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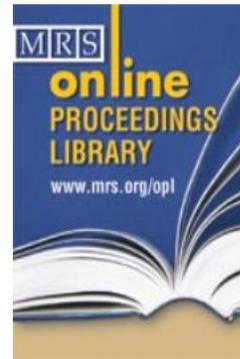
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Synthesis of TiO₂ Nanoparticles Using Chemical Vapor Condensation

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ABSTRACT

Nano-sized TiO₂ particles are of interest for many applications, including use as photocatalysts and in heat transfer fluids (nanofluids). In the present study, TiO₂ nanoparticles with controllable phase and particle size have been obtained through homogeneous gas-phase nucleation using chemical vapor condensation (CVC). The phase and particle size of TiO₂ nanoparticles under various processing conditions have been characterized using x-ray diffraction and transmission electron microscopy. Chamber temperature and pressure were found to be two key parameters affecting particle phase and size. Pure anatase phase was observed for synthesis temperatures as low as 600 °C with chamber pressure varying from 20-50 Torr. When the furnace temperature was increased to 1000 °C at a pressure of 50 Torr, a mixture of anatase and rutile phases was observed, with the predominant phase being anatase. The average particle size under all the experimental conditions was observed to be less than 20 nm.

INTRODUCTION

TiO₂ is widely used in many diverse applications, including photocatalysis, paint, and electronics, and heat transfer fluids. A nanocrystalline microstructure is desirable in many of these applications. For example, nano-sized TiO₂ particles exhibit unique photophysical and photocatalytic properties compared with bulk TiO₂ [1, 2]; the sintering temperature of nanocrystalline TiO₂ is much lower than that of micron-sized TiO₂; nanofluids containing TiO₂ nanoparticles are expected to have much higher thermal conductivity than that of the base fluids, leading to enhanced heat transport efficiency in heat transfer fluids[3, 4].

Many nanoparticle synthesis routes have been explored so far [5, 6], among which gas-phase synthesis techniques possess advantages including high purity, good size controllability and low cost. In the present study, chemical vapor synthesis (so-called chemical vapor condensation or CVC) of TiO₂ nanoparticles based on homogeneous gas-phase nucleation has been carried out. In this method, small clusters (monomers) form by decomposition of a metal-organic precursor. These monomers then aggregate to form larger clusters, *i.e.*, nanoparticles. Condensation of the particles occurs when the vapor is supersaturated. Similar procedures have been used in the past by others to produce powders or porous coatings [7, 8]. In the present study, the process was modified to allow dispersion of the nanoparticles into fluids. Observations of the thermal conductivity behavior of these nanofluids will be reported elsewhere [9]. Operation parameters affecting the particle phase and size have been investigated in this study. As will be demonstrated, the CVC process is found to be ideal for producing nanofluids containing oxide nanoparticles of size ≤ 20 nm and excellent dispersion properties.

EXPERIMENTS

TiO₂ nanoparticles were synthesized using chemical vapor condensation (CVC) in this study in a 3-zone furnace. This reaction system has three precursor delivery lines and three temperature zones at different furnace heights such that the temperatures in each zone can be varied independently. A schematic diagram of this system is shown in Figure 1. A quartz rod was inserted into the furnace and a glass beaker was placed around the furnace outlet at the bottom, both serving as particle collectors. A glass beaker containing base fluids serves as particle collector in case of making nanofluids (dispersion of nanoparticles in fluids). Titanium isopropoxide (Ti[OCH(CH₃)₂]₄, 99.999%, Alfa Aesar, Ward Hill, MA) was used as the metal-organic precursor. The liquid precursor was contained in a bubbler delivery system in an ethylene glycol bath. A heating element was used to control the temperature of the bath, which was stirred with pressured air to provide temperature uniformity. A precursor temperature of 60 °C was used for all studies reported here. The precursor was delivered into the furnace chamber from the precursor line 3 (shown in Fig. 1). The carrier gas was N₂ introduced from the top of the furnace chamber and O₂ was input as well for the chemical reaction. Flow rates of N₂ and O₂ typically used are 500 and 300 sccm, respectively. The operation temperature (temperature of zone 3) was varied from 1000 to 600 °C and chamber pressure was varied from 5-50 Torr.

The chemical and phase compositions together with the sizes of the particles under all conditions were investigated using x-ray diffraction (XRD, Phillips X'Pert-MPD x-ray diffractometer) and transmission electron microscopy (TEM, Phillips CM 30). The particle size was obtained both from TEM images and peak broadening in XRD patterns.

RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of TiO₂ particles synthesized at various temperatures with a chamber pressure of 50 Torr. Note that anatase phase is the predominant phase at all temperatures. Rutile phase is also observed at 700 °C, 800 °C and 1000 °C while only the anatase phase forms

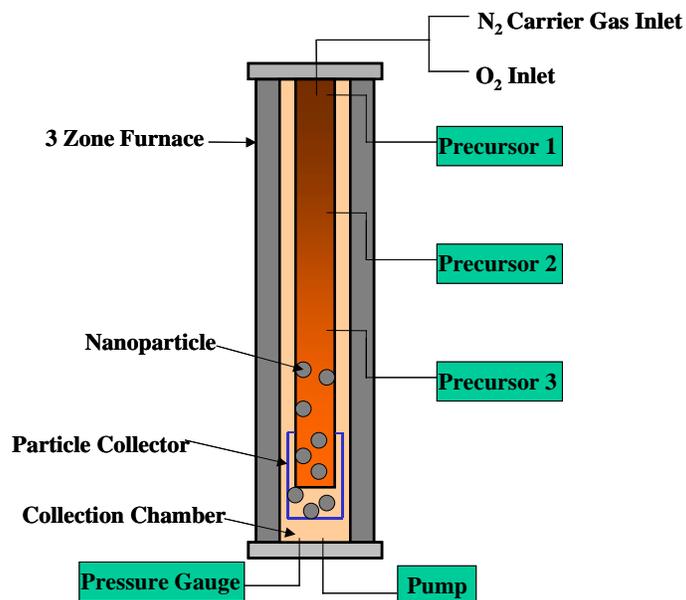


Figure 1. Schematic diagram of 3-zone furnace of chemical vapor condensation (CVC).

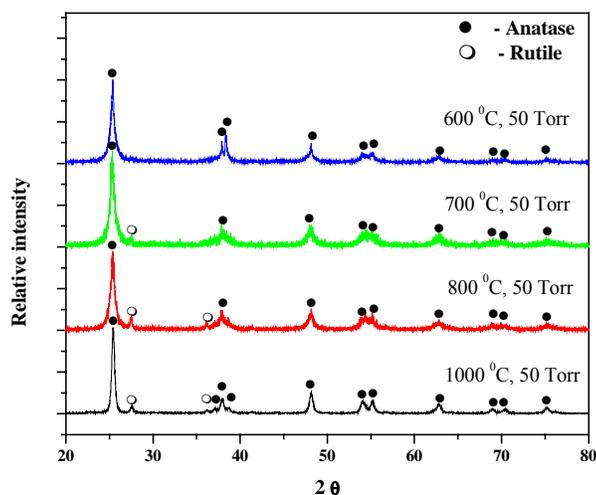


Figure 2. XRD patterns of TiO₂ particles synthesized at temperatures from 1000 °C to 600 °C at chamber pressure of 50 Torr.

when the synthesis temperature drops to 600 °C. The XRD peak intensities of the rutile phase decrease as the synthesis temperature decreases, indicating a decreasing rutile content in the mixture. Also it is noted that the XRD peaks broaden as the furnace temperature decreases, indicative of smaller nanoparticle formation.

Figure 3 shows the pressure dependence of particle phase and size of TiO₂ nanoparticles obtained from CVC. It is seen obviously from both figure 3(A) and figure 3(B) that the diffraction peaks broaden in the patterns at both 1000 °C and 600 °C as the chamber pressure decreases. At 1000 °C, a mixture of rutile and anatase phases was observed when the chamber pressure was 50 Torr with average particle size of ~ 20 nm, while pure anatase formed at 5 Torr with finer particle size (~ 7 nm). At 600 °C, TiO₂ nanoparticles of pure anatase phase form at chamber pressure of 50 Torr with particle size of ~ 14 nm and at 20 Torr with particle size of ~ 12 nm, respectively. No particles formed at 600 °C when the chamber pressure was decreased to 5 Torr.

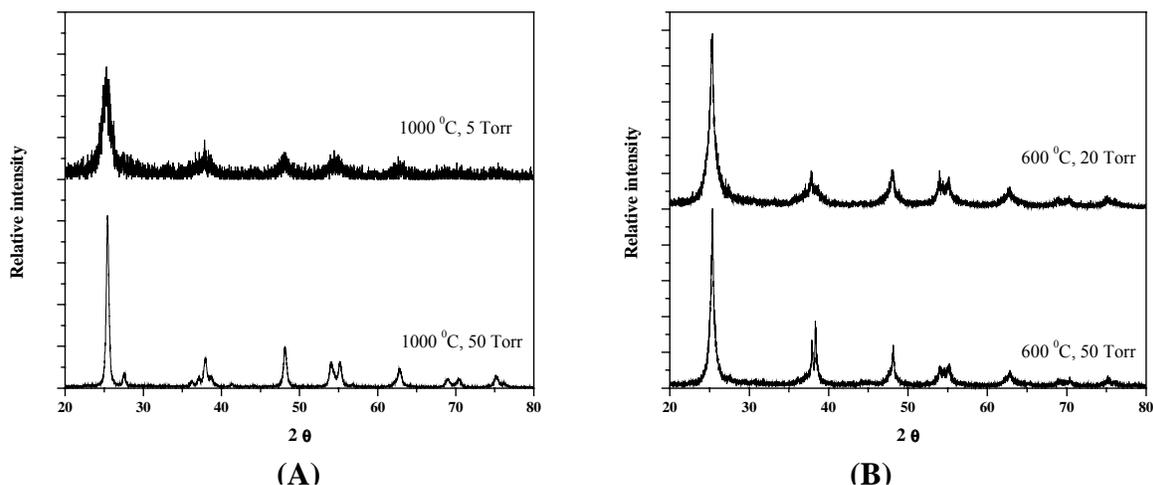


Figure 3. XRD patterns of TiO₂ particles at different chamber pressures at synthesis temperatures of (A) 1000 °C and (B) 600 °C.

To verify the results from XRD, the TiO₂ nanoparticles were investigated using TEM. Figure 4 (A) and (B) are the typical TEM images of TiO₂ particles obtained at 1000 °C, 50 Torr, and 600 °C, 50 Torr, respectively. Consistent with the XRD results, TiO₂ particles synthesized at 1000 °C and 50 Torr were a mixture of rutile and anatase with an average particle size of 20 nm. Synthesis at 600 °C and 50 Torr resulted in an average particle size of about 14 nm.

The formation of TiO₂ nanoparticles through CVC occurs in the following sequential steps : i) Titanium isopropoxide vapor is introduced into reaction chamber and is activated by collisions with carrier gas N₂. ii) TiO₂ monomers (small clusters) form from the reaction between precursor vapor and O₂ at high temperatures. iii) TiO₂ monomers condense into larger clusters by homogeneous gas-phase nucleation. iv) TiO₂ nanoparticles form in the gas phase and are transported by the carrier gas to the collectors (the surface of quartz rod and the wall of glass beaker) or into the liquids contained a glass beaker to form nanofluids.

According to the bulk equilibrium TiO₂ phase diagram [10], the transition temperature from the low-temperature anatase phase to the high-temperature rutile phase occurs about 700 °C. However, our experiments show that the anatase is still the predominant phase even at synthesis temperatures as high as 1000 °C. This is not unexpected since Zhang and Banfield [11] have pointed out that anatase becomes more stable than rutile when the particle size is smaller than certain critical value. According to the thermodynamic analysis, the phase boundary of anatase to rutile transformation can be calculated when the standard free energy of the phase transformation is equal to zero, *i.e.*,

$$\Delta G^0 = 0. \quad (1)$$

The ΔG^0 can be expressed as the following equation [11]:

$$\Delta G^0 = \Delta_f G^0 (T, \text{rutile}) - \Delta_f G^0 (T, \text{anatase}) + A_R \gamma_R - A_A \gamma_A, \quad (2)$$

where $\Delta_f G^0$ is the standard free energy of rutile and anatase formation, A is the molar surface area

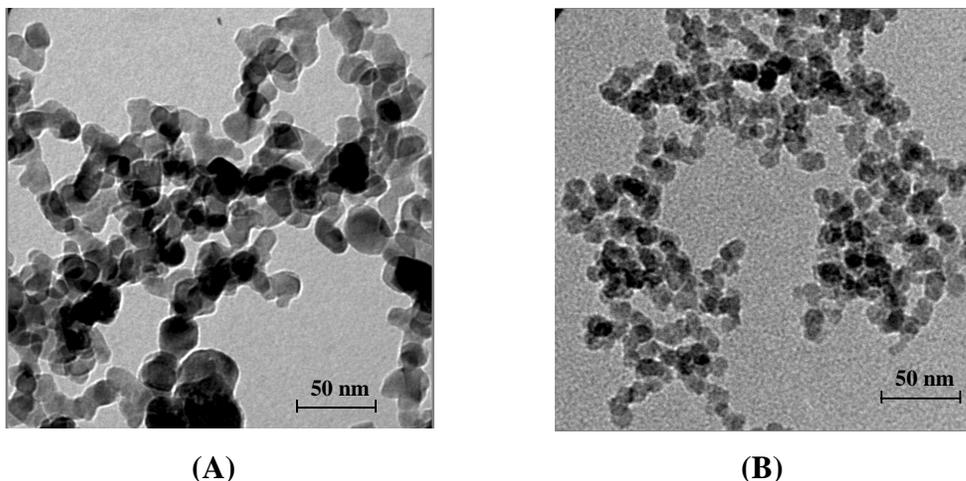


Figure 4. TEM images of TiO₂ particles at synthesis conditions of (A) 1000 °C, 50 Torr, and (B) 600 °C, 50 Torr.

and γ is the surface free energy. Subscripts R and A represent rutile and anatase, respectively. If we consider a spherical particle, the surface area can be described as

$$A = 3 \frac{V}{r}, \quad (3)$$

where V is the molar volume and r is the radius of the particles. Combining equations (1), (2) and (3), we know that the anatase to rutile transition occurs at certain temperature and certain particle size. Therefore, as particle size decreases, the anatase to rutile transformation temperature increases. Zhang *et al.* [11] have estimated that the average particle size of anatase when rutile was first detected is 14 nm in the temperature range 300–1000K.

CONCLUSIONS

In this study, nanocrystalline TiO₂ particles were synthesized using chemical vapor condensation with controllable phase and size. The particle phase and size varied with synthesis temperature and the pressure of furnace chamber. The particle size of TiO₂ decreases when we decrease the furnace temperature and/or lower the pressure of reaction chamber. Under the present experimental conditions, anatase is found to be the predominant phase.

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