Mössbauer investigation of the reaction between HCl and tin dopant ions located on the surface of Cr$_2$O$_3$ microcrystals

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The chemical behavior of surface-located tin dopant ions depends strongly on their valence state. At room temperature all Sn(II) ions readily react with gaseous hydrogen chloride while, under similar conditions, the predominant part of Sn(IV) ions is not affected by this gas. The results of this study, along with those previously obtained for both valence states of tin dopant exposed to a H$_2$S atmosphere, suggest that lower reactivity of Sn(IV) ions is essentially due to their higher coordination number and concomitant steric hindrance effects.

Introduction

Treatment under hydrogen atmosphere allows tin dopant ions to be located in the divalent state just on the surface of the chromium sesquioxide matrix crystallites. Further exposition of such a material to ambient atmosphere results in rapid oxidation of Sn(II) to Sn(IV), the latter having been shown to remain in surface sites. This system thus permits to apply usual $^{119}$Sn Mössbauer transmission spectroscopy to the study of the impact of exposure to different gases on the local surrounding of the surface-located dopant in both valence states. Such investigations have been recently performed, at room temperature, for hydrogen sulfide and halogens. In this paper we report first results concerning both Sn(II) and Sn(IV) surface-located ions exposed to HCl at 295 K.

Experimental

The starting material Sn(II)/Cr$_2$O$_3$, containing the dopant (enriched to 92% in $^{119}$Sn; overall atomic ratio Sn/Cr=0.003) on surface sites of the substrate grains, was obtained according to References 1–4 under H$_2$ flow in a quartz reactor. The reactor was equipped with a thin wall sample cell for in situ Mössbauer measurements prior to and after admitting HCl. This under Ar flow by reaction between NaCl and a concentrated solution of H$_2$SO$_4$, condensed and then twice purified by low-temperature distillation. $^{119}$Sn spectra were recorded using a conventional Mössbauer spectrometer operating in constant acceleration mode with a Ca $^{119}$SnO$_3$ source. Isomer shift values refer to a CaSnO$_3$ absorber at 295 K.

Impact of HCl on Sn(II) surface ions

The spectrum of Sn(II)/Cr$_2$O$_3$ recorded at 80 K (Fig. 1a) is in good agreement with those published earlier. According to Reference 2 it corresponds to the superposition of two distinct patterns, both arising from $^{119}$Sn combined quadrupole and magnetic interactions. The main difference between the two Sn(II)-sites concerns their cationic surrounding which determines the magnitude of the local magnetic field acting on the $^{119}$Sn probe. Predominant part (ca. 70%) of Sn(II) ions are surrounded by three Cr$^{3+}$ whilst the others have only one Cr$^{3+}$ neighbor. The formers are located in the topmost cationic layer, the latter just above this layer. As to the anionic environment, it is similar for both sites and involves three oxygen atoms of the matrix surface, the lone electron pair of Sn(II) being perpendicular to this oxygen triangle.

The spectrum recorded after admitting HCl (Fig. 1b) drastically differs. It shows the presence of two symmetric doublets with the following parameters:

- **Doublet 1**
  - $\delta_1 = 3.53 \pm 0.03$ mm/s, $\Delta_1 = 1.15 \pm 0.03$ mm/s,
  - $\Gamma_1 = 0.99 \pm 0.03$ mm/s, $A_1 = 47 \pm 2\%$

- **Doublet 2**
  - $\delta_2 = 3.85 \pm 0.03$ mm/s, $\Delta_2 = 0.98 \pm 0.03$ mm/s,
  - $\Gamma_2 = 0.99 \pm 0.03$ mm/s, $A_2 = 53 \pm 2\%$

where $\delta$ is the isomer shift, $\Delta$ is the quadrupole splitting, $\Gamma$ is the full width at half maximum, $A$ is the spectra contribution.

Two main effects associated with exposure to HCl are thus revealed by this spectrum: (1) The appearance of two new Sn(II)-sites, either containing Cl$^{-}$ anions in...
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Fig. 1. Mössbauer spectra of Sn(II)/Cr_2O_3 recorded before (a) and after (b) 30-minute exposure of the sample to HCl at 295 K; T_{\text{meas}} = 100 K (antiferromagnetic region)

the nearest surrounding. This is evidenced by the increased $\delta$ values, as compared to those concerning initial (oxygen surrounded) Sn(II)-sites ($\delta_1 = 2.81$ mm/s and $\delta_2 = 2.91$ mm/s), which now fall into the isomer shift region of stannous chloride compounds. The complete disappearance of spin polarization of the tin electron shell by neighboring Cr$^{3+}$ cations even at a temperature markedly lower than the Néel point of Cr$_2$O$_3$($T_N = 308$ K). This is evidenced by the absence of any magnetic perturbation in both doublets at 80 K (Fig. 1b).

Similar alteration of anionic surrounding and disappearance of spin polarization of Sn(II) were already observed in analogous experiments with H$_2$S and these both effects were shown to reflect the migration of Sn(II) into hydrogen sulfide adsorption layer. Thus, the same process may be a priori expected to occur in the presence of HCl as well. However, contrary to the experiments involving H$_2$S, where the unique new Sn(II)-site exhibits Mössbauer parameters close to those of SnS, two non-equivalent Sn(II)-sites appear upon exposure to HCl, both with parameters significantly different from those of the relevant stannous compound SnCl$_2$ ($\delta = 4.06$, mm/s, $\Delta = 0.66$ mm/s). Analysis of the available literature data does not allow any straightforward assignment of the doublets to be made. It is to be noted, however, that the Mössbauer parameters of doublet 2 are in reasonable agreement in those ($\delta = 3.80$, mm/s, $\Delta = 1.00$ mm/s) reported for NH$_4$Sn$_2$Cl$_5$. This compound is supposed to contain binuclear pentachlorodistannate(II) ions, in which both Sn(II) have three anionic neighbors due to the presence of a bridging chloride ion. Comparison with compounds containing discrete [SnCl$_4$]$^-$ ions (e.g., K$_2$SnCl$_7$ $\delta = 3.74$ mm/s, $\Delta = 0.77$ mm/s) allows greater difference to be evidenced. On the basis of these data the Sn arrangement in the surface species giving rise to doublet 2 seems therefore to be intermediate between that in SnCl$_2$ (unlimited chains of SnCl$_4$ groups with bridging chloride ions) and that in isolated [SnCl$_3$]$^-$ ions. As to doublet 1, its parameters – not very different from those of SnCl$_2$-H$_2$O ($\delta = 3.65$ mm/s, $\Delta = 1.25$ mm/s) may point to the location of the concerned Sn(II) ions in sites with [H$_2$O]SnCl$_3$-like mixed oxychloride surrounding. Further studies are obviously needed to clarify the precise nature of both Cl$^-$-containing surface species of tin revealed by these Mössbauer measurements.

Impact of HCl on Sn(IV) surface ions

The starting Sn(IV)/Cr$_2$O$_3$ sample was obtained by exposing the Sn(II)-containing material to ambient atmosphere. Its low-temperature spectrum (Fig. 2a) attests, as noted above, the essentially unchanged location of oxidized Sn(IV) ions over magnetically active sites in the topmost cationic layer ($H = 110$ Kq/oe) and just above this layer ($H < 60$ kOe). The sample was then exposed to flowing HCl and Mössbauer measurements were performed again. It is easily seen that the spectrum obtained (Fig. 2c) still contains the same magnetically split components. This indicates that Sn(IV) ions in the overhelming majority ($A = 90\%$), were not removed from their initial sites, in striking contrast with what was observed under similar conditions for the Sn(II) dopant. Another interesting feature concerns the minority of Sn(IV) ions which appear, after exposing to HCl, in hexachloride surrounding as indicated by the singlet with $\delta = 0.50$ mm/s and $\Gamma = 1.11$ mm/s (Fig. 2c) (e.g., for K$_2$SnCl$_6$ $\delta = 0.5$ mm/s, $\Delta = 0$ mm/s). Since exposure to HCl does not significantly change the relative contribution of surface Sn(IV) ions ($H = 110$ Kq/oe) and mainly decreases that of «oversurface» ones ($H < 60$ kOe) (Figs. 2b and d), it can be inferred that hexachloride Sn(IV) species essentially result from reaction of HCl with Sn(IV) ions located above the topmost cationic layer. It is significant that the same behavior, i.e., selective chemical reaction between the gas under investigation and «oversurface» Sn(IV) ions, was already observed in similar experiments involving H$_2$S.

Discussion

Comparison of the results here reported for Sn(II) and Sn(IV) ions exposed to HCl with those of previous similar studies concerning H$_2$S shows that the chemical nature of the gaseous medium is not the decisive factor affecting the extent of involvement of the dopant in surface reactions on the Cr$_2$O$_3$ substrate. In fact, higher