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Effects of oxygen on the properties of titania nanoparticles prepared by MOCVD

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Anatase titania nanoparticles are prepared using pyrolysis of titanium tetrabutoxide in oxygen free and oxygen containing atmospheres by MOCVD method. Influence of oxygen on the properties of the titania nanoparticles is investigated, followed by discussion. The results show that oxygen influences not only the particle size but also the particle size distribution of the nanoparticles. With increasing oxygen flow rates, the average grain sizes of the nanoparticles decrease and the particle size distributions become uniform. Oxygen exerts great influence on the nucleation rate of the nanoparticles and reaction kinetics occurred in the reactor. The formation of titania nanaoparticles by MOCVD is not a growth controlled process, but is a nucleation rate controlled process.

1. Introduction

Nanocrystalline materials are gaining increasing importance in many fields by virtual of their considerably different and evidently improved properties [1–3]. Titania nanoparticles play important roles in the technology fields such as pigments, catalysts and supports, cosmetics, ceramics and so on [4]. Traditionally, titania particles are prepared by the two main production routes, the sulfate and chloride processes. Very unfortunately, the two processes both have significant process sections operating under aggressive conditions [5]. Compared with sulfate route, the chloride method, which is a CVD method and a consecutive process, does not involve batch operation, a large quantity of liquid/solid byproducts' treatment, strong tendency of hard aggregates formation, and is a preferred method from the viewpoint of environment protection [6]. However, the chloride process is a high temperature process and the oxidation of titanium chloride vapor is carried out at high temperatures ranging between 1200 and 1723 K [7]. In order to lower preparation temperature, titanium alkoxide is selected as titanium source material instead of titanium chloride [8, 9]. The advantage of using titanium alkoxide liquid is that high surface area titania nanoparticles can be prepared at low temperatures without generating aggressive gases [10–12]. By using titanium alkoxide as titanium source material, titania nanoparticles were prepared mainly via pyrolysis or hydrolysis. For example, Okuyama *et al.* [13] prepared titania particles by thermal decomposition of titanium isopropoxide (TTIP) at temperatures ranging between 400 and 600°C and the effects of preparation temperature and TTIP vapor concentration on the microstructure, and particle size distribution were studied systematically. P. P. Ahonen *et al.* [14] found that anatase titania particles could be prepared via pyrolysis of titanium tetrabutoxide (TTB) at 500°C in nitrogen and 580°C in air, respectively, indicating that the microstructures of the particles were influenced by atmospheres. Shimakawa *et al.* [15] prepared titania particles at a low temperature of 257°C by hydrolysis of TTIP and studied the effects of water vapor on the particle size, surface area, and crystallization temperature of anatase. However, there is no detailed report on the preparation of titania nanoparticles by the oxidation of TTB, and the effects of oxygen in the oxidation of TTB on the properties of the nanoparticles and the mechanism of titania nanoparticle formation are far from fundamental understanding.

In addition, yokozawa *et al.* [16] originally studied titania films grown by thermal decomposition of TTIP in the presence of different concentrations of oxygen. The presence of oxygen greatly increased the film growth rate and the reaction appeared to be at least first order in oxygen concentration. The apparent activation energy for film formation in oxygen free atmosphere was estimated to be about 36 Kcal/mol, while it was about 6.5 Kcal/mol in oxygen containing atmosphere. Based on these results, it is suggested, therefore, that

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oxygen will exert great influence on the properties of the nanoparticles in the oxidation of TTB by oxygen, and decrease the particle size by increasing nucleation rate.

As we know, MOCVD technology has been widely used in the thin film preparation of superconductors [17], semiconductors [18], ferroelectrics [19] and metals [20]. Special MOCVD reactors have been designed and set up for the preparation of thin film materials [21, 22]. In our previous work [23–25], a special MOCVD apparatus is designed and set up for the preparation of nanoparticles. By this method, it is possible to deposit a very large variety of elements and compounds with controllable composition, structure, perfection, and purity that are difficult or impossible to attain by other techniques. It is also found in our previous paper [26] that high surface area anatase titania nanoparticles with weak agglomeration can be prepared by MOCVD at temperatures ranging between 500 and 1000°C. In this paper, we study the effects of oxygen on the properties of titania nanoparticles prepared by MOCVD and the mechanism of titania nanoparticle formation is also proposed.

2. Experimetal

Titania nanoparticles are prepared by hot wall low pressure MOCVD using titanium tetrabutoxide as starting precursor in oxygen free and oxygen containing atmospheres. The apparatus used is shown schematically in Fig. 1. A 1.2 meter-long quartz tube with internal diameter of 92 mm is used as reactor. Preparation temperatures are measured by three thermocouples that are inserted into the furnace. All gas lines have bypass capability, and the gas flow in each line and the reactor pressure can be controlled by a computer automatically. TTB, which is liquid at room temperature, is used as the organometallic precursor. The vapor of the OM precursor is carried by high purity argon gas to the reactor, and the gas line is heated by a heating tape to avoid condensation. Pure oxygen is used as oxidant. In a typical run, the system is pumped down and purged with argon gas for about 20 minutes before the heater is turned on. After the reactor temperature stabilizes, deposition is initiated by switching OM and oxygen gas from bypass line into the reactor. At the end of deposition, OM line, bypass line, and the reactor are purged by nitrogen gas for about 10 minutes. The details of the apparatus and experimental procedures can be found elsewhere [24].

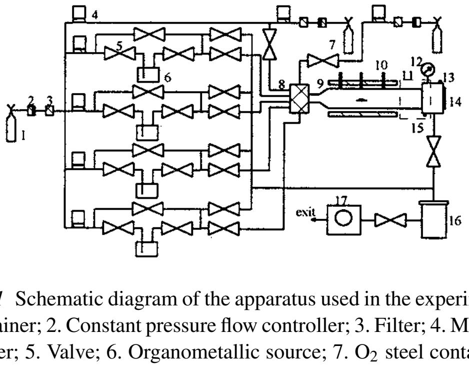

Figure 1 Schematic diagram of the apparatus used in the experiment. 1. Ar container; 2. Constant pressure flow controller; 3. Filter; 4. Mass flow controller; 5. Valve; 6. Organometallic source; 7. O_2 steel container; 8. Mixing chamber; 9. Furnace; 10. Thermocouple; 11. Collection zone; 12. Vacuum gauge; 13. Water outlet; 14. Water inlet; 15. Sample door; 16. Cold trap; 17. Pump.

The as prepared particles are collected in the collection zone by thermophoresis. The thermophoretic velocity v_{th} is proportional to the temperature gradient [27]:

$$v_{\text{th}} = k\nu \Delta T/T, \tag{1}$$

where k is a constant for a given particle size, ν the viscosity of the gas, and T the temperature. The collection efficiency of the particles can be found in reference [28].

X-ray diffraction (D/max-2400, Japan) is used to characterize the microstructure of the particles. Change in the average grain size of the particles is determined by using Scherrer formula [29]. Particle size distributions of the nanoparticles are studied by transmission electron spectroscopy (JEM-200CX, Japan).

3. Results and discussion

In order to study the effects of oxygen on the properties of titania nanoparticles prepared by MOCVD, the samples are prepared in oxygen free and oxygen containing atmospheres. Table I summarizes the average grain sizes of the nanoparticles prepared at different oxygen flow rates. The samples are prepared under the condition that total gas flow rate and carrier gas flow rate are kept constant at 1800 and 300 sccm (standard cubic centimeter per minute), respectively. The preparation temperature is 800°C and TTB source temperature is controlled at 125°C. It can evidently be seen from Table I that with the increase of oxygen flow rates, the average grain sizes of the particles decrease. The average gain size of the particles prepared in oxygen free atmosphere is 25.0 nm, while it decreases remarkably after adding oxygen in the reaction atmosphere. When the oxygen flow rate is 1500 sccm, the average grain size of the nanoparticles is decreased to 12.9 nm, indicating that oxygen exerts great influence on the average sizes of the particles. Moreover, the average grain size of the particles decreases very fast with increasing oxygen flow rate below 500 sccm, while it decreases very slowly with increasing oxygen flow rate above 500 sccm. The results clearly show that the presence of oxygen in the reaction atmosphere has great influence on the average grain size of the particles while oxygen flow rate exerts little influence on that in oxygen containing atmosphere.

The formation of titania nanoparticles by MOCVD consists of two processes, that is, homogeneous nucleation and growth. In oxygen free atmosphere, titania nanoparticles are prepared by pyrolysis of TTB according to the following reactions:

$$\mathrm{Ti(OC_4H_9)_4(g) \rightarrow TiO_2(g) + 4C_4H_8(g) + 2H_2O(g)} \tag{2}$$

$$n\mathrm{TiO_2(g) \rightarrow n(TiO_2)(s)} \tag{3}$$

TABLE I Average grain sizes of the nanoparticles prepared at different oxygen flow rates

Oxygen flow rate	0 sccm	500 sccm	1000 sccm	1500 sccm
Average grain size	25.0 nm	15.8 nm	14.1 nm	12.9 nm

However, in oxygen containing atmosphere, different reactions take place in MOCVD reactor compared with that in oxygen free atmosphere. In oxygen containing atmosphere, TTB vapor is decomposed first by pyrolysis which is the same as that in oxygen free atmosphere as shown in reaction (2). It is worth noting [30] that C_4H_8 can react with oxygen at 800°C according to

$$C_4H_8(g) + 6O_2(g) \rightarrow 4CO_2(g) + 4H_2O(g) \quad (4)$$

Therefore, total reactions that occur in oxygen containing atmosphere can be described as

$$\mathrm{Ti(OC_4H_9)_4(g)} + 24O_2(g) \rightarrow TiO_2(g) + 16CO_2(g) + 18H_2O(g) \quad (5)$$

$$n\mathrm{TiO_2(g)} \rightarrow \mathrm{n(TiO_2)(s)} \quad (6)$$

Then, the concentration of titania monomer vapor in the reactor increases with the proceeding of reaction (5) and the particles produced in the reactor by reaction (6) continue to grow to final particles as a result of particle-particle collision and adsorption-reaction-fusion mechanism.

From the above analysis, it can be clearly seen that after the addition of oxygen in the reaction atmosphere, reaction (2) shifts to the right-hand side. In this case, the reaction rate and therefore the nucleation rate of reaction (2) will increase. In fact, the particle size of the nanoparticles is determined by the relative magnitudes of nucleation rate and growth rate. Because the average grain size is almost equal to the particle size of the nanoparticles in MOCVD process under the conditions studied in the present work [20], it is reasonable that the average grain size of the particles decreases after the addition of oxygen in the reaction atmosphere. This can explain why the average grain size of the particles decreases very fast with increasing oxygen flow rate below 500 sccm. Moreover, that the average grain size of the nanoparticles decreases very slowly with increasing oxygen flow rate above 500 sccm maybe because the concentration of oxygen in the reactor has reached so sufficient level compared with that of TTB that oxygen exerts little influence on the nucleation rate of the particles.

This nucleation rate effect can also be briefly depicted in Fig. 2. In oxygen free atmosphere, the reactions occur in the reactor can reach completion in a long time, while in oxygen containing atmosphere the reactions can immediately reach completion. So all the reactant converts into particles in a very short time which prevents further growth of the particles. The particle size, therefore, decreases. It can also be deduced from Fig. 2 that the particle size distribution of the nanoparticles prepared in oxygen containing atmosphere should be more uniform than that prepared in oxygen free atmosphere because the differences in growth time between the particles are smaller in oxygen containing atmosphere. In order to examine this hypothesis, the particle size distributions of the nanoparticles prepared in oxygen free and oxygen containing atmospheres are studied by TEM and the results are shown in Fig. 3. It can be clearly seen from Fig. 3 that the particle size distributions of the nanoparticles become uniform after the addition of oxygen in the reaction atmosphere, indicating that the particle formation in MOCVD reactor is not a growth controlled process, but is a nucleation rate controlled process under the conditions studied in the present work.

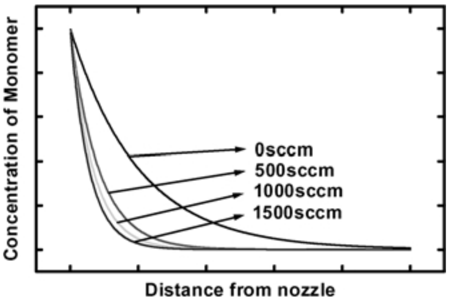

Figure 2 Effect of oxygen on monomer concentration.

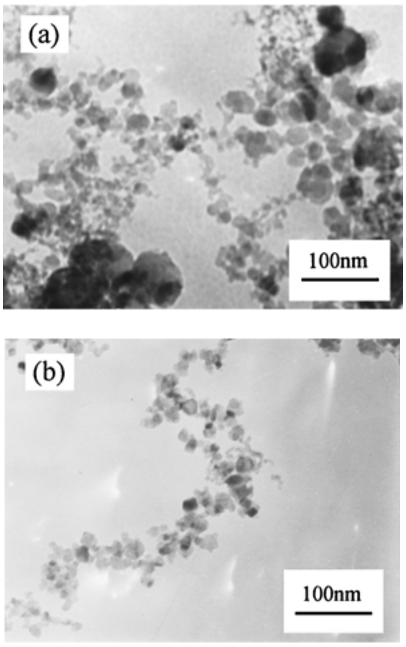

Figure 3 Particle size distributions of titania nanoparticles prepared in (a) oxygen free and (b) oxygen containing atmospheres.

4. Conclusions

Anatase titania nanoparticles are prepared using pyrolysis of titanium tetrabutoxide in oxygen free and oxygen containing atmospheres by MOCVD method. Effects of oxygen on the properties of titania nanoparticles are examined. Broadly speaking, oxygen exerts great influence on the particle size and particle size distribution of the nanoparticles. The particle size of the nanoparticles decreases very fast with increasing oxygen flow rate below 500 sccm, while it decreases very slowly with increasing oxygen flow rate above 500 sccm. After the addition of oxygen in the reaction atmosphere, the nucleation rate of the nanoparticles increases. Therefore, the particle size of the particles decreases very fast. However, when the concentration of oxygen in the reactor reaches a sufficient level (oxygen flow rate is greater than 500 sccm), it decreases very slowly with increasing oxygen flow rate. Because the differences in growth time between the nanoparticles are smaller in oxygen containing atmosphere, the particle size distribution of the nanoparticles prepared in oxygen containing atmosphere is more uniform compared with that in oxygen free atmosphere. The particle formation in MOCVD reactor is not a growth controlled process, but is a nucleation rate controlled process under the conditions studied in the present work.

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