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Interactions of Sn²⁺ dopant ions located on surface sites of anatase-type TiO₂ with adsorbed H₂S molecules studied using ¹¹⁹Sn Mössbauer spectroscopic probe

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ABSTRACT

Information provided by ¹¹⁹Sn²⁺ Mössbauer probe ions, located on surface sites of anatase-type TiO₂ microcrystals exposed, at room temperature, to a H₂S/H₂ mixture, has permitted to conclude that the interaction of H₂S molecules with the substrate surface leads to the dissociation of a fraction of the adsorbate molecules. This gives rise to the formation of elemental sulfur which oxidizes the neighboring Sn²⁺ ions, the produced Sn⁴⁺ ions being found coordinated only by S²⁻ anions. Subsequent exposure to ambient air is shown to result in the oxidation of S²⁻ ions, yielding both S⁰ and SO₄²⁻-like species, with concomitant stabilization of Sn⁴⁺ ions in coordination polyhedra where they are surrounded by only oxygen anions.

1. Introduction

Our recent *in situ* Mössbauer spectroscopic measurements, performed in hydrogen atmosphere with tin-doped anatase microcrystals [1], has permitted to develop synthesis procedures allowing tin dopant cations to be located in the +2 oxidation state immediately on the surface of crystallites. Oxidation of these Sn²⁺ ions, occurring upon subsequent exposing the samples to ambient atmosphere, was shown to produce the surface-located Sn⁴⁺ ions that can therefore be used, along with the Sn²⁺ pristine ions, to study surface chemical reactions with adsorbed molecules by means of ¹¹⁹Sn Mössbauer spectroscopy [2]. Investigation of the reactions occurring on the surface of titania particles is of technological significance given their numerous applications in heterogeneous catalysis. The mentioned room-temperature oxidation of surface-located Sn²⁺ by O₂ molecules, present in ambient air, was revealed by Mössbauer spectra as a drastic decrease in both the isomer shift δ and quadrupole splitting ΔE_Q values reflecting the disappearance of the Sn²⁺ 5s lone pair electrons. However, in this case the analysis of Mössbauer spectra of the ¹¹⁹Sn⁴⁺ oxidized ions did not permit to distinguish the newly incorporated O²⁻ anion from those already present in the coordination sphere of the pristine Sn²⁺. For

this reason, it would be very interesting to investigate the evolution of the spectral parameters of the surface-located ¹¹⁹Sn probe in the presence of oxygen-free molecules. In this paper, we report new results concerning ¹¹⁹Sn Mössbauer spectroscopic characterization of both the electronic state and local surrounding of Sn²⁺ cations on surface sites of anatase microcrystals exposed to an H₂S-containing atmosphere. The interactions of H₂S with undoped TiO₂ (1 1 0) surfaces were previously studied using ultraviolet photoelectron spectroscopy UPS [3]. The authors have observed two distinct phases in the adsorption of H₂S. The first phase, occurring at exposures equal or lower than 1 L (1 L = 1 Langmuir = 10⁻⁶ Torr s), was identified as dissociative adsorption of H₂S; the second phase occurring at higher amounts of hydrogen sulfide (exposures \geq 1 L) was tentatively identified as molecular H₂S adsorption. Thus, it would be interesting to compare these results, obtained by conventional surface-characterization technique, to the information on the interaction of H₂S with the surface of anatase particles provided by surface-located ¹¹⁹Sn Mössbauer probe ions.

2. Experimental

2.1. Synthesis method

Tin-doped anatase powder samples, containing 0.1 atom% Sn, were prepared using an impregnation procedure proven to allow the large majority of the tin dopant atoms to be located, in the +2

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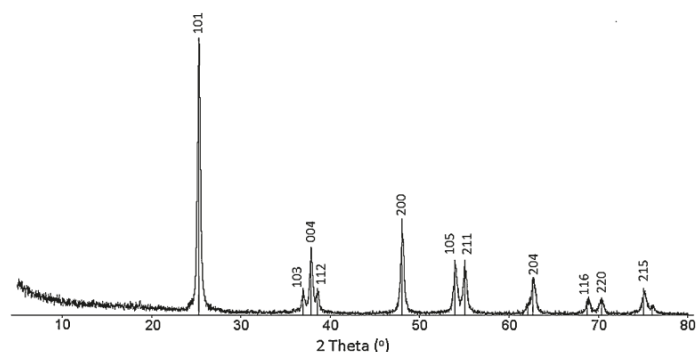


Fig. 1. X-ray diffraction pattern of undoped **1** exhibiting the anatase-type single phase composition (space group $I4_1/amd$).

oxidation state, on surface sites of crystallites [1]. This procedure is based on the precipitation of titanium(IV) hydroxide $Ti(OH)_4 \cdot xH_2O$ by the addition of concentrated ammonia solution to a solution containing 15 mM of $TiCl_4$ until the pH reaches ca. 8. To obtain the $TiCl_4$ solution, titanium hydride $TiH_{1.9}$, used as the starting material, was dissolved in a hot concentrated solution of HCl. To oxidize Ti^{3+} ions, initially formed upon dissolving titanium hydride, concentrated nitric acid was added dropwise to the obtained solution until the characteristic violet shade of Ti^{3+} has disappeared. The precipitated hydroxide was washed with deionized water, dried and then annealed in air for 3 h at 650 °C. As evidenced by X-ray diffraction (Fig. 1), the resulting powder (hereafter denoted as **1**) was a single-phase anatase. Its specific surface area S_{BET} determined by the BET method was found to be $57 \text{ m}^2 \text{ g}^{-1}$. A solution of $^{119}\text{SnCl}_4$ (0.015 mM) was then introduced by dropwise addition, onto the synthesized anatase powder. To obtain the $^{119}\text{SnCl}_4$ solution, metallic β -Sn, enriched with ^{119}Sn to 92%, was dissolved in a hot concentrated solution of HCl. To convert Sn^{2+} ions, initially formed upon dissolving, to the +4 oxidation state, a few drops of concentrated HNO_3 were added to the obtained solution. Prior to the addition of $^{119}\text{SnCl}_4$, the anatase powder **1** (15 mM) was impregnated with ammonia solution to ensure rapid hydrolysis of stannic chloride to $\text{Sn(OH)}_4 \cdot x\text{H}_2\text{O}$. After deposition of $\text{Sn(OH)}_4 \cdot x\text{H}_2\text{O}$, the powder was washed with deionized water, dried in an oven at 150 °C and then introduced in the quartz chemical reactor to be annealed at 400 °C for 2 h in hydrogen atmosphere. The resulting material (hereafter denoted as **2**) was cooled down to room temperature and characterized by *in situ* Mössbauer spectroscopic measurements. X-ray diffraction (XRD) patterns of **2**, recorded in ambient air, were identical to those obtained before hydrogen annealing. Hydrogen sulfide, used in the subsequent adsorption experiments, was synthesized by reacting molten elemental sulfur, at ca. 450 °C, with hydrogen released by a LaNi_5H_x source kept at room-temperature. All of the chemicals used were analytical grade.

2.2. Characterization techniques

XRD measurements were performed on a powder sample ARL X'TRA Thermo Scientific diffractometer using $\text{Cu } K\alpha$ radiation (wavelength $\lambda = 1.5418 \text{ \AA}$).

Mössbauer spectra were recorded on a MS-1104 spectrometer with a $\text{Ca}^{119\text{m}}\text{SnO}_3$ source. To allow *in situ* Mössbauer spectroscopy experiments with hydrogen-annealed powders, before and after their exposure to H_2S , the reactor was equipped with a lateral thin-window quartz sample-cell [4]. During the measurements, both the $\text{Ca}^{119\text{m}}\text{SnO}_3$ source and the sample cell filled with studied

powder (the absorber) were introduced into the hole of a copper bar immersed in a Dewar flask filled with liquid nitrogen. Under these conditions, the temperature of both the source and the absorber was close to 100 K, and, consequently, in all cases the observed isomer shift δ values were not affected by the second-order Doppler shift. Moreover, at 100 K, the spectral contributions of chemically different species could be considered as a more realistic estimate of their abundances as compared to the results of room temperature measurements. All Mössbauer spectra were analyzed by a least-square fitting program.

X-ray Photoelectron Spectroscopy (XPS) measurements were carried out with a K-Alpha X-Ray Photoelectron Spectrometer (ThermoFisher Scientific Inc.) using monochromatic $\text{Al } K\alpha$ radiation ($h\nu = 1486.6 \text{ eV}$), spot size: 200 μm , and charge compensation. Overview spectra were taken at pass energy $E_p = 200 \text{ eV}$ and high-resolution spectra at $E_p = 40 \text{ eV}$. Powder samples, to be analyzed in the as-prepared state, were pressed onto indium foil. Atomic concentrations were determined using areas of the $\text{Sn}3d5$ ($E_b = 487 \text{ eV}$ range), $\text{Ti}2p3$ ($E_b = 459 \text{ eV}$ range) and $\text{S}2p$ ($E_b = 160\text{--}170 \text{ eV}$ range) peaks with Scofield correction. High resolution spectra were fitted using AVANTAGE software provided by ThermoFisher Scientific Inc.

3. Results and discussion

3.1. *In situ* Mössbauer spectroscopic measurements (samples **2**, **3** and **4**)

In agreement with our previous results [1], *in situ* ^{119}Sn Mössbauer spectrum of the hydrogen annealed sample (sample **2**, Fig. 2) reveals the presence, besides the residual peak at $\nu = 0.06 \text{ mm s}^{-1}$ assignable to unreduced Sn^{4+} ions (the spectral contribution $A_0 = 9\%$), of a largely predominant asymmetric doublet at positive Doppler velocities. The latter can be represented by a superposition of two quadrupole doublets defined by the following parameters (Table 1): doublet I: $\delta_{(I)} = 3.22 \text{ mm s}^{-1}$, $\Delta E_{Q(I)} = 1.65 \text{ mm s}^{-1}$, the full width at half maximum of each doublet component $\Gamma = 0.83 \text{ mm s}^{-1}$ (the fixed value), $A_{(I)} = 45\%$; doublet II: $\delta_{(II)} = 2.89 \text{ mm s}^{-1}$, $\Delta E_{Q(II)} = 1.71 \text{ mm s}^{-1}$, $\Gamma = 0.83 \text{ mm s}^{-1}$, $A_{(II)} = 46\%$.

Both sets of $(\delta, \Delta E_Q)$ values should obviously be ascribed to covalent stannous species having valence electron configurations of the $5s^2\text{--}x5p^x$ type [5]. In fact, the s – p mixing allows one to account for the significant decrease in the observed isomer shift values, as compared to that for stannous cation in the $5s^25p^0$ pure ionic state ($\delta \geq 4 \text{ mm s}^{-1}$), as a result of reducing the total electronic density at ^{119}Sn nuclei. Moreover, the observed non-zero values

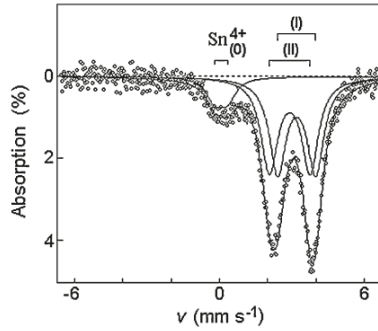


Fig. 2. *In situ* ^{119}Sn Mössbauer spectrum of 2.

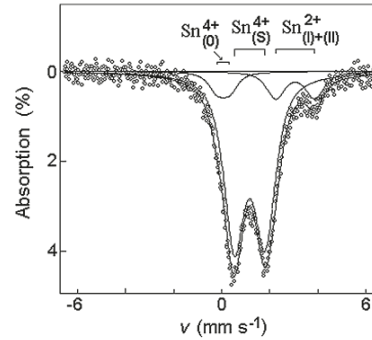


Fig. 3. *In situ* ^{119}Sn Mössbauer spectrum of 3.

of the quadrupole splitting reveal large electric field gradients acting at ^{119}Sn nuclei and, consequently, a non-spherical electronic charge distribution over the hybridized tin valence orbitals. This means that both considered stannous Sn^{2+} species possess a "stereochemically active 5s lone pair" (for more information about the relationship between the ^{119}Sn Mössbauer spectroscopic results and the degree of the lone pair stereochemical activity see, for instance, [6], [7]). This conclusion thus implies that these Sn^{2+} ions occupy the low-coordination sites, in agreement with their location on the surface of anatase microcrystals, as evidenced in [1]. According to [1], the appearance of two quadrupole doublets can be tentatively accounted for by the presence of Sn^{2+} ions both within and just above the outermost cationic layer of TiO_2 crystallites. As to the residual peak at $v = 0.06 \text{ mm s}^{-1}$, it can be attributed to Sn^{4+} ions, which have moved the farthest away from the surface towards the bulk of anatase particles upon preliminary air heating of the tin-impregnated sample in the oven.

Sample 2 was then exposed at ambient temperature to a H_2S -containing atmosphere. For this purpose, a mixture of hydrogen and hydrogen sulfide, obtained by heating molten elemental sulfur in flowing hydrogen and collected in a chilled glass vessel, was aspirated into the reactor, through a 3-way glass valve, by depression created upon the preceding cooling down the isolated reactor, containing H_2 -annealed 2, from 400°C to room temperature. In order to facilitate the penetration of hydrogen sulfide into anatase powder, the sample was displaced, prior to admission of H_2S , from the measurement cell to the bottom of the reactor. After aspiration of H_2S , the reactor has been disconnected from the glass vessel and left at room temperature for 19 h (the resulting sample is hereafter denoted as 3). Powder 3 was then displaced from the bottom into the simple cell to be characterized by *in situ* Mössbauer spectroscopic measurements.

The relevant ^{119}Sn spectrum (Fig. 3 and Table 1) has revealed two main drastic changes:

- (i) Very strong decrease in the total contribution of two doublets ascribed to Sn^{2+} ions coordinated by O^{2-} anions ($A_{(I)} + A_{(II)} < 10\%$). This effect, exhibiting the easy accessibility of tin, even at room temperature, to molecules as large as H_2S , can indeed be observed only for dopant ions located on surface sites.
- (ii) Appearance of a very intense and somewhat asymmetrically broadened doublet component defined by the following average values of Mössbauer parameters: $\delta_{(S)} = 1.16 \text{ mm s}^{-1}$, $\Delta E_{Q(S)} = 1.28 \text{ mm s}^{-1}$, $\Gamma_{(S)} = 1.03 \text{ mm s}^{-1}$ and $A_{(S)} = 83\%$.

The value of $\delta_{(S)}$ obviously cannot be assigned to a divalent tin coordinated by S^{2-} anions which is known to exhibit a much greater isomer shift (e.g. $\delta = 3.4 \text{ mm s}^{-1}$ for SnS and $\delta = 3.5 \text{ mm s}^{-1}$ for Sn^{2+} in Sn_2S_3 [8]). On the contrary, the observed value of $\delta_{(S)}$ is close to those reported for the tetravalent tin possessing an octahedral S^{2-} -surrounding ($\delta = 1.3 \text{ mm s}^{-1}$ for SnS_2 and $\delta = 1.15 \text{ mm s}^{-1}$ for Sn^{4+} in Sn_2S_3 [8]). Thus, the spectrum in Fig. 3 clearly indicates that Sn^{2+} ions were oxidized with concomitant breaking of the initial $\text{Sn}-\text{O}$ bonds. This, at first glance surprising oxidation of Sn^{2+} ions, can only be accounted for by the formation of elemental sulfur through the dissociative adsorption of H_2S molecules which themselves are known to exhibit reducing properties but not the oxidizing ones. Thus, the ^{119}Sn spectrum in Fig. 3 furnishes an original proof of dissociation of H_2S molecules adsorbed on the surface of anatase particles, as reported previously [3]. Moreover, this spectrum provides experimental evidence that elemental sulfur, produced by the dissociation of H_2S , can easily react, even at room temperature, with neighboring stannous ions. Taking into account the typical values of δ corresponding to an Sn^{4+} ion, octahedrally coordinated by either 6 O^{2-} ($\delta = 0 \text{ mm s}^{-1}$ in the case of SnO_2) or 6 S^{2-} ($\delta = 1.3 \text{ mm s}^{-1}$ in the case of SnS_2), the value of the isomer shift relative to Sn^{4+} ions, formed upon exposure of 2 to H_2S ($\delta_{(S)} = 1.16 \text{ mm s}^{-1}$), obviously cannot be ascribed to a site with

Table 1
Mössbauer spectroscopic parameters of the ^{119}Sn probe, located on surface sites of anatase microcrystals, determined before (sample 2) and after (sample 3) exposure to hydrogen sulfide.

	δ (mm s ⁻¹)	ΔE_Q (mm s ⁻¹)	Γ (mm s ⁻¹)	A (%)
Sample 2 (H_2 -annealed powder characterized, by <i>in situ</i> measurements, prior to exposure to H_2S) (Fig. 2)				
(O)	0.06 ± 0.03	0.5 ± 0.1	0.83	9 ± 5
(I)	3.22 ± 0.05	1.65 ± 0.07	0.83	45 ± 5
(II)	2.89 ± 0.05	1.71 ± 0.07	0.83	46 ± 5
Sample 3 (the previous powder exposed to H_2S at room temperature for 19 h) characterized by <i>in situ</i> measurements (Fig. 3)				
(O)	0.06 ± 0.03	0.5 ± 0.1	0.83	8 ± 5
(S)	(1.16 ± 0.05)	(1.28 ± 0.05)	(1.03)	83 ± 5
(I)+(II)	(3.1 ± 0.1)	(1.63 ± 0.05)	0.90	9 ± 5

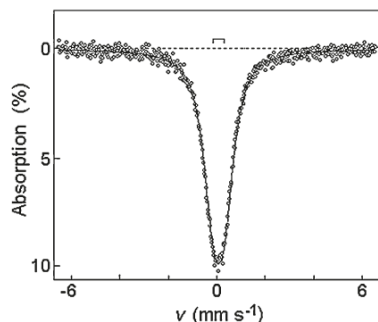


Fig. 4. *In situ* ^{119}Sn Mössbauer spectrum of 4.

a mixed anionic surrounding (*i.e.* to a Sn^{4+} ion coordinated by 3 O^{2-} and 3 S^{2-}). Hence, the observed $\delta_{(S)}$ value also implies the presence, at the anatase surface, of large amounts of undissociated H_2S molecules capable of saturating the coordination sphere of a pristine sulfur-oxidized Sn^{4+} ion to produce $[\text{SnS}_6]$ -like species. Therefore, the spectrum in Fig. 3 is also suggestive of H_2S adsorption layer formation on the surface of anatase particles. Besides, the value of $\Delta E_{Q(S)} = 1.28 \text{ mm s}^{-1}$ shows that the local surrounding of Sn^{4+} in the $[\text{SnS}_6]$ -like species is strongly distorted as compared to that of Sn^{4+} in SnS_2 whose Mössbauer spectrum is known to exhibit an unsplit resonance absorption peak ($\Delta E_Q \leq 0.5 \text{ mm s}^{-1}$ [9]). As revealed by the slightly asymmetric broadening of the main doublet component in Fig. 3, that is suggestive of the existence of distributions in both the $\delta_{(S)}$ and $\Delta E_{Q(S)}$ values, the $[\text{SnS}_6]$ coordination polyhedra are obviously distorted to somewhat different extents.

In this respect, it is worth mentioning that the observed behavior of Sn^{2+} ions on anatase microcrystals in the presence of H_2S , significantly differs from what was observed under the same experimental conditions for Sn^{2+} ions on surface sites of Cr_2O_3 [10]. While in the latter case the surface-located Sn^{2+} ions were also found to migrate from the sites with pure oxygen surrounding to be bonded only to S^{2-} ions, no oxidation of the divalent tin was revealed by the relevant *in situ* ^{119}Sn Mössbauer spectra [10]. Accordingly, the persistence of Sn^{2+} ions in the case of Cr_2O_3 shows that the interaction of this oxide with adsorbed molecules of H_2S is essentially molecular.

In order to get a better insight into the chemical behavior of tin ions in the presence of hydrogen sulfide we have also investigated Mössbauer spectrum of anatase particles doped with $^{119}\text{Sn}^{4+}$ oxidized pristine ions. For this purpose, the starting material was prepared according to [1] by mild heating of 2 in air at 200°C for 1 h (the resulting material is hereafter denoted as 4). Mössbauer measurements, performed after exposure of 4 to H_2S at 25°C for 19 h (Fig. 4), did not allow any tin sulfide species to be detected at positive Doppler velocities, all the parameters of the initial central peak, assigned to Sn^{4+} ions coordinated by 6 O^{2-} anions, being found to remain unchanged. Hence, contrary to what was observed for Sn^{2+} , exposure to H_2S under the same experimental conditions did not affect the nearest surrounding of Sn^{4+} pristine ions. The higher reactivity of surface-located Sn^{2+} ions with respect to H_2S may therefore be explained by the instability of the intermediate mixed anionic surrounding of Sn^{4+} sulfur-oxidized ions involving size-incompatible O^{2-} (ionic radii $r = 1.40 \text{ \AA}$ [11]) and S^{2-} ($r = 1.84 \text{ \AA}$ [11]) anions.

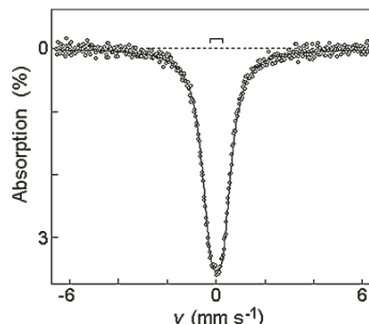


Fig. 5. ^{119}Sn Mössbauer spectrum of 5.

3.2. Mössbauer spectroscopy and XPS characterization of sample 3 after a long-term exposure to ambient air (sample 5)

We also took advantage of the opportunity to investigate, using both ^{119}Sn Mössbauer spectroscopic probe and XPS techniques, sample 3 which was exposed to ambient air for a period of 3 months (this sample is hereafter denoted as 5).

Mössbauer spectroscopic measurements (Fig. 5) have once again exhibited a drastic change in the local environment of Sn^{4+} ions pointing to the total replacement of their neighboring S^{2-} anions ($\delta_{(S)} = 1.16 \text{ mm s}^{-1}$ and $\Delta E_{Q(S)} = 1.28 \text{ mm s}^{-1}$) by O^{2-} anions ($\delta_{(O)} = 0.02 \text{ mm s}^{-1}$ and $\Delta E_{Q(O)} = 0.50 \text{ mm s}^{-1}$). Hence, the observed change in the ^{119}Sn hyperfine parameters has provided direct evidence for the oxidation, under ambient conditions, of the adsorbed H_2S by oxygen molecules. This reaction is found to result in the formation of H_2O and/or other oxygen-containing species capable of saturating the coordination sphere of Sn^{4+} to produce $[\text{SnO}_6]$ -like coordination polyhedra. Note, that in this experiment once again, Mössbauer spectra revealed no Sn^{4+} ions stabilized in a mixed $[\text{S}^{2-} + \text{O}^{2-}]$ anionic surrounding.

XPS characterization of 5 has provided the following results (Fig. 6 and Table 2):

- The binding energy values corresponding to $\text{Ti}2p3$ ($E_b = 458.8 \text{ eV}$) and $\text{Sn}3d5$ ($E_b = 487.0 \text{ eV}$) peaks are found to be virtually equal to those previously reported in [1] for a sample, similar to 4, but not exposed to H_2S . Thus, XPS spectra in Fig. 6a and b did not allow us to detect any change in the chemical state of both host and guest cations, which could be related to interactions of H_2S with the surface of tin-doped anatase microcrystals;
- On the contrary, XPS measurements revealed the $\text{S}2p$ spectrum (Fig. 6c) consisted of two chemically different main contributions defined by the binding energy values $E_b \sim 164 \text{ eV}$ and $E_b \sim 169.0 \text{ eV}$. According to [12], the former value is assignable

Table 2

Tin-to-titanium, tin-to-total sulfur, and elemental sulfur-to-sulfate molar ratios, relative to 3–5 nm thick surface-adjacent layers in 5 (this sample was first exposed to H_2S and then to ambient air), determined from XPS measurements at different locations of the X-ray spot.

Locations of the spot	$[\text{Sn}]:[\text{Ti}]$	$[\text{Sn}]:([\text{S}^0] + [\text{SO}_4^{2-}])$	$[\text{S}^0]:[\text{SO}_4^{2-}]$
1	0.024	0.21	1.52
2	0.023	0.33	0.54
3	0.025	0.46	0.46
4	0.023	0.43	0.38
5	0.023	0.33	0.73

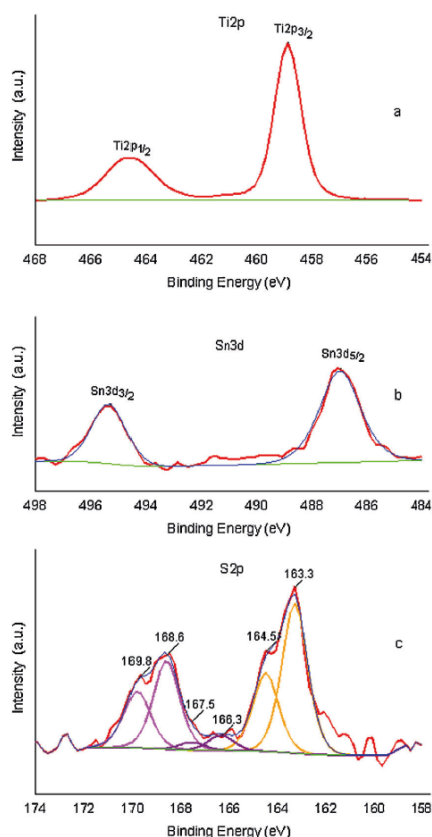


Fig. 6. Ti2p, Sn3d and S2p X-ray photoelectron spectra of air-exposed **5**. Both main S2p peaks were fitted taking into account the S2p_{3/2} and S2p_{1/2} contributions.

to elemental sulfur (S^0) and the latter to sulfate anion (SO_4^{2-}). Moreover, in the region between these main peaks, one can tentatively suggest the occurrence of two very weak peaks representing the +4 intermediate oxidation state ($E_b = 166\text{--}167$ eV being reported for the sulfite ion SO_3^{2-} [12]). Hence, all of these XPS results are consistent with the oxidation of S^{2-} ions revealed by the Mössbauer spectrum shown in Fig. 5.

The data presented in Table 2 also allow us to draw some conclusions based on comparing the $[Sn]:[Ti]$, $[Sn]:([S^0] + [SO_4^{2-}])$ and $[S^0]:[SO_4^{2-}]$ molar ratios. So, the observed tin-to-titanium molar ratio, $R_{[Sn]:[Ti]} = [Sn]:[Ti] = 0.023 \pm 0.002$, which appears to be virtually independent on the spot location, still implies an abnormally high (more than 20-fold) enrichment with tin of surface layers as compared to the overall molar ratio $[Sn]:[Ti] = 0.001$ defined by the amounts of tin and titanium used in the synthesis of **2**.

Moreover, the $R_{[Sn]:[Ti]}$ value, relative to **5**, is found to be even somewhat higher than the relevant value reported in [1] for a sample similar to **2**, but not exposed to H_2S ($R_{XPS} = [Sn]:[Ti] = 0.018$). As the overall $[Sn]:[Ti]$ ratio in both these samples was the same, a higher value of $R_{[Sn]:[Ti]}$ for the sample exposed to H_2S may be explained assuming that the presence of sulfur-containing species has preferentially affected the spectral contribution of Ti^{4+} ions that became too distant from the "sulfur-contaminated" anatase surface to be detected by XPS. Considering the values of $[Sn]:([S^0] + [SO_4^{2-}])$ and $[S^0]:[SO_4^{2-}]$ molar ratios, involving the sulfur-containing species that were not desorbed under high vacuum conditions of XPS measurements, one can see that these values exhibit large variations depending on the spot location. The obvious lack of correlation between Sn and S contents is thus quite consistent with the formation, upon long-term exposure of **3** to ambient air, of $[SnO_6]$ -like species revealed by the ^{119}Sn Mössbauer probe.

4. Conclusions

Our *in situ* Mössbauer spectroscopic measurements performed with $^{119}Sn^{2+}$ probe ions located on surface sites of anatase-type TiO_2 microcrystals and then exposed to a H_2S/H_2 mixture, have revealed the oxidation of these ions with concomitant stabilization of the resulting Sn^{4+} ions in a coordination polyhedra composed of only S^{2-} anions. This finding is accounted for by the dissociative adsorption of a fraction of the H_2S molecules retained by the studied TiO_2 substrate. In ambient air, oxidation of H_2S by O_2 results in the formation of both H_2O molecules and SO_4^{2-} anions responsible for the appearance of Sn^{4+} ions coordinated by only O^{2-} -containing species. In a broader sense, the results reported in the present study provide further evidence that the method of the surface-located $^{119}Sn^{2+}$ Mössbauer probe can be successfully applied to studying the adsorption phenomena at molecular scales.

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