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The effect of dopant's valence (+III and +V) on the anion/cation uptake properties of antimony-doped tin dioxide

Short Communication

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Abstract: Antimony is perhaps the most frequently used doping element of tin dioxide. Although antimony of different oxidation states have been used in the synthesis, the effect of dopant 's valence on ion exchange properties has not been investigated critically. In our study the valence of antimony had clear effects on the metal uptake properties of Sb-doped SnO_2 materials. Extremely high Tc uptake (Kd > 100 000 mL g^{-1}) on Sb(III)-doped material was observed in conditions under which Sb(V)-doped material did not show any Tc uptake. However, the Sb(V)-doped material showed good Ni^{2+} uptake properties (Kd up to 33 000 mL g^{-1}), even at pH values below the material's point of zero charge (pzc), while the Sb(III)-doped material showed Ni^{2+} uptake only at pH above its pzc. The cation uptake of Sb-doped SnO_2 resembles typical weakly acidic cation exchanger character but the uptake of TcO_4- does not follow a typical anion exchange pattern. Instead, we propose a sorption process related to redox reactions as the probable Tc uptake process.

Keywords: *Antimony-doped • Tin dioxide • Metal uptake • Technetium • Nickel*

1. Introduction

Antimony-doped tin dioxides possess interesting physical and chemical properties. These properties have a wide range of applications such as catalysis and optoelectronic devices. This is why such materials are intensively studied using a diverse range of analysis methods. Although there has been great interest in the effect of oxidation states of antimony on tin dioxide, the nature of the antimony sites in highly doped nanocrystalline tin dioxide is still not well understood [1]. However, it is widely accepted that antimony can and usually exist in both +III and +V oxidation states in the Sb-doped tin dioxide structures [1-3]. The +V oxidation state is in particularly tight association with sites inside the tin dioxide particle. This association is due to its slightly smaller ionic radii (60 pm) of antimony +V, which enables it to replace the tin ion (69 pm) more easily than does the lager antimony +III (76 pm) ion. On the other hand, the +III Sb ion tends to replace tin ions at the surface sites or at grain boundaries [2-5]. Antimony +V imparts n-type conductivity to nanocrystalline tin dioxide. In contrast, doping tin dioxide with antimony of oxidation state +III decreases its conductivity to that of an insulator [6]. A rough classification of the valence state can be made visually. Tin dioxide doped with antimony of oxidation state +V has a bluish color, whereas tin dioxide doped with antimony in an intervalence state (both +III and +V) is brownish in color [7-9]. Valence of antimony can also be dependent on thermal treatment. Annealing a material at 500°C has typically been used to oxidize Sb(+III) into Sb(+V): a change which has been verified by color change as well as careful spectroscopic measurements [1,2,4].

The basic ion exchange properties of hydrous tin dioxide have been well characterized in earlier works [10-15]. Antimony doping of hydrous tin dioxides usually enhances the material's cation exchange properties, particularly when the exchange occurs in acidic media. A clear effect on the distribution coefficients can be observed when progressive amounts of antimony are incorporated into the structure of hydrous tin dioxide [16,17]. Those studies focused on metal uptake properties of antimony-doped tin dioxide and how it is affected by the change in the oxidation state of antimony.

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2. Experimental Procedure

2.1 Reagents

All reagents were of analytical grade (Fluka, Merck, Aldrich, J.T. Baker) and used without further purification. Syntheses and ion exchange studies were performed in aerobic conditions at room temperature. Radioactive tracers, ^{63}Ni and ^{99}Tc, for ion exchange studies were obtained from Amersham International. The tracer concentrations were 1.2×10^{-11} and 1.6×10^{-8} M for ^{63}Ni and ^{99}Tc, respectively.

2.2 Synthesis

Detailed synthesis procedure is described elsewhere [17]. In short it is as follows: A 350.02 g (2 M) quantity of tin chloride ($SnCl_4\bullet5H_2O$) was dissolved into 500 mL of 6 M HCl. Either 3.0 g (26 mM) of $SbCl_3$ (Sb(III)material) or 1.3 mL (21 mM) of $SbCl_5$ (Sb(V)material) was added to the solution and mixed for 30 min using a magnetic stirrer. Pure and antimony-doped tin dioxides were precipitated by raising the pH of the synthesis solution to 2 by adding 25% aqueous NH_3 solution dropwise to the respective solution. The precipitate was washed with de-ionized water and oven dried at 70°C. Subsamples of the synthesized materials were heat treated at 450°C in normal atmosphere for 24 hours.

2.3 Characterization

Oven dried products were characterized by X-ray diffraction method. Powder X-ray diffraction (XRD) patterns were collected by a Phillips PW 1710 powder diffractometer (operating at 40 kV and 50 mA) with Cu K_α (1.54 Å) radiation. Elemental analyses of the metals were carried out using the X-ray fluorescence (XRF) method (with an Amptek 7 mm^2 Si(Li) XR-100CR detector and a 500mCi ^{241}Am excitation source). Point of zero charge (pzc) measurements were carried out using a Malvern Instruments NanoZs Zetasizer equipped with autotitration unit in 0.001 M NaCl media.

2.4 Ion exchange studies

The ion exchange properties of the product materials were studied by measuring their distribution coefficients (K_d) in batch experiments. In those experiments approximately 20 mg of finely ground and sieved (below 74 µm) synthesized material was placed in a polyethylene vial along with 10 mL of test solution. Samples were equilibrated in a constant rotary mixer (50 rpm) at room temperature for 24 hours, during which the solid/solution system reached equilibrium. The solid phase was then separated by centrifuging the vials at 3000 G for 10 minutes. Then 2 mL aliquots of the supernatant were pipetted and filtered through a 0.2 µm filter (I.C. Acrodisc, Gellman Sciences) for concentration measurements (β counting). The equilibrium pH in the remaining solution was measured. The distribution coefficient determines the extent to which the studied element was distributed from the initial solution into the solid material, and it was calculated as follows:

$$K_d = \frac{A_i - A_{eq}}{A_{eq}} x \frac{V}{m},$$

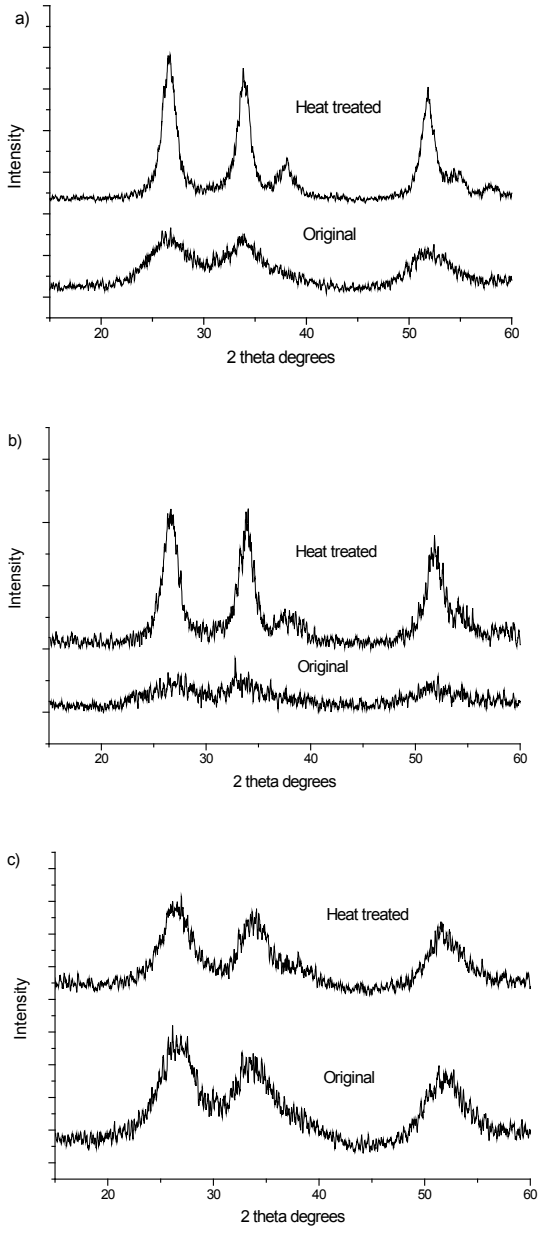

Figure 1. XRD diffractograms of a) tin dioxide and its analogous with b) Sb(III) and c) Sb(V) antimony doping. A material's XRD diffractogram after heat treatment has also been added to the figures.

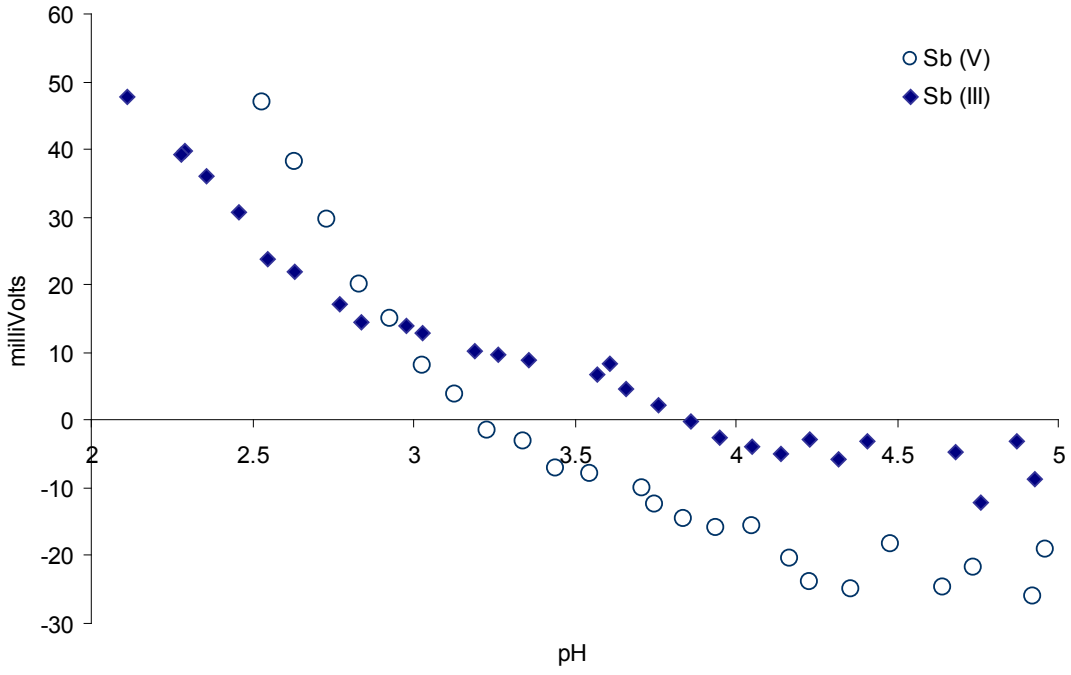

Figure 2. Point of zero charge (pzc) curves of (○) Sb(V) doped and (♦)Sb(III) doped tin dioxide in 0.001 M NaCl solution. The pzc of pure tin dioxide was at pH 5.3

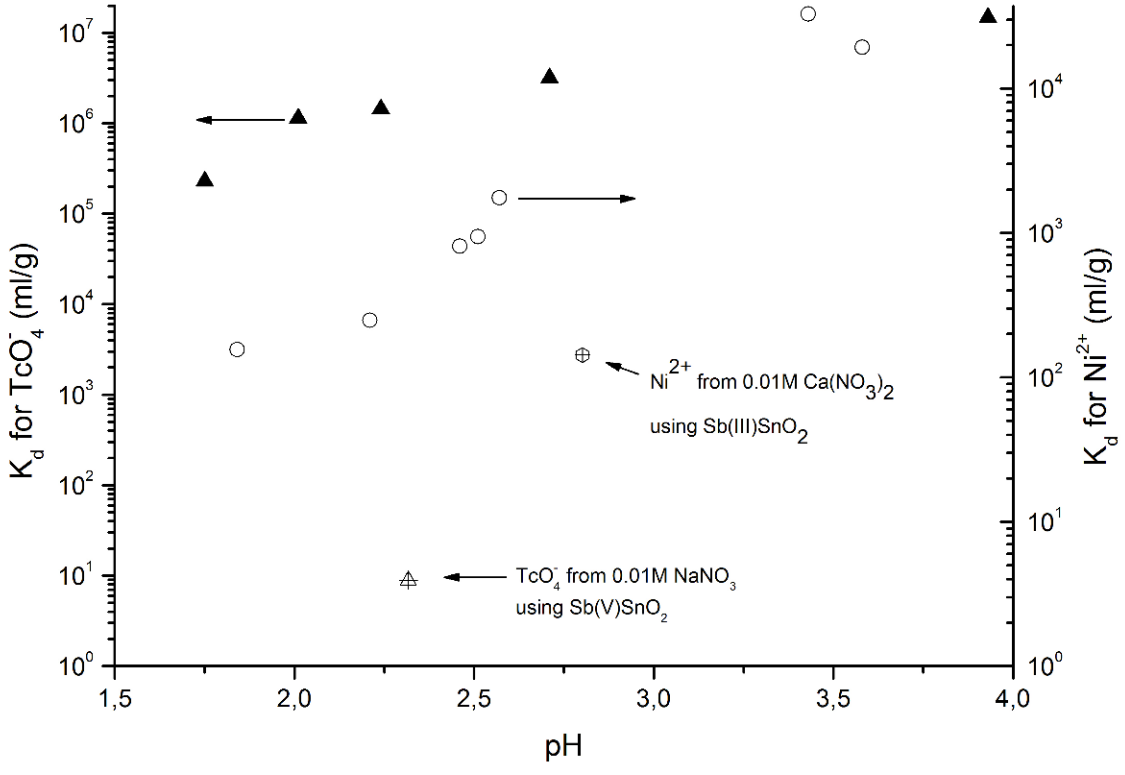

Figure 3. Distribution coefficients (K_d, mg L^{-1}) as a function of pH: (○) K_d for Ni^{2+} from 0.01 M $Ca(NO_3)_2$ solution using $Sb(V)SnO_2$ and (▲) K_d for TcO_4^- from 0.01 M $NaNO_3$ solution using $Sb(III)SnO_2$ material. Comparable Kd-values for Ni^{2+} and TcO_4^- uptake using pure hydrous SnO_2 were 42 at pH 2.8 and 1 at pH 2.9, respectively.

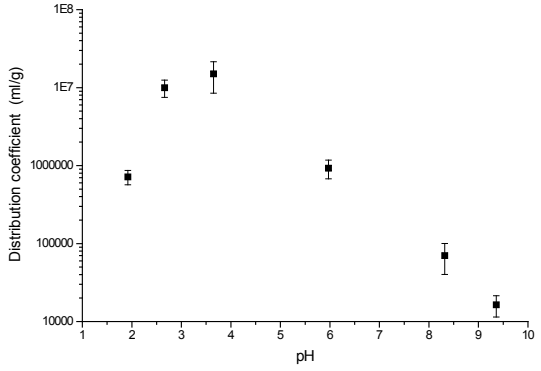

Figure 4. Distribution coefficients (K_d, mg L^{-1}) as a function of pH for TcO_4^- from 0.1 M $NaNO_3$ solution using Sb(III) SnO_2 material.

where A_i = initial metal concentration of the solution, A_{eq} = metal concentration of the solution at equilibrium, V = volume of the solution, m = mass of the solid material. When using radioactive tracers, the activity of the tracer can be used instead of the element concentrations. Consequently, ^{63}Ni and ^{99}Tc were used as radioactive tracers. Since they are pure beta-emitting nuclides with β^--energies of 65.9 and 293.7 keV, respectively, a liquid scintillation counter (Wallac 1217 BackBeta) was used during the measurements.

The obtained K_d-values were used to determine the material's selectivity for nickel and technetium that were informed of positively charged Ni^{2+} and negatively charged TcO_4^- ions in all the test solutions [18]. The selectivity determines how efficiently a certain element is removed from other elements. In practical applications such as radioactive waste treatment, those 'other elements' are usually present in high concentrations and that is why the K_d-values have to be high for meaningful separation applications.

Test solutions (0.01 M $Ca(NO_3)_2$ and 0.01 M $NaNO_3$) were chosen in order to have equal conditions for the competition of the materials ion exchange sites between the target element (Ni^{2+} and TcO_4^-, respectively) and solution matrix.

3. Results and Discussions

3.1 Material characterization

All the synthesized materials with or without antimony doping were typical nanocrystalline hydrous tin dioxides (Fig. 1). The degree of Sb-doping was 3% and 7% (metal percentage) for Sb(III)- and Sb(V)materials, respectively. Due to the same synthesis procedure, alike changes in color and XRD diffractograms were observed as a result of heat treatment. It was assumed that the synthesized material was very close to the one that was synthesized by Rockenberger *et al.*, which has been very thoroughly examined by XRD, EXAFS and XANES [1,8,9]. Based on their findings and general understanding, the Sb in the Sb(V)SnO_2 material was presumed to be of +V valence (> 90%) but for the Sb(III)SnO_2 material the ratio between +III/+V valences was taken to be ½ [4,19,20].

The point of zero charge (pzc) measurements of the material surface showed that the Sb-doping had acidified the materials from pH 5.3 of pure SnO_2 to significantly low values. In addition, small differences in the point of zero charges between the two Sb-doped materials were seen and pzc at pH values of 3.2 and 3.9 were measured for the Sb(V) and Sb(III) materials, respectively (Fig. 2). Reason for this 0.7 difference most likely originates from the relative easiness of smaller Sb^{5+} ion (60 pm) to replace Sn^{4+} ion (69 pm) in the SnO_2 lattice compared to larger Sb^{3+} ion (76 pm). This in turn will increase the electronegativity of the material. Thus, a decrease in the pzc value was observed. The measured pzc is very close to the one measured by Goebbert *et al.* (pH 3.7) which also confirmed that our material synthesis was successful [21].

3.2 Ion exchange properties

Although the structural differences between the different tin dioxides were small, the differences in the materials ion exchange properties were remarkable. The incorporation of antimony into the lattice of tin dioxide acidified the material as seen by the respective pzc curves (Fig. 2). Generally, only a very limited number of ions are exchanged close to the materials pzc. The Sb(V)SnO_2 material's cation (Ni^{2+}) uptake from acidic solution at pH well below its pzc was already significant and the uptake showed very high K_d-values at pH above the materials pzc value (Fig. 3). The uptake trend resembled a typical cation uptake of weakly acidic metal oxides. For comparison, only poor Ni^{2+} uptake (K_d 42 mL g^{-1} at pH 2.8) on pure hydrous SnO_2 was observed. The weakly acidic cation exchanger (WAC) behavior of Sb(V)SnO_2 material was further demonstrated by zero uptake of TcO_4^- at pH 5.1 but it is noteworthy that zero uptake was measured also at pH 2.7 which is below the materials pzc value. Similar zero Tc uptake was also observed using pure hydrous SnO_2. This lack of uptake can be explained by low selectivity of the material towards TcO_4^- from 0.01 M NO_3^- solution matrix. The Sb(III)SnO_2 material showed also cation exchange properties but the uptake of nickel was modest (K_d 35 and 6150 at pH 2.7 and 4.6, respectively) compared to Sb(V)SnO_2 material. However, the Sb(III) SnO_2 material showed excellent TcO_4^- uptake properties

(Figs. 3 and 4). Almost quantitative uptake of Tc was observed over a broad pH range (Fig. 4). The shape of TcO_4^- uptake as a function of pH was, however, somewhat disturbing since it has characteristics of both weak cation and weak anion exchange processes. The pzc of both materials was around pH 3.5. At low pH values the surface charges of both $SbSnO_2$ materials were positive, and the uptake of anions (TcO_4^-) should have increased with the acidic conditions due to the increase of charge of the material surface. However, our study showed that the TcO_4^- uptake of Sb(III)SnO_2 material followed a typical trend of cation uptake at low pH values (slow increase with increasing pH) and not the expected trend of anion uptake. At high pH values the trend was the opposite. Thus the Sb(III)SnO_2 material showed declining TcO_4^- uptake at higher pH values, typical for weakly basic anion exchanger.

One plausible explanation for this odd uptake behavior of Sb(III)material could be redox assisted precipitation of TcO_2 and its sorption on the material surface. It is widely accepted that doping SnO_2 with Sb^{3+} ions results in oxygen vacancies and reduction of Sn^{4+} to Sn^{2+} at the material surface [5,20,22,23]. These defect sites are considered as particularly strong Lewis acids where a reduction of Tc(VII) to Tc(IV), for example, is possible [20,24]. The sparingly soluble TcO_2 is well known for its strong sorption affinity on material surfaces [25] that enables a plausible way for technetium to be excluded from the solution phase.

4. Conclusions

Based on findings of this study it is concluded that Sb-doped tin dioxides possess ion exchange properties of weakly acidic cation exchanger. In addition, depending on the valence of the Sb in the synthesis the material may possess very good technetium uptake properties. However, the results indicate that the TcO_4^- uptake is probably not pure anion uptake process and it is emphasized that +III valent antimony has a significant role in the observed Tc-uptake. Whether this uptake is due to the precipitation TcO_2 on the SnO_2 surface after redox reactions is not known, and cooperation with laboratories that possesses more powerful analysis methods such as EXAFS, XPS and Mössbauer spectroscopy would be required for future studies.

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