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Synthesis of hydrous SnO_2 and SnO_2-coated TiO_2 powders by the homogeneous precipitation method and their characterization

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Hydrous SnO_2 and SnO_2-coated TiO_2 powders were synthesized by the homogeneous precipitation method using urea and the products were characterized by X-ray diffraction, thermogravimetry, differential thermal analysis, scanning electron microscopy and energy-dispersive X-ray microanalysis. Electrical conductivities were measured with an impedance analyser. Hydrous SnO_2 powder prepared under conditions without SO_4^{2-} ions was a bulky product containing 75 wt% of water. The addition of SO_4^{2-} ions to the solution changed bulky hydrous SnO_2 to a dense product; approximately spherical particles were obtained with an average particle size of $0.14 \pm 0.03\,\mu$m with 13.5 wt% of absorbed water. Antimony-doped hydrous SnO_2 prepared under conditions with SO_4^{2-} ions consisted of approximately spherical particles with an average particle size of $0.17 \pm 0.04\,\mu$m with 15.0 wt% of absorbed water. Hydrous SnO_2-coated TiO_2 powders with a good dispersion state and with various Sn/Ti ratios were prepared under conditions with SO_4^{2-} ions. All the as-prepared coated powders were white, but the products doped with Sb^{3+} ions were turned to pale blue by heat treatment at 600° C for 1 h and their electrical conductivities increased by orders of about 3.0 in comparison with those of the other two.

1. Introduction

It is important to develop a new kind of method to prepare fine ceramic powders coated with other kinds of substance. These new kinds of powder are useful because it is possible to make a new class of powder with two different properties. For example, SnO_2-coated TiO_2 powder has the shielding power and UV absorption of TiO_2 and the electrical conductivity of SnO_2, and is of practical interest as a filler for plastic films [1]. In the conventional methods of adding a precipitant as a base into a reaction solution from the outside, even a weak base added to the solution makes the pH locally high. This leads easily to a voluminous hydroxide with various impurities. On the other hand, the homogeneous precipitation method is one of the best methods to control the pH and to form pure and dense precipitates [2, 3], because it produces a precipitant slowly in the solution. Syntheses of TiO_2 [4], Al_2O_3 [5, 6], $MgAl_2O_4$ [7], Fe_3O_4 [8, 9], $Fe(OH)_2$ [10], hydrous Al_2O_3 and Al_2O_3-coated Cr_2O_3 powders [11] by this method using urea have already been reported by several authors.

This paper deals with the synthesis of SnO_2-coated TiO_2 powders using the homogeneous precipitation method as a coating process and their characterization. Hydrous SnO_2 was first prepared by this method and the preparation conditions were investigated, and then the method was applied to the preparation of SnO_2-coated TiO_2 powders. Hydrous SnO_2 and SnO_2-coated TiO_2 powders were characterized with scanning electron microscopy (SEM), thermogravimetry, differential thermal analysis (TG-DTA) and X-ray diffractometry (XRD). Electrical conductivities were also measured.

2. Experimental procedure

Hydrous SnO_2 powders were prepared under three conditions: (i) in the absence of SO_4^{2-} ions, (ii) in the presence of SO_4^{2-} ions, and (iii) in the presence of SO_4^{2-} ions and Sb^{3+} as a dopant to enhance the electrical conductivity of SnO_2. The SnO_2 samples prepared under these three conditions were named S-1, S-2, and S-3, respectively. SnO_2-coated TiO_2 powders prepared under the same three conditions were also named T-1, T-2 and T-3, respectively.

Fig. 1 shows a flow-chart for the preparation of various hydrous SnO_2 powders. All reagents used were of guaranteed grade (Wako Chemical Co.) except for TiO_2. 300 ml of an aqueous solution of $SnCl_4 \cdot 5H_2O$ (10^{-2} M) and urea (1 M) was prepared in a three-neck flask with a capacity of 300 ml. The initial pH was adjusted to 0.5 by adding concentrated HCl. It was hydrolysed at 85° C for 4 h and then cooled with ice-water. The product was separated with a centrifugal separator and washed with deionized water. This separation and washing procedure was performed four times. Finally, the product was dried in an electric oven at 120° C for 5 h. S-2 and S-3 were also prepared according to the preparation conditions and procedures shown in Fig. 1.

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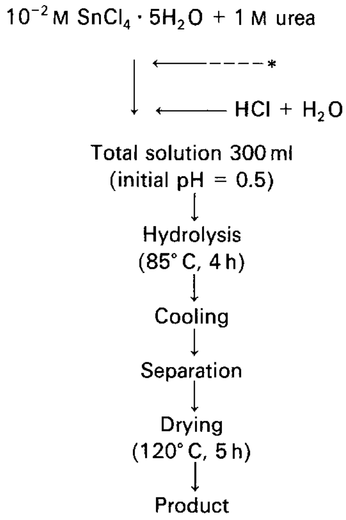

Figure 1 Flow-chart for the preparation of hydrous SnO_2 powders. The stages shown are for S-1; for others, the extra stage (*) involves the addition of 1.5×10^{-2} M $(NH_4)_2SO_4$ + 8.0×10^{-3} M H_2SO_4 for S-2, or 1.5×10^{-2} M $(NH_4)_2SO_4$ + 8.0×10^{-3} M H_2SO_4 + 10^{-3} M $SbCl_3$ for S-3.

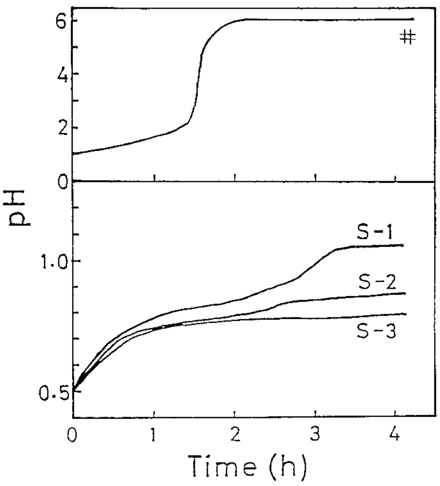

Figure 2 pH changes of the reaction solutions with reaction time at 85° C. (#) Blank test.

TiO_2 powder (rutile form) (Asahi Chemical Co.) consisting of approximately spherical particles with $0.2 \pm 0.04\,\mu m$ diameter was used to prepare SnO_2-coated TiO_2 powders. Various amounts of TiO_2 were added into the solutions for preparing the three kinds of hydrous SnO_2 as described above. Agitation was required throughout the hydrolysis in order to disperse TiO_2 particles in the reaction solution.

Characterizations of the synthesized powder were performed by several methods. Shapes and the agglomeration state of the particles were observed by SEM (Hitachi S-700). Particle sizes and the particle size distribution were measured with a digitizer and a personal computer. TG-DTA (Rigaku Denki Co.) was carried out in air, with a heating rate of 2° C min^{-1}. The crystallinity of the as-prepared and heat-treated hydrous SnO_2 was measured by powder XRD (Geigerflex, Rigaku Denki Co.). Electrical conductivities of pellets of prepared powders were measured by means of an a.c. two-terminal method with an impedance analyser (Yokogawa Hewlett Packard, LF4192A). Powder pellets with thickness approximately 1.0 mm and diameter 10 mm were prepared under a uniaxial pressure (1.28 ton cm^{-2}) and gold electrodes with diameter 7 mm were coated on both sides with an ion coater (Eiko IB-3). Sn/Ti ratios of SnO_2-coated TiO_2 powders were measured by an energy-dispersive X-ray microanalyser (EDX) (Kevex 7000).

3. Results and discussion

3.1. Formation of hydrous SnO_2 powder

Urea is hydrolysed to ammonia and carbon dioxide as follows:

$$CO(NH_2)_2 + H_2O \rightarrow 2NH_3 + CO_2$$

Urea is a good reagent for a hydrolytic process because of its very weak basic properties ($K_b = 1.5 \times 10^{-14}$) and higher solubility in water. It hydrolyses easily at 80 to 100° C and the hydrolysis can be quickly terminated at a desired pH by cooling the reaction mixture to room temperature. Moreover, the resulting carbon dioxide bubbles serve as an agitator.

Fig. 2 shows the pH change of the reaction solution. The curve designated by # shows the pH change when the solution of urea (2 M) with pH 1.0 is hydrolysed at 85° C for 4 h (blank test). This shows two inflections near pH 2.0 and 6.0. It was proved from this result that the hydrolysis of urea proceeds slowly up to pH 2.0 but over pH 2.0 it proceeds very fast.

In experiments on the formation of hydrous SnO_2,

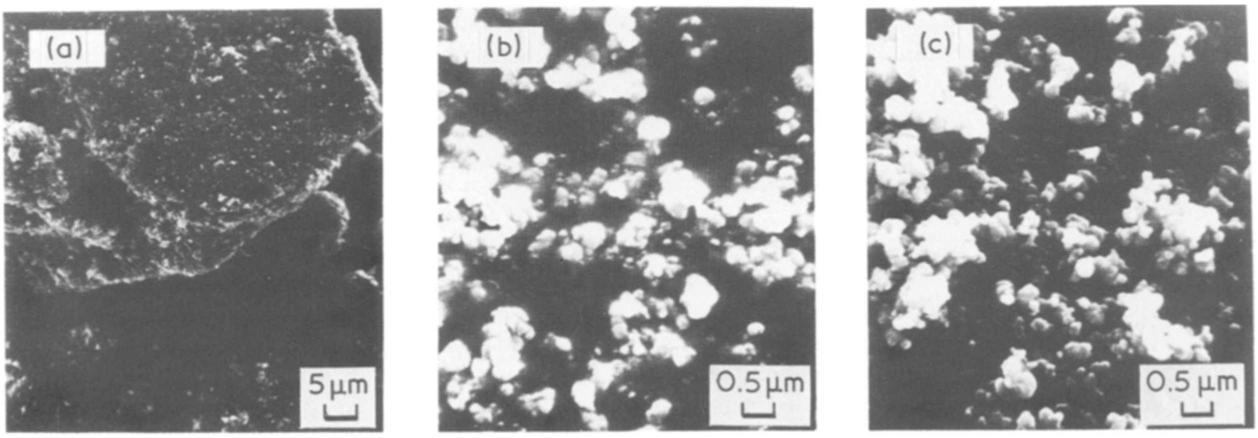

Figure 3 SEM photographs of hydrous SnO_2: (a) S-1, (b) S-2, (c) S-3.

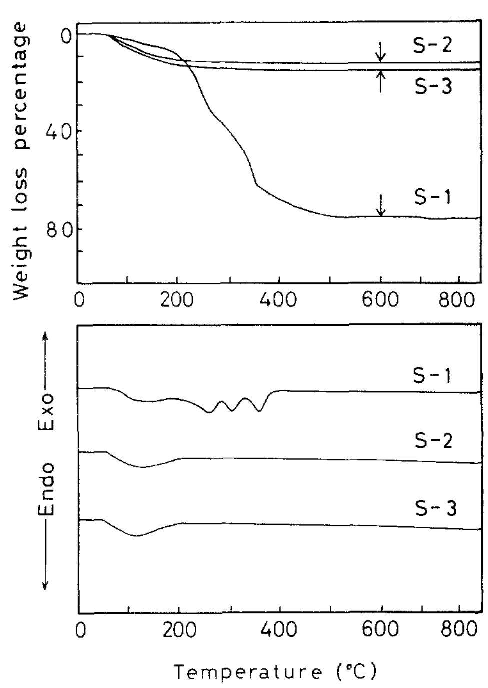

Figure 4 TG-DTA curves of hydrous SnO_2 powders.

the concentrations of 10^{-2} M $SnCl_4$ and 1.0 M urea were chosen, because when $[Sn^{4+}] > 10^{-2}$ M the resulting precipitate had a mushy and bulky form, and when $[Sn^{4+}] < 10^{-2}$ M a long reaction time was required. The initial pH was adjusted to 0.5 because the reaction ends at about pH 1.0.

S-1 began to be formed when the reaction time passed about 20 min. This was also observed as a change of the transparent reaction solution to become translucent. The S-1 formation continued for about 2 h. The slight rise of pH in the range of about 2.3 to 3.3 h is due to the decomposition of the remaining urea, and this indicates the completion of S-1 formation. The beginning of S-2 formation was delayed by 10 min beyond that of S-1, and this reaction also continued for about 2 h. The pH change of S-2 was smaller than that of S-1. This seems to be ascribed to the buffer action of SO_4^{2-} ions. S-3 began to be formed when the reaction time passed about 50 min. This was delayed by 30 min beyond that of S-1.

3.2. Characterization of hydrous SnO_2

All hydrous SnO_2 powders obtained were poorly crystalline products. Fig. 3 shows SEM photographs of these products. S-1 does not show a spherical product but S-2 and S-3 have approximately spherical shapes with some agglomeration. This can be understood by SO_4^{2-} ions in the reaction solution contributing to the formation of dense hydrous SnO_2. Average particle sizes, electrical conductivities and colours of these products are summarized in Table I. The average particle size of S-3 was larger than that of S-2, which seemed to be due to the prolonged reaction time. The electrical conductivity of S-1 could not be measured because its high water content (see TGA result) prevented us from preparing the pellets. S-3 had a higher electrical conductivity than S-2 as expected. Both electrical conductivities were increased by heat treatment at 600° C for 1 h. All heat-treated products except for S-3 were white powders.

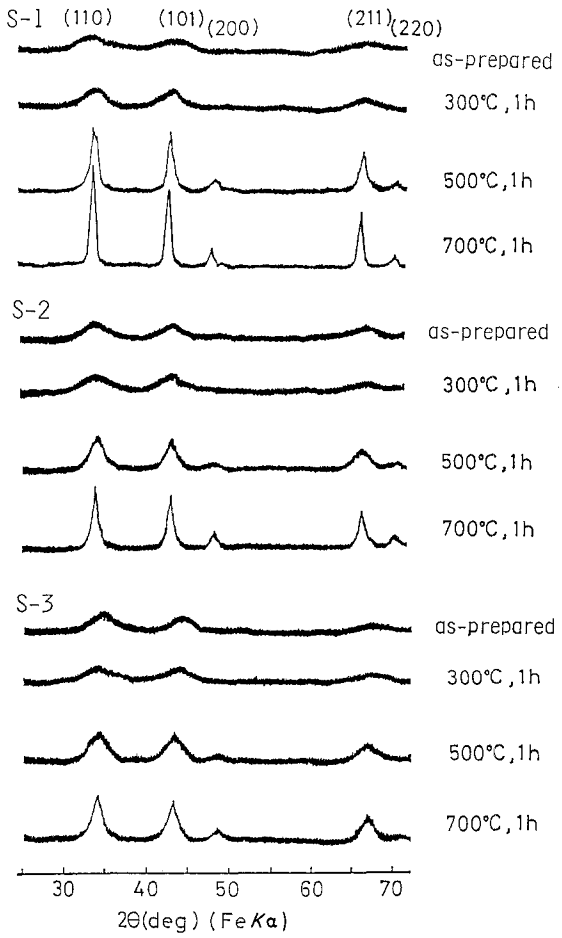

Figure 5 X-ray diffraction patterns of as-prepared and heat-treated SnO_2 powders.

Fig. 4 shows the TG-DTA curves of the hydrous SnO_2 powders. The weight of S-1 decreased mainly in the range 200 to 400° C, but those of S-2 and S-3 in the range 60 to 200° C. The weight loss for S-1 amounted to 75 wt % at 600° C and those for S-2 and

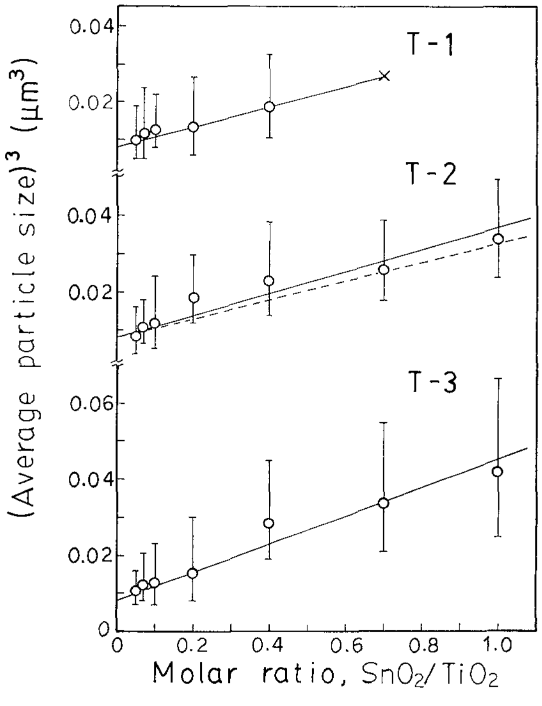

Figure 6 Variations of average particle size of various hydrous SnO_2-coated TiO_2 powders with SnO_2/TiO_2 molar ratio. (- - -) Theoretical variation of average particle size with SnO_2/TiO_2 molar ratio.

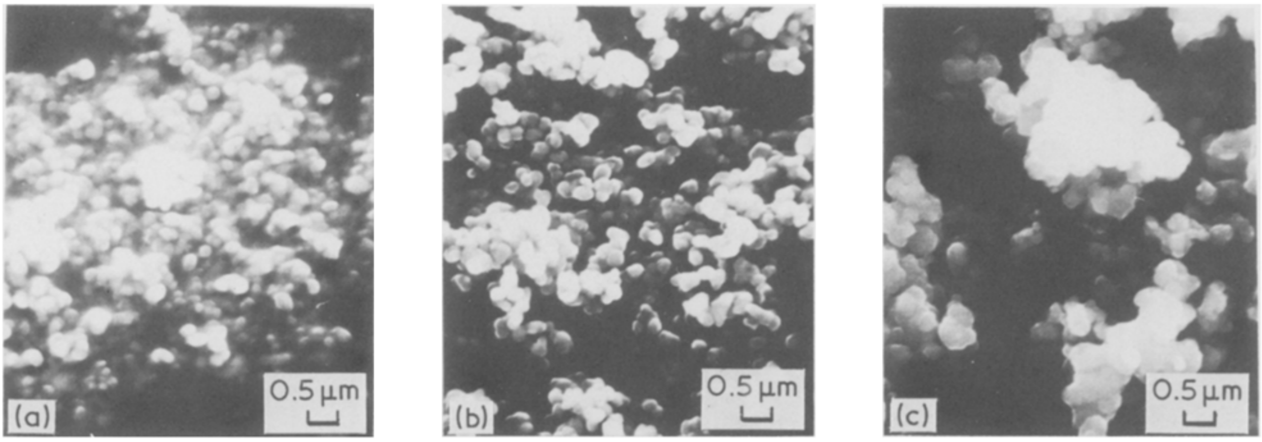

Figure 7 SEM photographs of hydrous SnO_2-coated TiO_2 powders. (a) TiO_2 only, (b) T-3 with SnO_2/TiO_2 = 0.1, (c) T-3 with SnO_2/TiO_2 = 1.0.

S-3 amounted to 13.4 and 15 wt % at 600° C, respectively. In DTA curves broad and weak endothermic peaks in the range 60 to 200° C were observed in all products. These correspond to the desorption of water. In addition to this peak, S-1 showed complicated endothermic peaks in the range of about 200 to 400° C. This seems to be due to the dehydration of its bonded water and to the decomposition of by-products such as NH_4Cl.

Fig. 5 shows the XRD patterns of as-prepared and heat-treated hydrous SnO_2 powders. These products corresponded to cassiterite. The crystallinities of S-1, S-2 and S-3 increased with an increase in heating temperature. The reason why S-1 showed a higher crystallinity with increasing heating temperature than the other two products is estimated to be due to its crystal growth resulting from the dehydration of bonded water. The fact that the crystallinity of S-3 was lower than that of S-2 is estimated to be due to the suppression of crystal growth by Sb^{3+} ions or the formation of a solid solution with Sb^{3+}.

3.3. Formation and characterization of SnO_2-coated TiO_2 powders

It is difficult to describe the formation mechanism of SnO_2-coated TiO_2 powders in detail. In general, TiO_2 powder has a high dispersibility in an aqueous solution and its surface is more active, compared with other metal oxides such as SiO_2, ZrO_2, MgO and ZnO [1]. Both TiO_2 and SnO_2 have the rutile type of structure. It is supposed that TiO_2 particles dispersed in the solution act as seeds or accelerators in the formation of hydrous SnO_2.

In order to confirm the formation of SnO_2-coated TiO_2 particles, it is preferable to observe cross-sections of the powders. This experiment was impossible because SnO_2-coated TiO_2 particles were of submicrometre size. Thus, indirect confirmation was used in this study; the products were characterized by the variation of particle size, weight loss, Sn/Ti ratio and electrical conductivity with increasing SnO_2/TiO_2 molar ratio.

Fig. 6 shows the variation of average particle size of the coated powders with increasing SnO_2/TiO_2 molar ratio. The relation between the average particle size D and the concentration of SnO_2, $[SnO_2]$, is expected to follow the relation $D^3 = a[SnO_2] + b$, where a and b are constants. The average particle sizes of these products were increased with an increase in SnO_2/TiO_2 ratio. The dotted line for T-2 in Fig. 6 shows a theoretical relation obtained under the assumption that the TiO_2 particles are spherical and SnO_2 forms a uniform layer on each particle. These straight-line relations were taken as an indirect proof of the formation of coated particles. However, T-1 with SnO_2/TiO_2 molar ratios of more than 0.4 aggregated strongly, so that the average particle size could not be measured. These results showed that SO_4^{2-} ions

TABLE I Data on average particle size and electrical conductivity of as-prepared and heat-treated hydrous SnO_2 powders and their colours

Sample name	Particle size (μm)		Electrical conductivity ($\Omega^{-1}\,cm^{-1}$)	Colour
	Average	Standard deviation		
S-1	–	–	–	White
S-2	0.14	0.03	3.41×10^{-5}	White
S-3	0.17	0.04	4.54×10^{-4}	White
S-1*	–	–	6.79×10^{-5}	White
S-2*	–	–	5.74×10^{-4}	White
S-3*	–	–	6.70×10^{-2}	Blue
BS-1†	0.20	0.04	6.10×10^{-8}	White

*Heat-treated at 600° C for 1 h.
†TiO_2 powder.

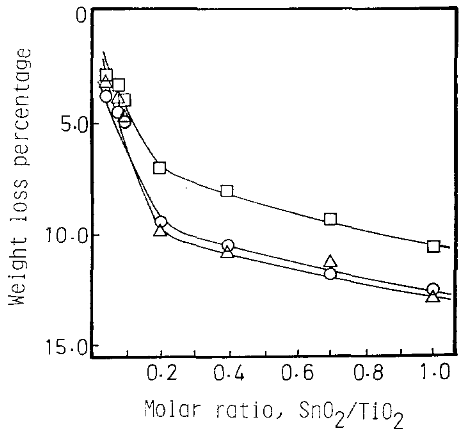

Figure 8 Variations of weight loss of hydrous SnO_2-coated TiO_2 powders with SnO_2/TiO_2 molar ratio, heated at 600° C. (○) T-1, (△) T-2, (□) T-3.

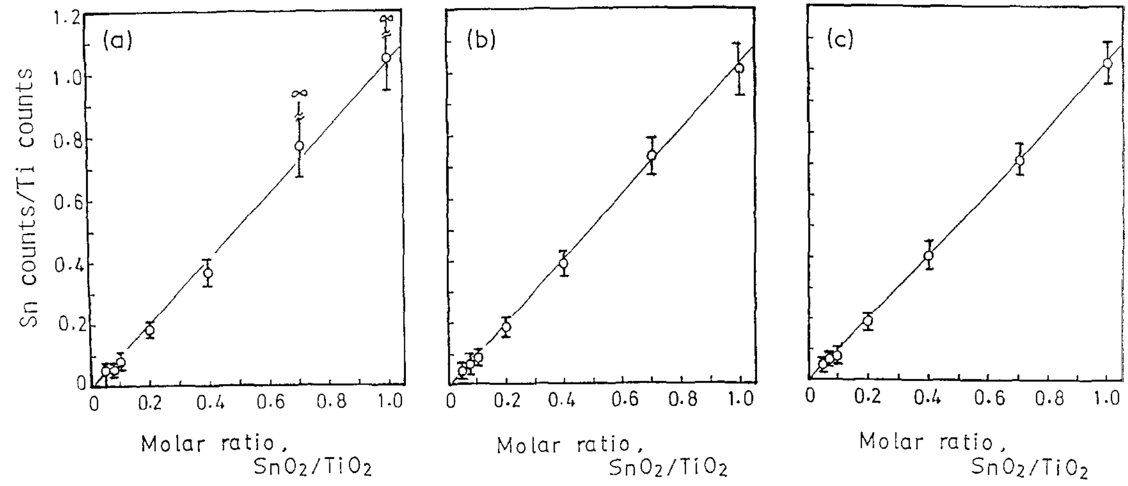

Figure 9 Sn/Ti ratios of hydrous SnO_2-coated TiO_2 powders with SnO_2/TiO_2 molar ratio. (○) Plane analysis, (⊢⊣) spot analysis. (a) T-1, (b) T-2, (c) T-3.

contributed to the formation of well-coated powders. Fig. 7 shows SEM photographs of the starting TiO_2 and two coated samples (SnO_2/TiO_2 = 0.1 and 1.0) of T-3. This shows the difference in their particle sizes between the starting TiO_2 powder and the other two coated ones.

Fig. 8 shows the weight loss of these coated powders heated at 600° C with increasing SnO_2/TiO_2 molar ratio. The weight losses also increased with an increase in SnO_2/TiO_2 molar ratio. The losses of T-2 and T-3 which were due to the desorption of water were similar to those of S-2 and S-3. The loss of T-1 was also similar to those of T-2 and T-3, in contrast to the fact that S-1 lost more water than S-2 and S-3. This may be ascribed to the action of TiO_2 particles as seeds or accelerators for SnO_2, or to the influence of the slightly dissolved Ti^{4+} ions from TiO_2.

In order to identify the element ratios of Sn/Ti in these coated powders EDX analysis was used. Fig. 9 shows X-ray count ratios of Sn/Ti for these products and the molar ratios of Sn/Ti in the starting solutions. Straight-line relations in Fig. 9 indicate that each particle contained the amount of SnO_2 and TiO_2 which was expected from the compositions of the starting solutions. This relation was also taken as an indirect proof of the formation of coated particles. However, in the case of T-1, some uncoated TiO_2 particles were observed in the product with SnO_2/TiO_2 molar ratio 0.05. In the products of SnO_2/TiO_2 molar ratios 0.7 to 1.0 some isolated hydrous SnO_2 particles were observed. The comparison of the results for T-1 and T-2 indicates that SO_4^{2-} ions contributed to the formation of well-coated powders.

Fig. 10 shows the electrical conductivities of as-prepared hydrous SnO_2-coated TiO_2 powders at room temperature. They increased with an increase in SnO_2/TiO_2 molar ratio but the expected trend was not obtained, showing a high electrical conductivity of T-3 in comparison with those of T-1 and T-2. The reason for this result could not be obtained directly because of various factors affecting the electrical conduction

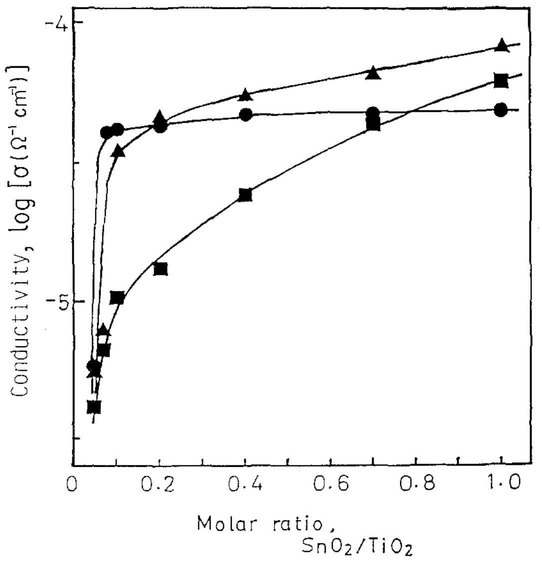

Figure 10 Variations of electrical conductivity of as-prepared hydrous SnO_2-coated TiO_2 powders with SnO_2/TiO_2 molar ratio at room temperature. (●) T-1, (▲) T-2, (■) T-3.

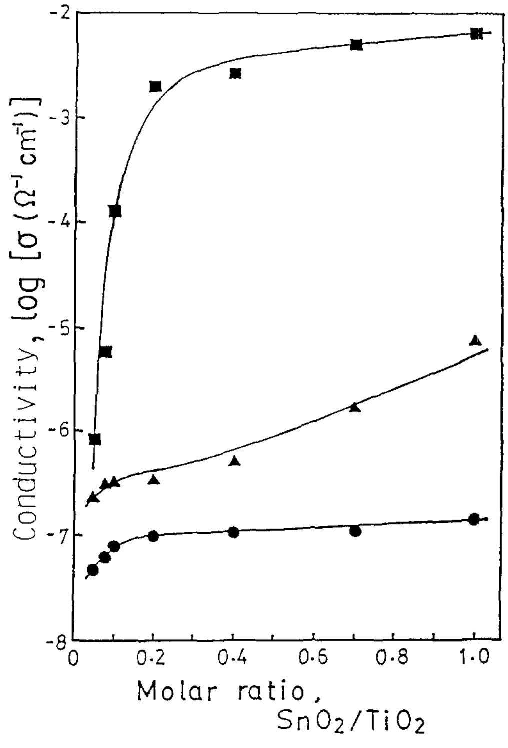

Figure 11 Variations of electrical conductivity of heat-treated SnO_2-coated TiO_2 powders (600° C, 1 h) with SnO_2/TiO_2 molar ratio at room temperature. (●) T-1, (▲) T-2, (■) T-3.

such as particle size and its distribution, shape and surface state of the particles, and so on [12]. Thus, in order to eliminate absorbed water and volatile impurities such as NH_4Cl, these products were calcined at 600° C for 1 h. Even after the heat treatment, a solid solution between SnO_2 and TiO_2 did not occur. Fig. 11 shows the electrical conductivities of these products at room temperature. Their electrical conductivities increased with an increase in SnO_2/TiO_2 molar ratio, showing the order of T-3 > T-2 > T-1 as expected.

T-1, T-2 and T-3 are white powders as well as hydrous SnO_2 powders, but heat treatment at 600° C for 1 h changed the colour of T-3 slightly to pale blue, which was caused by the presence of Sb^{3+} ions in SnO_2.

4. Conclusions

Hydrous SnO_2 and SnO_2-coated TiO_2 powders were synthesized by the homogeneous precipitation method using urea, and their characterization was carried out. The results obtained may be summarized as follows:

1. Hydrous SnO_2 prepared under conditions with out SO_4^{2-} ions was a bulky product containing 75 wt % water.

2. Hydrous SnO_2 prepared under condition with SO_4^{2-} ions consisted of approximately spherical particles with an average particle size $0.14 \pm 0.03\,\mu m$ containing 13.5 wt % of absorbed water.

3. Antimony-doped hydrous SnO_2 prepared by adding antimony ions into the solution along with the presence of SO_4^{2-} ions also showed approximately spherical particles with an average particle size $0.17 \pm 0.04\,\mu m$. Its water content amounted to 15.0 wt % of absorbed water and its electrical conductivity was higher than those of the other two.

4. Hydrous SnO_2-coated TiO_2 powders with a good dispersion state and with various Sn/Ti ratios were prepared under conditions with SO_4^{2-} ions.

5. Hydrous SnO_2-coated TiO_2 powders were changed to SnO_2-coated TiO_2 ones by heat treatment at 600° C for 1 h. The electrical conductivities of antimony-doped SnO_2-coated TiO_2 powders were increased by orders of about 3.0 in comparison with those of the other two.

6. All the as-prepared products were white, but the products doped with Sb^{3+} ions were turned to pale blue by heat treatment at 600° C for 1 h.

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