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ORIGINAL CONTRIBUTION

Formation of "monodispersed" SnO_2 powders of various morphologies

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Abstract Several procedures for the preparation of colloidal SnO_2 powders, consisting of particles of narrow size distribution and of various morphologies, are described. The hydrolysis of $SnCl_4$ aerosols in the presence of gaseous ammonia produces poorly crystalline SnO_2 spheres of modal diameters $< 2\ \mu m$. Depending on the preparation conditions, the forced hydrolysis of acidic (HCl) $SnCl_4$ solutions yields either prismatic particles or spherulites composed of tiny, strongly aggregated, elongated subunits. In both cases the particles are in the nanometer size range (< 100 nm) having crystalline rutile structure. Rod-like SnO_2 particles ($\sim 0.3\ \mu m$) of good crystallinity can be obtained by hydrolysis of $SnCl_4$ solutions in the presence of formamide. It is concluded that the hydrolysis of dissolved $SnCl_4$ tends to produce elongated SnO_2 particles which, depending on the experimental conditions, may be at different aggregation states.

Key words Aerosol of TiO_2 – hydrolysis of $TiCl_4$ – tin oxide (colloidal, nanosize)

Introduction

Owing to its transparency and conductivity, tin dioxide finds many technological applications such as gas sensor, transistor, electrode material, catalyst, as well as in optical-conductive films for solar cells, etc. For many of these uses, the availability of finely divided powders, consisting of particles uniform in size and shape ("monodispersed"), is highly desirable. These powders can provide appropriate model systems for studying their properties and they can also improve ceramic processing, for example, by decreasing sintering temperatures [1]. The latter can be further affected, if the particle size is in the nanometer range [2]. Recently, several techniques have been developed for the preparation of "monodispersed" inorganic colloids which include precipitation from homogeneous solutions and hydrolytic reactions in aerosols [3, 5]. In the first method, two different approaches can be used, i.e., forced hydrolysis of hydrated metal cations at moderately elevated temperatures (< 100 °C) or controlled release of precipitating anions (OH^-, for oxides) by decomposition of organic molecules, such as formamide [6]. In the aerosol process, droplets of one reactant are exposed to a coreactant in gaseous state, which yield a desired product [7, 8].

Uniform SnO_2 powders consisting of particles of various shapes and narrow size distribution have been recently obtained by hydrolysis of both $SnCl_4$ aerosols [9] and of $SnCl_4$ acidic solutions in the presence [10] or in the absence [11, 12] of formamide. The aim of this study is to compare the variables that control the respective processes in relationship to the characteristics of the resulting particles.

Experimental

Materials

Tin(IV) pentahydrate (98%, Alfa), tin(IV) chloride (anhydrous, Fluka), formamide (Eastman), and hydrochloric acid

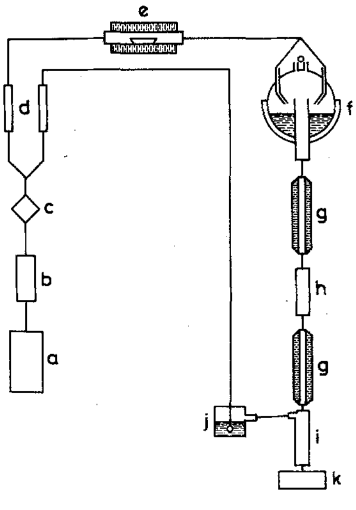
(Dilute-it concentrate) were used without further purifications.

Preparation of the particles

Hydrolysis of aerosols

Spherical SnO_2 particles of narrow size distribution were prepared by the hydrolysis of $SnCl_4$ aerosol droplets in the presence of NH_3 [9]. A schematic diagram of the apparatus is represented in Fig. 1, the components of which are described in the legend. The gas flow rate was adjusted between 0.05 and 0.4 $1\ min^{-1}$, while the temperature of the nuclei producing AgCl furnace (e) was kept constant in the range 620–720 °C. The $SnCl_4$ container (f) was thermostated between -3 and -16 °C. The $SnCl_4$ vapor collected by the carrier gas was condensed on AgCl nuclei at temperatures between -15 and -30 °C (g). Ammonia, necessary to hydrolyze the resulting droplets, was obtained by bubbling nitrogen at a flow rate between 0.9 and 1.6 $1\ min^{-1}$ through an ammonium hydroxide solution ranging in concentration between 0.5 and 0.2 $mol\,dm^{-3}$. Before analyses, the powders so prepared were washed with doubly distilled water to remove ammonium chloride generated as byproduct.

Fig. 1 Schematic diagram of the apparatus used to produce spherical tin(IV) hydrous oxide particles by hydrolysis of tin(IV) chloride aerosol droplets in the presence of ammonia: a) gas tank; b) drying column; c) filter; d) flow meters; e) nuclei generator (AgCl heated at a high temperature); f) $SnCl_4$ thermostated reservoir; g) condensers; h) re-evaporation chamber; i) hydrolysis chamber; j) ammonium hydroxide container; k) thermopositor



Precipitation from homogeneous solutions

Powders, identified as SnO_2, were obtained by aging acidic solutions of tin(IV) chloride in the absence (forced hydrolysis) or in the presence (controlled release of precipitating anions) of formamide at 100 °C for different periods of time [10, 11]. The concentrations of the tin(IV) salt, HCl, and of formamide were systematically varied in order to explore the influence of these parameters on the characteristics of the final products.

Characterization

The structure of the solids was determined by x-ray diffraction, and the crystallite size was estimated by the Scherrer procedure applied to the (211) reflection of cassiterite ($2\Theta \sim 52°$). The morphological characteristics of samples were elucidated by electron microscopy and infrared (IR) spectroscopy. The latter technique was shown to yield information on the shape and the state of aggregation of the particles that constitute the powder, in addition to their chemical composition [12–14]. While the IR data can be evaluated using different theories, in this work "the average dielectric constant" (TADC) approach was utilized, because it was previously demonstrated that this method was applicable to many oxides [8–14]. The infrared spectra were recorded for samples diluted with KBr.

The size distribution of the powders was obtained from the electron micrographs by counting several hundred particles.

Results and discussion

Hydrolysis of aerosols

The hydrolysis of $SnCl_4$ droplets by water vapor is not fast enough to produce solid particles in the short reaction time involved in the aerosol technique [15]. Since ammonium hydroxide is known to accelerate the precipitation of tin hydroxide, nitrogen was bubbled through ammonia solutions of different concentrations and then contacted with $SnCl_4$ droplets. Solid particles were detected if the concentration of ammonium hydroxide solutions exceeded 0.05 $mol\,dm^{-3}$, although at the last condition they were irregular in shape, indicating partial evaporation of droplets before the hydrolysis was completed. Full solidification was only attained, if the inert gas was bubbled through a $\sim 0.2\ mol\,dm^{-3}$ NH_4OH solution; still higher concentrations of ammonia resulted in the formation of a large number of very tiny particles. This effect may have been due to the release of gases (and possibly heat) generated by the reaction of ammonia vapor with $SnCl_4$ droplets, causing the latter to shatter.

Figure 2A illustrates spherical particles of a reasonably narrow size distribution obtained under the set of conditions described in the legend (sample I). The particle size analysis indicated a bimodal distribution, with a large fraction having a modal diameter (d_m) of 1.7 μm and a relative standard deviation (σ) of 0.042. The second mode ($\sim 10\%$) with $d_m = 0.54$ μm and $\sigma = 0.003$ is likely to be due to the autocondensation of some of the $SnCl_4$ vapor, which would produce smaller droplets than those formed by the condensation on nuclei.

Several other reaction parameters were altered to elucidate their influence on the morphological characteristics of the final powders. An increase in the temperature of the nuclei furnace from 620° to 720 °C yielded solid spheres of a size distribution quite similar to that of sample I, but of somewhat smaller diameters ($d_m = 1.55$ and 0.50 μm for the two modes), which was to be expected, since the number of nuclei was larger. An increase in the gas flow rate yielded a rather polydisperse system. A slower flow produced larger, mostly hollow particles of irregular shape, caused by an incomplete reaction The change in the temperature of the $SnCl_4$ reservoir from -10 to -16 °C resulted in spheres of broader size distribution with $d_m = 1.47$ μm. This effect was expected, since at lower temperatures less vapor was generated. An increase of the temperature from -10 to -3 °C did not produce significant changes in the characteristics of the final particles.

The x-ray diffraction of sample I (Fig. 3a) demonstrates the poorly crystalline nature of this powder (crystallite size ~ 20 Å). The infrared spectrum (Fig. 4a) shows bands corresponding to Sn-O vibrations (< 700 cm^{-1}), with an indication of a structural order by the presence of a low frequency band (300 cm^{-1}), characteristic of cassiterite [14]. In fact, using the TADC approach this spectrum can be accounted for by considering tiny, yet strongly aggregated cassiterite particles [16]. It is interesting to note that the hydrolysis of aerosols usually produces amorphous solids, since it involves a very fast reaction carried out at room temperature. The low crystallinity obtained in the present case could be due to a local temperature increase

Fig. 2 Electron micrographs of the SnO_2 samples obtained by different experimental procedures. A) Hydrolysis of a $SnCl_4$ aerosol in the presence of NH_3 (Table 1, sample I): Nuclei over temperature (Fig.1e) : 623 °C; $SnCl_4$ reservoir (f) temperature -10 °C: condensation (g) temperature -30 °C; N_2 flow rate for the aerosol generation 0.1 l min^{-1}; N_2 flow rate bubbled into the ammonium hydroxide solution 0.9 l min^{-1}, ammonium hydroxide concentration 0.2 mol dm^{-3}. B) Forced hydrolysis of a 0.003 mol dm^{-3} $SnCl_4$ solution at 100 °C for 2 h in the presence of 0.3 mol dm^{-3} HCl (sample II). C) Forced hydrolysis of a 0.1 mol dm^{-3} $SnCl_4$ solution in the presence of 1 mol dm^{-3} HCl at 100 °C for 6 days (sample III). D) Hydrolysis of a 0.001 mol dm^{-3} $SnCl_4$ solution in the presence of 0.15 mol dm^{-3} formamide and 0.6 mol dm^{-3} HCl at 100 °C for 1 week (sample IV)

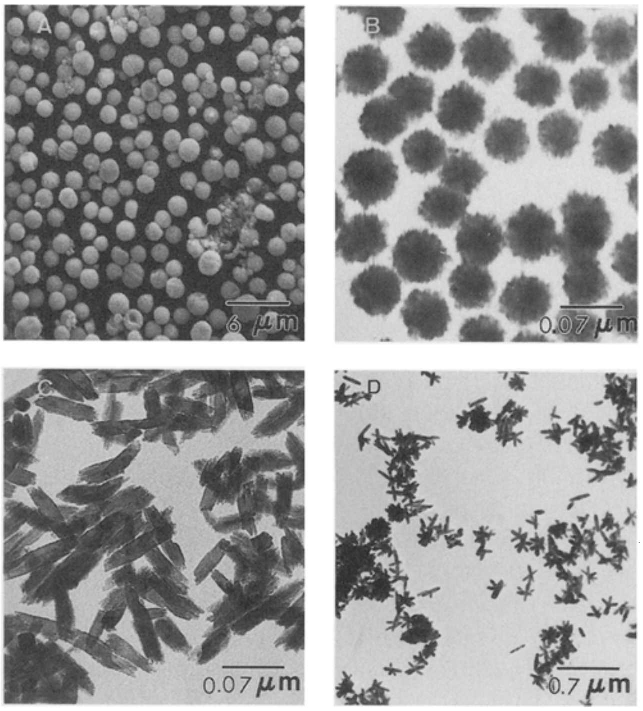


Fig. 3 X-ray diffraction patterns of: a) sample I (Table 1, Fig. 2); b) sample II; c) sample III; and d) sample IV

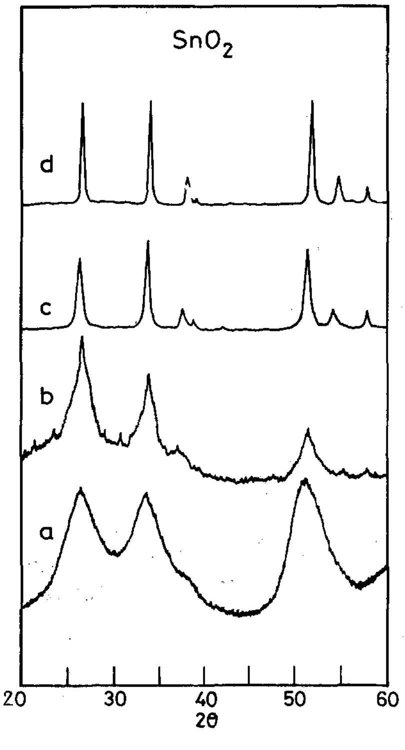
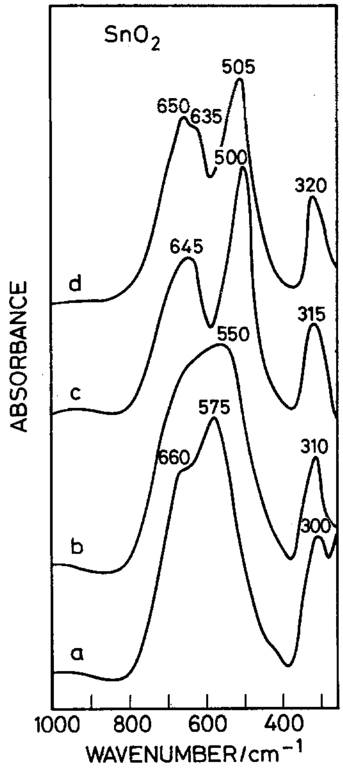


Fig. 4 Infrared spectra of:
a) sample I (Table 1, Fig 2);
b) sample II; c) sample III; and
d) sample IV



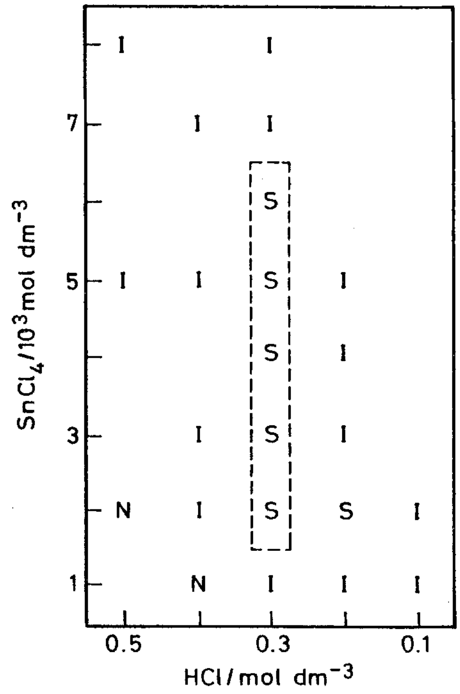


Fig. 5 The precipitation domain for solutions containing $SnCl_4$ and HCl in varying concentrations, aged at 100 °C for 2 h. Symbols designating different kinds of particles: S = spherical, I = irregular, N = no precipitation. The more uniform systems are surrounded by dashed lines

in the particles as a consequence of the $SnCl_4$ hydrolysis, which is strongly exothermic in the presence of ammonia.

Precipitation from homogeneous solutions

The main requirement to produce monodispersed systems by this procedure is to control the kinetics of the generation of solutes that are precursors to precipitation, which can be achieved by the adjustment of the concentration of reagents, pH, and temperature [3, 4].

Forced hydrolysis

This method is based on the enhancement of the deprotonation of hydrated metal ions. Depending on the hydrolizability of cations, this process can take place even under very acidic conditions at a sufficiently high temperature, eventually leading to the precipitation of colloidal metal (hydrous) oxides [3–5].

The precipitation domain obtained by aging $SnCl_4$ solutions in the presence of HCl at 100 °C for 2 h (Fig. 5) indicates the nature of precipitated solids at different reactant ($SnCl_4$ and HCl) concentrations under otherwise same conditions. Spherical particles of narrow size distribution having spherulitic microstructure are obtained only using solutions of tin(IV) chloride ranging from 0.0020 to 0.0060 mol dm^{-3}, in the presence of 0.3 mol dm^{-3} hydrochloric acid. The mean particle size of the uniform powders decreases slightly as the concentration of the tin salt increases, the diameter ranging from 0.06 μm for the less concentrated solutions (0.0020–0.0030 mol dm^{-3}) to ~0.04 μm for the more concentrated one (0.0060 mol dm^{-3}). A typical example (sample II) is given in Fig. 2B, which clearly demonstrates that these solids are composed of aggregated tiny elongated subunits. Uniform particles consisting of much smaller entities, have been previously observed with other inorganic colloids, including metal oxides [3, 17]. The lowest temperature that caused precipitation in sample II was 80 °C and no effect on the final particle size could be noted when the aging was carried out at temperatures up to 150 °C. Finally, it was also observed that the minimum aging time required for the formation of the final particles was 2 h.

The x-ray diffraction pattern of sample II (Fig. 3b) shows that the solid consists of polycrystalline cassiterite (crystallite size ~50 Å) as expected from the composite nature of the particles. The corresponding infrared spectrum (Fig. 4b) shows variations in the position and in the width of the maxima with respect to that calculated for uniform spheres of SnO_2 using the TADC method. This finding indicates internal heterogeneity of the particles and deviation from sphericity [10].

Uniform SnO_2 particles of other shapes may be obtained under experimental conditions different from those described in Fig. 5. Nanocrystalline prismatic SnO_2 dispersions of narrow size distribution can be prepared by aging at 100 °C for 6 days solutions 0.10 to 0.25 mol dm^{-3} in $SnCl_4$ and 0.9 to 1.0 mol dm^{-3} in HCl (Fig. 6). An increase in the particle size was observed with higher tin salt concentrations. Figure 2C is the electron micrograph of nanocrystalline SnO_2 particles produced under the conditions described in the legend (sample III). The x-ray diffraction pattern of this sample (Fig. 3c) is characteristic of cassiterite having higher crystllinity than sample II. These particles appear to be composed of smaller aggregated fibrils, when observed in the transmission electron microscope, yet the electron diffraction indicated that they were monocrystalline.

The particle size analysis carried out with sample III gave a mean length and width of 0.062 and 0.017 nm, respectively, with a relative standard deviation (σ) of 0.22 in both cases. The particle thickness of 0.010 nm was estimated from the analysis of the IR spectrum of this sample (Fig. 4c) [11].

The morphological differences between samples II and III could be explained by stability and kinetic considerations. Thus, at the higher pH values (sample II) the hydrolysis reaction is faster, resulting in a larger number of nuclei, which – after a short period of growth – aggregate to minimize the high free energy of the system. In contrast, at the lower pH (sample III) the hydrolysis is slower, producing fewer nuclei, which remain stable either due to their higher surface charge and/or to the lower surface energy. These nuclei can then grow to larger sizes by the incorporation of hydrolyzed solutes.

Controlled release of precipitating anions

It is well known that formamide ($HCONH_2$) decomposes upon heating, generating hydroxide anions which enhance the hydrolysis [6]. Figure 7 shows the precipitation domain obtained by aging for 1 week at 100 °C tin(IV) chloride solutions containing formamide and 0.6 mol dm^{-3} HCl. Under certain conditions rod-like particles are generated as illustrated in Fig. 2D (sample IV).

The concentration of the hydrochloric acid was found to greatly influence the precipitation process. Thus, in the system of 0.0010 mol dm^{-3} $SnCl_4$ and 0.15 mol dm^{-3} formamide (sample IV), no precipitation took place when the HCl concentration was raised to 0.7 mol dm^{-3}, whereas increased agglomeration was observed if the HCl concentration was lowered to 0.5 mol dm^{-3}.

The x-ray diffraction pattern of sample IV is characteristic of cassiterite of rather good crystallinity (Fig. 3d), while its infrared spectrum (Fig. 4d) is very similar to that of the prismatic particles (Fig. 4c). The only appreciable differences between these two solids is in the slight shift of the position of the bands and a shoulder at ~635 cm^{-1} in the spectrum of the rods, which are mainly related, according to the TADC [6], to the presence of oblate spheroids in

Fig. 6 The precipitation domain for solutions containing $SnCl_4$ and HCl in varying concentrations aged at 100 °C for 6 days. Symbols: P = prismatic, I = irregular particles, and N = no precipitation. The region in which nanocrystalline (≤ 100 nm) solids are formed is shown by dashed lines

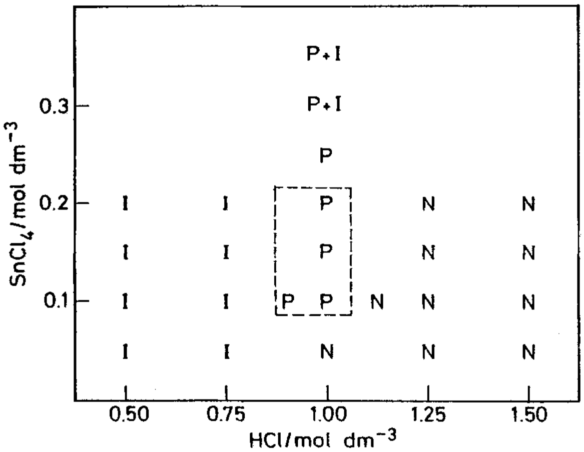


Fig. 7 The precipitation domain for solutions of varying concentrations of $SnCl_4$ and formamide, at a constant concentration of 0.6 mol dm^{-3} HCl, aged at 100 °C for 1 week. Symbols: R = rods, A = agglomerates, I = irregular small particles, and N = no precipitation

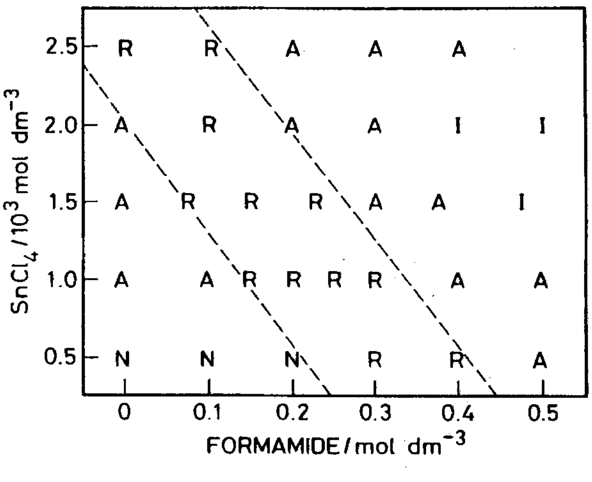


Table 1 Morphological characteristics and crystallite size of uniform SnO_2 particles prepared by different procedures

Sample	Preparation method	Particle morphology	Particle size (μm)	Crystallite size (Å)
I	Aerosol hydrolysis	Spherical	Bimodal; 1.7 and 0.54	~20
II	Forced hydrolysis	Spherulitic	0.06	~50
III	Forced hydrolysis	Prismatic	0.062 × 0.0017 × 0.01	monocrystals
IV	Controlled release of hydroxide ions	Rod-like and aggregates	0.3 × 0.045	monocrystals

sample IV. Indeed, the electron micrographs show the powder to consist of a mixture of single rods and agglomerates that assume oblate shape (Fig. 2d). The interpretation of the spectrum suggests that the aggregation is not physical in nature, but rather it is caused by chemical bond formation.

Summary

Table 1 summarizes the characteristics of the SnO_2 powders produced by the hydrolysis of $SnCl_4$ aerosols and $SnCl_4$ solutions. The former method generates, under a very restrictive set of conditions, spherical particles of poor crystallinity having a bimodal size distribution. The hydrolysis of $SnCl_4$ in solution tends to produce elongated particles which, depending on the experimental conditions, can appear in different states of aggregation.

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