

SULFUR ADSORPTION AND REACTION WITH A TiO₂(110) SURFACE: O \leftrightarrow S EXCHANGE AND SULFIDE FORMATION

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Upon sulfur adsorption on TiO₂(110) at 600 K, all surface oxygen is replaced by sulfur. High-resolution photoemission data show a complete loss of oxygen from the surface layer, a large binding energy shift and attenuation of Ti core levels, and the presence of three different S species. The bonding of sulfur is examined using first-principles density-functional calculations and the periodic supercell approach. At saturation the top layer of the oxide surface is converted to sulfide, with the majority of sulfur buckled above the Ti lattice plane and the remaining sulfur bonded in bridging sites. A mechanism for this self-limiting thermodynamically unlikely surface reaction is proposed.

Keywords: Sulfur; Titanium oxide; Photoemission spectroscopy; Sulfidation; DFT calculations; Surface reactions; Heterogeneous catalysis.

Sulfur-containing molecules in feedstock are regarded as a major environmental liability of modern industrial society¹. The poisoning effect of S on catalyst performance has sizeable impact on the energy cost of many chemical and petrochemical processes^{2,3}. Understanding on a molecular level of the sulfur interaction with surfaces of model catalysts may lead to design of better catalysts for hydrodesulfurization and/or sulfur tolerant catalysts^{4,5}.

The majority of sulfur interaction studies is conducted on metal surfaces, while oxides are investigated less often. Nevertheless, it is the oxides such as alumina or titania that are used on a large industrial scale in sulfur-removal catalytic process from the H₂S-containing gases⁶. Although TiO₂ can be investigated using ultra-high vacuum (UHV)-compatible surface probes without an adverse effect of surface charging, only a few studies of S interaction have been carried out on well-defined single-crystal TiO₂ surfaces so far. In the case of single-crystal Al₂O₃ surfaces, where the surface charge buildup is a serious problem for surface science studies, we are not aware of any investigation.

Our knowledge of the elementary steps of the original Claus reaction⁶, $\text{H}_2\text{S} + 1/2 \text{O}_2 \rightarrow \text{H}_2\text{O} + 1/n \text{S}_n$, and its latter modification, where one third of H_2S is first burned ($\text{H}_2\text{S} + 3/2 \text{O}_2 \rightarrow \text{SO}_2 + \text{H}_2\text{O}$) and SO_2 reacts catalytically with the rest of H_2S ($2 \text{H}_2\text{S} + \text{SO}_2 \rightarrow 2 \text{H}_2\text{O} + 3/n \text{S}_n$), is limited. Catalytic studies were carried out mainly on high-surface area aluminas and titanias where detailed characterization of the active surface is difficult^{4,6,7}. Examples of work on model single-crystal TiO_2 surfaces are few and include the adsorption of H_2S (ref.⁸) and SO_2 (ref.⁹). While the H_2S interaction with the $\text{TiO}_2(110)$ surface is very weak, formation of SO_3^{2-} and SO_4^{2-} ions was observed as well as conversion of TiO_2 to TiS_2 after reaction of the TiO_2 surface with SO_2 . Recently, the interaction of elemental sulfur was studied with scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and X-ray photoemission spectroscopy (XPS) (ref.¹⁰). Two different adsorption sites were identified: at room temperature, S adsorbed on the Ti rows, while at 600 K, S replaced oxygen in bridging oxygen rows, forming a (3×1) superstructure at higher coverages. The adsorption site change is accompanied by a 2 eV binding energy shift of the S 2p core levels and a Ti^{3+} shoulder developed at the Ti 2p_{3/2} core level spectrum. High-resolution photoemission data show that at least three different types of sulfur species coexist on the $\text{TiO}_2(110)$ surface at room temperature¹¹.

In this paper we present new data from high-resolution photoemission and results of density-functional (DF) calculations modeling sulfur adsorption on a semiconducting $\text{TiO}_2(110)$ surface. We show that at 600 K, all surface oxygen, *i.e.* bridging and in-plane, is replaced by sulfur and the top oxide layer is transformed to a sulfide. The process is activated and driven by the enhanced surface segregation of bulk vacancies at elevated temperatures in the presence of adsorbed S.

EXPERIMENTAL

Photoemission experiments were carried out at the U7A beamline of the National Synchrotron Light Source. UHV chamber (base pressure $ca 5 \cdot 10^{-8}$ Pa) is equipped with a hemispherical energy analyzer and multichannel detector, and optics for LEED. A second UHV chamber (base pressure $< 1 \cdot 10^{-8}$ Pa) was equipped with an Auger electron spectrometer (AES), LEED, mass spectrometer and a temperature programmer. The same TiO_2 crystal mounted in a Ta frame and sandwiched between Ta plates was spot-welded to Ta heating legs of a manipulator capable of cooling to 80 K and heating to 1 100 K and used in both chambers.

The sample was cleaned by procedures suggested by Hebenstreit¹⁰ and Chen¹² that consisted of the initial sample heating to 1 000 K for 1 h, followed by many cycles of sputtering at room temperature and 10 min anneal to 1 000 K. This preparation leads to a dark blue

sample with no detectable impurities as judged by AES and XPS and displays a perfect (1×1) LEED pattern.

The geometry of the $\text{TiO}_2(110)$ (1×1) surface is shown schematically in Fig. 1. The ideal surface consists of a coplanar lattice of Ti and O ions with every other [001] Ti row capped with bridging oxygen. Exposed five-fold coordinated Ti ion rows alternate with bridge-bonded six-fold coordinated Ti ion rows. For the stoichiometric surface, the formal oxidation state of titanium is Ti^{4+} . Although titanium(IV) is the most stable and common oxidation state, Ti(IV) compounds are generally covalent and Ti^{4+} ion does not really exist. We will, however, follow the convention used in the surface science literature and use Ti^{n+} to indicate Ti oxidation states. The reduced surface prepared by vacuum annealing of the stoichiometric one has lost some of the bridging oxygen ions thus leaving the adjacent titanium ions in the Ti^{3+} oxidation state to maintain neutrality.

The spectroscopic differences between the stoichiometric and reduced surfaces are reflected in high-resolution photoemission data (Fig. 2). Only a single doublet of the Ti 2p core level with the binding energy at 458.08 eV of the Ti $2p_{3/2}$ line is needed to fit the photoemission curve acquired for the stoichiometric surface prepared by adsorption of oxygen on the clean sample at elevated temperatures¹³. Upon annealing, an additional doublet shifted to lower binding energy by 1.70 eV is required to fit the shoulder on the photoemission line, suggesting the presence of Ti^{3+} ions at the sample surface. Partial occupation of Ti d levels as a result of Ti sites reduction leads also to band-gap photoemission, color changes of the crystal and a large increase in the electronic conductivity¹⁴. Due to the

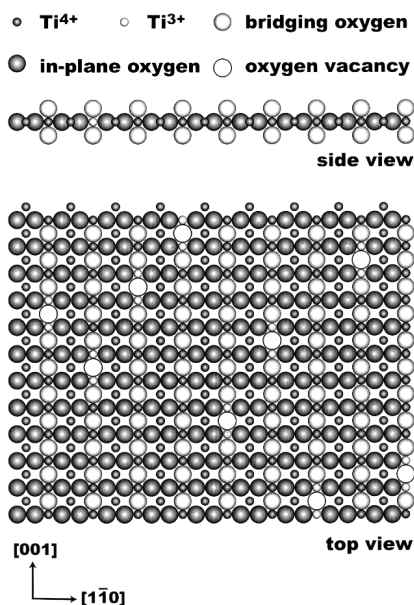


FIG. 1

A schematic model of the $\text{TiO}_2(110)$ surface with bridging oxygen vacancies

low kinetic energy of the photoelectrons (≈ 160 eV) used in the present experiment, only the first two layers are contributing to the measured signal (mean free path of the 160 eV electron is about 0.6 nm). The integrated Ti^{3+} signal makes 12% of the total Ti 2p integrated intensity. Removal of a single oxygen atom exposes two Ti^{3+} ions and we can therefore estimate the surface oxygen vacancy concentration. The value of $\approx 6\%$ agrees well with recent measurements by STM, where the authors measured oxygen vacancy density of $\approx 7\%$ per surface unit cell¹⁵.

Sulfur was deposited from a UHV-compatible electrochemical source described in the literature¹⁶. Pellets of AgI_2 and AgS were assembled together with metal disks in ceramic heating tube to form the $\text{Ag}/\text{AgI}_2/\text{AgS}/\text{Pt}$ cell. The elemental sulfur is produced by electrolysis of AgS at potential above 210 mV and at temperatures above 440 K, where AgI_2 is transformed to a fast ion conductor¹⁷. Elemental sulfur segregates on AgS surface and desorbs. As seen in Fig. 3, more than 80% of sulfur from the electrochemical source is in the form of sulfur dimers, S_2 .

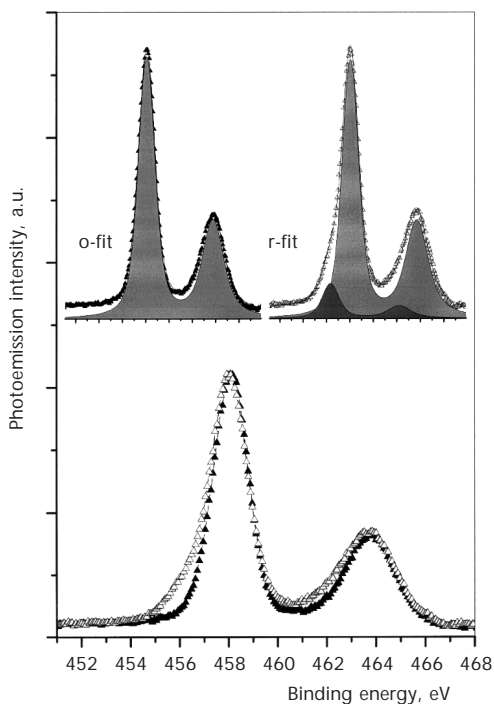


FIG. 2

Bottom panel: Ti 2p photoemission spectra of a clean $\text{TiO}_2(110)$ sample with oxidized (\blacktriangle) and reduced (\triangle) surfaces. Top panel: Results of the curve fitting of photoemission spectra ($h\nu = 625$ eV) in the bottom panel. To fit these spectra, a Shirley background was subtracted from the raw data and spectra were fit with the Gaussian-Lorentzian sum and an asymmetric peak function

The geometries and bonding energies of sulfur on adsorption sites of $\text{TiO}_2(110)$ were calculated using a commercial version of Cambridge Serial Total Energy Package (CASTEP) available from Molecular Simulations Inc. CASTEP has an excellent track record in predicting geometry and energetics for the adsorption of molecules on oxides systems¹⁸. More details about calculations of S on $\text{TiO}_2(110)$ can be found in a recent paper¹¹.

RESULTS AND DISCUSSION

Auger spectra of a clean $\text{TiO}_2(110)$ surface are shown in Fig. 4 (curve A) together with data acquired after saturation of surface with sulfur at 300 K (curve B) and at 600 K (curve D). Sulfur adsorbed at 300 K attenuates the Ti LMM and O KLL signals equally: there is almost no change of the O/Ti Auger signal ratio between a clean and S-covered surface. However, for the 600 K adsorption, sulfur concentration is much higher and the O/Ti signal ratio is significantly lower as seen in Table I.

It is evident from this data set that sulfur adsorption at 300 K leads only to a small build-up of surface concentration of sulfur without replacement of the surface lattice oxygen. This conclusion is in agreement with results

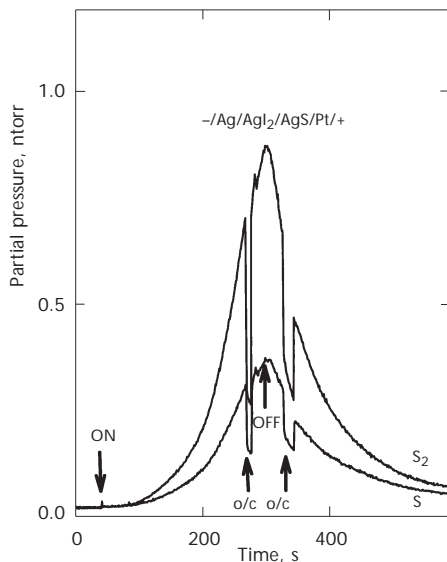


FIG. 3

Time dependence of the mass spectra of sulfur from the UHV-compatible electrochemical doser. The cell held at 200 °C was run for ca 250 s. The sulfur flux was interrupted by closing and opening of a shutter

of recent STM (ref.¹⁰) and photoemission studies¹¹, where the authors had shown sulfur adsorbing on the exposed titanium rows and filling in oxygen vacancies of the bridging oxygen rows. At higher adsorption temperatures, however, the Auger data suggest replacement of the surface lattice oxygen with sulfur and conversion of oxide to sulfide.

Figures 5 and 6 show a set of Ti 2p and O 1s spectra, respectively, acquired at room temperature after nine incremental exposures of the clean TiO₂(110) surface to sulfur at 600 K. A large reduction and significant line shape changes in the Ti 2p are accompanied by a very large loss of the O 1s intensity. These changes are summarized in the insets of both figures as the integrated intensity of the photoemission peaks vs time of sulfur exposure plots.

TABLE I
S adsorption on TiO₂(110): Auger data

Sample	S, a.u.	S/Ti	O/Ti
Clean	0	n.a.	1.37
S (300 K)	0.76	0.61	1.36
S (700 K)	2.13	2.92	0.91

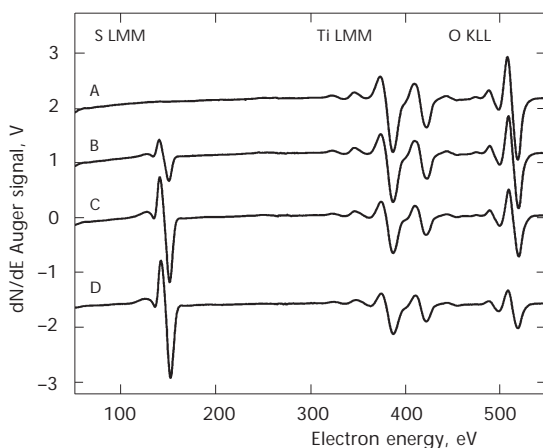


FIG. 4

Auger spectra of a clean (A) and sulfur-covered TiO₂(110) surface. Surface saturated at room temperature (B), intermediate S exposure at 600 K (C), S saturation at 600 K (D)

With increasing sulfur exposure, a weak low-binding energy shoulder develops first, intensifies and finally dominates the Ti 2p spectrum at saturation (Fig. 5). The new core level is found at 455.60 eV, shifted by -2.5 eV from the Ti 2p position of the clean surface. Similarly, low binding energies were reported for sputtered^{19,20} and thin-metal-film-covered²¹ TiO₂(110) surfaces and assigned to Ti²⁺ initial state or a Ti³⁺/Ti²⁺ final state. As noted above, the binding energy of Ti³⁺ ions on the vacuum-reduced surface is shifted only by 1.7 eV (Fig. 2). In addition to chemical reduction of rutile surface, a loss of more than 50% of metal core level intensity implies also structural changes in the probed sample volume.

The O 1s core level position and its line shape are not affected by reaction with sulfur (Fig. 6). However, the oxygen integrated intensity drops down to 3% of its original value after saturation at 600 K. Because the mean free path (or sampling depth) of photoelectrons with ≈ 100 -eV kinetic en-

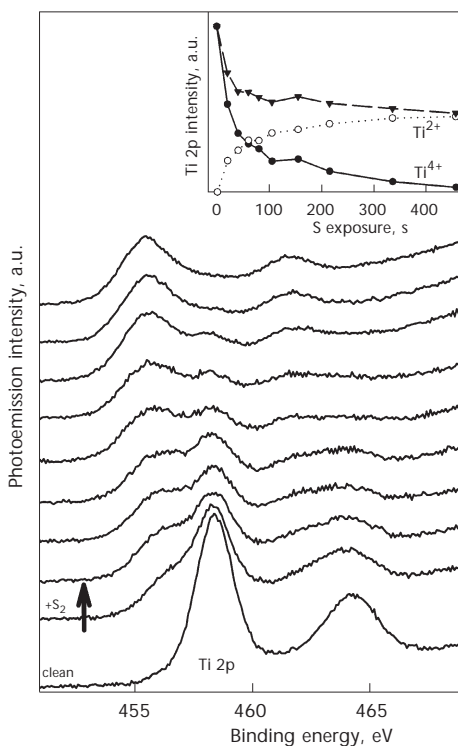


FIG. 5

Ti 2p photoemission spectra for the adsorption of sulfur on a TiO₂(110) surface at 600 K ($h\nu = 625$ eV). Inset: Dependence of integrated Ti 2p intensity on sulfur exposure

ergy is ≈ 0.5 nm, there is no oxygen present in the top one or two surface layers. This particular data imply that the high-temperature reaction is not limited to removal of bridging oxygen only¹⁰ and the in-plane oxygen ions have to be removed in the course of the surface reaction as well.

The S 2p core level spectra are shown in Fig. 7 together with the inset displaying the sulfur uptake curve. With increasing S exposure, we can see growing doublets and changes in their line shape. Sulfur adsorption saturates and no additional changes are observed for exposure times longer than 200 s. Notice that similar results were obtained by XPS (ref.^{10b}). Spectra were fitted with a set of S 2p_{3/2,1/2} doublets to account for the observed line shapes and their variations. After a Shirley background subtraction the sum of Lorentzian and Gaussian functions was used while constraining the spin orbit energy splitting to 1.20 eV and the branching ratio to 2. The results of fitting for the lowest and the highest S coverages curves from Fig. 7 are shown in Fig. 8. A set of three doublets is needed for the fit of both

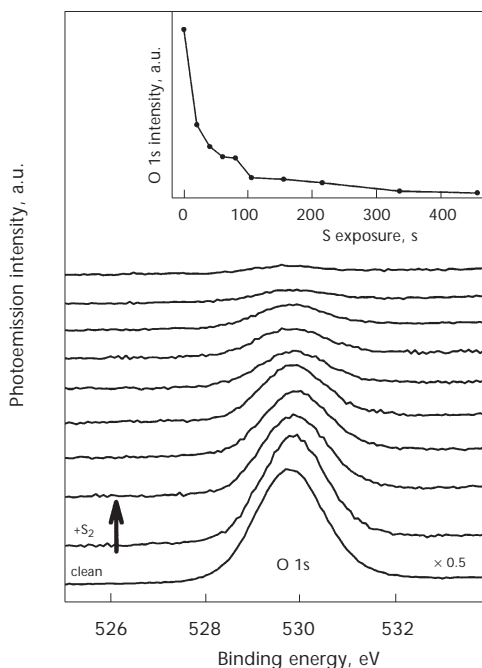


FIG. 6

O 1s photoemission spectra for the adsorption of sulfur on a TiO₂(110) surface at 600 K ($h\nu = 625$ eV). Inset: Dependence of integrated O 1s intensity on sulfur exposure

spectra. $2p_{3/2}$ components are found at 160.60, 161.10 and 161.85 eV for low S coverage and at 160.50, 161.10 and 161.90 eV for saturation. All three S species are present throughout the sulfur uptake in different relative concentrations. The use of either one or two doublets leads to unsatisfactory and physically meaningless fits.

Use of synchrotron-based high-resolution photoemission for studies and identification of several surface sulfur species with distinct electronic properties^{3,22} proved to be quite successful due to narrow line shape of S 2p core levels, their large chemical shifts and high sensitivity. In our previous work¹¹ we have shown that at 300 K, sulfur fills vacancies in bridging oxygen rows and adsorbs on top of the Ti rows. The characteristic binding energies of the corresponding S $2p_{3/2}$ core levels were ≈ 161.6 eV for S at bridging position and at ≈ 163 eV for S at Ti rows. The bonding of S on Ti rows is relatively weak and these sulfur species desorbed below 600 K. It is therefore not surprising that we do not see any S species at 163 eV in Fig. 7.

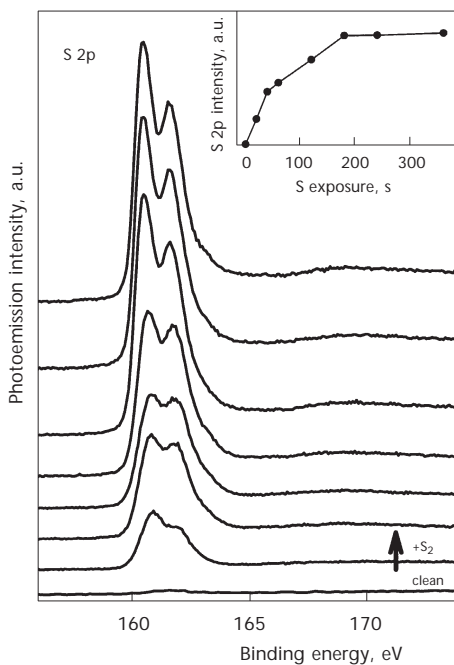


FIG. 7

S 2p photoemission spectra for the adsorption of sulfur on a $\text{TiO}_2(110)$ surface at 600 K ($h\nu = 260$ eV). Inset: Sulfur uptake curve

We argue that the S 2p core levels seen in Figs 7 and 8 can be assigned to S species that replaced *all surface oxygen* on the $\text{TiO}_2(110)$ surface.

Auger data provided the first indication of extensive $\text{S} \leftrightarrow \text{O}$ exchange at elevated temperature (Fig. 4). Both Ti 2p and O 1s photoemission sets measured with very high surface sensitivity (Figs 7 and 8) showed clearly that O in the top layer of $\text{TiO}_2(110)$ is almost completely absent and all Ti^{4+} in the layer sampled by photoemission is reduced to Ti^{2+} or Ti^{3+} . Sulfur is therefore replacing both in-plane and bridging oxygen. Since there are two in-plane oxygen ions and only one bridging one in the original surface unit cell of $\text{TiO}_2(110)$, the more intense leading doublet at 160.5 eV is assigned to the in-plane S species, while less intense doublet at 161.1 eV is assigned to the bridging position. The third doublet reflects most probably the existence of an unknown surface site formed by lattice distortion due to accommodation of larger S anions in place of oxygen. The presence of molecular

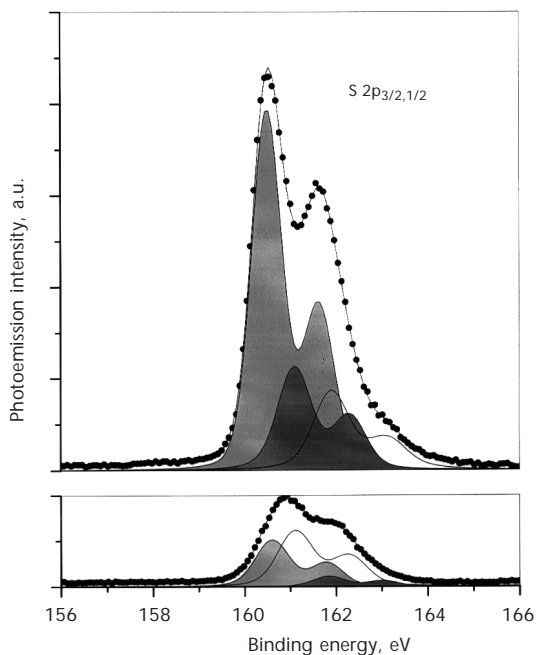


FIG. 8

Results of the curve fitting of two photoemission spectra from Fig. 7. To fit these spectra, a Shirley background was subtracted from the raw data and spectra were fit with Gaussian-Lorentzian sum functions

species S_n can be ruled out as they appear at much higher energy on TiO_2 (ref.¹¹) and other substrates²³.

Hebenstreit *et al.*¹⁰ proposed a structure model of the sulfided $TiO_2(110)$ surface based on a combined STM, LEED and XPS study. At higher temperatures (>450 K) and lower S coverages (≈ 0.3 monolayers (ML), where 1 ML corresponds to 1 S atom per surface unit cell), they observed a (3×1) superstructure made of chains of S atoms aligned in the $[110]$ direction together with narrow isolated rectangles made of S pairs aligned along $[001]$. At higher S coverages (≈ 0.5 ML), a (3×3) superstructure developed and large areas were covered by bright double S rows running in $[001]$ direction. At saturation coverage (0.9 ML), a new (4×1) superstructure is observed and identified with stripes of S pairs running along $[110]$ direction at the adsorption sites of the in-plane oxygen. S adsorbed in bridging position, occupying every 3rd oxygen site, forms the chains of S atoms and all remaining bridging oxygen is removed. The S pairs in rectangles, rows and stripes are replacing neighboring in-plane oxygen in different structural arrangement of sulfur, including (3×3) and (4×1) superstructures. In their model, sulfur at saturation replaces half of the in-plane oxygen and there is no oxygen or sulfur left in the bridging position.

This model cannot account for our photoemission data. As has been shown above, all surface oxygen from both sites (bridging and in-plane) is removed during S adsorption. Moreover, there are three different types of S species observed and only one type of Ti sites. Finally, a loss of all bridging oxygen should lead to the Ti 2p intensity increase and not to its decrease. Possible reasons for this disagreement are different conditions of sample preparation that may alter the oxygen vacancies concentrations and differences in sulfur coverages.

Bonding of sulfur to $TiO_2(110)$ was examined using density-functional generalized gradient corrected (DF-GGA) calculations. The $TiO_2(110)$ surface was represented by a three-layer slab imbedded in a three-dimensionally periodic supercell. A vacuum of 1.2 nm was placed on the slab top to insure negligible interactions between periodic images normal to the surface¹⁸. By removing oxygen atoms from the bridging rows and filling every other vacancy with sulfur together with replacement of all in-plane oxygen, a first layer sulfide was created on the top of a TiO_2 bulk. The first layer of the slab was allowed to relax during the DF calculation while the other two layers were kept fixed in the geometry of bulk TiO_2 . The results of geometry optimization are shown in Fig. 9.

We can see that all sulfur as a 1 : 1 replacement of the in-plane oxygen can be accommodated by outward relaxation and formation of buckled

layer. The “in-plane” sulfur has moved 0.112 nm above the plane of the Ti layer. The “in-plane” S–S distance along the [001] direction is expanded to 0.309 nm in the presence of the bridging sulfur and contracted to 0.285 nm in its absence when compared to the original value of 0.297 nm for the in-plane O–O distance in the $\text{TiO}_2(110)$. The S–S distances are shorter (0.265 nm) along [110] across Ti rows and shorter still (0.260 nm) between the “in-plane” and bridging sulfur ions. There is, however, no dimerization or pairing of “in-plane” sulfur as proposed previously¹⁰. Relaxed and crowded sulfur on the top of the Ti plane forms a separate layer that attenuates more effectively photoelectrons from Ti core holes thus explaining a large drop of the Ti 2p intensity.

Rutile is one of the most stable oxides known with a ΔH_f^0 value of -943 kJ/mol while TiS and TiS_2 have ΔH_f^0 values of -238 and -334 kJ/mol, respectively²⁴. The formation of sulfide in preference to the oxide is thermodynamically very unlikely. The reaction heat of sulfidation is $+770$ kJ/mol for the $\text{TiO}_2 + 1/2 \text{S}_2 \rightarrow \text{TiS} + \text{O}_2$ reaction and $+738$ kJ/mol for the $\text{TiO}_2 + \text{S}_2 \rightarrow \text{TiS}_2 + \text{O}_2$ reaction, both clearly energetically uphill at 300 K. At higher temperatures, the presence of bulk oxygen vacancies and their mobility changes the bulk physical properties of rutile and oxygen vacancies segregate at surface during vacuum annealing. In our previous work¹¹, we have argued that sulfur adsorption starts at vacancies in the bridging oxygen rows at room temperature. At higher temperature, the loss of oxygen is complete and limited exclusively to the surface layer.

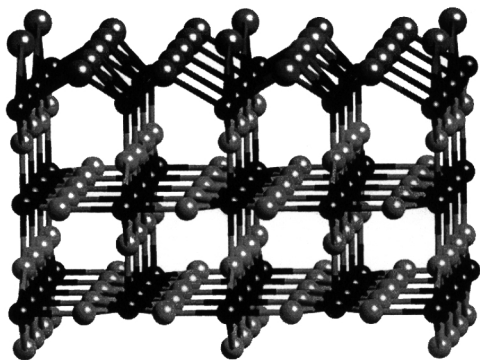


FIG. 9

Perspective view of an S-saturated $\text{TiO}_2(110)$ surface. The “in-plane” sulfur atoms are no longer coplanar with the Ti layer and no dimers or S pairs are formed. This structure was obtained after relaxing a $\text{TiS}_x/\text{TiO}_2$ interface in DF-GGA calculations

We suggest that the $O \leftrightarrow S$ place exchange surface reaction at elevated temperatures is driven by *enhanced* segregation of bulk oxygen vacancies to the surface. As shown in model calculations, there is a large driving force for surface segregation of oxygen vacancies in the presence of adsorbed sulfur. While on a clean surface, the energy difference between the near surface and surface vacancies (< 8 kJ/mol) is within the accuracy of calculated parameters, a difference of ≈ 125 kJ/mol is calculated for the same in the presence of sulfur bonded in bridging position. It is the ease of vacancy segregation on the surface that is driving this thermodynamically impossible reaction. Once all the surface oxygen diffused into the bulk and all vacancy sites were occupied by sulfur, the sulfidation process terminates, as there are no additional reactive defect sites created since a bulky sulfur atom cannot penetrate and diffuse into the bulk of rutile. Similar self-limiting growths²⁵ are known but this is the first example of a self-limiting thermodynamically uphill surface reaction driven by vacancies segregation.

CONCLUSIONS

Upon sulfur adsorption on $TiO_2(110)$ at 600 K, all surface oxygen is replaced by sulfur. Surface-sensitive synchrotron-based photoemission results show a complete loss of oxygen from the surface. At the same time, a large binding energy shift of Ti 2p core levels by 2.5 eV towards lower binding energy suggests complete reduction of the Ti^{4+} surface layer. The intensity of Ti core levels is lowered by one half and the S 2p data show the presence of three different S species. At sulfur saturation, the top layer of the oxide surface is converted to sulfide, with the majority of sulfur bonded above the Ti lattice plane and the remaining sulfur bonded in bridging sites. The thermodynamically unlikely surface sulfidation, being facilitated by segregation of oxygen vacancies to the surface, is self-limiting due to the inability of sulfur to diffuse into the bulk of oxide.

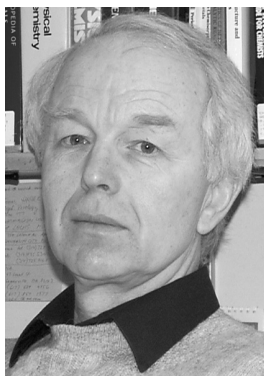
There are obvious implications of these findings for the behavior of TiO_2 as a catalyst in the Claus process, and we are currently examining the reactivity of the sulfided rutile surface to relevant simple molecules.

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