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Effects of reaction medium on the synthesis of TiO_2 nanocrystals by thermal decomposition of titanium (IV) *n*-butoxide

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Abstract

Thermal decomposition of titanium (IV) *n*-butoxide (TNB) in organic solvents yields nanosized anatase titania without the contamination of other phases. The formation of anatase titania crystals and their phase transformation are investigated by using X-ray diffraction (XRD), SEM, BET techniques. It is suggested that anatase titania synthesized in 1,4-butanediol is the result from direct crystallization while titania synthesized in toluene is transformed from precipitated amorphous intermediate. Thermal stability of products investigated by calcination at various temperatures and photocatalytic activity evaluated from ethylene decomposition reaction suggest that amount of defect structures in titania synthesized depends upon the solvent used.

Keywords: A. Powders: chemical preparation; C. Chemical properties; D. TiO_2; Synthesis

1. Introduction

Titanium (IV) dioxide or titania (TiO_2) has been recognized as one of the most important oxide used in industrial applications because of its physical and chemical properties, such as catalytic activity [1], photocatalytic activity for pollutant removal [2], good stability toward adverse environment [3], sensitivity to humidity and gas [4], dielectric character [5], photo-electrochemical conversion [6], nonlinear optics [7], photoluminescence [8]. Its applications include the use as catalysts, catalyst supports, cosmetics, pigments and filler coating. Nevertheless, photocatalysis is one of the most important uses of titania. Titania is known to have three natural polymorphs: rutile, anatase, and brookite. Rutile is thermodynamically stable polymorph, but anatase is more suitable form for catalytic applications.

There are many variables that influence the photocatalytic activity of titania, such as particle size, reactive surface area, incident light intensity and crystal structure. Among these factors, the crystal structure and crystallinity of titania are considered as important factors. Amorphous titania has negligible photocatalytic activity because of the recombination between the pair of photoexcited electron and hole in the amorphous structure [9]. For crystalline titania, only anatase is generally accepted to have significant photocatalytic activity [10–12]. Photocatalytic activity was reported to be strongly dependent on the heat treatment as well [10].

Many methods have been proposed to synthesize titania in anatase polymorph. In this work, nanocrystalline titania was synthesized via thermal decomposition of titanium alkoxide in organic solvent. This method has been used to successfully synthesize various types of nanosized metal oxides with large surface area, high crystallinity and high thermal stability [13–18]. This work presents the effect of reaction medium, i.e. organic solvent, to the characteristic of

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the nanocrystalline titania obtained. Phase transformation, thermal stability and photocatalytic activity of the products were also investigated.

2. Experimental

2.1. Sample preparation

Titanium (IV) *n*-butoxide (TNB) was used as starting material for titania synthesis. Various amounts of TNB, in the range of 5–25 g, was suspended in 100 cm^3 of organic solvent, i.e. 1,4-butanediol or toluene, in a test tube, which was then placed in a 300 cm^3 autoclave. The gap between the test tube and the autoclave wall was filled with 30 cm^3 of the same solvent used in the test tube. The autoclave was purged completely by nitrogen before heating up to the desired temperature, in the range of 200–300 °C at a rate of 2.5 °C/min. Autogeneous pressure during the reaction gradually increased as the temperature was raised. Once the prescribed temperature was reached, the temperature was held constant for desired period of time, in the range of 0–4 h, before the system was cooled down to room temperature. After the system was cool, the resulting powders were repeatedly washed with methanol and dried in air.

For phase transformation and thermal stability study, part of the synthesized product was calcined in a box furnace with a heating rate of 10 °C/min. The calcination was done at the temperature in the range of 400–1000 °C for 1 h.

2.2. Characterization

Powder X-ray diffraction (XRD) analysis was done by using a SIEMENS D5000 diffractometer with Cu Kα radiation. The crystallite size of the product was determined from the broadening of its main peak, using the Scherrer equation. Fraction of rutile in the product was calculated according to the following equation [19]:

$$\%\text{Rutile} = \frac{1}{((A/R) \times 0.884) + 1} \times 100$$

where A and R are the peak area for the major anatase and rutile phases, respectively. It should be noted that brookite was not found in this work. Infrared (IR) spectra were recorded on a NICOLET FT-IR Impact 400 spectroscopy. Morphology of the products was observed on JEOL Scanning Electron Microscope and JEOL TEM-200cx Transmission Electron Microscope. Specific surface area of the samples was measured by using the BET multipoint method.

2.3. Photocatalytic activity evaluation

The decomposition of ethylene via photocatalytic reaction was employed to evaluate photocatalytic activity of products obtained. The prepared titania was spread in a horizontal quartz reactor. The air containing 0.1% ethylene was continuously supplied at a constant flow rate with GHSV of 120 h^{-1}. The reaction temperature was set at 40 °C. For each run, an air stream with 0.1% ethylene was first passed through the reactor without illumination until reaching gas–solid adsorption equilibrium (typically 120–180 min) as indicated by identical inlet/outlet ethylene concentration. Then, UV light was illuminated on the surface of the catalyst by using 500 W mercury lamp. The outlet gas was sampled and analyzed at regular intervals by using a SHIMADZU GC-14B gas chromatograph equipped with the flame ionized detector.

3. Results and discussion

3.1. Formation of titania in different solvents

Nanosized titania crystal was successfully synthesized by using the method described above. The XRD patterns, as shown in Figs. 1 and 2, confirm that the products obtained are anatase titania without contamination of other phases, e.g. rutile or brookite. TEM micrographs of the as-synthesized products prepared in both solvents are shown in Fig. 3. The crystallite sizes of products calculated from the Scherrer equation are in the range of 9–15 nm, which agree with the TEM observation. Therefore, it is suggested that each primary particle observed by TEM is a nanosized single crystal titania.

Physical properties of products synthesized at 300 °C for various period of reaction time are shown in Table 1. The products grow slightly with an increase in the reaction holding time, while the crystallite sizes of product from both solvents are relatively the same. However, SEM micrographs reveal that morphology of the products obtained from 1,4-butanediol and toluene are different (see Figs. 4 and 5). The products synthesized in toluene agglomerated into spherical micron-sized particle, which is called secondary particle. The spherical shape of the secondary particle is more apparent when the reaction holding time is prolonged. On the other hand, in case of reaction in 1,4-butanediol, irregular aggregates of nanometer particles are observed for all reaction holding period investigated. This difference in morphology suggests that the colloidal stability of the precipitate in toluene is different from that in 1,4-butanediol. The results can be explained by the difference in the dielectric constant of the organic solvents, which affect the colloidal stability and morphology of the product [20].

Table 1 also shows BET surface area (S_{BET}) measured by nitrogen adsorption and the surface area calculated from a particle size (S_{XRD}), assuming that the particles are non-porous spheres. It is noticed that S_{BET} is smaller than S_{XRD} for all powders synthesized in 1,4-butanediol, which is attributed to the agglomeration of titania crystals. However, for powders synthesized in toluene, S_{BET} is generally greater than S_{XRD}. Kominami et al. [21] proposed that this behavior was the result of an amorphous-like phase contaminated in

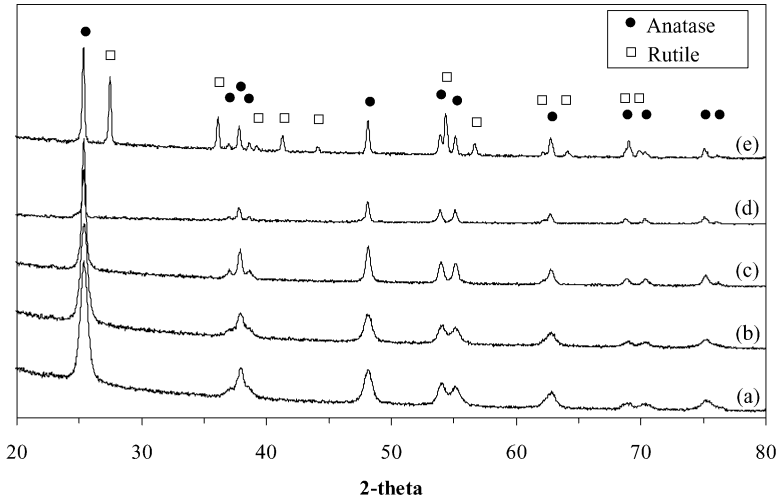

Fig. 1. The XRD patterns of titania synthesized by the reaction in 1,4-butanediol and subsequently calcined at various temperatures: (a) as-synthesis, (b) calcined at 400 °C, (c) calcined at 600 °C, (d) calcined at 800 °C and (e) calcined at 900 °C.

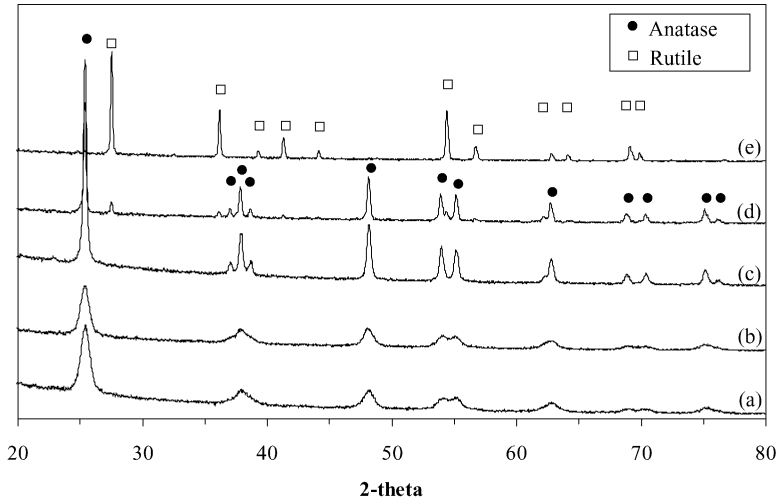

Fig. 2. The XRD patterns of titania synthesized by the reaction in toluene and subsequently calcined at various temperatures: (a) as-synthesis, (b) calcined at 400 °C, (c) calcined at 600 °C, (d) calcined at 800 °C and (e) calcined at 900 °C.

Table 1
Crystallite size and surface area of titania products synthesized at 300 °C for various period of reaction time

Solvent	Reaction holding time (h)	Phase	Crystallite size, d (nm)	S_{BET} (m^2/g)	S_{XRD}[a] (m^2/g)
1,4-Butanediol	0	Anatase	10	150	156
	0.25	Anatase	9	170	174
	0.5	Anatase	9	166	174
	1	Anatase	11	128	142
	2	Anatase	13	110	120
	4	Anatase	15	100	104
Toluene	0	Amorphous	–	204	–
	0.25	Anatase	9	163	174
	0.5	Anatase	10	156	156
	1	Anatase	10	161	156
	2	Anatase	12	145	130
	4	Anatase	13	143	120

[a] Calculated surface area assuming that the particles are nonporous spheres and using the density of anatase (3.84 g/cm^3).

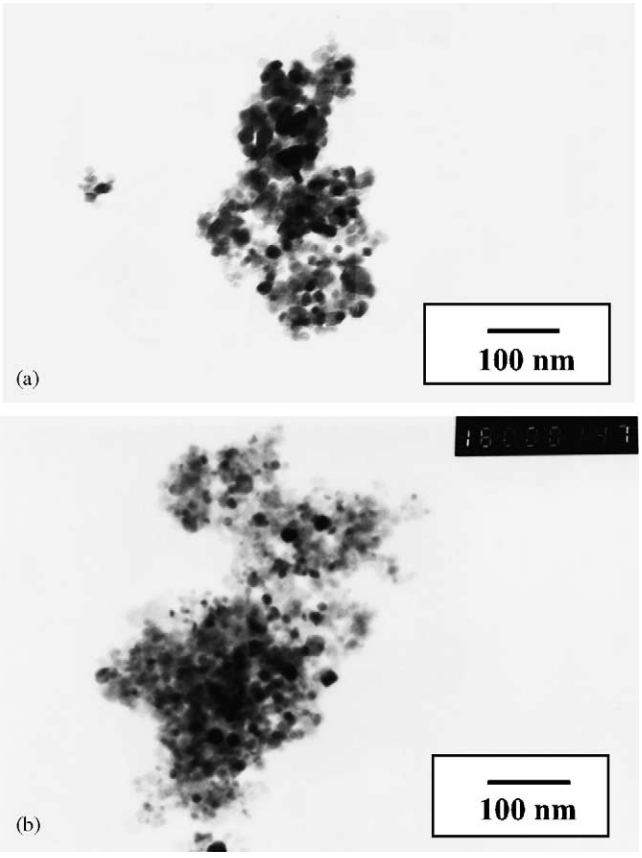

Fig. 3. TEM micrographs of the as-synthesized products prepared in: (a) 1,4-butanediol and (b) toluene.

the particles. Therefore, it is suggested that the product synthesized in toluene may contain small amount of amorphous-like phase, while titania synthesized in 1,4-butanediol is crystalline.

The major difference between the reaction in 1,4-butanediol and in toluene is that amorphous product was obtained from the reaction in toluene when there was no holding period. It is, therefore, suggested that the reaction mechanisms in both solvents are different. Further investigation of the reaction with no holding period was conducted by varying the reaction temperature from 300 °C to 250 and 220 °C, respectively. The results are shown in Table 2. It is found that the products obtained from the reaction with no holding time are always amorphous when toluene is used as the reaction medium. On the other hand, for the reaction in 1,4-butanediol, anatase titania is obtained. It should be noted that amount of product obtained was smaller when the reaction temperature was decreased and no solid product was obtained at 220 °C. The reaction temperature of 220 °C is too low to form any product within such short time. According to the results in Table 2, it is suggested that, when 1,4-butanediol is employed as reaction medium, anatase crystals are formed by crystallization when the temperature in the autoclave reaches about 250 °C. The subsequent heating results in growth of the crystals. On the other hand, for the reaction in toluene, amorphous product initially precipitates from the solution. Then, the solid state transformation from the amorphous product to anatase titania occurs during subsequent heating period. The unconverted amorphous phase remains in the particles and corresponding to the difference in S_{BET} and S_{XRD} as discussed earlier.

Table 2
Phase of titania products synthesized at various reaction temperatures

Reaction temperature (°C)	Product obtained[a]	
	1,4-Butanediol	Toluene
300	Anatase (9)	Amorphous
250	Anatase (6)	Amorphous
220	No product	No product

[a] The number in parenthesis represents crystallite size in nm.

3.2. Thermal stability and photocatalytic activity of products

Thermal stability of the product was investigated by calcining the as-synthesized product at various temperatures for 1 h. The product that transforms from anatase to other forms at lower calcination temperature is considered to have lower thermal stability. Low thermal stability is undesirable, especially for the use of titania as photocatalyst since rutile has long been considered to have less photocatalytic activity [22].

It has been generally accepted that the thermal stability of anatase titania depends upon the synthesis method. Jung and Park synthesized anatase titania by sol–gel process and found that the products transformed to rutile at temperature in the range of 400–500 °C [23]. Kominami et al. [21] employed the hydrolysis of titanium alkoxide in organic solvent and reported that their products transformed to rutile at temperature in the range of 600–950 °C. In this work, according to the XRD patterns shown in Figs. 1 and 2, our products transform from anatase to rutile at temperature in the range of 600–900 °C. This is in the same range as those reported by Kominami et al. [21] since the synthesis method is based on the same fundamental concept of metal alkoxide decomposition.

For the product synthesized in 1,4-butanediol, anatase phase was preserved even at 800 °C, while rutile phase was observed at this temperature in case of the product synthesized in toluene. The fraction of rutile in the calcined

Table 3
Fraction of rutile observed in titania calcined at various temperatures

Calcination temperature (°C)	Fraction of rutile[a] (%)	
	1,4-Butanediol	Toluene
As-synthesis	0	0
400	0	0
600	0	0
800	0	11.63
900	43.55	100
1000	100	100

[a] Calculated according to equation proposed by Fu et al. [19].

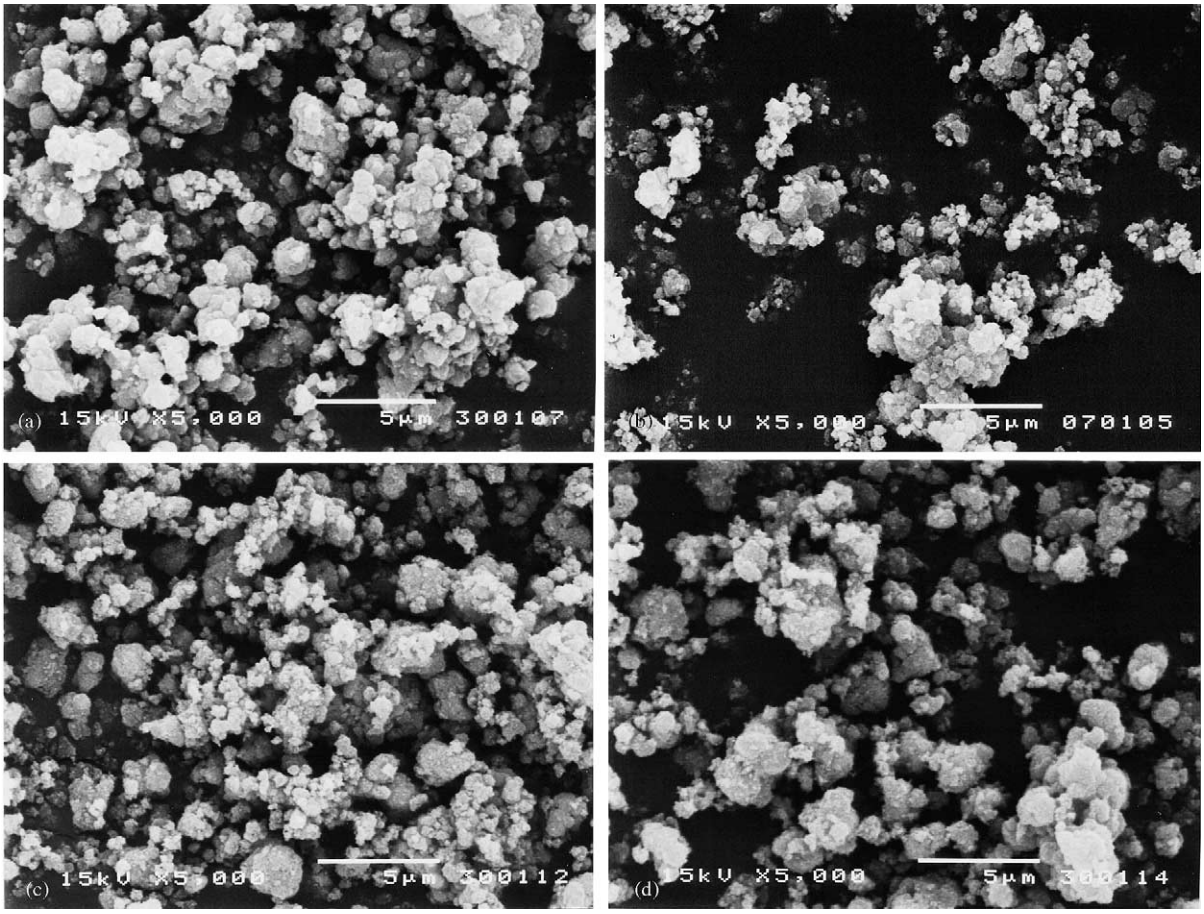

Fig. 4. SEM micrographs of the products synthesized in 1,4-butanediol for various holding time: (a) 0 h, (b) 0.25 h, (c) 2 h and (d) 4 h.

product as shown in Table 3 clearly indicates that anatase products obtained from the reaction in toluene start transforming into rutile at lower calcination temperature than the products obtained in 1,4-butanediol. Therefore, it may be referred that the former has lower thermal stability than the latter. In conjunction with the results discussed earlier, it is suggested that the formation route of titania significantly influences morphology and/or structure of crystals which further affects the phase transformation of titania product. Namely, anatase titania formed via direct crystallization in an organic solvent, i.e. the product formed in 1,4-butanediol, has feature that suppresses the phase transformation into rutile. On the contrary, anatase titania formed via solid state transformation of amorphous precursor, i.e. the product formed in toluene, transforms into rutile at lower temperature. This finding also agrees with the fact that the thermal stability of titania product synthesized by sol–gel method is relatively low comparing to those obtained from the decomposition of alkoxide because the sol–gel process involves formation of amorphous intermediate prior to heat treatment to form titania crystals.

Several variables corresponding to the phase transformation of nanocrystalline TiO_2 have been reported [24–28]. These parameters include particle size, surface stress, loading pressure, impurities and defect. Particle size effects are clearly important for transformation kinetics and phase stability of very fine crystalline materials. The smaller particle size and large surface area have been suggested to favor the transformation [25]. A critical particle size of anatase to transform into rutile was calculated thermodynamically to be 13 nm with consideration of surface stress [29]. The phase transformation of anatase titania, therefore, depends on the growth rate of anatase particles to attain the critical size.

As shown in Table 1, the products synthesized in both reaction mediums are anatase phase with relatively the same crystallite size and BET surface area. Therefore, the effects of crystallite size and surface area on the phase transformation of both products can be eliminated. According to Ding and Liu [30], the defects formed in titania are potential nucleation sites and the concentration of defect is rate limiting factor for the phase transformation from anatase to rutile at low temperature. It is, thus, suggested that the difference in thermal stability of our products results from different amount of defect structures or crystallinity obtained by different synthesis routes.

The amount of defect structures in titania was also evaluated from the photocatalytic reaction for the decom-

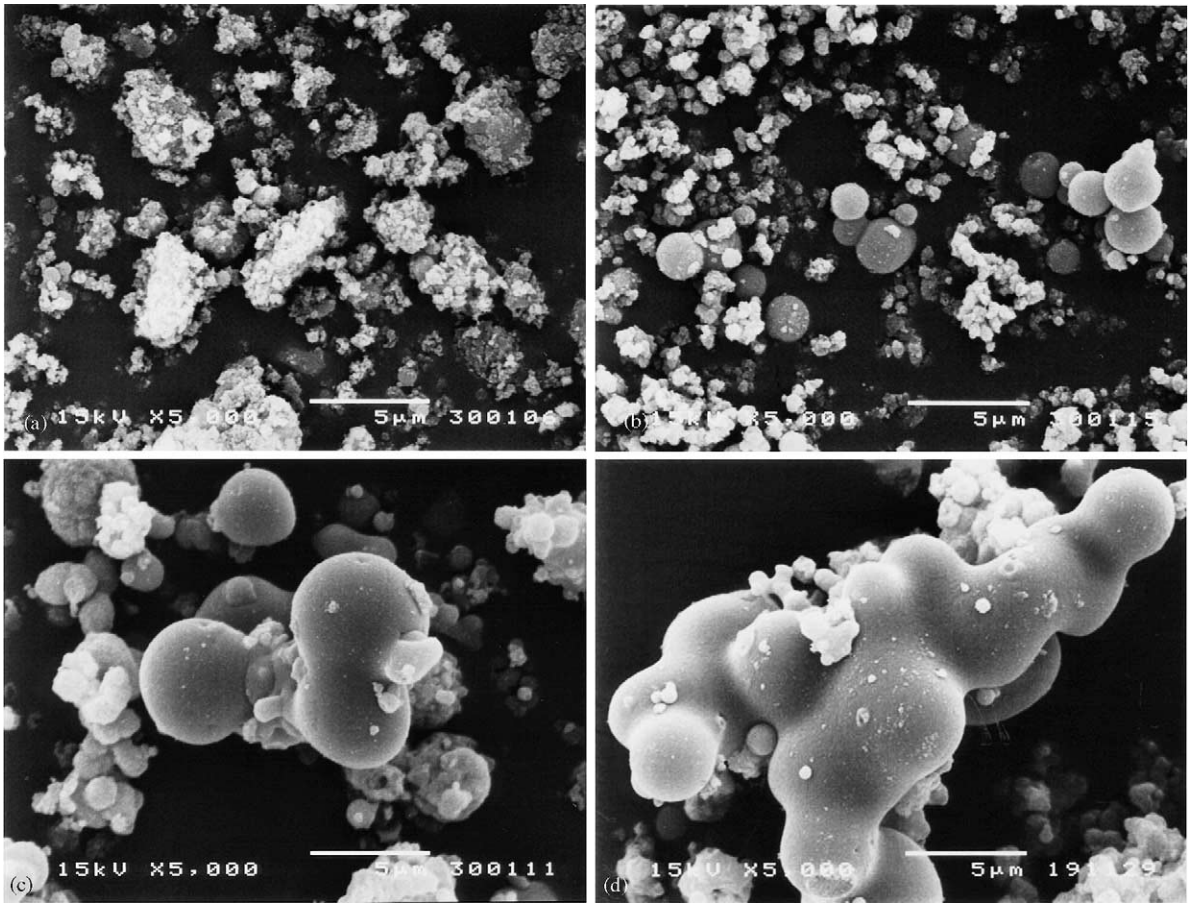

Fig. 5. SEM micrographs of the products synthesized in toluene for various holding time: (a) 0 h, (b) 0.25 h, (c) 2 h and (d) 4 h.

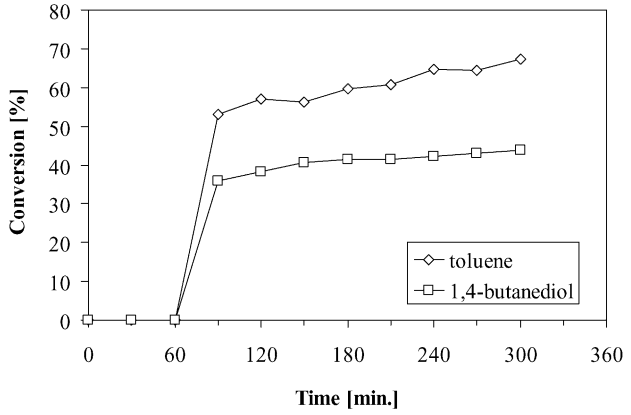

Fig. 6. Results for photocatalytic activity of titania synthesized in different solvents.

position of ethylene. As is shown in Fig. 6, the conversions from anatase titania prepared in different organic solvents are evidently different, which is the result from different amount of defect structure in titania. This result also supports the above findings that anatase titania synthesized via different routes, i.e. direct crystallization or solid state transformation of amorphous intermediate, contains different amount of defect structures in the crystals.

4. Conclusion

Nanocrystalline anatase titania can be prepared via thermal decomposition of TNB in organic solvents. The mechanisms for the formation of anatase crystal are different depending upon the organic solvent used. Nanocrystalline anatase titania prepared in 1,4-butanediol crystallized directly from the solution. On the other hand, for the reaction in toluene, crystalline anatase titania was obtained from solid state transformation of precipitated amorphous product. Thermal stability as well as photocatalytic activity evaluations suggest different amount of defect structures in titania synthesized in these two solvents.

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