ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 5, pp. 1060–1069. © Pleiades Publishing, Ltd., 2008.
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5s5p Element Dopant Cations: Møssbauer Probes for Studying Chemical Reactions at the Solid–Gas Interface

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Received September 5, 2007

Abstract—Annealing in reducing atmosphere allows stabilization of the Sn^{4+}, Sb^{5+}, or Te^{6+} dopant cations in a lower oxidation state. Due to its stereochemical activity, the lone electron pair of the resulting Sn^{2+}, Sb^{3+}, or Te^{4+} favors the location of these species in low-coordination sites, immediately on the surface of the substrate-compound crystallites. This allows ^{119}Sn, ^{121}Sb, or ^{125}Te Møssbauer spectroscopy to be applied for studying the processes occurring at the solid-gas interface. Results of such studies, mainly devoted to the Cr_2O_3 antiferromagnetic substrate, were discussed, along with the prospects of searching appropriate substrate-compounds of other types.

DOI: 10.1134/S1070363208050393

INTRODUCTION

Møssbauer spectroscopy, in its most widespread version, is based on measuring absorption spectra and is not a surface-sensitive method. The reason is a high penetrability of gamma radiation, responsible for the fact that the resulting spectrum characterizes primarily the state of the inner atoms, and the contribution from the atoms occurring on the particle surface is mostly negligible. The situation, however, radically changes when two requirements are satisfied

(1) the Møssbauer atoms are those of dopant elements specially introduced into the examined substance which is free from these elements;

(2) the electronic structure of such Møssbauer atoms (typically occurring as cations) is responsible for their occurrence immediately at the solid–gas interface.

In that case, the Møssbauer spectra are not veiled by the contribution from inner atoms, and the information about hyperfine interactions, provided by the probe atoms, will concern surface atoms and their local surrounding only. From the viewpoint of the amount of information derived from the Møssbauer spectra, the most favorable is the situation when the probe cation is diamagnetic, and the substance examined, on the contrary, is formed by magnetically active (3*d*) cations whose moments pass to the magnetically ordered state at not too low temperatures. In this case, 3*d* cations that surround the probe cation will induce spin polarization of its electron shell. This will be responsible for appearance in the Møssbauer spectrum of a nonmagnetic element of a system of magnetic hyperfine splitting lines. Analysis of this system can easily demonstrate that the probe cation belongs to the substance examined. Also, the parameters of this magnetically split spectrum become specifically sensitive to the cation surrounding of the probe atom.

LOCALIZATION OF DOPANT CATIONS ON THE CRYSTALLITE SURFACE

We observed for the first time the spontaneous passing of diamagnetic dopant cations from the crystallites bulk to the surface in the Møssbauer spectroscopic examination of the hyperfine interactions of ^{119}Sn in the antiferromagnetic Cr_2O_3 oxide [1, 2]. We found that annealing in hydrogen of Cr_2O_3, or its precursor $Cr(OH)_3$, containing coprecipitated Sn^{4+} cations results in tin stabilization in the oxidation state +2 in low-coordination sites [coordination number

(CN) of 3]. This precludes the occurrence of such cations in the crystallite bulk (at sites with CN = 6). In situ Møssbauer experiments in an H_2 atmosphere showed that the magnetic hyperfine splitting is manifested in the ^{119}Sn spectrum starting from the temperature coinciding with the Neel point of Cr_2O_3. Hence, the dopant cations participate in magnetic interaction of Cr_2O_3, but, in order to have a CN < < 6, they should occur on the crystallite surface. This conclusion was validated by analysis of the spectrum of ^{119}Sn upon the sample contacted air at room temperature. The spectrum revealed instantaneous tin oxidation, which suggests that it is readily accessible for oxygen molecules. At last, the occurrence of tin at crystallite surface sites was independently confirmed by "abnormally" high enrichment in tin of the near-surface layers of the crystallites, revealed by an XPS examination. The ratio of the atomic concentrations [Sn]/[Cr] at a depth of no greater than 2–3 nm was approximately 40 times the nominal content of tin in the sample as a whole.

Along with unexpected at a first sight accumulation of tin dopant cations on the crystallite surface, those experiments revealed an abnormally high stability of tin in the oxidation state +2; it did not pass to metal upon annealing in H_2 at temperatures reaching 900°C. This unambiguously suggested that Sn^{2+} causes the energy of the neighbor Cr^{3+} cations to substantially decrease. In other words, to preserve the most favorable octahedral coordination, the $3d^3$ chromium cations prevented splitting of the O^{2-} anion which is bound to them and simultaneously belong to the neighbor Sn^{2+} cation.

Passing of the tin dopant ions from bulk to the surface was also revealed by more recent studies of other oxides with the corundum structure: V_2O_3, γ-Al_2O_3, $Cr_{2-x}Al_xO_3$ [3]. This allowed application of Møssbauer spectroscopy in studying various aspects of chemical reactions of the surface atoms with gases, taking several isostructural oxides as an example. Passing of the dopant cations from the Cr_2O_3 bulk to the surface and their stabilization in an intermediate oxidation state were revealed for isoelectronic Møssbauer cations $^{121}Sb^{3+}$ and $^{125}Te^{4+}$ [4, 5]. The sp^3 hybridization is responsible for stereochemical activity of the lone electron pair, which allowed the Sb^{3+} and Te^{4+}, as well as Sn^{2+} cations to occupy low-coordination sites, energetically unfavorable for the major cations. This provides model systems with a set of isoelectronic probe cations differing in the oxidation state, ionic radius, and electronegativity, suitable for studying the chemical behavior of dopant cations and their possible modifying action on the surface-sensitive properties of the substance. However, because of a much higher labor intensity of the Møssbauer experiments with ^{121}Sb and ^{125}Te nuclei, most of the studies concerned with reactions of the surface atoms with gases utilized ^{119}Sn probe cations. In those works, Cr_2O_3 was most often used as the substrate. This compound has an experimentally convenient Neel temperature T_N = 308 K [6]; it is distinguished by a high chemical stability in most gases, and, importantly, exhibits a catalytic activity in numerous heterogeneous reactions whose study was of special interest.

REACTION OF $^{119}Sn^{2+}$ IONS ON THE Cr_2O_3 SURFACE WITH OXIDIZING GASE

Reaction with O_2 [1, 7]

The first chemical evidence of the surface localization of Sn^{2+} was obtained in the reaction with oxygen proceeding at a high rate at room temperature which is clearly insufficient for oxygen diffusion into the crystallite bulk. In situ Møssbauer spectroscopic examinations at different temperatures revealed two magnetically split subspectra corresponding to Sn^{2+} at sites with nonequivalent cation surrounding of two types [8]. The sites characterized by a weaker magnetic field (at 10 K, H = 11 kOe) were attributed to the Sn^{2+} ions containing only one Cr^{3+} magnetic cation in its nearest surrounding (i.e., to tin cations above the first cationic surface layer), and the Sn^{2+} ions subjected to a stronger spin polarization (H = 47 kOe) were attributed to sites with three neighbor Cr^{3+} cations, i.e., to positions in the first cationic surface layer. At the tin content of 0.3 at % the occupancy of the sites of the second type ("layer sites") proved to be approximately 2.5 times higher. Fast tin oxidation in samples contacting air was accompanied by approximately threefold increase in H for sites of both types without appreciable change of the ratio of their spectral contributions. This suggests that the reaction with O_2, responsible for enhancement of the spin polarization of the electron shell of ^{119}Sn (owing to now possible 3*d*-5*s* electron transfer [1]), did not change the cation surrounding of tin proper. The fact that the oxidized Sn^{4+} ions were preserved on the surface allowed comparison of their rms amplitudes of thermal fluctuations $<u^2>$ with those of the Sn^{4+} ions in the crystallite bulk (i.e., in a sample annealed in air at 900°C).

A higher <u^2> value for surface Sn^{4+} cations confirmed the expected weakening of the chemical bond with the surrounding anions [7]. This reaction allowed examination of how the valence state of the surface probe cation affects its reaction with other gases in the case of the samples that preliminarily did not contact (Sn^{2+}/Cr_2O_3) or contacted (Sn^{4+}/Cr_2O_3) air.

Reaction with Halogens [9]

For surface Sn^{2+} ions, steric factors are of less significance than for the bulk, which should favor the formation of a mixed (oxohalide) anionic surrounding for the tin oxidized with a halogen. In situ Møssbauer experiments showed that a 7-min contact of Sn^{2+} with Cl_2, Br_2, or I_2 is sufficient for exhaustive oxidation of tin. However, these experiments did not prove the presence of Sn^{4+} in the coordination polyhedrons containing both oxygen and halogen anions. For example, the spectra in the paramagnetic area at 315 K were characterized by the same, within the measurement accuracy, isomer shift relative to $BaSnO_3$, $\delta = 0.15 \pm 0.04$ mm s^{-1}, and the observed quadruple splitting (Δ ~0.6–0.7 mm s^{-1}) proved to be even smaller than that for the ions yielded by oxidation of the surface Sn^{2+} cations with oxygen ($\Delta = 0.82 \pm 0.03$ mm s^{-1}) [7]. At the same time, the experiments in which the samples were quenched in liquid nitrogen after keeping in the reaction medium at room temperature for different periods revealed a clear change of the spectral parameters of the already oxidized $^{119}Sn^{4+}$ ions. A special study of the reaction of Sn^{2+} with Cl_2 showed that the initial anion surrounding of Sn^{4+} at room temperature is unstable. Most of these cations are stabilized at sites at which they are surrounded by O^{2-} anions only and are subjected to spin polarization by Cr^{3+} cations ($\delta = 0.02$ mm s^{-1}, H = 110 кOe at 100 K). At the same time, a smaller proportion of Sn^{4+} occupied sites with a chloride surrounding ($\delta = 0.39$ mm s^{-1} corresponds to $[SnCl_6]^{2-}$ groups) in which the spin polarization at 100 K was completely lacking. This suggested that, upon exposure to Cl_2, some Sn^{4+} ions were detached from the surface of the antiferromagnetic oxide. Thus, the number of the ligands in the coordination sphere of the surface cation is not always the sum of those bound to it before the reaction ($3O^{2-}$) and attached as a result of the reaction ($2Cl^-$). The instability of the oxochloride (as well as oxobromide or oxoiodide) surrounding could be associated a priori with a too strong difference between the sizes of the oxygen vacancies in the neighborhood of Sn^{2+} (i.e., of the ionic radius of O^{2-}), on the one hand, and the ionic radii of considerably larger Cl^-, Br^-, and I^- anions, on the other.

This presumption was denied by the Møssbauer spectroscopic data on Sn^{2+}/Cr_2O_3 oxidation with XeF_2 [10]. In that case, the Sn^{4+} ions are stabilized at sites with a uniform anionic surrounding of two types: magnetic sites with an oxygen surrounding and nonmagnetic sites of hexafluoride groups $[SnF^6]^{2-}$ ($\delta = -0.27$ mm s^{-1}). In that case, the ionic radius of F^- (0.133 nm) was smaller than that of the O^{2-} anion (0.14 nm) [11]. Therefore, the instability of Sn^{4+} in the oxofluoride surrounding, revealed by that experiment, could by no means be associated with insufficient size of the oxygen vacancy. This allowed a presumption that degradation of the initial surrounding of Sn^{4+} is due to the fact that, in the case of interest, the interaction of an impurity defect with a foreign gas results in the partial cleaning of the surface owing to separation of interconnected oppositely charged defects, rather than in the appearance of new defects (F^-) on the surface.

REACTION WITH HYDROGEN HALIDES [12–14]

The experiments that allowed comparison of the surface cations in different oxidation states, as regards their chemical behavior, utilized two hydrogen halides, HCl and HF. In HCl the ionic radius of the anion (R_{Cl} = 0.181 nm) exceeds that of the oxygen anion (R_O = 0.14 nm) [11], by contrast to HF. In situ Møssbauer experiments showed that virtually all surface tin cations (Sn^{2+}) react with both acid gases, and the Sn^{4+} cations, in a fairly small number.

Reaction between HCl and Sn^{2+}/Cr_2O_3 Sample

A 30-min exposure to the HCl atmosphere caused the Sn^{2+} ions to exhaustively pass to the Cl^- anion surrounding. This is suggested by the spectrum of ^{119}Sn measured at 100 K, which is a superposition of two quadruple doublets, those with $\delta_1 = 3.85$ mm s^{-1}, $\Delta_1 = 0.98$ mm s^{-1} and $\delta_2 = 3.53$ mm s^{-1}, $\Delta_2 = 1.15$ mm s^{-1}, respectively, which make nearly equal spectral contributions. The lack of indications of spin polarization of Sn^{2+}, despite the fact that the spectra were measured at $T << T_N$, suggests that the HCl exposure caused rupture of the Cr–O–Sn chains that bound tin to the magnetically ordered chromium cations. Comparison of the δ and Δ parameters with the published data suggests that the former doublet corresponded to the Sn^{2+} ions in the $[SnCl_3]^-$ groups, isolated or interconnected via bridging chloride anions. The parameters of the latter doublet are fairly close to those of $^{119}Sn^{2+}$ in $SnCl_2 \cdot 2H_2O$ structure, which suggests the presence of the corresponding tin ions in the $[(H_2O)SnCl_2]$ groups.

Reaction between HCl and Sn^{4+}/Cr_2O_3 Sample

In this experiment, before HCl exposure, the Sn^{2+}/Cr_2O_3 sample was taken out of the reactor into air for 30 min. As noted above, this resulted in oxidation of tin and enhancement of its spin polarization at sites of the first cationic surface layer and immediately above this layer (at 100 K, H = 110 and H ≤ 60 kOe, respectively). The spectrum obtained upon 30-min exposure of the sample to HCl suggests that, by contrast to Sn^{2+} in the above-described case, the overwhelming majority (90%) of the Sn^{4+} ions retained their initial sites. Also, it was found that, before the Sn^{4+} ions passed to the hexachloride surrounding of the $[SnCl_6]^{2-}$ type (as evidenced by the appearance of the singlet with $\delta = 0.50$ mm s^{-1}), they occupied primarily the sites above the first cationic layer. This experiment showed that air exposure decelerated further chemical corrosion in the acid gas, which resulted in passivation of the oxide surface. On the other hand, the ^{119}Sn spectra showed that the Cl^- anions more readily replace the terminal O^{2-} (or OH^-) anions connected to the Sn^{4+} ions above the first cationic layer compared to the bridging O^{2-} anions in the coordination sphere of the cations in this layer.

Reaction between HF and the Sn^{2+}/Cr_2O_3 Sample

The exposure of this sample to an HF/Ar mixture caused spectral changes similar to those observed upon exposure to HCl [14]. As a result of reaction with HF, the Sn^{2+} ions appeared in the composition of the fluoride-containing groups of two types; the groups of one type were similar to those in the α-SnF_2 structure, and the other, to those in the α-Sn_3F_8 structure. In both types of fluorides the Sn^{2+} coordination polyhedron can be represented by a trigonal pyramid with the apexes occupied by the F^- anions and a lone electron pair of tin. Upon exposure to HF, tin escaped its initial sites where it was surrounded by O^{2-} anions. The detachment of tin from the oxide substrate was manifested as the loss of spin polarization of ^{119}Sn at $T << T_N$ because of the absence in the Sn^{2+} surrounding of the Cr^{3+} cations participating in magnetic interaction of Cr_2O_3. Thus, the behavior of the surface Sn^{2+} cations, observed in the case of HCl exposure, was unaffected by a decrease in the ionic radius (F^-). This allowed a presumption that the change of the local surrounding of tin when contacting both hydrogen halides is associated with the dissociative adsorption of their molecules by the substrate, followed by replacement of the Sn^{2+} cations by the protons formed.

Reaction of Sn^{2+}/Cr_2O_3 with O_2 Traces upon Exposure to HF

To record the spectra of this sample, the latter was transferred in a dry box filled with argon to a hermetically sealed cell for measurements in a helium cryostat. The Møssbauer experiments showed that, despite the precautions, Sn^{2+} was partially oxidized [14]. This once again demonstrated a high sensitivity of the tin cations, for which the change of the charge could be achieved in the presence of even trace amounts of oxygen. The unexpected isomer shift of 0 mm s^{-1} suggested that, like in the reference $BaSnO_3$ sample, the resulting Sn^{4+} ions were surrounded by the O^{2-} anions. The lack of magnetic fields on the $^{119}Sn^{4+}$ nuclei even at 5 K unambiguously suggested that these cations were detached from the Cr_2O_3 surface. This allowed a presumption that, even before the reaction with O_2, the $[SnF_3]^-$ groups contained in their surrounding the H_2O molecules (or hydroxy groups). These molecules, or groups, first, allowed an increase in the number of the anions surrounding the Sn^{4+} ions to six ($3F^- + 3O^{2-}$), and, second, they replaced the F^- anions from the resulting coordination sphere. This suggested that the exposure to HF resulted not only in hydroxylation of the oxide surface but also in passing of a portion of surface “lattice” O^{2-} anions to the fluorine-containing envelope covering the crystallites. Thus, the spectra of ^{119}Sn showed that exposure of the Sn^{2+}/Cr_2O_3 sample to an HF atmosphere resulted in corrosion of the crystallite surface.

Reaction between HF and the Sn^{4+}/Cr_2O_3 Sample

Like in the above-described experiments, the Sn^{4+}/Cr_2O_3 sample was obtained upon the Sn^{2+}/Cr_2O_3 sample was brought into contact with oxygen [14]. According to the Møssbauer data, upon exposure to HF, most of the Sn^{4+} ions in this case also remained in layer sites (at 100 K, $\delta = 0.01$ mm s^{-1}, H = 110 kOe). Thus, the preceding contact with the O_2 molecules once again resulted in passivation of the crystallite surface. The nonmagnetic component was characterized by the isomer shift $\delta = -0.15$ mm s^{-1}, which suggests the oxofluoride surrounding for the corresponding Sn^{4+} ions. Its formation is consistent with the fact that the number of the H_2O molecules was insufficient for replacement of all the fluorine anions in the coordination sphere of the Sn^{4+} ions detached from the oxide surface. Thus, in this case, the passivating effect of the O_2 adsorption on the reactivity of the Cr_2O_3 surface affected the isomer shift of the most active Sn^{4+} cations.

REACTION WITH HYDROGEN SULFIDE [15–17]

Early studies of the reaction of H_2S with chromium oxide surface, using ^{119}Sn probe cations, date back to the time preceding the experiments with halogens and hydrogen halides. In situ measurements showed that, upon exposure in H_2S of the samples containing Sn^{2+}, these cations, irrespective of the initial sites, pass into the sulfide surrounding similar to that in the crystalline SnS. In the case of samples containing Sn^{4+} cations, the exposure in H_2S did not affect tin in the composition of the first cationic layer, while the Sn^{4+} cations above this layer passed into the sulfide surrounding. The Møssbauer parameters of the latter (δ = 1.05 mm s^{-1}, Δ ~0 mm s^{-1}) are identical to the published data for crystalline sulfide SnS_2. Introduction of minor amounts of O_2, along with H_2S, into the atmosphere above the Sn^{2+}/Cr_2O_3 sample also gave rise to a singlet with δ = 1.05 mm s^{-1} corresponding to the Sn^{4+} ions in the sulfide surrounding. Since in this case the O_2 molecules acted as oxidizers, this experiment confirmed the preference given by Sn^{4+} to the surrounding comprised of anions of the same kind (i.e., the S^{2-} anions available in a sufficient amount). The spectra of ^{119}Sn showed the lack of the Sn^{4+} ions with the coordination sphere comprised exclusively of oxygen anions, which suggests that the exposure of the Sn^{2+}/Cr_2O_3 sample in H_2S (by contrast to HF) was not accompanied by corrosion of the crystallite surface. Thus, the spectral changes caused by exposure to H_2S can be treated as associated with passing of the Sn^{2+} cations to the adsorption layer on the crystallite surface.

In this connection, we will mention a completely different chemical behavior of the Sn^{2+} ions on the α-Al_2O_3 surface in the presence of H_2S. In that case, the spectra of ^{119}Sn revealed formation of "SnS_2," which suggested oxidation of Sn^{2+} [15]. This could be associated exclusively with formation of elemental sulfur from degradation of the H_2S molecules in the neighborhood of the sites occupied by tin.

Upon annealing in hydrogen of the samples containing the Sn^{4+} ions that passed into the sulfide surrounding, the Sn^{4+} ions detached from the surface once again (now in the bivalent state) occupied their initial magnetic sites on the Cr_2O_3 surface, rather than were reduced to the metal, as expected at 600°C. This clearly demonstrated that the behavior of the dopant cations is governed, above all, by the coordination demands of the surface Cr^{3+} cations. This experiment validated the originally suggested explanation to passing of the tin ions from the Cr_2O_3 bulk to the surface [1].

DYNAMIC CHARACTERISTICS OF THE Sn^{2+} DOPANT CATIONS DETACHED FROM THE Cr_2O_3 SURFACE

Our studies discussed above [14, 17] were concerned with the dynamic characteristics of the surface Sn^{2+} cations in the fluoride and sulfide groups. We found that the Møssbauer lattice temperature Θ_M governing the temperature dependence of the rms amplitudes of thermal fluctuations $<u^2>$ of the Sn^{2+} ions in both cases is much lower than that for these ions before contacting HF or H_2S. This is consistent with the fact that the Θ_M parameters for crystalline tin halides and chalcogenides are lower than those for the oxides. Therefore, for surface Sn^{2+} ions, a decrease in Θ_M, evidently, was mainly indicative of the weakening of the interaction of tin with the ligands, not associated with the surface localization of $[SnF_3]$ or $[SnS_3]$ groups. On the other hand, the Θ_M parameters for surface Sn^{2+} cations in the sulfide or fluoride surrounding differed fairly insignificantly from the corresponding parameters for crystalline SnS [18] or α-SnF_2 and α-Sn_3F_8 [19] phases. This suggested that the $<u^2>$ (as well as δ and Δ) parameters of the Sn^{2+} ions are determined, above all, by their coordination polyhedron. The lack of major changes in Θ_M suggests that the content of the tin surface species can be estimated from their spectral contributions using the f factor (the proportion of zero-recoil transitions) for the corresponding crystalline compounds.

In [16], we revealed the anisotropic nature of the rms amplitudes of thermal fluctuations of tin for the surface $[SnS_3]$ groups [16]. A growing difference between the intensities of the quadruple doublet components with increasing temperature (Goldanskii–Karyagin effect [20]) suggests that $<z^2>$, the rms amplitude of the Sn^{2+} fluctuations parallel to the plane formed by the three neighboring S^{2-} anions exceeded $<z^2>$, the rms amplitude of the Sn^{2+} fluctuations perpendicular to this plane (at 230 K, $<x^2> - <z^2> = 0.6 \times 10^{-18}$ cm^2). The revealed sharp increase in the asymmetry of the quadruple doublet and its decrease in intensity at temperatures above 230 K were attributed to activation of the fluctuations of the surface $[SnS_3]$ groups.

APPLICATION OF ^{119}Sn, ^{121}Sb, AND ^{125}Te PROBE CATIONS IN ELUCIDATING THE MODIFYING ACTION OF THE DOPANTS ON THE CATALYTIC PROPERTIES OF Cr_2O_3

Chromium oxide exhibits a catalytic activity in CO and hydrocarbon oxidation, butane dehydrogenation, ethylene hydrogenation, and ethylene and propylene polymerization, as well as in paraffin dehydrocyclization to aromatic compounds, methanol synthesis, nitrogen monoxide reduction with carbon monoxide or ammonia, etc. (see, e.g., references in [21]). This made Cr_2O_3 doped with the ^{119}Sn, ^{121}Sb and ^{125}Te probe cations suitable as a model system for elucidation of the mechanism by which the dopants affect the catalytic properties. Importantly, in this case the Møssbauer spectra allowed not only in situ determining the valence state of the dopant but also characterizing its distribution over the catalyst surface.

Oxidation of CO with Oxygen in the Presence of Sn^{4+}/Cr_2O_3 (Sb^{5+}/Cr_2O_3, Te^{4+}/Cr_2O_3) Catalyst [22–24]

Catalytic experiments with the samples prepared under identical conditions (the undoped reference sample and a sample, whose crystallite surface contained the Sn^{4+} cations) showed that, in the presence of minor tin amounts (for a sample as a whole, $[Sn]/[Cr] = 0.0033$) the activation energy E_a substantially increased (63 and 93 kJ mol^{-1}, respectively). At the same time, in the sample containing the same amount of Sn^{4+}, though in the crystallite bulk, no significant changes in E_a were observed. This suggested a change of the nature of the active catalytic centers in the sample containing surface Sn^{4+} cations. An earlier chromatographic study showed that the number of active oxygen atoms O_S on the Cr_2O_3 surface (without dopants), $(4.3–6.3) \times 10^{18}$ O_S m^{-2}, only slightly depends on the method of synthesis of the samples. This suggests that, in the reference, the O_S concentration should be of the same order of magnitude. A Møssbauer spectroscopic examination of the local surrounding of tin on the Cr_2O_3 surface, in turn, yielded the number of oxygen vacancies V_O in the surrounding of every Sn^{2+} cation ($3V_O$) and, hence, in every oxidized Sn^{4+}cation ($2V_O$). Based on the known specific surface area of the sample and the amount of tin introduced, the total number of the vacancies bound to Sn^{4+} and occurring in the neighborhood of the coordination-unsaturated Cr^{3+} cation was estimated at 3.8×10^{18} V_O m^{-2}. This is close to that expected for the reference on the basis of the chromatographic data. This suggested that the difference between the tin-doped and tin-undoped samples consisted in that, in the former, the crystallite surface near V_O contained simultaneously Cr^{3+} and Sn^{4+} cations, while that in the latter, Cr^{3+} cations only. Hence, the revealed increase in E_a of the CO oxidation reaction is associated with a stronger retention of the oxygen adsorbed in the neighborhood of the highly-charged Sn^{4+} cation. This conclusion was validated by analysis of the Cr_2O_3 sample with even more highly-charged Sb^{5+} cations on the crystallite surface: They caused an additional increase in E_a by ~30 kJ mol^{-1}. By contrast, E_a for the tellurium-doped samples proved to be close to that of the reference. This allowed the following interpretation of the ^{125}Te spectra: The doped tellurium stabilized on the surface as Te^{4+} cations preserved its oxidation state both under contact with air and under CO oxidation conditions. This suggests that a lone electron pair which favors the location of this cation in low-coordination sites was still located in the valence shell of tellurium. This precluded oxygen adsorption in the neighborhood of Te^{4+}, so that (unexpectedly at a first sight) the activation energy was unaffected by this dopant.

A Møssbauer Spectroscopic Examination of the Action Mechanism for Tin, Antimony, and Tellurium Dopants on the Isopropanol Transformations [25–27]

Published data suggest that, in the presence of Cr_2O_3, isopropanol transformation takes two parallel routes: dehydration and dehydogenation. This reaction was of interest for elucidating the factors affecting the selectivity of the catalytic process. Also, by contrast to CO oxidation with oxygen, isopropanol is dehydrated (dehydrogenated) in a reducing medium, which could affect the valence state of the dopants utilized and the properties of the catalyst.

Influence of dopants localized on the crystallite surface. Like in the above-described experiments, the tin, antimony, or tellurium cations were localized on the surface via annealing of the hydroxide precursor in hydrogen. The Møssbauer data suggest that the annealed tin, antimony, and tellurium samples differently behaved in air. The Sn^{2+} ions were rapidly oxidized to Sn^{4+} already at room temperature; the conversion of the surface Sb^{3+} ions to Sb^{5+} required a slight heating (T~100°C), and the valence state of the Te^{4+} ions remained unchanged even upon calcination in air at ~500°C. Thus, before the onset of the catalytic process, the dopants occurred in the catalyst as Sn^{4+}, Sb^{5+}, and Te^{4+}.

The data for the catalyst containing 0.3 at % Sn suggest that tin on the crystallite surface did not affect the selectivity of the process. The influence exerted by the dopants on other catalytic characteristics was elucidated for the dehydration reaction. Examination of the temperature dependence of the dehydration rate constants showed that, in the case of the reference and the tellurium-doped catalyst, the changes associated with an increase and a decrease in temperature were reversible. In the case of the catalysts with tin or antimony, by contrast, a hysteresis was observed starting from ~340°C. In situ Møssbauer measurements under the conditions simulating those of a catalytic reaction showed that, specifically at this temperature, Sn^{2+} and Sb^{3+} were formed. Thus, in the course of the catalytic process, all the three elements occurred in an isoelectronic state as Sn^{2+}, Sb^{3+}, and Te^{4+} cations, and, correspondingly, had a lone electron pair. Strong quadruple interaction manifested in the spectra of ^{119}Sn, ^{121}Sb, and ^{125}Te suggested that the lone electron pair is "stereochemically active", i.e., occupies the site of one of the ligands in the coordination sphere. Thus, the hydroxy group which is typically included into the active catalytic site in the examined process cannot enter into the coordination sphere of either of the Sn^{2+}, Sb^{3+}, or Te^{4+} cations. This explains why the dopants discussed do not affect the selectivity and activation energy (like in the case of the reference, $E_a = 110–115$ kJ mol^{-1}).

Influence of the bulk-localized dopants. Analysis of the temperature dependence of the catalytic activity of the samples whose crystallites contained highly charged Sn^{4+}, Sb^{5+}, or Te^{6+} cations in the bulk showed that these dopants do not markedly affect E_a. The very fact that their presence did not affect the nature of the active sites is itself consistent with the conclusion that these cations occurred in the bulk, as suggested by the Møssbauer data. An unexpected result was that the presence of Sn^{4+} and, in an even greater extent, of Sb^{5+}, was responsible for enhancement of the catalytic activity. At the same time, a much weaker effect was observed for the samples doped with Te^{6+} cations, although they bear the highest charge. The spectra of the probe cations suggested the following explanation. We showed earlier [28–30] that the excess positive charge on Sn^{4+}, Sb^{5+}, and Te^{6+} in the Cr_2O_3 lattice is balanced via formation of the appropriate number of chromium vacancies V_{Cr}, specifically, $1V_{Cr}$ per $3Sn^{4+}$, $2V_{Cr}$ per $3Sb^{5+}$, and $3V_{Cr}$ per $3Te^{6+}$.

Binding two defects as the dopant–V_{Cr} pair is equivalent to rupture of one of the magnetic bonds responsible for the magnetic field H on the diamagnetic cation nucleus. Therefore, the arising of such associates results in the appearance of a spectral component at a weaker field. It was found that, in the catalysts examined, approximately one third of the total number of Sn^{4+} and Sb^{5+} cations occupied the sites with complete cationic surrounding (i.e., they had no V_{Cr} vacancy in their surrounding), while virtually all the tellurium cations occurred as Te^{6+}–V_{Cr} pairs. Considering these data, the influence exerted by the dopants on the catalytic activity was attributed to the fact that Sn^{4+} and Sb^{5+} cations with locally unbalanced charge act as traps for V_{Cr} vacancies, that are intrinsic defects of chromium oxide, whose concentration is especially high on the crystallite surface. Therefore, such cations in the near-surface layer are capable of "pulling" into it the surface chromium vacancy. Its position will be occupied by the Cr^{3+} cation with a coordination-unsaturated surrounding (which existed when the site considered was vacant), which will be responsible for the appearance of an increased adsorption potential on the cation that escaped to the surface. Therefore, such Cr^{3+} can be a base for new active sites (bridging hydroxy groups) due to increase in the probability of the dissociative adsorption of the water molecule. The Møssbauer spectra showed that the content of the Sn^{4+} cations with unbalanced charge in the catalysts examined was approximately identical to that of Sb^{5+} cations. The Sb^{5+} cations bearing a higher charge should exert a stronger influence than the Sn^{4+} cations, as really observed in the catalytic experiments. This mechanism of the modifying action also explains why the Te^{6+} cations exert a considerably weaker influence (in the catalyst utilized, virtually all of them were already bound to the V_{Cr} vacancies in the crystallite bulk).

The above-discussed examples suggest that Møssbauer spectroscopy with diamagnetic cations is fairly attractive for examination of chromium oxide-based catalysts.

SEARCH FOR NEW OXIDES SUITABLE FOR SURFACE STABILIZATION OF 5*s*5*p* ELEMENT CATIONS

The compounds tested till 2005 as candidate substrates for surface localization of tin cations, Cr_2O_3, α-Al_2O_3, $Cr_{2-x}Al_xO_3$, and V_2O_3 [2, 3], all belonged to the same crystallographic group ($R\bar{3}c$). However, not all representatives of this group proved to be suitable for this purpose. Among the oxides that did not stabilize the Sn^{2+} cations on the crystallite surface is α-Fe_2O_3, the first simple antiferromagnetic oxide for which well-resolved hyperfine splitting spectra of $^{119}Sn^{4+}$ at the substitution sites in the bulk were obtained [31, 32]. This interesting compound decomposed in the course of annealing in a reducing atmosphere, required for surface stabilization of Sn^{2+}. However, α-Fe_2O_3 samples with a high content of the Sn^{4+} cations in the near-surface layers of the crystallites were prepared more recently by mechanochemical methods [33, 34]. In that case, the ^{119}Sn spectra were a superposition of a large number of components reflecting the nonequilibrium distribution of tin. Identification of individual sites of Sn^{4+} in such samples was a difficult task. Distribution of the Sn^{4+} ions over the sites for which the spin polarization was weaker than that observed for individual $^{119}Sn^{4+}$ sites in the α-Fe_2O_3 bulk was also determined in a study of the $(Fe_2O_3)_{0.8}(SnO_2)_{0.2}$ nanocomposite [35]. That was the case of tin oxide segregation as islands on the surface of the smallest α-Fe_2O_3 particles. Annealing of such samples resulted in tin segregation as a SnO_2 microphase, which suggested nonequilibrium distribution of the components in the case of the $(Fe_2O_3)_{0.8}\cdot(SnO_2)_{0.2}$ nanocomposite as well.

Thus, ^{119}Sn (and, especially, inconvenient ^{121}Sb and ^{125}Te Møssbauer isotopes) can be for different reasons unsuitable for diagnostics of the processes occurring at the interface. At the same time, our studies showed that stabilization of the surface sites of 5*s*5*p* elements is not an exclusive privilege of oxides with the corundum structure.

Distribution of ^{119}Sn Dopant Ions over Titanates with the Ilmenite $MnTiO_3$ Structure [36, 37]

Crystallographically, ilmenite ($FeTiO_3$) and corundum (α-Al_2O_3) have related structures. However, by contrast to simple oxides, ilmenite-type titanates $MTiO_3$ (M = Mn, Fe, Co, Ni, or Mg) exhibit regular alternation of the (111) planes formed by the M^{2+} and Ti^{4+} cations. As a result, external (111) faces of the crystallites will also contain cations or either kind. Therefore, in this case, localization of Sn^{2+} is a priori possible on the faces with different chemical compositions. By now, among the titanates with the ilmenite structure, only $MnTiO_3$ was tested as a substrate for tin. The choice of this compound was dictated by the fact that, by contrast to other 3d cations, Mn^{2+} exhibits chemical stability toward annealing in H_2. On the other hand, this titanate favorably compares with $MgTiO_3$, also resistant to annealing in H_2, in that it contains magnetic cations. The ability of the Mn^{2+} cations to induce spin polarization of ^{119}Sn, by contrast to diamagnetic Ti^{4+} cations, should simplify identification of the sites occupied by tin. Analysis of the sample with 0.5 at % Sn^{4+} in the crystallite bulk showed, that the overwhelming majority of the probe cations occurred in the manganese layer in the neighborhood of the charge-balancing vacancy V_{Mn} (at 5 K H = 52.5 kOe [36]). However, annealing of this sample in H_2 at 800° C resulted in tin segregation from the titanate lattice as β-Sn clusters, rather than in formation of Sn^{2+} [37]. This suggests that, under the actual conditions, the Sn^{2+} ions are unstable on the $MnTiO_3$ faces, in particular, those formed by the Mn^{2+} cations. The formation of β-Sn, which suggests a weak stabilizing action of Mn^{2+} and unsuitability of the manganese faces for accommodation of the Sn^{2+} ions, was also revealed in annealing in H_2 of the MnO sample with Sn^{4+} dopants in the crystallite bulk [38].

Distribution of the Dopant ^{119}Sn Ions over the MgO Cubic Oxide [39]

Along with MnO, the only oxide among the listed bivalent cations forming titanates with the ilmenite structure, capable to resist annealing in H_2 is MgO. For this reason, it was also examined, despite its diamagnetic properties. In situ Møssbauer experiments showed that, upon annealing in H_2, the Sn^{4+} ions passed from a site in the crystallite bulk to the Sn^{2+} state (δ = 2.56 mm s^{-1}, Δ = 2.44 mm s^{-1}). Localization of the Sn^{2+} cations on the surface once again was manifested in their ability for rapid oxidation when contacting air (appearance of a singlet with $\delta = 0.08$ mm s^{-1}) and in an abnormally high content of tin in the near-surface layers, as revealed by an XPS examination. These experiments demonstrated that tin can be stabilized on the surface of the oxide from a new important group of compounds with the NaCl structure.

CONCLUSION

Thus, Møssbauer spectroscopy of 5*s*5*p* dopant elements in Cr_2O_3 is a unique tool for diagnostics of the condition and processes occurring on the crystallite boundary surface. The spectra of the probe cations provided explanation to the influence exerted by dopants on the catalytic properties of Cr_2O_3. Such information is useful both for development of new and improvement of the characteristics of the existing catalysts. Stabilization of the tin cations at the surface sites is not an exclusive privilege of oxides with the corundum structure. In this connection, a search for new materials suitable for Møssbauer spectroscopic diagnostics of the solid–gas interface is expedient. It can be expected that Sn^{2+} can be stabilized not only on the surface of cubic MgO, but also in titanate $MgTiO_3$ on the faces formed by Mg^{2+} cations. The applications of the method are not limited by heterogeneous catalysis. It could be expected that, owing to the improved characteristics, some surface-modified oxides would find application as sensitive elements of semiconductor sensors. Rapid development of nanomaterial studies will pose new questions concerning the mechanism by which the surface affects the properties of substances, which can be answered with the use of Møssbauer probe cations.

ACKNOWLEDGMENTS

This study was financially supported by the Russian Foundation for Basic Research (project nos. 94-03-099, 97-03-33179 and 06-03-32007) and the General Council, Loire-Alantique Department, France (in 1993–1995).

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