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Ceramics International 38 (2012) 2233–2237

CERAMICS INTERNATIONAL

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Sol–gel derived mesoporous titania nanoparticles: Effects of calcination temperature and alcoholic solvent on the photocatalytic behavior

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Received 15 June 2011; received in revised form 12 October 2011; accepted 31 October 2011

Abstract

In this study, titania nanoparticles were successfully prepared by a sol–gel process, employing titanium (IV) tetraisopropoxide ($Ti[OCH(CH_3)_2]_4$; TIP) as a starting precursor. Either ethanol or isopropanol was used as an alcoholic solvent. The as-synthesized mesoporous titania was calcined at different temperatures in the range of 300–700 °C. The aim of this study is to investigate the effects of calcination temperature and the types of solvent on the photocatalytic behavior of titania. The results indicate that crystallinity and crystalline phase are important factors influencing the degree of photocatalytic activity of titania. It was found that the photocatalytic property of titania consisting predominantly of anatase crystallites has been markedly improved in the degradation of methylene blue under UVC light. Compared to ethanol, enhanced photocatalytic activity is obtained with isopropanol solvent through the thermal stability of anatase phase.

Keywords: A. Calcination; Nanocrystalline titania; Sol–gel process; Hydrolysis; Photocatalysis

1. Introdution

Recently, many research attentions have been focused on the fabrication of titania (TiO_2) material due to its novel properties such as good photocatalytic activity, low cost, non-toxicity, and large energy bandgap. A wide range of applications making use of its advantages include dye sensitized solar cells, sensor devices, and photocatalysts for the degradation of organic pollutants [1–3]. The photocatalytic activity of titania strongly depends on many factors such as morphology, particle size and distribution, porosity, crystallinity and crystal structures of titania. Among three crystalline polymorphs of titania (anatase, rutile and brookite), anatase phase is found to have the greatest photocatalytic activity, while rutile has the highest chemical stability [4,5]. However, previous researches [6,7] have shown that the photocatalytic activity of mixed phase titania nanoparticles can be higher than pure anatase phase.

The most common and widely used wet chemical technique for the synthesis of mesoporous nanoparticles is the sol–gel method due to its low cost, low temperature requirement and simple process. Based on sol–gel chemistry, titania nanoparticles can be prepared by the hydrolysis and condensation reactions of appropriate precursors (i.e., titanium alkoxide). The sol–gel derived nanoparticles are sensitive to many processing parameters such as pH, reaction temperature, catalysts, concentration and precursor composition. Recent research studies on the controllable hydrolysis rate of titanium alkoxide for the synthesis of titania nanoparticles have revealed that high hydrolysis rate could induce uncontrolled precipitation and the formation of rutile phase, resulting in poor photocatalytic activity [8–10]. Since the photocatalytic reaction is strongly dependent upon the kinetics of the sol–gel reactions, understanding factors affecting these reactions is significant and allows the controllable properties of final titania materials. The primary purpose of this work is to investigate the effects of crystalline phases and the hydrolysis rate on the photocatalytic activity of titania by varying calcination temperatures and alcoholic solvent types.

2. Experimental procedure

Titania nanoparticles were prepared by sol–gel method, employing tetraisopropoxide (TIP) as a starting precursor. In a preparation procedure, 5.5 ml of TIP was dissolved in 55 ml

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doi:10.1016/j.ceramint.2011.10.072

ethanol. The mixture of 19 ml distilled water and 1.5 ml HCl was then added dropwise under vigorous stirring at room temperature. The mixture was further stirred for 3 h and the obtained gel was centrifuged, washed to remove excess reactants and catalyst, and dried in the oven at 80 °C for 24 h. The samples prepared in the above-described way were labeled as E1. Following the drying process, the samples were calcined at 300 °C, 500 °C, or 700 °C for 3 h at a heating rate of 5 °C/min, and the calcined materials were labeled as E1-300, E1-500, and E1-700, respectively. In order to compare the effects of alcoholic solvent (ethanol or isopropanol), 72 ml of isopropanol, which is equivalent to the same mole ratio of TIP/ethanol, was added in the mixture. The samples were then calcined at 500 °C and labeled as I1-500.

The morphology and size of the particles were observed by JEOL JEM-1230 transmission electron microscopy (TEM). X-ray diffraction (XRD) patterns were recorded on a BRUKER AXS: D8DISCOVER system using Cu Kα radiation to analyze the crystal structure. The pore characteristics and specific surface area were determined using BET method by Autosorb-1 instrument (Quantachrome, USA).

The photocatalytic activity of titania nanoparticles was evaluated by photocatalytic degradation of methylene blue solution under UVC light irradiation (20 W UVC ultraviolet Tokiva lamp, $\lambda_{max} = 254$ nm). All batch equilibrium experiments were conducted in the dark. In each test, 0.031 g of TiO_2 nanoparticles was added to 50 ml of 2×10^{-5} M methylene blue aqueous solution. The degree of dye decomposition was evaluated by decoloration or a change in concentration of methylene blue solution under different UVC irradiation time. The suspensions were centrifuged, and the concentration of methylene blue was determined using a UV–vis spectrophotometer (Shimadzu UV-1800).

3. Results and discussion

Fig. 1 shows XRD patterns of as-synthesized (E1) and calcined (E1-300, E1-500, and E1-700) titania nanoparticles prepared from ethanol solvent. All of the peaks observed for E1 and E1-300 samples are indexed as a pure anatase phase (A). As sintering continues, the anatase begins to transform into rutile (R), and the degree of crystallinity is increased. An additional phase of rutile was observed when the samples are calcined at 500 °C (E1-500), indicating the anatase–rutile transformation. The complete transformation from anatase to rutile takes place at 700 °C (E1-700). The anatase crystallite size of as-synthesized and calcined titania was estimated by employing Debye–Scherrer equation. From the XRD patterns, the percentage of anatase phase can be calculated using the following equation [11].

$$\%\text{anatase} = 100 \cdot \left(\frac{1 + I_R}{0.8 I_A}\right)^{-1}$$

where I_A and I_R is the intensity of strongest diffraction line of anatase (1 0 1) and rutile (1 1 0) phase, respectively. The calculated data are listed in Table 1. An increase in crystallite size with increasing calcination temperatures indicates an enhancement of crystallite growth of titania nanoparticles. With isopropanol (I1-500) as a replacement of ethanol (E1-500), the anatase content is increased from 20% to 55%, as shown in Fig. 2.

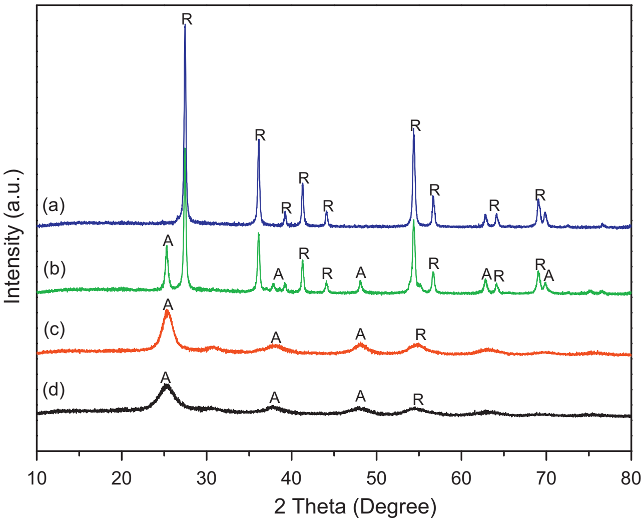

Fig. 1. XRD patterns of (a) E1-700, (b) E1-500, (c) E1-300 and (d) E1 (R – rutile, A – anatase).

Fig. 3 shows typical TEM micrographs of as-synthesized and calcined titania. The average particle sizes of as-synthesized (E1) and titania nanoparticles calcined at 300 °C (E1-300), 500 °C (E1-500) and 700 °C (E1-700) are approximately 10, 16, 20, 58 nm in size, respectively. The close agreement in the particle size by TEM and crystallite size by XRD indicates that there is no significant agglomeration of titania nanoparticles. The size of titania nanoparticles is, however, slightly increased with the use of isopropanol. Bernards et al. [12] have reported that, due to more alkoxide groups, the hydrolysis rate in the sol–gel process of tetra-alkoxysilanes in ethanol is higher than that in isopropanol. A slower hydrolysis rate of titanium alkoxide in isopropanol solvent

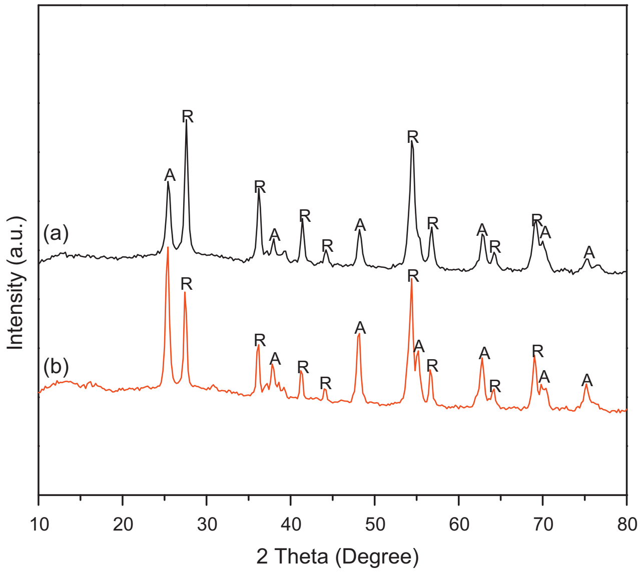

Fig. 2. XRD patterns of (a) E1-500 and (b) L1-500 (R – rutile, A – anatase).

Table 1
Particle size, percentage of anatase phase, specific surface area, pore volume and mean particle size of the titania nanoparticles.

Samples	TIP (ml)	EtOH/isopropanol (ml)	HCl (ml)	H_2O (ml)	Calcination temperature (°C)	Particle size (nm)	Anatase crystallite size (nm)	% Anatase	Surface area ($m^2\ g^{-1}$)	Pore volume ($cc\ g^{-1}$)	Average pore size (nm)
E1	5.5	55/–	1.5	19	As-synthesized	10	4	100	152	0.11	3
E1-300	5.5	55/–	1.5	19	300	16	6	100	111	0.12	4
E1-500	5.5	55/–	1.5	19	500	20	16	20	29	0.08	11
E1-700	5.5	55/–	1.5	19	700	58	35	0	1	0.00	3
I1-500	5.5	–/72	1.5	19	500	27	19	55	26	0.08	13

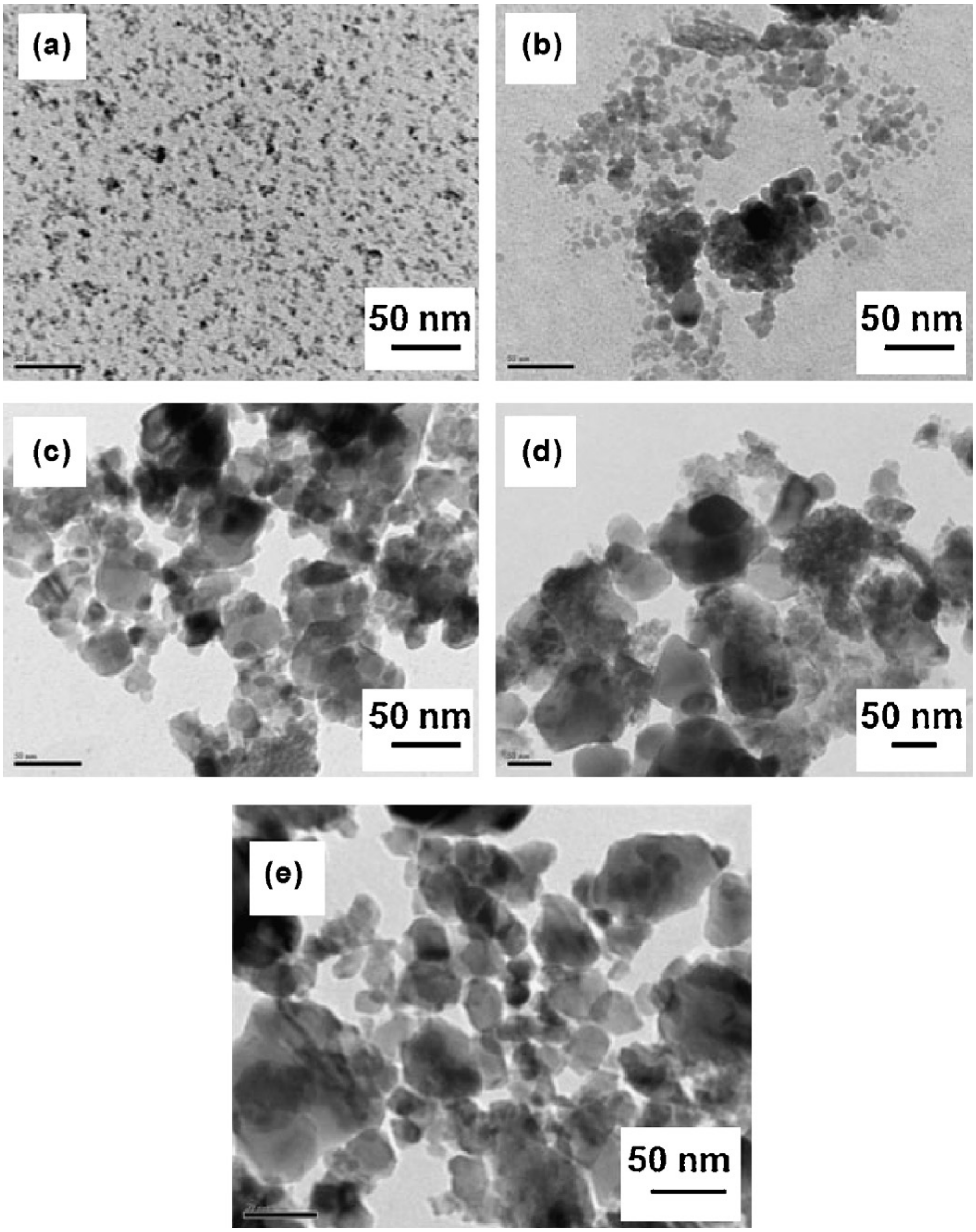

Fig. 3. TEM photographs of (a) E1, (b) E1-300, (c) E1-500, (d) E1-700 and (e) I1-500 (scale bar: 50 nm).

then allows particles to grow, resulting in larger particle size. In addition, the %anatase formation is reportedly increased when the rate of hydrolysis is reduced [13]. Consistent results were observed in XRD patterns (Fig. 2), which confirmed that anatase crystallization could be promoted through slow hydrolysis of titanium alkoxide in isopropanol solvent. The specific surface area was determined by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was obtained from the nitrogen adsorption–desorption isotherms. The measured BET specific surface area decreases with increasing calcination temperature (Table 1). This is due to a collapse of the pore structure and an increase of particle size. No significant difference in BET specific surface area is observed between different alcoholic solvents, and the values are in range of 26–29 $m^2 g^{-1}$ when calcined at 500 °C. Fig. 4 shows nitrogen adsorption–desorption isotherms of titania nanoparticles calcined at 500 °C. Both E1-500 and I1-500 samples exhibit type IV adsorption isotherms, which are a characteristic of mesoporous materials [17]. As-synthesized titania nanoparticles, however, exhibit a hysteresis loop at low relative pressure range, indicating the presence of micro- and lower range of mesopores. A slight increase in adsorption between $P/P_o = 0.95$ and 1.00 indicates that all calcined nanoparticles exhibit a small amount of macroporosity, which can be attributed to N_2 adsorption between nanoparticles.

Average pore size of titania increases with increasing calcination temperature and decreases rapidly when calcined at 700 °C due to sintering effects (Table 1). Typical pore size distribution curves for the synthesized titania are shown in Fig. 5. Without calcination, titania (E1) has much larger microporosity and pore volume than titania calcined at 500 °C (E1-500). Nevertheless, fairly narrow monomodal pore size distributions of 5–10 nm and 5–17 nm are achieved for E1-500 and I1-500, respectively.

Fig. 6 shows a gradual decrease in the concentration of methylene blue solution as a function of UVC irradiation time in combination with titania photocatalysis. More than 20% decrease in methylene blue concentration was observed after 120 min irradiation. At the calcination of 500 °C, titania nanoparticles exhibit the highest rate of photocatalytic degradation due to an increase in the crystallinity of anatase phase. Despite resulting in lower specific surface area, the use of isopropanol solvent could play a crucial role in anatase–rutile phase transformation. Compared to ethanol (E1-500), the rutile phase content of titania calcined at 500 °C is reduced, leading to an enhanced photocatalytic activity. These observations are consistent with the results on the hydrolysis of tetra-alkoxysilanes or tetraethyl orthosilicate, reported elsewhere [12,14]. In addition, previous works have also reported that higher concentration of Ti^{3+} sites is obtained when isopropyl alcohol is used as the solvent [15]. These Ti^{3+} sites are active sites for water decomposition during the photocatalytic process, and hence better photocatalytic activity is displayed [16].

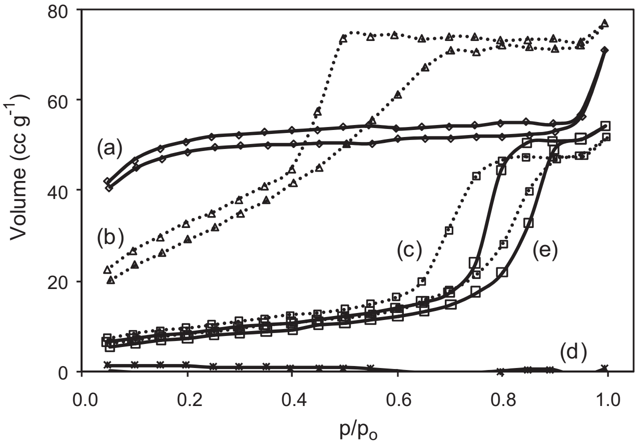

Fig. 4. N_2 adsorption–desorption isotherms of (a) E1, (b) E1-300, (c) E1-500, (d) E1-700 and (e) I1-500.

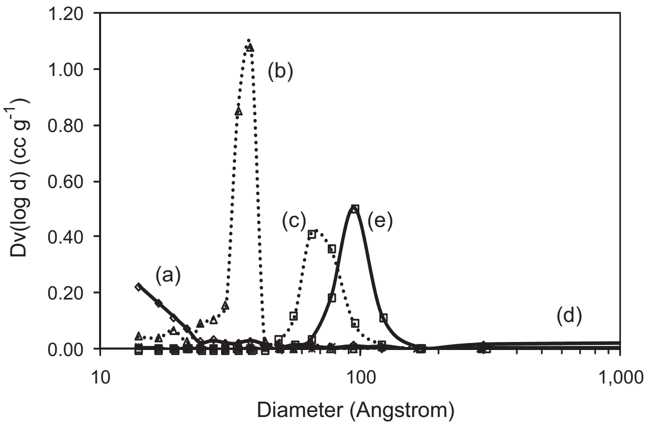

Fig. 5. BJH pore size distributions from adsorption of (a) E1, (b) E1-300, (c) E1-500, (d) E1-700 and (e) I1-500.

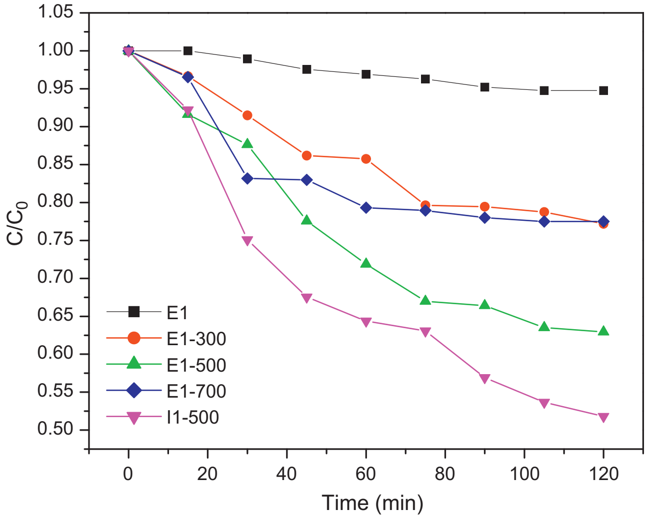

Fig. 6. Degradation of methylene blue with photocatalysts.

4. Conclusion

The effects of crystal structure, crystallinity, and crystallite size on the photocatalytic activity were investigated through varied calcination temperatures and solvent types. The results showed that as-synthesized titania nanoparticles were porous and had low anatase crystallinity. With an increase in calcination temperatures, pore collapsing, crystallite growth, and anatase–rutile phase transformation have occurred. It is clear that specific surface area, crystal structure, and the crystallinity are crucial factors controlling the photocatalytic behavior of titania. The use of isopropanol solvent was likely to inhibit the anatase–rutile transformation through the control of hydrolysis rate. As a consequence, a higher mass fraction of anatase phase retained at elevated temperatures, and better photocatalytic activity was achieved.

Acknowledgements

This work is supported by Silpakorn University Research and Development Institute (SURDI 54/01/41). The authors also wish to thank Department of Materials Science and Engineering, Faculty of Engineering and Industrial Technology, Silpakorn University, and National Center of Excellence for Petroleum, Petrochemicals and Advanced Materials for supporting and encouraging this investigation.

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