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Preparation of Tin(II) Oxide by a Homogeneous Precipitation Method

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Synopsis. The production of tin(II) oxide from tin(II) chloride and urea was found to depend on the concentration of urea. An amorphous compound was produced for a lower concentration of urea, $5SnO \cdot 2H_2O$ was produced for a higher concentration of urea, and tin(II) oxide was produced for a middle-range concentration of urea.

In order to prepare tin(II) oxide from solution, the following process is generally undertaken. Tin(II) hydroxide, which is prepared by adding an alkaline solution to a tin(II) salt solution, is mixed with a mother liquid solution and boiled for several hours.[1—5] Through this process, however, it is difficult to obtain tin(II) oxide in good reproducibility regarding particle shape or size. A homogeneous precipitation method makes it possible to prepare a homogeneous precipitate which has a constantly identical composition as well as properties with good reproducibility.[6,7] The precipitation of tin(II) oxide by the homogeneous precipitation method has not been reported yet. Since tin(II) oxide is thermally unstable, it has not been utilized as a ceramic material. On the other hand, tin(IV) oxide is a chemically stable semiconductor, and has been utilized as a gas sensor. One of the preparative methods of tin(IV) oxide is to oxidize tin(II) oxide. Since the particle shape and size of the power depend on the preparative method, those of tin(IV) oxide prepared by this method depend on the quality of the original tin(II) oxide. Therefore, in this study the preparation of tin(II) oxide by the homogeneous precipitation method was made at various concentrations of tin(II) chloride and at various $(NH_2)_2CO/SnCl_2$ molar ratios.

Experimental

0.1 mol dm^{-3} hydrochloric acid was used as a solvent in order to keep aqueous solution of tin(II) chloride strongly acidic; otherwise, an aqueous solution of tin(II) chloride hydrolyzes to form a precipitation of the basic salt.[8] A mixed solution of 1 dm^3 of an aqueous solution containing tin(II) chloride dihydrate (0.01 to 0.05 mol dm^{-3}) and that containing urea (0.01 to 10.0 mol dm^{-3}) was heated at 95—97 °C in a steam bath for one hour. The precipitate was filtered, washed by distilled water, and dried under vacuum at room temperature. All of the chemicals used in this experiment were first-grade reagents of Wako Junyaku Kogyo Co., Ltd. An X-Ray diffraction analysis was carried out with an X-ray diffractometer (Rigaku Denki Co., Ltd., model D-6C). A thermal analysis (DTA-TG) were carried out in air at a heating rate of 10 °C min^{-1} using a Rigaku Denki Co., Ltd., model PTC-10A. The amount of tin in the precipitates was determined by a chelatometric titration method using sample solutions which were prepared by alkali fusion.

Results and Discussion

Tin(II) chloride is soluble in both cold and hot water,[9] and its dilute solution becomes thick with a basic salt to produce precipitates.[10] It was therefore examined whether tin(II) chloride produces a precipitate or not under various concentration conditions of tin(II) chloride in 0.1 mol dm^{-3} hydrochloric acid (excluding urea) and on heating at 95—97 °C for one hour. A solution of tin(II) chloride with a concentration higher than 0.06 mol dm^{-3} produced a precipitate. Thus, the concentration of tin(II) chloride was kept lower than 0.05 mol dm^{-3}. Figure 1 shows the X-ray diffraction patterns of the obtained samples. Figure 2 shows DTA and TG curves of the corresponding samples. In Fig. 1 the diffraction pattern of sample(A) almost coincides with that of No. 6-395 (SnO) on an

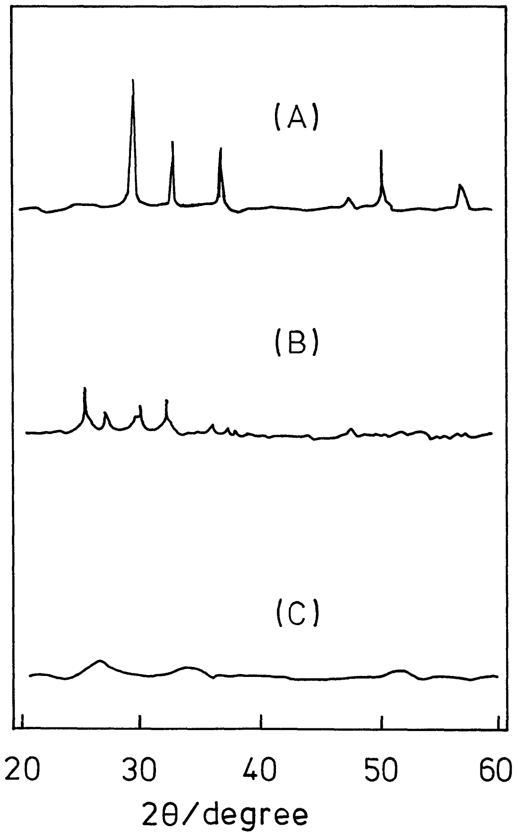

Fig. 1. X-Ray diffraction patterns of a sample prepared from the aqueous solution (1 dm^3) containing both $SnCl_2$ (0.02 mol dm^{-3}) and $(NH_2)_2CO$ of various concentrations: (A) 0.6 mol dm^{-3}, (B) 2.0 mol dm^{-3}, (C) 0.4 mol dm^{-3}.

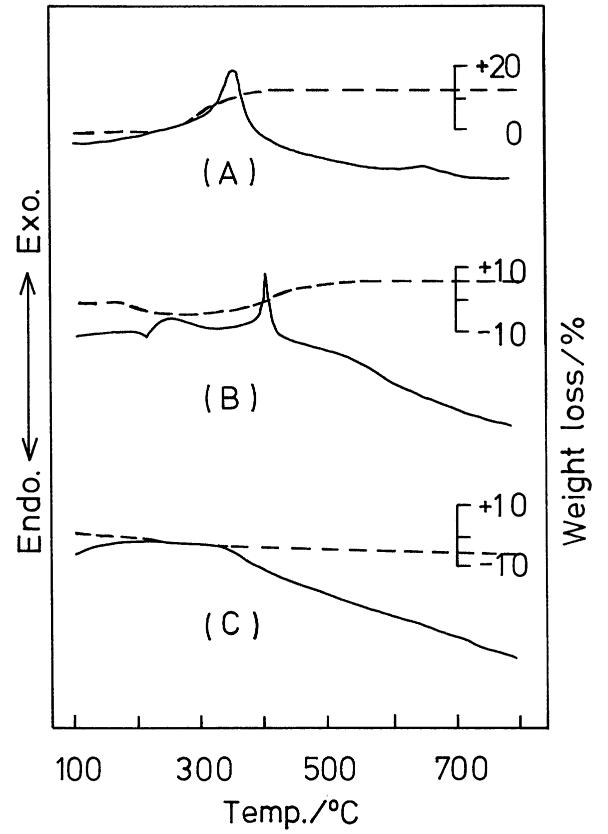

Fig. 2. DTA and TG curves of a sample prepared from the aqueous solution (1 dm^3) containing both $SnCl_2$ (0.02 mol dm^{-3}) and $(NH_2)_2CO$ of various concentrations: (A) 0.6 mol dm^{-3}, (B) 2.0 mol dm^{-3}, (C) 0.4 mol dm^{-3}. —: DTA, ---: TGA.

ASTM card; that of sample(B) almost coincides with that of No. 14-140 ($5SnO \cdot 2H_2O$) on an ASTM card; and that of sample(C) resembles No. 21-1250 (SnO_2) on an ASTM card. The DTA and TG curves show that sample(A) gains about 12% in weight with an exothermic reaction around 300 °C; sample(B) loses about 4% in weight with an endothermic reaction around 200 °C and gains 10% in weight with an exothermic reaction around 400 °C. Sample(C) showed a gradual loss in weight. The results of a chemical analysis showed a tin content in sample(A) of 87.5%, 82.7% in sample(B), and 75.3% in sample(C).

It has been theoretically deduced that SnO changing into SnO_2 gains 11.9% in weight, and that $5SnO \cdot 2H_2O$ changing into SnO by dehydration loses 5.1% in weight. The tin content in SnO is 88.1%, that in $5SnO \cdot 2H_2O$ 83.7%, and that in SnO_2 78.8%. From the results of X-ray diffraction, DTA and TG analyses, as well as chemical analyses, it is presumed that sample(A) is SnO; sample(B) is $5SnO \cdot 2H_2O$; and sample(C) is an amorphous compound. This amorphous compound before drying changed into tin(II) oxide upon aging in a solution with a pH above 3; it did not change upon drying at room temperature. It is thus presumed that the substance after drying (sample C) is SnO_2; the property of the amorphous compound changes according to the drying. The amorphous compound is very easily oxidized. Figure 3 shows the relationship between the preparative conditions and the kind of product. When a solution of tin(II) chloride at a concentration of 0.01 mol dm^{-3} was used,

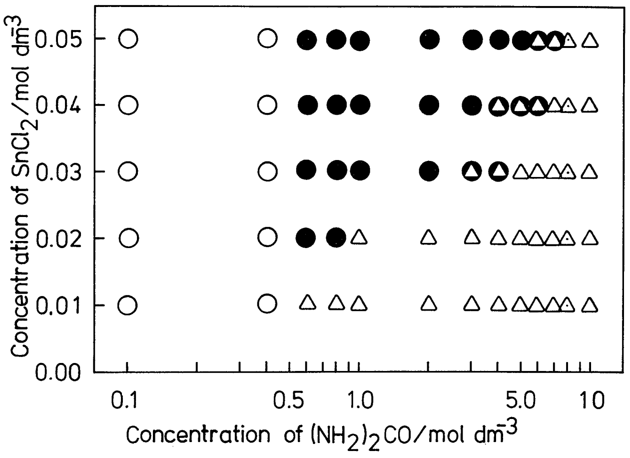

Fig. 3. Relationship between preparative conditions and the kind of products. The volume of the aqueous solution containing both $SnCl_2$ and $(NH_2)_2CO$ is 1 dm^3. ○: Amorphous compound, ●: tin(II) oxide, **○** mixtures of tin(II) oxide and $5SnO \cdot 2H_2O$, △: $5SnO \cdot 2H_2O$.

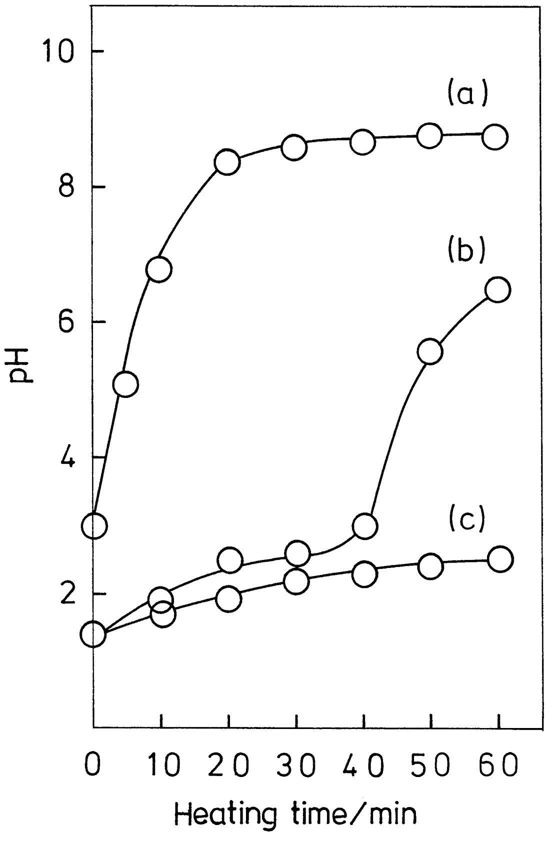

Fig. 4. Relationship between pH and the heating time of the aqueous solution (1 dm^3) containing both $SnCl_2$ (0.05 mol dm^{-3}) and $(NH_2)_2CO$: (a) 9.0 mol dm^{-3}, (b) 1.0 mol dm^{-3}, (c) 0.4 mol dm^{-3}.

tin(II) oxide was not produced. A tin(II) chloride solution with urea at a concentration lower than 0.4 mol dm^{-3} produced an amorphous compound; and tin(II) chloride solution with urea at a concentration higher than 0.6 mol dm^{-3} produced $5SnO \cdot 2H_2O$. The range of the concentration of urea which produced tin(II) oxide depended on the concentration of tin(II) chloride. The higher the concentration of tin(II) chloride, the wider was the range where tin(II) oxide was exclusively produced. Besides, a mixture of tin(II) oxide and $5SnO \cdot 2H_2O$ was produced from a tin(II) chloride solution with urea at a concentration higher than 0.6 mol dm^{-3}. $5SnO \cdot 2H_2O$ was produced exclusively from a solution of tin(II) chloride with urea at a higher concentration than the former one. When the solution of tin(II) chloride which produced tin(II) oxide was heated, a white precipitate was produced first. As the heating time was prolonged, the surface of the precipitate which had been kept in contact with the mother liquid changed, and a black precipitate was also directly produced from the mother liquid.

Figure 4 shows the relationship between the pH and the heating time of a solution of tin(II) chloride of 0.05 mol dm^{-3} with urea of 0.4, 1.0, 9.0 mol dm^{-3} concentration. When urea (0.4 mol dm^{-3}) was added to a tin(II) chloride solution, the pH gradually rose with the heating time. After 60 minutes, an amorphous compound was formed in the solution. When 1.0 mol dm^{-3} of urea was added, the pH gradually rose with the heating time, nearly settled for a while, and then rose again abruptly. After 60 minutes, tin(II) oxide was formed in the solution. When 9.0 mol dm^{-3} of urea was added, the pH abruptly rose with the heating time, and then nearly settled for a while. After 60 minutes $5SnO \cdot 2H_2O$ was produced in the solution. Both the amorphous compound before drying and $5SnO \cdot 2H_2O$ changed into tin(II) oxide upon aging in a solution of pH above 3.

These results have shown that the products which were formed in the solution with urea under heating were an amorphous compound, tin(II) oxide, and $5SnO \cdot 2H_2O$, and that the range producing these three compounds depended on the concentration of urea.

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