

INFLUENCE OF THE pH VALUES OF THE SOL–GEL STATE ON THE PROPERTIES OF SnO₂ POWDERS OBTAINED FROM A SOL–GEL ROUTE

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The evolution of the specific surface area and crystallite size of SnO₂ powders, prepared from a sol-gel process, was studied as a function of the calcination temperature of the stannic hydroxyde colloid, and for two different pH values (7.5 and 12.5) of the colloidal state. The samples were characterized by TGA, IR spectroscopy, BET, and XRD techniques. The crystallite size and specific surface area were strongly affected not only by the calcination temperature, but unexpectedly, by the initial pH value of the colloidal state. A framework model, relating the pH dependence to the resulting properties, is presented.

1. INTRODUCTION

Stannic oxide is an *n*-type semiconductor with a tetragonal rutile structure¹ and a large indirect band energy gap. It has attracted considerable attention due to the variety of applications related to its unique electrical, optical, and catalytic properties. For example, stannic oxide is used in transparent heaters for windshield defrosting, in anti-reflection coating for solar cells, as a transparent electrode for electrochromic devices, as a sensing material for combustible gas sensors, and as an electrocatalyst for organic oxidation reaction.^{2–4} For the last two applications, finely grained SnO₂ powders are used. These powders have generally been obtained through two different methods: one involves the oxidation of elemental tin with acids (HNO₃, H₂SO₄ etc.) and the other utilizes the well-known sol-gel route.^{3–4}

We have prepared fine particles of SnO₂ powder from this conventional sol-gel method. It involves the dispersion of stannic hydrate in aqueous ammonia to give a sol. The sol is later “solidified” through stages of stiffening and polymerization to give a gel (gelation). The gel so obtained is thoroughly washed with distilled water, filtered, dried, and finally heated to high temperatures to obtain the required material. The evolution of the properties of SnO₂ powders, prepared with this

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TABLE 1

Sample identification

sample	sol-pH values	gel-calcination temperature
7-350	7.5	350
12-350	12.5	350
7-550	7.5	550
12-550	12.5	550

technique, has been previously investigated as a function of reaction temperature, time, and ambient calcination.⁵ In this paper, we report the correlation between the pH value of the stannic hydroxyde colloidal state and the physical properties of the resulting powders.

2. EXPERIMENTAL

SnO₂ powder preparation:

A stannic hydrate precipitate was obtained by dropwise addition of 28% ammonium water to a solution of stannic chloride up to pH 12.5. The temperature of the stannic chloride solution was maintained near 3°C with an ice-water bath. The excess of ammonium water and ammonium chloride was removed by repeatedly washing with distilled water followed by filtering.

The pH of the stannic hydrate gel progressively decreased from an initial value of 12.5 after the first filtering to 7.5 after washing and filtering nine times.

Two kind of SnO₂ powders were investigated here as a function of the calcination temperature of the gel, one obtained from a stannic hydroxide gel at pH = 12.5, the other from a gel at pH = 7.5.

The sample name, gel pH value and calcination temperature for each sample is listed in table 1.

The rate of heating and cooling during calcination was 1°C/min and was controlled using an Eurotherm controller.

Sample characterization:

TGA analysis was carried out up to 600°C in dry air with a heating rate of 3.3°C/min, using a Setaram thermobalance. The infrared spectra of SnO₂ powders, initially dried at 200°C for 2 hrs, were measured at room temperature using the KBr technique. The samples were manipulated in an argon filled dry box in order to prevent water absorption after drying. A Perkin-Elmer infrared spectrometer (model PE 983) was used to obtain the absorbance of samples in the range of 200 ~ 4000 cm⁻¹.

X-ray powder data were obtained with a Philips Spectrogoniometer (P.W 1050) using filtered Cu K α radiation. The Scherrer⁶ and Warren formula⁷ were used to calculate the average crystallite size from the width of the main diffraction peak at half height (the factor β was corrected using the x-ray diffraction pattern of standard silicon powder).

The specific surface area of the samples was measured by BET using a Micromeritics system (Accusorb) and nitrogen as the adsorbate gas. All samples were out-gased at 150°C for 5 hrs.

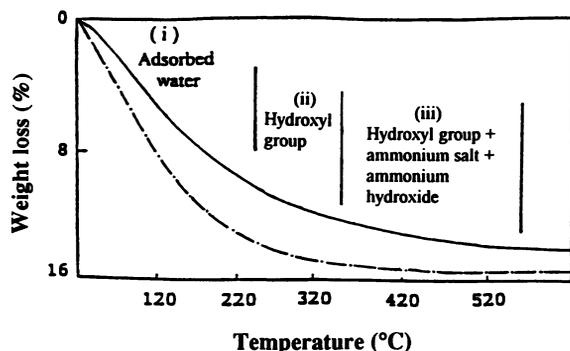


FIGURE 1 TGA profiles of hydrated SnO_2 gels, recorded in dry air. (— pH = 7.5 pH = ---12.5.) Before measurements the samples were “pre-dried” in dry air at 60°C , for 2 hrs.

Electrical conductivity measurements were carried out on samples that were isostatically pressed at $5 \text{ tons}/\text{cm}^2$ in a steel die of diameter 13 mm. The two-probe DC method was used and the experiments were performed under dynamic vacuum (10^{-3} Torr) between 223 K and 375 K. For the determination of conductivity, a bias voltage of 1.0 V was applied across the pelletized sample and the resulting current was measured using a picoammeter/voltage source (Keithley 487). Silver paste was used for electrical contacts.

3. RESULTS AND DISCUSSION

TGA results of pH 7.5 and pH 12.5 stannic hydrate gels are shown in fig. 1. The weight loss ($\sim 16\%$) reported in fig. 1 accounts for a smooth decomposition continued until the temperature reaches $\sim 550^\circ\text{C}$. Our observations of weight loss in agreement with the reports of other workers.⁸ The two samples exhibited a difference in weight loss at 350°C and 550°C of 2.9% and 1.4%, respectively. The decomposition takes place in two or three stages ((i), (ii), (iii)) depending on whether the pH of the gel is 7.5 or 12.5, as depicted in the figure. Stages (i) and (ii) corresponds to the removal of adsorbed water and hydroxyl groups, respectively. Adsorbed molecular water is entirely removed by drying at about 200°C .⁹ On the other hand, hydroxyl groups, which are more strongly bound to the cations than adsorbed water are, therefore, removed at higher temperature. Residuals of hydroxyl groups, ammonium salt (NH_4Cl), and ammonium hydroxide remaining from the synthesis, are likely to occur for the gel being at pH 12.5, and account for stage (iii). The IR spectrum of sample 12-350 reported on fig. 2a reveals an absorption peak at $1400 \sim 1420 \text{ cm}^{-1}$ (ν_4 mode of NH_4^+ ¹⁰). This indicates that unwashed, NH_4Cl , which is present in the stannic hydrate gel at pH 12.5, remains up to a calcination temperature of 350°C (sample (12-350)). It is likely that NH_4Cl has little interaction with the SnO_2 framework. The ammonium chloride probably behaves as a co-precipitate, which has little or no interaction with the SnO_2 framework.

The broad features between 3040 and 3500 cm^{-1} observed for samples 12-350 and 7-350 (IR spectra of fig. 2a and b) have been assigned to hydroxyl groups

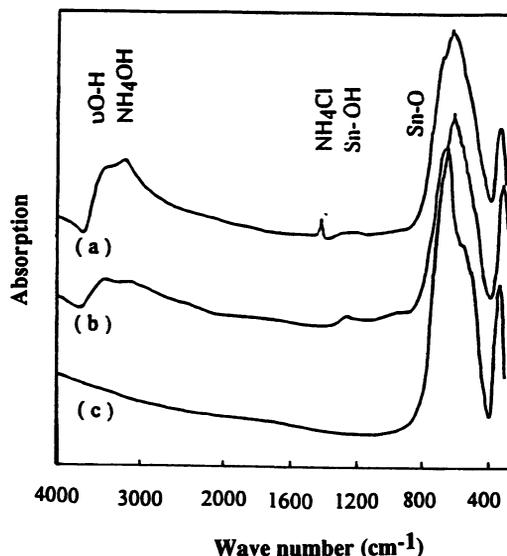


FIGURE 2 Infrared absorption spectra; (a): sample 12-350, (b): sample 7-350, (c): samples 12-550, 7-550.

associated with surface cations in the SnO_2 rutile structure.^{11,12} As expected, no adsorbed water, characterized by its deformation mode δOH_2 at 1620 cm^{-1} , was revealed in the IR spectra. On the other hand, the traces of ammonium ions, which would occur for sample 12-350, also contribute to the $3040 \sim 3500\text{ cm}^{-1}$ absorption band in fig. 2a ($\nu_1(3040\text{ cm}^{-1})$ and $\nu_3(3145\text{ cm}^{-1})$ modes of NH_4^+ ¹³).

It is of interest to examine whether the ammonium chloride, the hydroxyl, and ammonium groups, present in the stannic hydrate gel at pH 12.5, influence the physical properties of the resulting SnO_2 powders. Fig. 3 shows the x-ray diffractograms (XRD) for samples 7-550 and 12-550, from which the average crystallite sizes have been estimated. The XRD are characteristic of the SnO_2 rutile structure, as expected. However, and most interestingly, the crystallite size is significantly different: $\sim 75\text{ \AA}$ for 7-550 and $\sim 506\text{ \AA}$ for 12-550, although the calcination conditions are identical. On the other hand, the powders obtained from the two stannic hydrated gels calcinated at lower temperature ($T < 350^\circ\text{C}$) have similar crystallite sizes (fig. 4).

The specific surface area of the powders varies inversely with the calcination temperature. When the calcination temperature is larger than 350°C (fig. 5), it varies inversely with the size of the particles (the accepted definition being that many crystallites make a particle). For lower calcination temperatures ($T < 350^\circ\text{C}$), the departure of adsorbed water and, probably, of weakly bound hydroxyl groups is responsible for the increase of the specific surface area. The specific surface area of sample 12-350 is larger than that of 7-350 (fig. 5) even though the crystallite size appears to be nearly the same by x-ray diffraction. That can be explained as follows. We have shown that hydroxyl and ammonium groups and, also, ammonium chloride are present in higher proportions for sample 12-350. It is likely that these species are in the pores of the particles and could cause larger pore volume, as depicted in schematically fig. 6. Consequently, this would result in larger specific

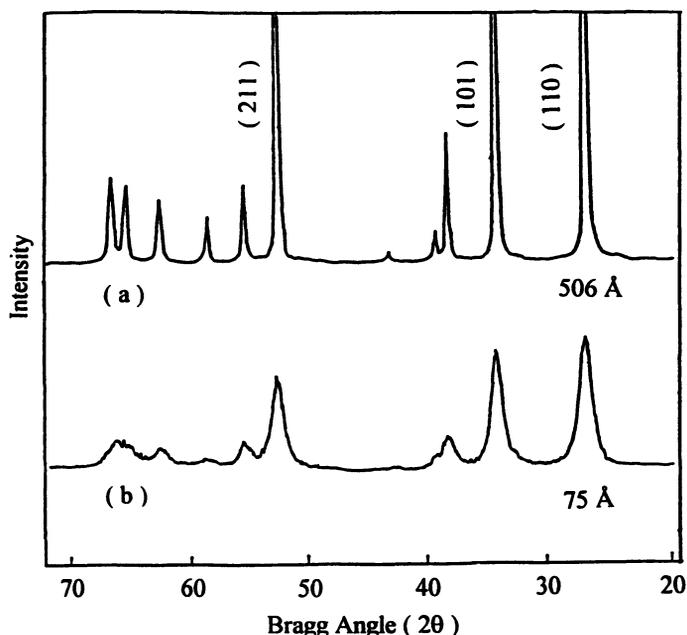
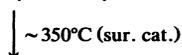


FIGURE 3 X-ray diffractograms of, 12-550, (a), and 7-550 (b) samples ($\pm 6 \text{ \AA}$).

surface area, as observed for sample 12-350 (fig. 5). Thus, the sharpest decrease of the specific surface area for $T > 350^\circ\text{C}$, observed for the powders from the gel at pH 12.5 (fig. 5), is induced by the complete departure of the above mentioned species, leading to a closing of pores. The overall reaction accounting for the departure of the species might be expressed as follows,



In fact, the surface of the tin oxide, very likely might act as catalyser for the departure of the hydroxyl and ammonium species. Indeed, ammonium chloride begins to be sublimated and decomposed above $\sim 350^\circ\text{C}$.¹⁴ According to (1) and (2), oxygen deficient tin oxide powders, $\text{SnO}_{2-y} \square y$, arise from the calcination of the stannic hydrate gel at pH 12.5. Moreover, the hydrogen involved in (1) might enhance the reduction process and, therefore, enhances the oxygen-vacancy concentration. On the other hand, it is well established that oxygen deficiency (as well as interstitial Sn) gives rise to *n*-type conductivity.^{15,16} Under such a circumstance, the conductivity of sample 12-550, for instance, should be significantly higher than that of sample 7-550, which should be more stoichiometric. The large difference in the conductivities between the two samples (fig. 7) supports this hypothesis. It also explains the observed darker (greyish) coloration of sample 12-550 compared with 7-550. However, the higher rate of oxygen vacancies in the oxide 12-550 does not account, in itself, for its much higher conductivity. Recall from fig. 3 that the oxide 12-550 does not account, in itself, for its much higher

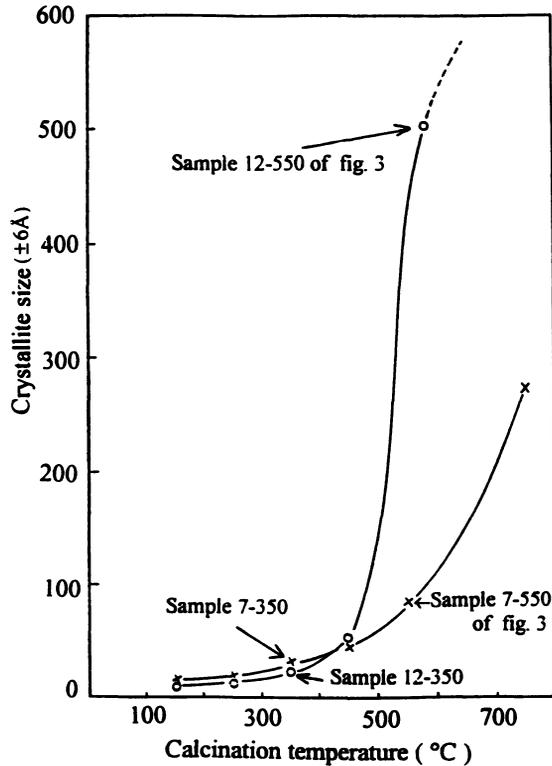


FIGURE 4 Evolution of the crystallite-size as a function of the calcination temperature of the two stannic hydrated gels (o: pH 12.5, x: pH 7.5).

conductivity. Recall from fig. 3 that the oxide 12-550 produces larger crystallites than the oxide 7-550. Consequently, the grain boundary effect, which inhibits the DC conduction, is minimized in sample 12-550, so that its conductivity is larger. It also suggests that the reaction (1) causes not only the closing of the pores but, in addition, promotes the crystal growth process. Indeed, the closing of the pores results in the “matching” of crystal site atoms (---Sn---O---Sn---). It means that the crystallite size is sharply increased by $(d_1 + d_2)$, as seen in fig. 4 and 6, in the 350 ~ 550°C range. Let us finally recall that no significant difference between the size of the crystallites of the two oxides will be observed if the calcination temperature is lower than ~ 350°C (fig. 4). Indeed, at these calcination temperatures, ammonium chloride is not sublimated¹⁴ and, consequently, reaction (1) cannot proceed.

CONCLUSION

The specific surface area and crystallite size of SnO_2 powders are affected not only by the calcination temperature, but also by the pH values of the colloidal state. Hydroxyl groups, ammonium hydroxide, and ammonium chloride are present in the gels prepared at pH 12.5. They account for the larger pore volume, and as well

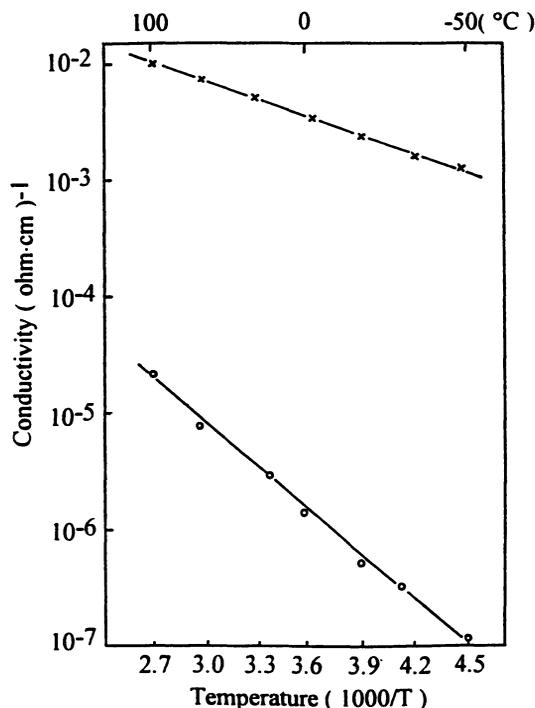


FIGURE 7 Electrical conductivity as a function of temperature for 12-550 (x) and 7-550 (o) samples.

as higher specific surface area observed for the SnO₂ powders calcined below 350°C. When the powders are heated above 350°C, these species volatilize. This results in a sharp decrease of the specific surface area, and a large increase in the crystallite size.

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