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Impurity level in SnO_2 materials and its impact on gas sensing properties

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ABSTRACT

Using the same protocol for precipitation of tin hydroxide and its hydrothermal treatment (HT), we synthesize SnO_2 from three precursors – tin(IV) acetate, tin(IV) hydroxide acetate and tin(IV) chloride pentahydrate. After annealing on sensor substrates the materials were found to be very similar from structural point of view. However, their sensing properties (responses to CO and H_2 as a function of humidity) were discovered to be very different, which was related to different impurity level in the samples. High amount of chlorine and potassium (ca. 300 ppmw) in two samples corresponded well to notably high water vapor effect. Differences in surface areas (within 20–60 m^2/g) and pore volumes (between 0.11 and 0.19 cm^3/g), found for the materials in question, seem to play minor role if the impurities are present.

1. Introduction

As has been widely accepted, the first step in wet chemistry processing is to choose the precursor. Careful selection is very important since precursors play at least the same role as pH, concentration, temperature and solvent media in tuning final properties of the polycrystalline material [1]. A vast majority of the research efforts in the field of "precursor effect" has been focused on studying how the nature of precursor affects chemistry of polycondensation reactions [2–5] and morphology of the grains [6–9]. Few addressed the problem of residual ions in the post-synthesis procedures. However, specifically the residual ions account for the wide spread of physical and chemical properties of similarly synthesized oxide materials.

Chlorides are probably the most widely used precursors for many functional materials. However, the role of contamination with chlorides has been studied mainly in the field of catalysis. For example it is known that chlorine can replace OH groups on oxides' surface and upon calcination it causes dramatic grain growth, sintering and loss of porosity [10,11]. Chlorine has been reported many times as severe poison in oxidation of hydrocarbons [12–15] and CO [16,17]. Its inhibiting effect is related to formation of stable and less active oxychloride species ($Met_xO_yCl_z$) which block the active surface sites and may produce chlorinated products competing with the reactants [12,13]. In addition, surface chlorine was found to decrease rate of isotope exchange of oxygen [18] and water [19], increase induction periods in CO and H_2 oxidation [18,20] and cause higher affinity of the contaminated oxide surface towards adsorbed hydrogen and water [16,19].

Sulfates and sulfur-containing precursors, being cheap and easy to handle as chlorides, are often used in laboratories as well. But contamination with sulfur is also known to inhibit many catalytic processes including oxidation of hydrocarbons [13,20,21]. Effect of alkali and alkaline earth metals present as impurities in oxidation catalysts is less studied. However, these elements are very common contaminants and their role in the surface chemistry might be dramatic, similarly to Co-supported catalysts in the Fischer–Tropsch synthesis [21–23].

Studies in the field of gas sensors related to the effect of common impurities and residuals are very scarce. Despite the fact that in many papers authors acknowledge the need to remove precursor residuals (e.g. [24]), the issue has never been studied systematically. Son et al. investigated the effect of chlorine residuals in SnO_2 materials on sensing performance [25]. Authors found that heavily

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contaminated tin oxides (5.1 and 2.6 wt% Cl) dramatically lost their surface area upon annealing at 650 °C after 2 h, which is in agreement with the findings reported above for the supported catalysts. As chlorine content decreased from 5.1 to 0.5 wt% sensor responses to CO increased. In contrast, responses to CH_4 and C_3H_8 were almost the same for 2.6–0.7 wt% Cl, and slightly higher for 5.1 wt% Cl.

Contamination with several weight percent of chlorine, having notable electronic effect, is typical for those materials, which are washed shortly. Good practice for synthesis of sensing materials implies checking the drain water with $AgNO_3$ test, which detection limit is ca. 2 ppm at room temperature (RT) [26]. Combining thorough washing and annealing at 400–600 °C, one typically achieves a concentration of Cl in a sensing material between 2000 and 400 ppmw [10,24]. Washing and annealing at 1000 °C remarkably decrease contamination with chlorine [25], and might bring it even down to 100 ppmw [27]. But as mentioned above it is achieved at high cost: dramatic loss of surface area. Use of chlorine free-precursors makes it possible to synthesize SnO_2 with rather low Cl amount (below 100 ppmw). However, in this case other impurities (e.g. carbon, S, Na, etc. [28]) should be taken into account and their influence on sensing properties should be at least qualitatively estimated.

In this paper we compare sensing properties of pure SnO_2 materials synthesized through hydrothermal treatment using inorganic and metalorganic precursors: $SnCl_4$, $Sn(OH)_xAc_y$ and $SnAc_4$. We used the same synthetic protocol, as well as the same post-synthetic procedures for all materials. Different analytic techniques have been carried out to study the impurity level of the materials. After analyzing structural and textural features of the porous oxides, the contaminations appear to be the only reason for very different sensing properties of the undoped tin dioxides.

2. Experimental

2.1. Material synthesis

Three materials, compared in this study, were synthesized as follows. Tin(IV) hydroxide acetate (synthesized from metallic tin and glacial acetic acid, as described elsewhere [29,30]), tin(IV) acetate (Aldrich, p/n 345172) and tin(IV) chloride pentahydrate (Aldrich, p/n 244678), dissolved in pure glacial acetic acid (the first two) and deionized water (only the latter), were added dropwise to ammonia hydrocarbonate aqueous solution upon stirring at RT. The resulting precipitates of tin hydroxide were washed first two times (for 3 h) with 0.6 M solution of NH_4NO_3 to remove Cl^- ions and then 5 times (for 12 h) with deionized water to remove other water-soluble impurities. The drain solutions were checked with $AgNO_3$ to ensure the absence of chloride ions. For hydrothermal treatment 7.0 ± 0.5 g of the washed precipitates was mixed with 200 ml of water. pH of the resulting colloid was adjusted to 10.5 through addition of NH_4OH. The mixture was transferred to an autoclave and hydrothermally treated. The colloid was heated up to 200 °C in N_2 atmosphere under continuous stirring. After 3 h at 200 °C the autoclave was allowed to cool down naturally. The obtained transparent sols of SnO_2 particles were evaporated and dried at 150 °C for 1 h. Hence, the three materials, being different only in their precursors, will be referred to as SnO_2 OHAc, SnO_2 AldrAc and SnO_2 Cl, respectively.

2.2. Material characterization

Just synthesized colloids of SnO_2, stable to sedimentation, were analyzed by laser particle analyzer (LPA) Malvern ZEN 3600. However, our main goal was to study sensing properties, thus the synthesized materials will be compared here chiefly after they have been deposited and annealed on sensor substrate or Al foil.

The SnO_2 powders were mixed with 1,2-propanediol and screen-printed on the front side of a planar Al_2O_3 substrate (containing Au electrodes for read out of the resistance) or Al foil annealed at 600 °C for 3 h prior to the deposition. After the deposition, the substrates were kept at RT for 12 h and then annealed in humid air (54% RH at 24 °C). The annealing protocol assumed heating at 100, 200 and 300 °C with 3 h of dwell at each temperature, followed by annealing at 400 °C for 12 h and 580 °C for 3 h.

Materials deposited on sensor substrates were analyzed by means of X-ray photoelectron spectroscopy using an AXIS-NOVA (Kratos Analytical, Japan) at pass energy of 80 eV. Those materials which were deposited on Al foil were characterized by means of TEM, XRD, FTIR and N_2 physisorption (BET analysis). TEM was performed using a FEI Tencai F20 microscope operating at 200 kV. X-ray diffraction patterns were recorded using a RINT 2100 diffractometer (Rigaku Denki) operating at 60 kV with Cu Kα radiation. FTIR transmission spectra were recorded at RT using a Jasco 4100 spectrometer operating at resolution of 2 cm^{-1} and with 100 scan times. The samples (1.3 ± 2 mg) were dispersed in the KBr matrix (105 ± 1 mg) and pressed to form self-supporting discs. BET surface areas were calculated from N_2 adsorption–desorption isotherms using a BELSORP-mini II surface analyzer. Before the BET analysis, all the samples were degassed in vacuum (10 Pa) at 150 °C for 1 h. Elemental analysis was performed with an EMAL-2 laser spark mass-spectrometer for 22 most abundant elements. Each material has been analysed once. Results of the analysis are given in ppmw, i.e. ppm by weight. Standard deviation of the instrument for the selected elements with atomic masses below 40 is about 40 ppmw, for all heavier elements the deviation is below 40 ppmw.

2.3. Photometric analysis of Cl ions

Amount of chloride ions in SnO_2 (after annealing at 580 °C without organic binder) has been indirectly estimated using a photometric analysis of those ions desorbed from the oxides into deionized water upon heating and sonication. The annealed materials were added to 28 ml of water and ultrasonically dispersed before heating at 80 °C. The heating alternated with ultrasonic dispersion was carried out simultaneously for all the samples and lasted 2 days. Then the obtained suspensions were centrifuged and the drain waters ware analyzed using a spectrophotometric method of Iwasaki et al. [31].

In this method mercury thiocyanate reacted with chlorine ions to produce mercury chloride and thiocyanate. The latter ions reacted with iron (dissolved in the form of perchlorate), which resulted in a raspberry pink iron thiocyanate. The concentration of the colored compound was measured by spectrophotometer V-660 Jasco in the visible spectrum with the absorbance maximum at 468 nm. The method was reported to obey the Beer law in the concentration range of 0.05–5 ppmw Cl^-. To determine concentration of Cl^- a set of standard solutions has been prepared and tested to give the Beer law.

2.4. Resistance measurements

After deposition of sensing materials, four substrates with the same material were placed into the sensor chamber and annealed as described above in a flowing air (100 ccm) containing water concentration of 0.016 atm (ca. 54% RH at 24 °C). Once the annealing has been finished the working temperature was set to 300 °C and the 4 sensors were stabilized under the same humidity rate for 7 days. Responses to CO and H_2 were measured starting from the highest water pressure of 0.016 atm and down to dry air with water content below 10 ppm. Sensor response is defined as resistance ratio: R_a/R_g,