

Mössbauer Study of the Impact of Hydrogen Fluoride on Tin Probe Ions Located on the Surface of Cr₂O₃ Microcrystals

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IN HONOR OF PROFESSOR PAUL HAGENMULLER ON THE OCCASION OF HIS 80TH BIRTHDAY

Room-temperature exposure of tin-doped Cr₂O₃ surfaces to HF induces in the ¹¹⁹Sn Mössbauer spectra changes that depend on the valence state of the tin probe and show differences between the Sn(II)- and Sn(IV)-containing Cr₂O₃ crystallite surfaces. In the Sn(II)-doped samples (Sn(II)/Cr₂O₃), the Sn and Cr surface cations are coordinatively unsaturated, and upon exposure to HF chemical corrosion occurs. Preliminary contact of Sn(II)/Cr₂O₃ with oxygen results in oxidation of Sn(II) to Sn(IV) and concomitant saturation of the coordination sphere of the surface cations; the apparent activity of HF then drastically decreases (passivation effect). Similar phenomena were previously observed for Sn(II)/ and Sn(IV)/Cr₂O₃ samples exposed to HCl or H₂S, i.e., acid gases containing anions much larger than F⁻. Thus, the behavior of the dopant cations in the presence of acid gases should not be imputed to size incompatibility between oxygen vacancies and foreign anions coming onto the surface from its gaseous surrounding. © 2001 Elsevier Science

Key Words: Mössbauer spectroscopy; ¹¹⁹Sn; chromium sesquioxide; hydrogen fluoride; surface; corrosion.

1. INTRODUCTION

Mössbauer spectroscopy is intrinsically a bulk technique. However, it can be used as a powerful tool in the study of surface phenomena, provided that a Mössbauer dopant can be placed in surface sites of the matrix to be studied, particularly if the dopant is diamagnetic and the matrix is magnetically ordered. Effectively, in this case, the Mössbauer

spectra of the probe provide information concerning not only its anionic neighborhood (through isomer shift and quadrupole splitting values) but also its cationic environment thanks to the magnetic effects observed. This possibility has already been illustrated in the case of chromium sesquioxide (1), which can be surface-doped with Sn(II) (the corresponding product is referred to as Sn(II)/Cr₂O₃). Cr₂O₃ is antiferromagnetic and, below its Néel temperature ($T_N = 308$ K (2)), the magnetic moments of the Cr(III) cations produce spin polarization of the electron shell of the neighboring tin ions, which results in Zeeman splitting of the ¹¹⁹Sn Mössbauer spectra. These magnetic spectra therefore permit one to get specific information on the cationic surroundings of the diamagnetic Mössbauer probe, i.e., on the cations present on the Sn/Cr₂O₃ crystallite surface. Such information can be efficiently used in various chemical studies; e.g., it permitted the elucidation of the modifying action of tin dopant on the catalytic properties of Cr₂O₃ in the reaction of oxidation of CO by O₂ and gain an insight into active oxygen species (3). Consequences of exposure of Sn(II)/Cr₂O₃ to various gases, O₂ (1), HCl (4), and H₂S (5) among others, have been investigated on this basis. One of the purposes of these studies was, using Sn/Cr₂O₃ as a model system, to elucidate the influence of different factors on the insertion of gas molecules or their fragments in the coordination sphere of the surface cations, i.e., on the surface reactivity mechanism. Upon contact with oxygen, Sn(II) is readily oxidized to Sn(IV), which remains located on the surface of the resulting Sn(IV)/Cr₂O₃ crystallites. Upon exposure of Sn(II)/Cr₂O₃ to HCl or H₂S, oxygen is quickly and completely replaced in tin surroundings by foreign anions supplied by the acid gas (at the same time the Sn–O–Cr interactions responsible for the spin polarization

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of the probe disappear as evidenced by the disappearance of Zeeman splitting in the Mössbauer spectra). The failure in observing an intermediate state with tin nearest environment involving lattice oxygens along with species coming from the reactive atmosphere thus points to the instability of such mixed configurations. It is significant in this respect that the ionic radii of the related anions are larger than that of oxygen. For this reason the instability of mixed anionic surroundings might in principle reflect size incompatibility between the available surface oxygen vacancies and the foreign anions. With the ionic radius of F^- being slightly smaller than that of O^{2-} (1.33 and 1.40 Å, respectively (6)), study of the reaction of tin probe ions with hydrogen fluoride was undertaken with the aim to check the validity of this hypothesis of size effect. This study concerns not only Sn(II)/Cr₂O₃, but also Sn(IV)/Cr₂O₃ in order to evidence the eventual reactivity difference between Sn(II)- and Sn(IV)-doped surfaces.

2. EXPERIMENTAL

The starting material, ¹¹⁹Sn(II)/Cr₂O₃, to be exposed to HF was obtained according to the method described in (1). The initial stage of this process involves coprecipitation of Cr(III) and Sn(IV) ions in the form of X-ray amorphous hydroxide (atomic ratio Sn:Cr = 0.003; 92% enrichment of the dopant in ¹¹⁹Sn Mössbauer isotope). The precipitate is then washed with water and dried in air. The final treatment is performed under H₂ flow at 1200 K for 10 h in a quartz reactor equipped with a lateral thin-window sample cell for *in situ* Mössbauer measurements. At the end of this annealing the tin ions are reduced to the + II state and located at the interface {Cr₂O₃ crystallites/H₂} (1,7). This surface location is in particular reflected by the high sensitivity of the Sn(II) ions to air exposure which results in their instantaneous reoxidation to the + IV state. The daughter Sn(IV) species remain surface-located as shown by XPS measurements: the Sn/Cr ratio derived from XPS data is found to be 40 times greater than the overall ratio, and Ar⁺ ion bombardment rapidly removes an appreciable part of the tin ions (1).

In order to study the effects of HF on tin-doped Cr₂O₃ crystallite surface, the samples were exposed to a mixture of hydrogen fluoride and pure argon obtained as follows. Potassium hydrofluoride KHF₂ was placed in a copper tube and dried in flowing Ar at 390 K. After shutting off the argon flow, HF was liberated from the source compound by decomposition at 850 K (8). The HF/Ar gas mixture was then admitted into the reactor containing Sn(II)/Cr₂O₃, using the depression resulting from previous cooling from 1200 K after the treatment under H₂ flow. The gas volume introduced corresponded to a [F]/[Sn] atomic ratio of ca. 20:1. For experiments involving Sn(IV)/Cr₂O₃,

Sn(II)/Cr₂O₃ was exposed at room-temperature to dry O₂/Ar mixture prior to HF/Ar admission.

¹¹⁹Sn spectra were recorded using a conventional Mössbauer spectrometer operating in constant acceleration mode with a Ca^{119m}SnO₃ source (isomer shift values refer to a CaSnO₃ absorber at 295 K). The Sn(II)/Cr₂O₃ starting material was first characterized by *in situ* Mössbauer measurements. For this purpose, the powder to be investigated was *in situ* transferred from the bottom of the reactor to entirely fill the measurement cell. Not being sealed off from the reactor, the cell was then introduced in vertical position into the cavity of a copper cold conductor immersed in a Dewar vessel filled with liquid nitrogen. During the measurements the temperature of the sample was 100 ± 2 K. For exposure to HF, the measurement cell was removed from the Dewar vessel and the powder was transferred back to the bottom of the reactor. The powder was then left for 1 h in contact, at room temperature, with the HF/Ar atmosphere and several times shaken up in order to favor efficient contact prior to being retransferred into the *in situ* measurement cell. Temperature-dependent measurements aiming to determine the Mössbauer lattice temperatures Θ_M required transfer of the material from the reactor measurement cell to another cell usable in a regular cryostat: in a glove box filled with high purity argon, the powder was quickly transferred into a double cuvette plastic cell which was hermetically sealed and then introduced into the cryostat already cooled down to 5 K.

3. RESULTS AND DISCUSSION

3.1. Exposure of ¹¹⁹Sn(II)/Cr₂O₃ to HF

3.1.1. *In situ* measurements. The *in situ* spectrum of the starting material Sn(II)/Cr₂O₃ (Fig. 1a) can be described as superposition of two ¹¹⁹Sn hyperfine splitting systems with parameters (Table 1) consistent with those reported in (7) for lower temperature measurements (*T*_{meas.} = 10 K). According to (7), the spectrum reflects the presence of Sn(II) in sites of two types, both possessing similar anionic environment (three oxygen ions of the matrix surface, the lone electron pair of Sn(II) being directed perpendicularly to this oxygen triangle) but having different numbers of neighboring Cr(III) cations as evidenced by the different H values. Predominant part of the Sn(II) ions are surrounded by three Cr(III) inducing H = 47.2 kOe while the others have only one Cr(III) neighbor (H = 11.2 kOe). The first are located in the topmost cationic layer, the last just above this layer ("over-surface" positions) (7). The *in situ* spectrum (Fig. 1a) allows the same interpretation and thus shows that the synthesized material is suitable for further experiments.

The *in situ* spectrum recorded after exposure to HF (Fig. 1b) is drastically different from the initial spectrum (Fig. 1a) since it consists of the superposition of two

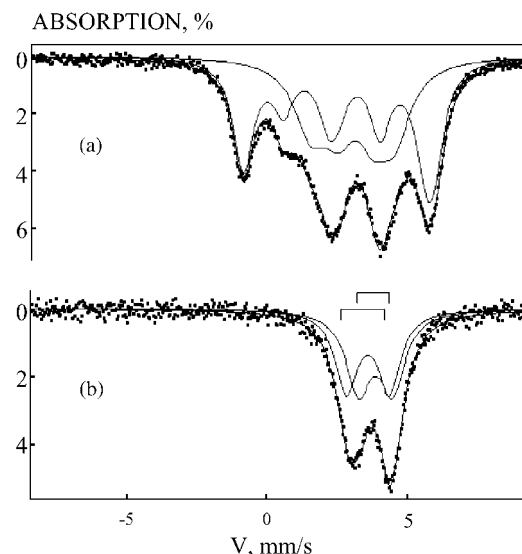


FIG. 1. *In situ* Mössbauer spectra of Sn(II)/Cr₂O₃ at 100 K (a) before exposure to HF and (b) after room-temperature exposure to HF for 1 h.

symmetrical doublets. Comparison of the δ^{HF} and Δ^{HF} values (Table 2) with those reported for various tin-containing fluorides shows that the parameters of doublet 1 are close to those of α -SnF₂ ($\delta = 3.50$ mm/s, $\Delta = 1.60$ mm/s (9)) while the parameters of doublet 2 are consistent with those of Sn(II) in mixed-valence α -Sn₃F₈ ($\delta = 3.89$ mm/s, $\Delta = 1.33$ mm/s (10)). In both of these fluorides the coordination polyhedron of Sn(II) is a triangular pyramid with three fluoride ions and the Sn(II) lone electron pair at the apexes (9, 10). The spectrum in Fig. 1b thus shows

TABLE 1
Parameters of the *in Situ* Mössbauer Spectrum (100 K)
of the Starting Material Sn(II)/Cr₂O₃

| | System 1 | System 2 |
|-----------------|-----------------|-----------------|
| δ (mm/s) | 2.71 ± 0.01 | 2.86 ± 0.02 |
| e^2qQ (mm/s) | 4.10 ± 0.02 | 4.02 ± 0.02 |
| H (kOe) | 42.1 ± 0.2 | 10.0 ± 0.2 |
| θ (°) | 82 ± 1 | 76 ± 2 |
| φ (°) | 90 ± 12 | 90 ± 15 |
| η | 0.10 ± 0.01 | 0.12 ± 0.04 |
| Γ (mm/s) | 1.00 ± 0.01 | 1.31 ± 0.04 |
| A (%) | 60 ± 5 | 40 ± 5 |

Note. δ is the isomer shift, $e^2qQ = 2\Delta/(1 + \eta^2/3)^{1/2}$ is the quadrupole coupling constant, η is the asymmetry parameter ($0 \leq \eta \leq 1$), θ is the polar angle, and φ is the azimuthal angle giving the direction of the magnetic hyperfine field H with respect to the electric field gradient. Γ is the full-width at half-maximum of the individual lines of a hyperfine splitting pattern and A is the relative contribution of a subspectrum to the absorption area.

TABLE 2
Parameters of the *in Situ* spectrum (100 K) of Sn(II)/Cr₂O₃
after Exposure to HF

| | Doublet 1 | Doublet 2 |
|-----------------------------|-----------------|-----------------|
| δ^{HF} (mm/s) | 3.59 ± 0.04 | 3.86 ± 0.04 |
| Δ^{HF} (mm/s) | 1.52 ± 0.06 | 1.21 ± 0.06 |
| Γ^{HF} (mm/s) | 0.97 ± 0.07 | 1.07 ± 0.07 |
| A ^{HF} (%) | 48 ± 2 | 52 ± 2 |

that exposure to HF results in stabilization of Sn(II) in surroundings similar to those existing in α -SnF₂ and α -Sn₃F₈. This means that action of HF results in removing Sn(II) from its initial lattice-oxygen coordination. Removing tin from the oxide substrate surface correlates with the disappearance of the spin polarization of the ¹¹⁹Sn electron shell (nonmagnetic ¹¹⁹Sn spectrum). Effectively, this disappearance indicates that the dopant has no longer neighboring Cr(III) ions with ordered magnetic moments, i.e., cations involved in the magnetic interactions of the Cr₂O₃ matrix. These spectral changes are similar to those previously observed for similar experiments with HCl and H₂S (3,5). They can be accounted for by dissociative adsorption of HF molecules followed by replacement of the surface-Sn(II) ions by the resulting protons. Thus, this spectrum shows that the ionic radius of the foreign anions is not responsible for the absence of mixed anionic surrounding of surface Sn(II) ions.

3.1.2. *Spectra recorded after transferring the sample into the cryostat measurement cell.* Temperature-dependent measurements were performed in order to determine the Mössbauer lattice temperatures, Θ_M , for the fluorine-surrounded Sn(II) ions in our sample and to compare these values with those reported for similar tin-containing units in the bulk of α -SnF₂ and α -Sn₃F₈.

The first spectrum, recorded at 5 K (Fig. 2a), shows that the precautions taken against oxidation did not impede partial oxidation of Sn(II) to Sn(IV) as demonstrated by the broad line at $v \approx 0$ mm/s. This oxidation shows that the oxygen traces present in the argon glove box atmosphere had easy access to Sn(II), due to its unsaturated coordination sphere. Nevertheless, measurements at higher temperatures were performed on this sample as far as Sn(II) contribution remained predominant. As it will appear below, and precisely due to the presence of Sn(IV), this sample allowed further information to be obtained concerning the HF impact.

All the spectra recorded over the 5–240 K temperature range contain three components, two Sn(II) doublets and

the Sn(IV) broad line, the only significant thermal evolution concerning the relative contribution of the different sub-spectra. Three of these spectra are presented in Fig. 2; the parameters of their different components are given in Table 3. Comparison of the parameters of the two Sn(II) doublets at 100 K (Fig. 2b) with those observed *in situ* at the same temperature (Fig. 1b) shows that the appearance of Sn(IV) ions has little effect on tin remaining in the divalent state, even if the Γ_2 value increases: only slight shift of both doublets toward lower velocities and slight increase of Δ can be discerned. Nevertheless these changes indicate that the heterovalent tin ions are not completely independent. The isomer shift value of the Sn(IV) component itself is more surprising and calls for reconsideration of the HF impact on the Sn(II)-containing surface of Cr_2O_3 : it is nearly zero (Table 3), which suggests an octahedral oxygen surrounding (as in the CaSnO_3 reference). The Sn(IV) ions resulting from reaction of O_2 with $[\text{Sn(II)F}_3]$ units, a mixed anionic environment ($3\text{F} + \text{O}$), could have been expected, with an isomer shift intermediate between 0 mm/s (Sn(IV) with only oxygen neighbors) and -0.39 mm/s (Sn(IV) in pure fluorine octahedral surrounding (11)). The fact that it is not the case suggests that water molecules (or hydroxyl groups) were already present in the vicinity of the $[\text{SnF}_3]$ species, prior to reaction with O_2 , allowing thus the oxidized

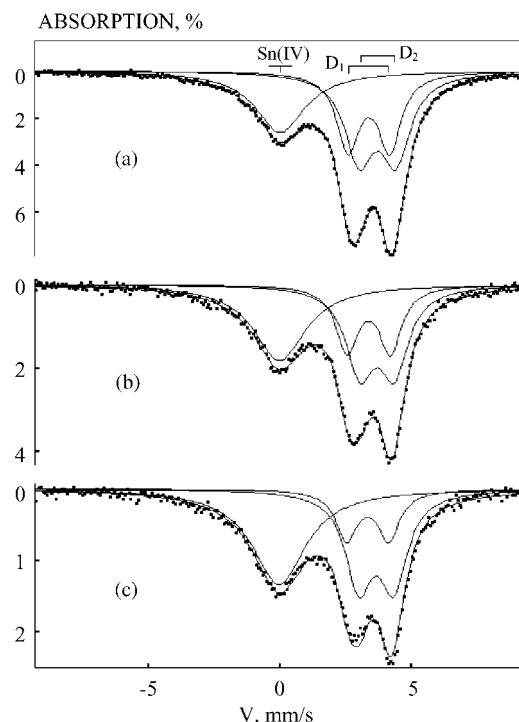


FIG. 2. Three typical Mössbauer spectra of Sn(II)/ Cr_2O_3 exposed to HF (the sample partly oxidized upon transferring into the helium cryostat): (a) $T = 5$ K, (b) $T = 100$ K, and (c) $T = 240$ K.

TABLE 3
Parameters of the Components Present in Three Typical Mössbauer Spectra of Sn(II)/ Cr_2O_3 Exposed to HF (the Partly Oxidized Sample)

| T, K | Dopant | Parameters | | | |
|------|---------------------|------------------|-----------------|-----------------|------|
| | | δ , mm/s | Δ , mm/s | Γ , mm/s | A, % |
| 5 | Sn(II) ₁ | 3.44 ± 0.01 | 1.59 ± 0.02 | 1.05 ± 0.02 | 32 |
| | Sn(II) ₂ | 3.77 ± 0.02 | 1.40 ± 0.01 | 1.35 ± 0.02 | 43 |
| | Sn(IV)* | 0.06 ± 0.01 | — | 2.36 ± 0.04 | 25 |
| 100 | Sn(II) ₁ | 3.42 ± 0.01 | 1.60 ± 0.02 | 1.03 ± 0.01 | 28 |
| | Sn(II) ₂ | 3.75 ± 0.03 | 1.34 ± 0.02 | 1.34 ± 0.02 | 41 |
| | Sn(IV)* | 0.03 ± 0.01 | — | 2.40 ± 0.05 | 31 |
| 240 | Sn(II) ₁ | 3.37 ± 0.02 | 1.60 ± 0.02 | 1.01 ± 0.02 | 19 |
| | Sn(II) ₂ | 3.70 ± 0.02 | 1.32 ± 0.02 | 1.27 ± 0.04 | 41 |
| | Sn(IV)* | -0.01 ± 0.02 | — | 2.50 ± 0.05 | 40 |

Note. *The broadening of the Sn(IV) component was assumed to be the result mainly from a distribution of the electric field gradient values. The contribution of this component was calculated as the sum of four discrete doublets with the same δ (to be fitted for each temperature), a fixed $\Gamma = 1.0$ mm/s, and nonconstrained $\Delta(i)$ and $A(i)$ values (e.g., at $T = 5$ K $\delta = 0.06$ mm/s, $\Delta(1) = 0.51$ mm/s, $A(1) = 16\%$, $\Delta(2) = 2.05$ mm/s, $A(2) = 7\%$, $\Delta(3) = 3.97$ mm/s, $A(3) = 3\%$, $\Delta(4) = 7.39$ mm/s, $A(4) = 2\%$). The two “doublets” with lowest contributions correspond to Δ values which are unrealistically large for Sn(IV), which consequently prohibits their assignment to quadrupole splitting. Their presence very likely reflects magnetic hyperfine splitting exhibited by a mere fraction of Sn(IV) ions. Their contribution is too weak to be properly fitted.

cations² to adopt octahedral configuration ($3\text{F} + 3\text{O}$) and further replacing F^- in their coordination sphere.

The presence of such H_2O molecules signifies that action of HF results not only in hydroxylation of the surface but also in departure of part of the surface “lattice” oxygen anions (likely together with chromium cations) into the fluorinated shell adsorbed on the Cr_2O_3 crystallites. In this respect, we can see that the oxidized tin cannot be surrounded by lattice oxygen since in this case magnetic splitting of the corresponding component would have been observed. Thus, the concerned spectra not only imply changes in local surroundings of the probe ions but they also reveal corrosion of the oxide surface as a whole. The anticipated migration of a number of Cr(III), along with the Sn ions, to the fluorinated shell allows one to account for the presence in the *in situ* spectrum (Fig. 1b) of a doublet with parameters close to those relative to Sn(II) in $\alpha\text{-Sn}_3\text{F}_8$ (10).

²The nearly zero isomer shift in fact refers to Sn(IV) in the sample at 100 K, the source being kept at room temperature. This means that the considered tin ions have a very small negative isomer shift which is compensated by the second-order Doppler shift ($\delta_T = +0.06$ mm/s). Some Sn(IV) ions can therefore contain an isolated F^- among their nearest neighbors. However, the observed value certainly prohibits assignment to Sn(IV) still containing three fluorine ligands in their coordination sphere.

In this fluoride (12), each $[\text{Sn(II)F}_3]$ unit is linked via shared F^- anions to two other units of the same type, and to one $[\text{Sn(IV)F}_6]$ group in ... $\text{F-Sn(II)-F-Sn(IV)-F-Sn(II)-F}$... zigzag chains. Although the sample contains only divalent tin after exposure to HF, as attested by the *in situ* spectrum (Fig. 1b), structural fragments similar to those in $\alpha\text{-Sn}_3\text{F}_8$ can be present with Cr(III) instead of Sn(IV) in the octahedral sites. At 5 K, the Sn(IV) line width (Γ) is large (Table 3), which could be related to magnetic effects ($T_N[\text{Cr}_2\text{O}_3] = 308$ K). However, it cannot be the case since Γ does not decrease for higher measurement temperatures. It thus appears more plausible that the broadening of the Sn(IV) component reflects a distribution of the electric field gradient (EFG) values. Such a weakly temperature-dependent broadening could arise from nonuniform distortion of tin-containing polyhedra. In this respect it is to be reminded that some Sn(IV) can be expected to have a lone F^- neighbor that could become a new source of distribution in EFG values. In addition, presence of a lone F^- in the vicinity of some Sn(IV) ions would allow the formation of Sn(IV)-F-Sn(II) bridges, which would explain the broadening of the doublet 2 components (at 100 K, $\Gamma_2 = 1.34$ mm/s) with respect to the *in situ* experiment ($\Gamma_2^{\text{HF}} = 1.07$ mm/s).

3.1.3. Mössbauer Lattice Temperatures Θ_M For each of the three spectral components, linear evolution of the logarithm of the normalized absorption area is observed in the 50–240 K temperature range. On the basis of Debye's model in the high-temperature approximation, the Θ_M values were calculated for Sn(II) relative to doublet 1 (157 ± 6 K), Sn(II) relative to doublet 2 (204 ± 7 K), and Sn(IV) (265 ± 9 K). The $\Theta_M[\text{Sn(II)}_2]$ value is in good agreement with that reported for Sn(II) in $\alpha\text{-Sn}_3\text{F}_8$ (13), which is the highest Θ_M known for divalent tin in fluorides ($\Theta_M = 181$ K). Moreover, $\Theta_M[\text{Sn(II)}_2]$ is even ca. 20 K larger than this value, which evidences a particularly strong bonding of the $[\text{SnF}_3]$ entities not only to each other but also to the oxide substrate surface (possibly due to the hydrogen bonds appeared after reaction between the Cr_2O_3 surface and HF). Taking into account the similarity of the Sn(II)-containing polyhedra related to doublets 1 and 2, formation of hydrogen bonds can be expected to produce similar increase in $\Theta_M[\text{Sn(II)}_1]$. The same correction of ca. -20 K should therefore be applied to the observed value. This yields the corrected $\Theta'_M[\text{Sn(II)}_1] = 134$ K, in fair agreement with the value reported for $\alpha\text{-SnF}_2$ ($\Theta_M = 139$ K (13)). Thus, both $\Theta_M[\text{Sn(II)}_1]$ and $\Theta_M[\text{Sn(II)}_2]$ values point to the fluoride phases which have already been selected as reference compounds on the basis of the (δ , Δ) values.

The situation is different for the Sn(IV) ions present as well in the fluorinated shell. While they are mainly surrounded by oxygen anions, their Θ_M value (265 K) is obviously lower than those reported for Sn(IV) ions produced

upon exposure of Sn(II)/ Cr_2O_3 to air (314 K (14)) and for Sn(IV) ions located in the bulk of Cr_2O_3 (400 K (14)). Therefore the decreasing sequence of $\Theta_M = 400$, 314, and 265 K reveals the increase in mean-square amplitudes of thermal vibrations of Sn(IV) upon going from the bulk to the surface, and further, in a hydrated state, to the chemically modified shell. The particularly low Θ_M for Sn(IV) ions within the fluorinated shell is thus consistent with the non lattice nature of their oxygen ligands.

3.2. Exposure of $^{119}\text{Sn(IV)}/\text{Cr}_2\text{O}_3$ to HF

This part of the study aimed to reveal the effect of the valence state of tin on the information provided by the ^{119}Sn spectra. The sample containing Sn(IV) surface-located ions (Sn(IV)/ Cr_2O_3) was obtained from Sn(II)/ Cr_2O_3 by action of a dry oxygen-argon mixture. Its spectrum was recorded at 100 K before exposure to HF and is shown in Fig. 3a; the relevant field distribution function $P(H)$ obtained by the method of Hesse and Rübartsch (15) is given in Fig. 3b. The predominant contribution ($H = 110$ kOe) corresponds to Sn(IV) located within the top-most cationic layer, where they are surrounded by three Cr(III) (1). The splitting structure related to H of ca. 60 kOe corresponds to Sn(IV) located above this layer and having only one Cr(III) neighbor (3). The weak contribution of intermediate H value is attributable to a minor fraction of Sn(IV) ions with two Cr(III) neighbors.

In the experiments involving HF the reactor was filled with a gas mixture having the same composition as in the similar experiments with divalent tin. In order to favor contact of the Sn(IV) probe ions with HF, the sample was

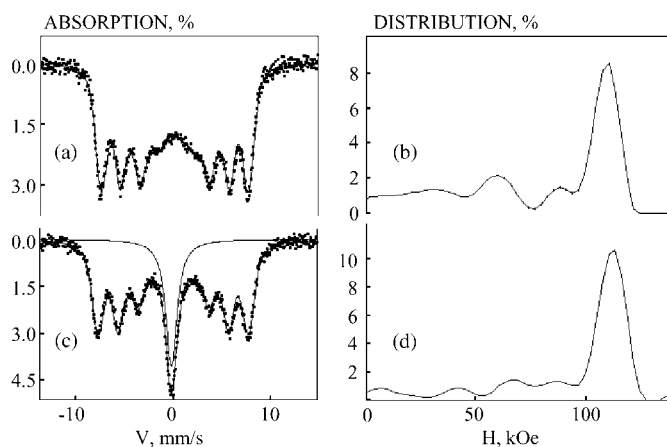


FIG. 3. *In situ* Mössbauer spectra of Sn(IV)/ Cr_2O_3 at 100 K and relevant $P(H)$ distribution curves: (a) spectrum recorded after passage of O_2 over Sn(II)/ Cr_2O_3 , (b) $P(H)$ distribution curve relative to (a), (c) Spectrum recorded after subsequent room-temperature exposure of the oxidized sample (a) to HF for 48 h, and (d) $P(H)$ distribution curve relative to (c).

kept under the reaction atmosphere for 48 h, and several times shaken, before starting the Mössbauer measurements. An *in situ* spectrum recorded at 100 K is shown in Fig. 3c. It allows the two following features to be immediately noted:

— in contrast with what happens upon exposure of $^{119}\text{Sn(II)/Cr}_2\text{O}_3$ to HF, the predominant contribution to the spectrum of $^{119}\text{Sn(IV)}$ is still associated to spin-polarized tin ions ($\langle\delta\rangle = 0.01$ mm/s, $H = 110$ kOe);

— the nonmagnetic component which appeared in the central part of the spectrum exhibits unambiguously negative isomer shift.

Fitting of the spectrum on the basis of the “model of discrete number of subspectra” leads to the following parameters for the nonmagnetic component:

$$\delta = -0.15 \pm 0.03 \text{ mm/s}, \Gamma = 1.37 \pm 0.05 \text{ mm/s},$$

$$A = 22 \pm 3\%.$$

After subtraction of this component, analysis of the magnetically split contribution (method of Hesse and Rübartsch) leads to the P(H) distribution given in Fig. 3d. Comparison of this curve with the initial curve (Fig. 3b) shows that exposure to HF virtually did not affect the Sn(IV) ions associated to the largest field $H = 110$ kOe (i.e., the ions located in the top-most cationic layer), and that the contribution of the Sn(IV) exhibiting weaker H values has decreased. The absence of significant decrease of the contribution with $H = 110$ kOe thus reveals that preliminary exposure of the Cr_2O_3 substrate to O_2 suppresses the corrosion of the surface by HF. The δ value relative to the nonmagnetic component (-0.15 mm/s) shows that the corresponding Sn(IV) have adopted mixed coordination involving both oxygen and fluoride anions. As noted above, prior to HF exposure these ions had a smaller number of Cr(III) neighbors and consequently a greater number of nearest terminal anions (hydroxyls). Further, it is to be stressed that these Sn(IV) ions exhibit more negative shift than that observed for the Sn(IV) ions formed during glove-box handling of the HF-exposed $^{119}\text{Sn(II)/Cr}_2\text{O}_3$ sample. At first sight it might appear surprising that stabilization of tin mainly in oxygen surrounding (as attested by zero isomer shift) could just occur upon unpremeditated oxidation of $[\text{Sn(II)F}_3]$ units, i.e., upon their oxidation by mere traces of O_2 . However, such a behavior can be accounted for by the presence, after corrosion, of H_2O molecules (or OH^- groups) which can replace F^- ions in the coordination sphere of Sn(IV). In contrast, suppression of the corrosion process in the sample preliminarily exposed to O_2 results in a deficiency of H_2O molecules (or OH^- groups) which forces the most reactive (“over-surface”) Sn(IV) ions to adopt an oxyfluoride-like environment upon exposure to HF. All these results thus demonstrate the oxide surface passivation induced by contact with oxygen.

4. CONCLUSION

The different changes induced in the ^{119}Sn spectra by room temperature exposure to HF of two surface-doped Cr_2O_3 samples, Sn(II)/ Cr_2O_3 and Sn(IV)/ Cr_2O_3 , are shown to reflect the different states of both the probe ion itself and the substrate surface it belongs to.

Sn(II)/ Cr_2O_3 synthesized in H_2 atmosphere contains coordinatively unsaturated surface cations, and HF easily reacts with the crystallite surface. This leads to the formation of a fluorinated shell containing the Sn(II) dopant in the form of $[\text{SnF}_3]$ units analogous to those occurring in $\alpha\text{-SnF}_2$ and $\alpha\text{-Sn}_3\text{F}_8$, without mixed coordination sphere (O + F) of the probe. Similar absence of mixed coordination spheres (O + S or O + Cl) previously evidenced in similar experiments involving H_2S or HCl cannot thus be imputed to size-incompatibility between oxygen vacancies and foreign anions supplied by the reactive atmosphere. Upon contact of HF-exposed Sn(II)/ Cr_2O_3 with mere traces of O_2 the arising Sn(IV) ions are stabilized in an essentially oxygen-containing environment which reveals the presence of H_2O molecules (or OH^- groups) in the fluorinated shell.

In the case of Sn(IV)/ Cr_2O_3 , obtained by contact of Sn(II)/ Cr_2O_3 with O_2 , tin oxidation is accompanied by saturation of the coordination sphere of the surface cations. As a consequence, further exposure to HF no longer affects the predominant part of the tin dopant, which clearly demonstrates the suppression of surface corrosion. Only the Sn(IV) ions weakly bonded to the Cr_2O_3 surface are found to react with HF and adopt an oxyfluoride coordination reflecting the deficiency of H_2O molecules on a surface resistant to corrosion.

The above results demonstrate that O_2 adsorption inhibits the reactivity of chromium sesquioxide toward acid gas media, due to the suppression of coordinatively unsaturated surface cations. The catalytic properties of this material (and of other catalysts) can be affected as well by similar phenomena.

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