculated $\Gamma_{BK,max}$ based on trimeric coverage as Si$_{sol}$ approaches saturation with respect to SiO$_2$(am).

The isotherms with $\Gamma$ given as surface concentrations ($\Gamma_{SA}$ as $\mu$mol m$^{-2}$) are shown in Figure 3b. For both rutiles the $\Gamma_{SA}$ were calculated using the measured SSA’s. The TiO$_2$(am) $\Gamma_{SA}$ are shown based on the highest BET value (430 m$^2$g$^{-1}$) and the theoretical SSA (800 m$^2$g$^{-1}$) while the theoretical maximum value of $\Gamma_{SA}$ ($\Gamma_{SA,MAX}$) is independent of the amount of TiO$_2$ aggregation. Comparing the TiO$_2$(am) $\Gamma_{SA,MAX}$ to values calculated using the two SSA’s implies that the true SSA for the TiO$_2$(am) in suspension is closer to the theoretical value of 800 m$^2$g$^{-1}$. At low $\Gamma_{SA}$ there is a clear trend where $\Gamma_{SA}$ is largest on R180 with the most crystalline surface and lowest on TiO$_2$(am), even assuming 430 m$^2$g$^{-1}$ SSA. Assuming 800 m$^2$g$^{-1}$ SSA the $\Gamma_{SA}$ of the TiO$_2$(am) are lowest over the whole isotherm. All measured R180 $\Gamma_{SA}$ lie above those of R60. Bearing in mind the uncertainties in the surface area assessments this order of the isotherm curves agrees with the hypothesis that the arrangement of $\equiv$TiOH groups on the rutile 110 face favors H$_4$SiO$_4$ coordination and condensation and this is further explored below using ATR-IR and XPS.
Figure 3 The $H_4SiO_4$ isotherms on the three TiO$_2$ phases at pH 9, 0.1 M NaCl and with 48-60 h equilibration time. (a) solid phase Si shown as the bulk phase Si/Ti from microprobe analysis (b) $H_4SiO_4$ surface concentrations calculated from the data in (a) and each TiO$_2$ phases specific surface area. Calculated $\Gamma_{\text{MAX}}$ are shown as horizontal lines (m.c. based on monomer cover only, o.c. based on oligomer cover). The $H_4SiO_4$ solubility limit with respect to SiO$_2$(am) is the solid vertical line, dotted vertical arrows are the $S_{\text{isol}}$ used in the ATRIR experiments.

In situ ATR-IR spectra of 0.2 mM $H_4SiO_4$ sorbing on the three TiO$_2$ surfaces:

The IR spectra measured over time as 0.2 mM $H_4SiO_4$ reacts with films of the three types of TiO$_2$ are shown in Figure 4. The spectra of all three TiO$_2$ materials have the same general trends as previously reported for TiO$_2$(am)\cite{16} in which maximum absorbance initially occurs at $\approx 950$ cm$^{-1}$ due to the initial adsorption of monomeric species with Si-O-Ti and terminal Si-O bonds. Over time a feature centred at $\approx 1010$ cm$^{-1}$ becomes increasingly dominant in all spectra due to the formation of oligomeric silicate species with Si-O-Si bonds.\cite{1, 39-43} Given that the $S_{\text{isol}}$ in these experiments is $\approx 10$ times below the solubility of amorphous silica, the role of the TiO$_2$ surfaces in promoting silicate condensation is evident. The $S_{\text{isol}}$ is above the solubility of quartz however quartz does not precipitate form solution for
kinetic reasons. From the shape of the spectra on the different oxides it is also evident that for TiO$_2$ reacting with 0.2 mM H$_4$SiO$_4$ the extent of interfacial silicate oligomerization is greatest on the well crystalline rutile (R180) and lowest on the TiO$_2$(am) phase with the poorly crystalline R60 being intermediate. This order in the ATR-IR spectra is consistent with the expectation from the supposed significance of the rutile (110) face in acting as a template for oligomerization.

![Figure 4](image.png)

**Figure 4** ATR-IR spectra measured over time as H$_4$SiO$_4$ adsorbed on the surface of TiO$_2$(am), R60 and R180 at pH 9 and 0.1 M NaCl. Spectra at selected time intervals are labeled. Final concentration of H$_4$SiO$_4$ is 0.2 mM.
For each TiO$_2$ phase the initial peak was at 950 - 960 cm$^{-1}$ and there was no change in the shape of the spectra collected over the first 10 minutes of each experiment with 0.2 mM H$_4$SiO$_4$. This suggests that only the monomeric surface silicate species is formed. However there are differences in the shape of the monomer spectra on the three TiO$_2$ phases which are shown in Figure 5 together with the solution H$_4$SiO$_4$ spectrum. The solution H$_4$SiO$_4$ spectrum has a triply degenerate asymmetric $\nu$(Si-O) mode ($\nu_3$) at 939 cm$^{-1}$ which is clearly split into three $\nu_3$ peaks for the H$_4$SiO$_4$ sorbed on TiO$_2$(am). Interestingly only two $\nu$(Si-O) peaks are evident for H$_4$SiO$_4$ sorbed on both rutile phases and the splitting is particularly well defined on the R180. This could mean that the monomeric silicate is adsorbed via a monodentate complex on the rutile but a bidentate complex on the TiO$_2$(am). Alternatively two of the three $\nu_3$ modes on rutile could be sufficiently close together that they are not resolved in the spectrum. To explore this possibility the $\nu$(Si-O) frequencies were calculated from a single point calculation using Hartree-Fock level of theory and a 6-31G basis set for the structures in Figure SI4 which have a silicate monomer on a section of rutile or TiO$_2$(am) with hydrogen atoms on the terminal oxygen atoms. On the rutile surface the SiO$_4$ $\nu_3$ modes occurred at 953, 962, and 987 cm$^{-1}$ while on the TiO$_2$(am) the SiO$_4$ $\nu_3$ modes occurred at 958, 1028, and 1111 cm$^{-1}$. It is evident that the splitting on the rutile surface is substantially smaller than that on TiO$_2$(am) and the calculations suggest that it is reasonable to consider that, even though a bidentate complex on the rutile surface has symmetry of C$_{2v}$ or lower, the spectrum may only show two resolved $\nu_3$ modes, especially given the width of the ATR-IR bands. In contrast the same calculated frequencies for a monomeric silicate on a section of the TiO$_2$(am) surface are each quite distinct which is consistent with the three bands in the spectrum.
Figure 5 ATR-IR spectra for H$_4$SiO$_4$ in solution and as a monomer adsorbed on the surface of TiO$_2$(am), R60 and R180 (at time $\approx 10$ min). The negative second derivatives (Savitsky Golay) are also shown.

It is also informative to compare the shapes of the IR spectra for H$_4$SiO$_4$ sorbed on the three TiO$_2$ phases at the end of the experiments with 0.2 mM H$_4$SiO$_4$. The spectra at the end of these experiments represent a mix of monomeric and oligomeric silicates (Figure 6). The intensity of the IR absorbance in the region of 950 cm$^{-1}$ is TiO$_2$(am) > R60 > R180 as expected from the above arguments. However the order of IR absorbance at $\nu > 1000$ cm$^{-1}$ is R60 > TiO$_2$(am) > R180 because the R180 spectrum decreases more rapidly than the R60 or TiO$_2$(am) as $\nu$ increases from 1000 to 1250 cm$^{-1}$. This is counter to the general observed trend and may indicate that the oligomeric silicate on the R180 has a differently shaped spectrum compared to the R60 and TiO$_2$(am) and this will be explored in relation to the ATR-IR spectra measured with higher surface coverage.

1200 1100 1000 900 800
ν (Si-O)
δ (Si-O-H)
H$_4$SiO$_4$ on TiO$_2$(am)
H$_4$SiO$_4$ on R60
H$_4$SiO$_4$ on R180
H$_4$SiO$_4$ in solution

Absorbance

Wavenumber (cm$^{-1}$)
$\frac{dA}{d\lambda}$
**Figure 6** ATR-IR spectra from the end of the experiments with 0.2 mM H₄SiO₄ adsorbed on the surface of TiO₂(am), R60 and R180.

*In situ ATR-IR spectra of 1.5 mM H₄SiO₄ sorbing on the three TiO₂ surfaces:*

The υ(Si-O) region of IR spectra measured over time as 1.5 mM H₄SiO₄ sorbs onto TiO₂ (Fig 7) are similar in shape for each of the three types of TiO₂ with the maximum IR absorbance occurs at ≈1010 cm⁻¹ after ≈0.5 h and the position of the maximum does not change after this time. To highlight the more subtle differences in shapes the spectra are shown in Figure 7 with IR absorbance normalized and the unscaled spectra are shown in Figure SI5. Apart from the different spectral shape for the rutile samples at low Γ_Si the major differences between the spectra occur around 1100 cm⁻¹ where 3 dimensional SiO₂ polymers absorb in the IR. After ≈16 h there is little change in IR absorbance around 950 cm⁻¹ on the TiO₂(am) and also little change in IR absorbance around 1100 cm⁻¹. In contrast to this on the R60 there is little change in IR absorbance around 950 cm⁻¹ after ≈3h but the IR absorbance around 1100 cm⁻¹ increases over time producing a distinct peak indicating that at higher Γ_Si a greater degree of polymerization is occurring beyond the formation of 1 dimension oligomers. For silicates on the R180 there is little change in IR absorbance around 950 cm⁻¹ after ≈0.5 h but the IR absorbance...
around 1100 cm$^{-1}$ increases over time again indicating polymerization beyond 1 dimension at higher $\Gamma_{\text{Si}}$. While a greater degree of 3 dimensional polymerization occurs on the rutile compared to the TiO$_2$(am) the dominant surface silicate phase on all TiO$_2$’s was oligomeric and not 3 dimensional polymers even when the Si$_{\text{sol}}$ is within 70 % of solubility limit for SiO$_2$(am).

![ATR-IR spectra](image_url)

**Figure 7** ATR-IR spectra measured over time as H$_4$SiO$_4$ adsorbed on the surface of TiO$_2$(am), R60 and R180 at pH 9 and 0.1 M NaCl. All spectra have absorbance normalized and spectra at selected time intervals are labeled. Final concentration of H$_4$SiO$_4$ is 1.5 mM and this does not change appreciably over the experiment because the amount of TiO$_2$ is so low.

*A quantitative analysis of sorbed silicate speciation from the ATR-IR spectra*

To quantify the differences between the IR spectra for silicates on the three TiO$_2$ phases MCR-ALS was used to decompose the data matrix for each oxide (termed D) into the product of two matrices; the
spectra matrix (termed $S$) represents the spectra of each of the three pure surface species and the composition matrix (termed $C$) represents the contribution of each of the three surface species to each measured spectrum.\textsuperscript{35} This requires initial estimates of the spectra of each of the three pure surface species and these initial estimates can either be fixed (it is known with) or optimized to fit $D$. The measured spectra for $H_4SiO_4$ on $TiO_2$(am) were well described with $S$ fixed to the values from Swedlund et al\textsuperscript{16} (termed $S_{am}$) and the evolution of the surface speciation over time is shown in Figure 8 with typical fits to spectra shown in Figures SI6a, SI7a and SI8a. The pure species spectrum for R60 ($S_{R60}$) had the monomer spectrum fixed to the R60 spectrum in Figure 5 while the initial estimates of the pure oligomeric and polymeric spectra were taken from $S_{am}$ because of the similar shape of the R60 and $TiO_2$(am) spectra at high surface coverage. The matrix $S_{R60}$ and the fits to the R60 spectra were not altered appreciably if the oligomeric and polymeric silicate spectra were optimized. The evolution of the surface speciation over time for R60 is shown in Figure 8 with typical fits to spectra shown in Figures SI6b, SI7b and SI8b. The pure species spectrum for R180 ($S_{R180}$) had the monomer spectrum fixed to the R180 spectrum in Figure 5 while the initial estimates of the pure oligomeric spectrum was taken as the R180 spectrum in Figure 7 because of the different shape of the R180 compared with the R60 and $TiO_2$(am) spectra at high surface coverage. The pure polymeric phase spectrum was taken from $S_{am}$. The $S_{R180}$ matrix and the fits to the R180 spectra were not altered appreciably if the spectra of the R180 oligomeric and polymeric species were optimized. The evolution of the surface speciation over time for R180 is shown in Figure 8 with typical fits to spectra shown in Figures SI6c SI7c and SI8c.

The effect of the rutile (110) structure on interfacial silicate oligomerization is very clear from Figure 8. As $TiO_2$ reacts with 0.2 mM $H_4SiO_4$ the disappearance of monomeric silicate occurs more rapidly and to a greater extent on the most ordered rutile compared to the $TiO_2$(am) as expected from the arrangement of monomer sorption sites acting as a template for oligomerization. The less ordered R60 rutile has silicate polymerization that is between that of the R180 ordered rutile and the $TiO_2$(am). As $TiO_2$ reacts with 1.5 mM $H_4SiO_4$ the disappearance of monomeric silicate also occurs more rapidly on the most ordered rutile and in addition to this the formation of higher polymers is promoted on the most
ordered rutile surface. This is expected based on the argument that the high curvature of the TiO$_2$(am)surface inhibited further condensation between silicate trimers. Again the less ordered rutile behaviour is between that of the ordered rutile and the TiO$_2$(am).

![Graphs showing the evolution of surface silicate species](image)

**Figure 8** The evolution over time of surface silicate species as TiO$_2$ reacts with H$_4$SiO$_4$ at either 0.2 mM (a) or 1.5 mM (b) as estimated from the area of spectral components fitted using MCR-ALS. Solid symbols are monomeric and open symbols are polymeric (only present in b). Oligomers make up the total to 100 %.

*XPS spectra of H$_4$SiO$_4$ on the TiO$_2$ surface*

The Si 2s XPS spectra (Figure 9) of the reference minerals show the expected shift to higher binding energy (BE) as the silicate changes from the isolated SiO$_4$ monomers in the mineral almandine to the 3 dimensional polymer of quartz. Similarly the Si 2s peak shifts to higher BE as the surface concentration of silicate increases on the TiO$_2$(am) phase as was observed for silicate on the iron oxide ferrihydrite. Considering silicate polymerization as replacing Si-O-H bonds with Si-O-Si bonds then the systematic
shift in the Si 2s BE to higher energy as the degree of silicate polymerization increases\textsuperscript{30} occurs because of the very electropositive Si cation with a formal 4\textsuperscript{+} charge. The Si 2s BE will be different for Si in different polymerization states, such as those on the end or in the middle of a linear oligomer. However, the resolution of the XPS signal is not sufficient to distinguish the individual Si states and the spectrum from each sample has one broad symmetrical peak. The Si 2s peak occurs at $\approx 153.5$ eV for silicates on both the TiO$_2$(am) and the ferrihydrite at high surface coverage. This position lies midway between the quartz and almandine peak and occurs in the region of linear silicate mineral phases such as orthopyroxene ((Mg,Fe)SiO$_3$) which has a Si 2s BE of 153.4 eV\textsuperscript{30}. The lowest surface Si/Ti was 0.11 for TiO$_2$(am) and the lowest Si/Fe was 0.03 for ferrihydrite and for these samples the Si 2s peaks occurred at 153.1 and 152.7 eV respectively compared to the almandine peak at 152.9 eV.

\textbf{Figure 9} The Si 2s peak in the XPS spectra of (a) silicates in the minerals almandine ($\text{Fe}^{11/3}\text{Al}_2\text{(SiO}_4\text{)}_3$)) and quartz (SiO$_2$) (b) silicates on TiO$_2$(am) and (c) silicates on ferrihydrite. The XPS determined Si/Ti or Si/Fe mole ratios are shown.
Despite the lack of resolution of the Si 2s peaks the XPS spectra have the advantage of providing a surface Si/Ti mole ratio in conjunction with a peak whose position which is indicative of the degree of silicate polymerization. The position of the Si 2s peak for H₄SiO₄ on the surface of the three TiO₂ oxides is shown as a function of the XPS determined surface coverage in Figure 10 with the corresponding data for the Si 2s peaks for H₄SiO₄ on ferrihydrite. Compared to the Si of ferrihydrite the Si on the TiO₂ phases have a Si 2s BE in the narrow range between 153.1 eV and 153.4 eV but within this range there is a clear trend where for a given surface coverage a higher Si 2s BE is observed on the more ordered rutile surface and the lowest Si 2s BE on the disordered surface.

![Figure 10](image_url)

**Figure 10** The position of the Si 2s peak in the XPS spectra of silicates on the surfaces of TiO₂(am), R60, R180 and ferrihydrite.

**CONCLUSIONS**

The relationship between surface structure and interfacial H₄SiO₄ oligomerization was explored using three TiO₂ phases; a rutile phase having well developed (110) faces (R180), a rutile phase with poorly developed (110) faces (R60) and an amorphous TiO₂ (TiO₂(am)). *In situ* ATR-IR spectra measured over time as 0.2 mM H₄SiO₄ reacted with TiO₂ were quite different on the 3 TiO₂ phases. The percentage of the surface H₄SiO₄ that was present as oligomers increased over time on all phases but after 20 h almost all H₄SiO₄ on the R180 surface was oligomeric while the H₄SiO₄ on TiO₂(am) was predominantly...
monomeric. The extent of H₄SiO₄ oligomerization on R60 was intermediate. When the TiO₂ phases reacted with 1.5 mM H₄SiO₄ the ATR-IR spectra showed oligomeric silicates dominating the surface of all three TiO₂ phases, however after 20 h the percentage of the surface H₄SiO₄ present as three dimensional polymers was ≈ 30, 10 and 0 % on R180, R60 and TiO₂(am) respectively. In the XPS spectra the Si 2s BE at any given Γ₅ were in the order R180 > R60 > TiO₂(am) indicating that the extent of silicate polymerization was in the same order. These results support the existing model for interfacial H₄SiO₄ oligomerization where linear trimeric silicates are formed by insertion of a solution H₄SiO₄ between suitably orientated adjacent bidentate sorbed monomers. The regular arrangement of TiO₆ octahedra on the rutile (110) face means that sorbed H₄SiO₄ monomers on adjacent rows of singly coordinated oxygen atoms are oriented so as to favor linear trimer formation. Similarly higher silicate polymers can form between adjacent trimers and this is favored on the rutile (110) surfaces compared to the TiO₂(am).

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REFERENCES


44. McIntosh, G. J.; Swedlund, P. J.; Sohnel, T., Experimental and theoretical investigations into the counter-intuitive shift in the antisymmetric ν(Si–O) vibrational modes upon deuteration of solvated silicic acid (H4SiO4). *Physical Chemistry Chemical Physics* **2011**, *13*, 2314-2322.
≈2 nm spheres of amorphous TiO$_2$

Rutile 110 face