In-Situ TEM Observation on Phase Formation of TiO_2 Nanoparticle Synthesized by Flame Method

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Abstract

TiO_2 nanoparticle was synthesized by the flame method, which was controlled by varying the ratio and flow rate of gas mixtures consisting of oxygen (oxidizer), methane (fuel) and nitrogen (carrier gas). The crystalline phases of TiO_2 nanoparticle depended strongly on the temperature distribution in the flame, whereas the morphology was not sensitive. We proved that the anatase phase formed without the phase transformation in the flame and the rutile phase generated through several phase transformations.

Keywords : titania, flame method, aerosol, nucleation, phase transformation

1. Introduction

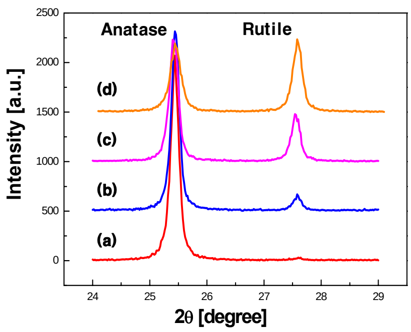
It has been well known that the photocatalytic properties of the titania (TiO_2) nanopowder which has polymorphic structures [1] are decided by the anatase to rutile ratio [2]. Therefore, many researchers have tried to control the phase ratio of anatase and rutile during the manufacture of TiO_2 nanopowder.

To date, the synthesis of nanopowder using the flame method have focused on the effects of various operating parameters on the size, shape and phases of TiO_2 nanopowders [2-7]. In the flame method, on the other hand, the formation behavior of TiO_2 nanoparticle has been reported that the nanoparticle is manufactured by the coalescence of tiny particles and the crystal structure is decided on the highest peak temperature of flame [6-7]. It is known that the high peak temperature leads to the formation of anatase phase. However we did not find the systematic study on the phase formation and evolution of TiO_2 nanoparticle. In this work, we tried to investigate the formation behavior of the anatase and rutile nanoparticle in flame using in-situ TEM observation.

2. Experimental and Results

A precursor of TiO_2 tetraisopropoxide (TTIP) was used for synthesizing TiO_2 nanoparticle. The TTIP was vaporized in the oil bath and transported into the horizontal burner nozzle by nitrogen. The used gases were oxygen (oxidizer), methane (fuel) and nitrogen (carrier gas) [6].

Fig. 1 shows the X-ray diffraction [(XRD) Philips XRD 3003] of TiO_2 nanoparticle manufactured with the different temperature gradient controlled by changing the mixing ratio of gases. We could control the phase ratio of anatase and rutile by changing the gas ratio.



$O_2/CH_4/N_2$
(a) 1.0/0.9/0.5
(b) 0.2/0.3/0.5
(c) 0.3/0.3/0.5
(d) 1.0/0.3/0.5

Fig. 1. XRD spectra of TiO_2 nanoparticles synthesized at the various flow rates

We observed that the phase ratio of anatase and rutile strongly depends on the distribution curve of the flame temperature. According the gas condition, various temperature distributions were made in the flame. The anatase TiO_2 nanoparticle was manufactured in the temperature distribution, which the flame is compressed in the total length of flame (<50 mm) and has a stiff cooling rate. On the other hand, the rutile TiO_2 nanoparticle was formed in the temperature distribution of the flame which spreads out long.

The microstructures of TiO_2 nanoparticles synthesized at the flow rates of oxygen/methane/nitrogen = 0.5/0.3/0.5 (100% anatase) and 1/0.6/0.5 (50% rutile). Although the particles were synthesized by the different flame condition, the general morphologies (spherical shape about 70 nm) of nanoparticle were similar.

Figs. 2 shows the flame photos, its temperature distributions, and TEM SAD patterns of TiO_2 synthesized by two distinguishable flame conditions, the condition of 100% anatase and 95% rutile, respectively. In Fig. 2(a), TiO_2 nanoparticle was an anatase phase at all the positions of flame. In the Fig. 2(a), the TiO_2 nanoparticle shows a broad anatase ring pattern (SAD I) and subsequently has a sharp anatase ring pattern without the transformation to rutile phase (SAD II, III, and IV). It means that the crystallinity of the anatase particle is more enhanced in the flame.

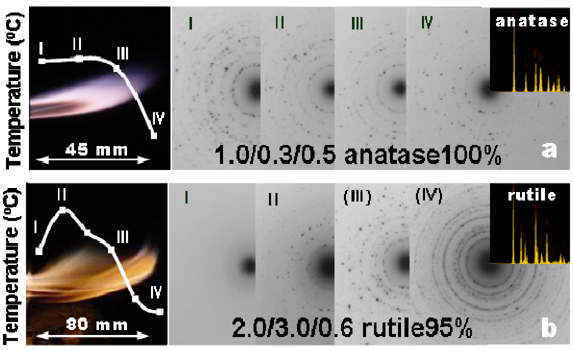


Fig. 2. The temperature distribution of flame and SAD patterns of TiO_2 nanoparticles.

The flame of Fig. 2(b) had a long and wide temperature distribution rather than Fig. 2(a). In this flame condition, TiO_2 formed the fully amorphous (I), the mixed phase of anatase and rutile (II), the rutile phase with a broad ring pattern (III), and close to perfect rutile phase (IV). Here the volume fraction of rutile phase was 95%.

It is generally well known that the particles in flame are formed by a homogeneous nucleation. In this work, the two kinds of particles (amorphous and anatase) in the initial stage of flame also are formed by the homogeneous nucleation. The phase of TiO_2 nanoparticle formed in flame depends on the various flame parameters affecting the homogeneous nucleation. In this view point, the flame of Figs. 2(a) and 2(b) is clearly different.

The anatase TiO_2 was first nucleated rather than amorphous (Fig. 2(a)), of which the flame is under the condition of the high starting temperature and the short flame length. The relatively smaller flow rate than one of Fig. 2(b) results in the rapid cooling rate of the temperature distribution of the flame. Therefore the homogeneously nucleated anatase nanoparticles have finally kept the anatase phase without the phase transformation.

At the the low temperature and long flame (Fig. 2(b)), however, it is hard to make a perfect crystal from the initial stage of nucleation. The other reason is due to an imperfect combustion with red color in Fig. 2(b). Therefore the nucleation in initial stage forms TiO_2 nanoparticles with amorphous phase. Since then, the amorphous TiO_2 nanoparticles are transformed to anatase or rutile phase by the subsequent-influxing heat from the long flame. From the results of SAD in Fig. 2(b), we can suggest that the many fraction of rutile phase is attributed to the phase transformation such as amorphous→anatase→rutile. The rutile phase was nucleated heterogeneously from the amorphous or anatase particles.

3. Summary

TiO_2 nanoparticles with the anatase, anatase and rutile mixture or rutile phases were successfully manufactured in various flame conditions. The anatase TiO_2 nanoparticle was predominantly synthesized at the high flame temperature and rapid flame cooling condition. The nucleation of anatase phase was homogeneous and the anatase nanoparticles have finally kept the anatase phase without the phase transformation any more in the flame.

At the flame condition having the low temperature and long flame, it was hard to make a perfect crystal from the initial stage of nucleation and it was easy to form the TiO_2 nanoparticle with the amorphous structure in the initial stage of flame. The amorphous TiO_2 nanoparticle was transformed to the rutile phase through the anatase phase by the subsequent-influxing heat from the long flame.

The rutile TiO_2 nanoparticle was not formed directly and homogeneously in flame, and was manufactured by the phase transformation such as amorphous→anatase→rutile. The rutile phase was nucleated heterogeneously from the amorphous or anatase particles.

4. References

1. J.C. Bailar, H.J. Elemeleus, R. Nyholm and A.F. Trotman-Dickenson: *Comprehensive Inorganic Chemistry* (Pergamon Press, UK 1973)
2. T. Ohno, K. Sarukawa, K. Tokieda and M. Matsumura: J. Catalysis Vol. 203 (2001) p. 82
3. S. Morooka, T. Yasutake, A. Kobata, K. Ikemizu and Y. Kato: Int. Chem. Eng. Vol. 29 (1989) p. 1
4. M. Akhtar, Y. Xiong and S. Pratsinis: AIChE J. Vol. 37 (1991) p. 10
5. Y. Suyama, K. Ito and A. Kato: J. Inorg. Nucl. Chem. Vol. 37 (1975) p. 1883
6. S.E. Pratsinis, W. Zhu and S. Vemury: Powder Tech. Vol. 86 (1996) p. 87
7. G. Yang, H. Zhuang and P. Biswas: NanoStruct. Mater. Vol. 7 (1996) p. 675