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Preparation of nanosize SnO_2 particles in an aerosol reactor by pyrolysis of tetra-*n*-butyl tin

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Possibility of preparing nanosize SnO_2 particles from alkyl metal by pyrolysis was tested. SnO_2 particles with a diameter of 10 to 45 nm were obtained from tetra-*n*-butyl tin (TNBT) in a tubular aerosol reactor. Crystalline SnO_2 particles began to be formed over 500 °C. The size of SnO_2 particles was increased with increasing concentration of precursor and decreasing reaction temperature. The number density in the reactor was in the order of 10^{14}/ml. IR spectrum showed that the alkyl group was completely removed and the color became bright white as the reaction temperature was increased. Oxygen concentration was found to be around 80% for complete removal of alkyl group.

1. Introduction

SnO_2 is widely used as a basis of gas sensor and materials for solar cell and conductive particles. SnO_2 is a n-type semiconductor with a wide band-gap. The conductivity of SnO_2 is improved by the addition of adequate doping materials. Doped SnO_2 particles are used as materials of a light transparent conductive film because SnO_2 particles have properties such as IR reflection and visible light transmission.

The particles used as materials in light transparent conductive films have a diameter ranging from 10 to 100 nm. Nanosize particles have special physical and chemical characteristics. These particles are more active than bulk materials due to their high surface-to-volume ratio. Nanosize particles have wide range of applications either as conductive particles or in the form of sintered nanophase materials.

Nanosize SnO_2 particles were prepared in liquid phase by precipitation method [1] and sol-gel method [2, 3]. These particles were also made in gas phase by sputtering method [4], evaporation-oxidation of bulk tin metal [5, 6] and spray pyrolysis method [7, 8].

Precursors used in preparation of tin oxide are mainly tin chloride, tin sulfate, and tin acetylacetonate. These precursors have to be dissolved in water or alcohol for the particle preparation. If an aerosol reactor is to be used for the production, precursors with high vapor pressure is needed. However, most of precursors of high vapor pressure are in alkoxide or akyl metal form. So the incompletely decomposed carbon becomes a source of low performance in transparency and conduction.

In this study, tetra-*n*-butyl tin (TNBT) was used as a precursor for producing nano-sized SnO_2 particles in a furnace type aerosol reactor. The possibility of using alkyl metal as precursor and controlling of particle size by varying the concentration of precursor and temperature was tested.

2. Experimental

The experimental system for preparing nanosize SnO_2 particles was shown in Fig. 1. The length and diameter of reactor are 120 and 5 cm respectively. The rate of feed flow was maintained at 3 l/min O_2 and 1 l/min N_2, and the auxiliary flow was fixed at 1 l/min O_2. The residence time for TNBT vapor in the aerosol reactor was 28.2 sec. The decomposition of TNBT in aerosol reactor is carried out by the following equation.

$$Sn(C_4H_9)_4 + 26O_2 \rightarrow SnO_2 + 16CO_2 + 18H_2O$$

The apparent rate of decomposition of TNBT was obtained from measuring the change of conversion of TNBT with changing reaction variables. The influence of initial precursor concentration and reactor temperature on the decomposition of TNBT was analyzed with gas chromatograph with flame ionization detector. IR study of SnO_2 particles prepared in this work was conducted to know if any unreacted precursor was remained in the particles. Particle size was measured with transmission electron microscope (TEM). Formation of crystal phase of SnO_2 particles was checked with XRD.

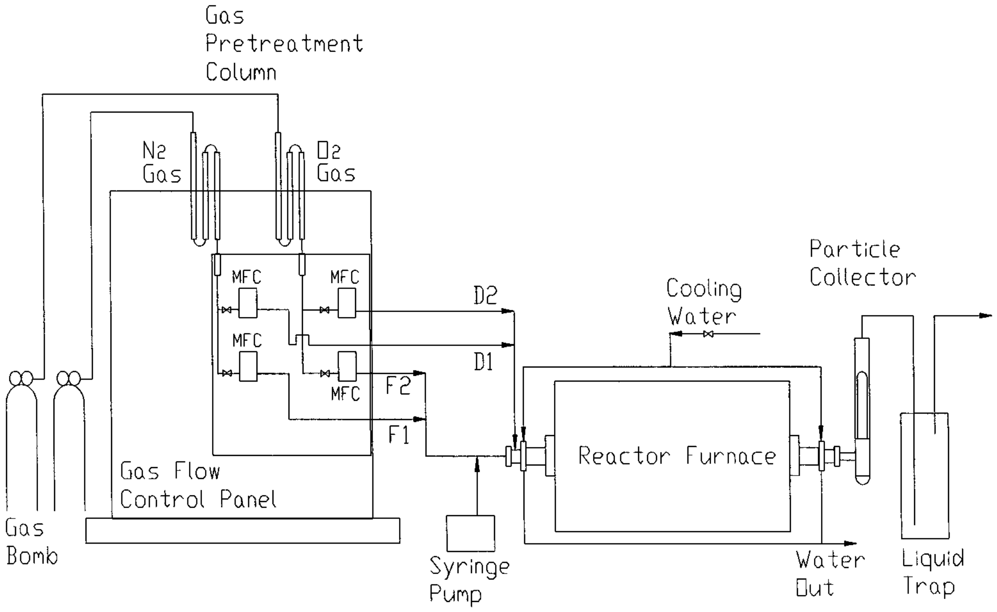

Figure 1 Experimental system for producing nanosize SnO_2 particles.

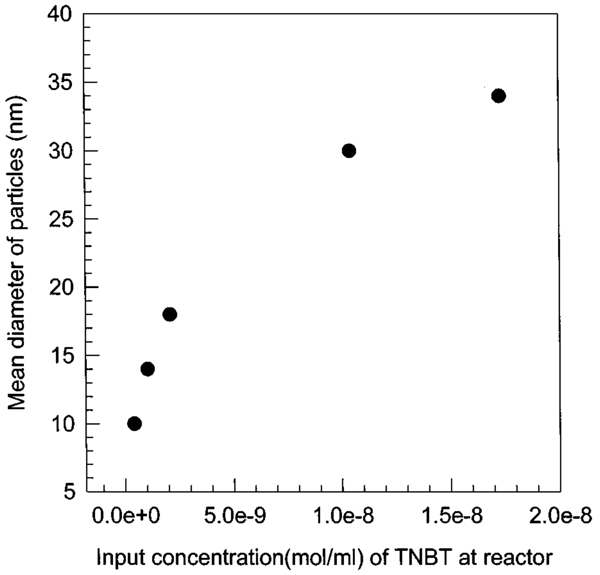

Figure 2 Change in particle size of SnO_2 with input concentration on TNBT.

3. Results and discussion

When TNBT was decomposed at low oxygen concentration, the color of the produced particles was black because of the incomplete decomposition of precursor. Therefore, 80% of oxygen gas was used as a carrier gas for complete decomposition of the precursor.

The estimation of reaction order and rate constant was carried out at an excess oxygen condition. The theoretical mole ratio for complete removal of alkyl group was 26 to 1. In this work, input mole flow rate of oxygen gas was 100 times higher than that of hydrocarbon gas produced. The conversion of the decomposition reaction of TNBT was independent of the input concentration of precursor at constant temperature, which indicated that the decomposition of TNBT was the first order reaction. The activation energy was −5147.8 J/K·mol. The apparent rate equation of decomposition reaction of TNBT was the following.

$$-r_A = 7.361e^{\frac{-5147.8}{RT}} C_A \quad (\text{mol/ml·min})$$

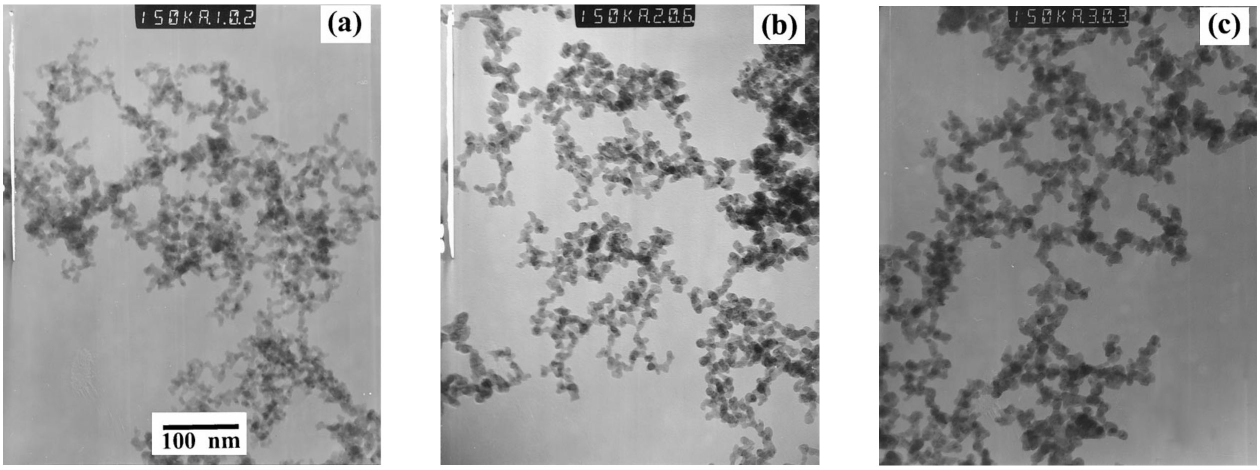

Figure 3 TEM Photographs of produced SnO_2 particles. Input concentration of TNBT is (a) 4.16×10^{-10} (b) 1.04×10^{-9} (c) 2.08×10^{-9} (d) 1.04×10^{-8} (e) 1.73×10^{-8} mole/ml. (*Continued*).

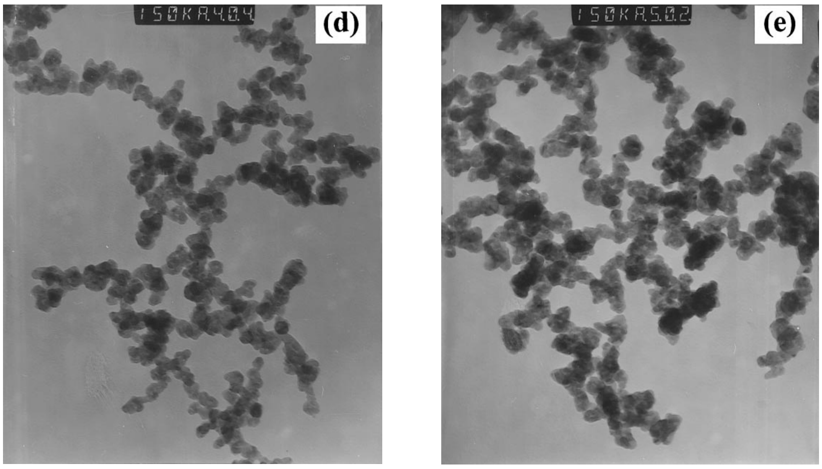

Figure 3 (*Continued*).

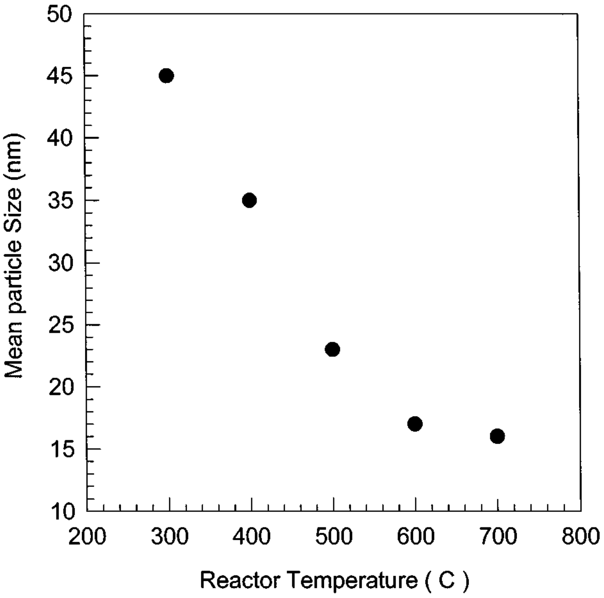

Figure 4 Change in particle size of SnO_2 with reaction temperature.

The mean size of particles with changing the initial concentration of TNBT is shown in Fig. 2. The reactor temperature was set at 600 °C at which the conversion of TNBT was unity. The mean size of particles was increased from 10 to 34 nm with increasing initial concentration of TNBT from 4.16×10^{-10} to 1.73×10^{-8} mol/ml. The TEM photographs of SnO_2 particles produced at the corresponding concentrations are shown in Fig. 3. The number concentration of particles from the precursor concentration and the measured particle size was ranged from 2.52×10^{14} to 3.21×10^{14}. Considering that the precursor concentration was changed by a factor of 40, this change in the number concentration is taken to be almost constant over the concentration range of this experiment.

Temperature effect on the formation of SnO_2 particles was examined and the results were summarized in Fig. 4. TEM photographs of these particles at the corresponding temperatures were shown in Fig. 5. The mean size of SnO_2 particles was decreased from 40 to 17 nm with increasing reaction temperature from 300 to 700 °C . The initial mole flow rate of TNBT was fixed at 3.05×10^{-5} mol/min. This temperature dependency of particle size can be explained by the densification of fluffy particles as the reactor temperature is increased. Fliedlander showed that the temperature dependency of titania, alumina, and niobia particles were consistent with the prediction based on the solid diffusivity of each components [9].

The particles produced at 300 °C was yellowish color. The color was changed into white with increasing reaction temperature. From the apparent rate equation, the conversion of TNBT at 300 °C was calculated to be 0.42. Therefore, unreacted TNBT was adsorbed on the produced SnO_2 particles. The color change with

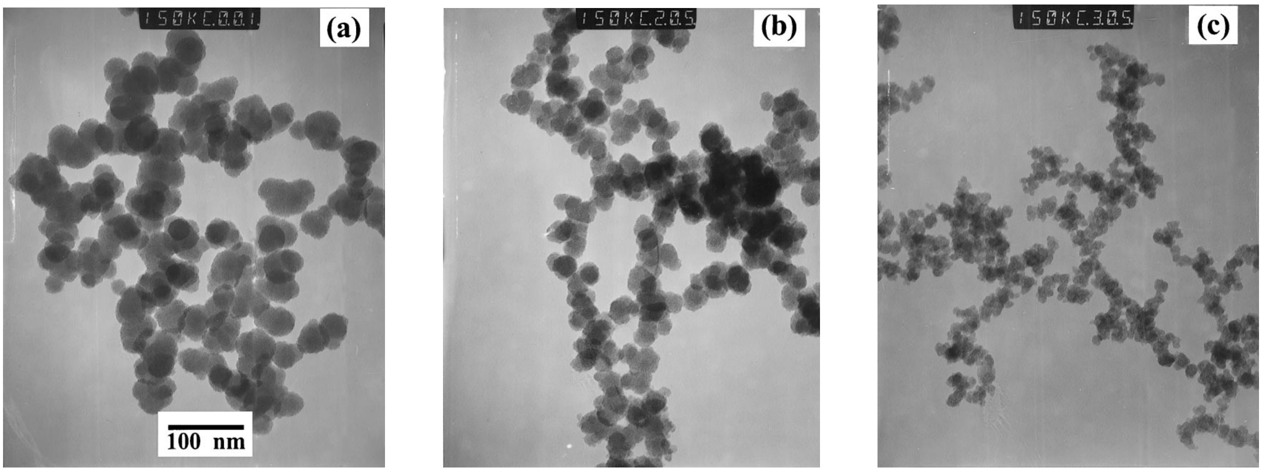

Figure 5 TEM photographs of produced SnO_2 particles at (a) 300 °C (b) 400 °C (c) 500 °C (d) 600 °C (e) 700 °C. (*Continued*).

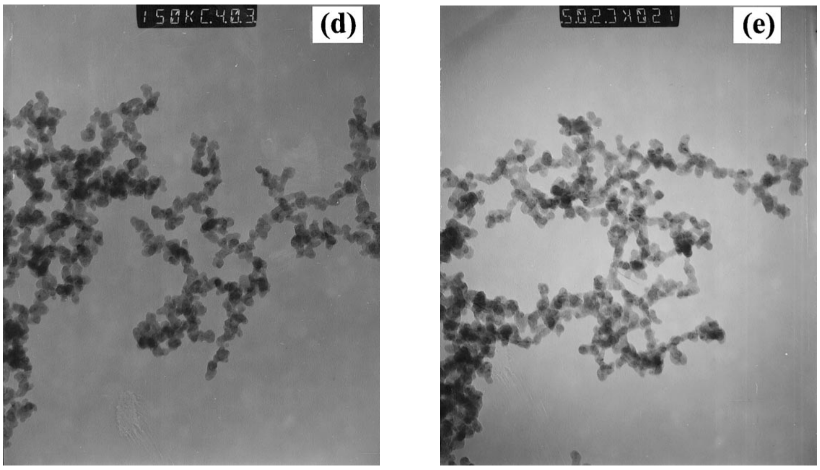

Figure 5 (*Continued*).

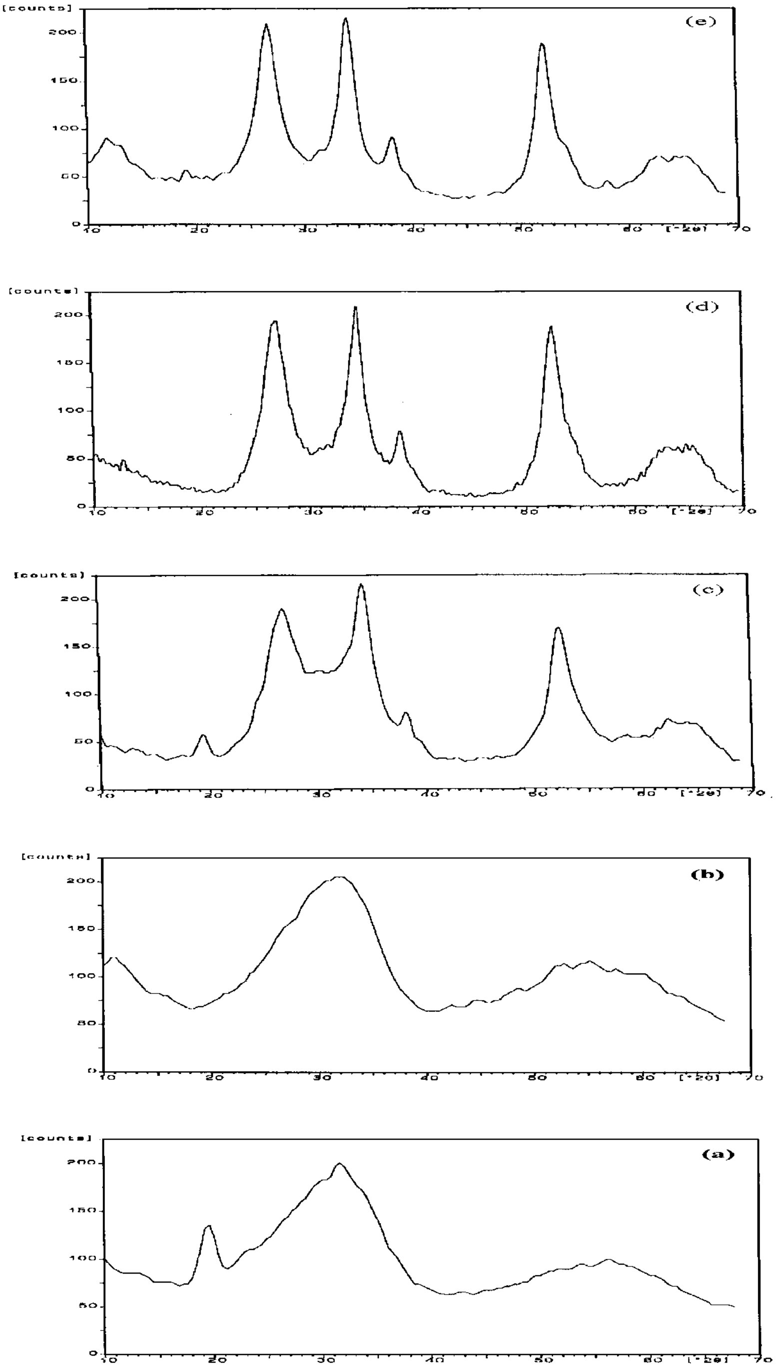

Figure 6 X-ray diffraction pattern of SnO_2 particles at (a) 300 °C (b) 400 °C (c) 500 °C (d) 600 °C (e) 700 °C.

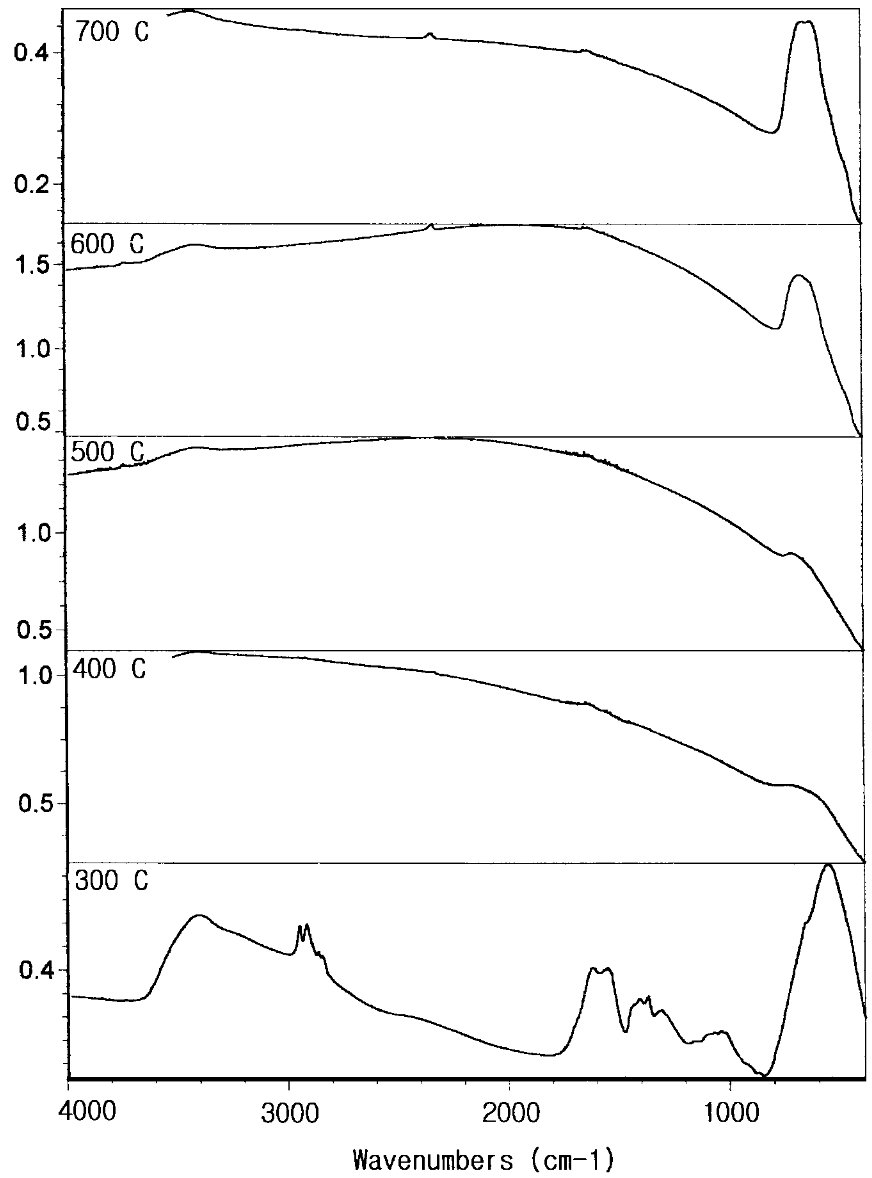

Figure 7 IR spectra of SnO_2 particles.

increasing temperature was summarized in Table I. The quantification of color was carried out with Minolta Chroma Meter (model CR-200). The x and y values based on CIE 1931 (x, y)-Chromaticity Diagram.

The IR spectra of SnO_2 particles are shown in Fig. 6. The particles prepared at 300 °C were shown band stretching at wave number 2900 to 3000 and 1300 to 1500 for alipahatic C-H and CH_2 or CH_3, respectively. These band stretching disappeared and Sn-O peak at wave number 600 to 700 was developed with increasing reaction temperature. According to the XRD spectrum, as shown in Fig. 7, SnO_2 particles produced at low temperature had an amorphous phase, however, the particles produced over 500 °C had distinct crystal phase.

TABLE I Color change of SnO_2 particles with increasing temperature

Temp (°C)	300	400	500	600	700
Lightness	54.92	42.99	45.57	66.16	77.17
x value	0.3633	0.3218	0.3152	0.3096	0.3184
y value	0.3653	0.3296	0.3245	0.3193	0.3310
Color	Yellowish	Gray	Gray	Dark white	Bright white

4. Conclusion

Thermal decomposition of TNBT was found to be the first order with respect to the TNBT in the tubular aerosol reactor. The apparent rate equation for TNBT decomposition was $-r_A = 7.361e^{\frac{-5147.8}{RT}} C_A$. The SnO_2 particles with a crystal phase was started to be formed over 500 °C. The mean size of particles was increased from 10 to 34 nm with increasing the initial concentration of TNBT from 4.16×10^{-10} to 1.73×10^{-8} mol/ml at 600 °C. The mean size of SnO_2 particles was decreased from 40 to 17 nm with increasing reaction temperature from 300 to 700 °C. Alkyl group of the precursor was completely removed and the color became bright white as the reactor temperature was reached up to 700 °C.

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