

Preparation of Mesoporous and Meso-macroporous Tin Dioxide Powders and Their Application to Sensor Materials

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Mesoporous SnO₂ (mp-SnO₂) and meso-macroporous SnO₂ (m·mp-SnO₂) powders were prepared by employing SnCl₄·5H₂O as a Sn source. Mesoporous structure was controlled by C₂₀H₃₇O₇SNa (AOT), while macroporous structure was controlled by polymethylmethacrylate (PMMA) microspheres. The mp- and m·mp-SnO₂ powders with and without SiO₂ and Sb₂O₅ additives were also prepared. Gas sensing properties of mp- and m·mp-SnO₂ pellet-type sensors to 1000 ppm H₂ were measured in the temperature range of 300 - 500°C. The addition of 9 wt% SiO₂ was effective for enhancing the specific surface area (SSA), but the simultaneous addition of Sb₂O₅ resulted in a decrease in SSA. The addition of Sb₂O₅ up to 10 wt% was found to reduce the sensor resistance in air, but beyond that it led to an increase in resistance. Among the sensors tested, mp-SnO₂ added with only 5 wt% Sb₂O₅ showed the highest H₂ response at 400°C.

1. Introduction

In recent years, a particular focus is currently being given to nano-structured SnO₂ powders as sensor materials. The present study is, therefore, directed to preparing thermally stable mp-SnO₂ and m·mp-SnO₂ powders aiming at improving their gas sensing properties. The effects of the addition of SiO₂ and Sb₂O₅ on the microstructure and H₂ gas sensing properties have also been examined.

2. Experimental

mp-SnO₂ and m·mp-SnO₂ powders were prepared by employing SnCl₄·5H₂O as a Sn source. Mesoporous structure was controlled by AOT, while macroporous structure was controlled by PMMA microspheres with a diameter of 800 nm.

Table 1 Preparation conditions and specific surface area of m·mp-SnO₂.

Sample	The amount of MO added to SnO ₂		SnCl ₄ ·5H ₂ O	Mesopore template (AOT)	Macropore template	pH adjusted	SSA (m ² g ⁻¹)
	MO: Sb ₂ O ₅ (using SbCl ₃)	MO: SiO ₂ (using TEOS)					
A	non	non	1.753 g	4.452 g	non	non	152.1
A-P							143.2
A-PT							262.7
A-PTS1	1 wt%	9 wt%			0.35 g	8.5	253.2
A-PTS5	5 wt%	non					220.8
A-S5					non	8.5	164.3
A-TS5							9 wt%
A-PS5	10 wt%	non			0.35 g	8.5	150.2
A-PTS10							218.2
A-PTS17							17 wt%
A-PTS33			33 wt%	171.6			
A-PTS50	50 wt%	168.9					

Typical preparation procedure of mp-SnO₂ and m·mp-SnO₂ was as follows. A given amount of each constituent listed in Table 1 was mixed in 400 ml of ultrapure water and the pH value of the resulting mixture was adjusted by adding an NH₃ aqueous solution to be 8.5 in some cases. As for tetraethoxysilane (TEOS) and SbCl₃, the amounts necessary to produce the given amounts of SiO₂ and Sb₂O₅ were added to the solution. The mixed solution was kept at 20°C for 3 days. The solution was evaporated to dryness in an oven at 80°C overnight. The resultant powder was then treated with a 0.1 mol m⁻³ phosphoric acid solution for about 2 h.

The powder was molded into the pellet at a pressure of 1000 kg cm⁻². Then the pellet was calcined in air at 600°C for 5 h. A pair of Pt electrodes was prepared on the pellet surface by screen printing. Hereafter each sample and sensor will be expressed by the abbreviations listed in Table 1. The gas sensing properties of the mp- and m·mp-SnO₂ pellet-type sensors to 1000 ppm H₂ were measured at a flow rate of 0.1 dm³ min⁻¹ in the temperature range of 300 - 500°C. Magnitude of the response was defined as the ratio (R_a/R_g) of sensor resistance in air (R_a) to that in 1000 ppm H₂ balanced with air (R_g).

3. Results and Discussion

Table 1 shows the specific surface area (SSA) of all the samples prepared. The SSA remained almost unchanged by the PMMA addition (compare A and A-P), but increased significantly by the 9 wt% SiO₂ addition (see A-PT). However, SSA decreased clearly with increasing the amount of Sb₂O₅ (see a series of A-PTS10 to A-PTS50).

Figure 1 shows variations in resistance of m·mp-SnO₂ sensors (A-PTS series) with the Sb₂O₅ amount added. It was revealed that the addition of Sb₂O₅ up to 10 wt% was found to reduce the sensor resistance in air. But, beyond that, it led to an increase in resistance with increasing the Sb₂O₅ additive amount, probably due to the solubility limit of Sb₂O₅. Thus, the A-PTS10 sensor showed the lowest resistance in air at 400°C. The resistance decrease can be explained by the valency control, i.e. partial substitution of Sn⁴⁺ sites with Sb⁵⁺ ions, producing free electrons, as described in Eq. (1).

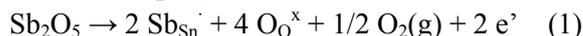


Figure 2 shows the temperature dependence of response to 1000 ppm H₂ of sensors. Among the sensors fabricated by the addition of Sb₂O₅ from 0 wt% to 50 wt%, A-TS5, i.e. m·mp-SnO₂ added with 9 wt% SiO₂ plus 5 wt% Sb₂O₅, showed the highest H₂ response (see Fig. 2 (a)). Fig. 2(b) compares the effect of introduction of macropores on the H₂ sensing properties of sensors added with 5 wt% Sb₂O₅ as well as 9 wt% SiO₂ plus 5 wt% Sb₂O₅. A-S5, i.e. mp-SnO₂ added with 5 wt% Sb₂O₅ showed the highest H₂ response among all the sensors tested. By comparing A-PS5 and A-PTS5, or A-S5 and A-PS5, the introduction of macropores was confirmed to be effective for shortening the recovery time.

From these results, it was revealed that the addition of SiO₂ was found to increase the SSA of the m·mp-SnO₂ powder. The sensor resistance in air could be reduced by the addition of Sb₂O₅. The recovery time could be reduced by the introduction of macropores.

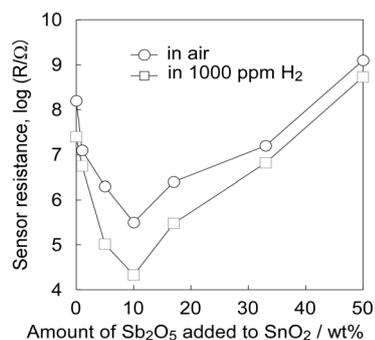


Fig. 1 Variations in resistance of m·mp-SnO₂ sensors (A-PTS series) with the Sb₂O₅ amount added.

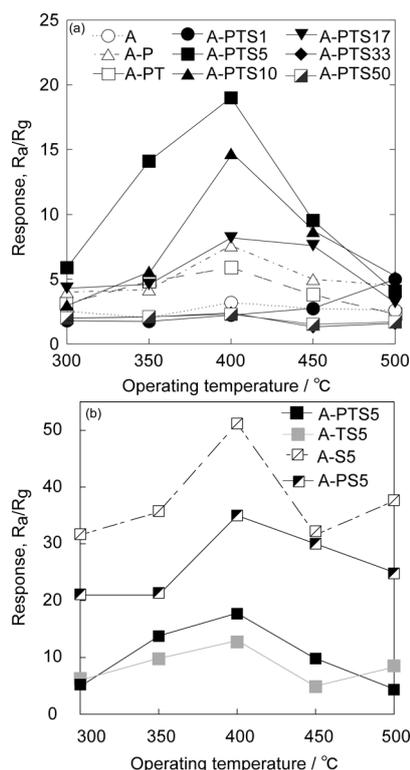


Fig. 2 Temperature dependences of response of sensors to 1000 ppm H₂.