The Role of CMC to Increase the Surface Area of TiO_2

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Abstract

The aim of this work was to find the optimum condition for synthesis of titania particles by sol-gel technique using precursor solution of titanium (IV) isopropoxide in toluene and 2 mol L^{-1} aqueous solution of potassium hydroxide. The concentration of precursor solution was 0.3, 0.5 and 0.7 mol L^{-1}. The obtained sol was dried at 80°C for 2 h and calcined in air at 400, 500 and 700°C for 2 h. The effect of carboxy methyl cellulose (CMC) on physical properties of prepared titania was studied by addition of 1-2 mL of 1% w/v of CMC aqueous solution in 0.7 mol L^{-1} of precursor solution. The obtained titania particles was characterized by XRD and SEM. Brunauer-Emmett-Teller surface areas have also been determined. The results showed that all titania particles were anatase phase, the particles size was in range of 5.49-26.30 nm and the average surface area of titania particles were in the range of 27.75-196.30 m^2g^{-1}. It was also found that titania with 2mL of CMC solution loading gave the highest average surface area.

1. Introduction

The anatase crystalline TiO_2 is well known to have interesting properties and potential applications, e.g., photocatalysts [1-3], photoelectrodes [4], gas sensors [5] and electrochromic display devices [6,7]. Anatase particles show a long catalytic lifetime [8], but for many applications, porous particles with a large surface area are desired. In recent years,photocatalytic activity of anatase has received considerable attention. Many papers have been published on the preparation of porous titania using the sol-gel method [9], sputtering techniques [10] and direct deposition from TiF_4 aqueous solutions [11]. For preparation of highly porous materials, supercritical drying process is well known, but it requires high temperatures and pressures. Several other methods at ambient pressure [12], such as solvent exchange [13] and the method that using polymer additives [14,15] have been proposed. The sol-gel technique is one of the most suited processes to prepare the TiO_2 particles [16]. In this paper, a novel method to increase the surface areas of sol-gel-derived TiO_2 particles by using polymer additive is reported.

The TiO_2 particles of large surface

area have been prepared via adding Carboxy Methyl Cellulose (CMC)

during preparation of TiO_2 particles by sol-gel technique.

2. Experimental

The TiO_2 particles were prepared by dissolving titanium (IV) isopropoxide (97%, Aldrich) in toluene solution.

The concentrations of precursor solution were 0.3, 0.5 and 0.7 mol L^{-1}. The 2 mol L^{-1} of KOH was added to each concentration of precursor by dropwise until the pH value of mixed solution reached to 9-10 under vigorous stirring the obtained white precipitates were filtered and thoroughly washed several times with distilled water. 1 mol L^{-1} of acetic acid was then dropped to precipitates until the pH value reached 4.5. Finally, the resulting sol was dried at 80°C for 2 h. The as-dried precipitates were calcined in air at 400, 500

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and 700°C for 2 h to produce TiO_2 particles. The effect of CMC on physical properties of prepared TiO_2 was studied by addition of 1-2 mL of 1% w/v of CMC aqueous solution to 0.7 mol L^{-1} precursor solution. For characterization of TiO_2 particles, Scanning Electron Microscope (Flow sorb 2300) and X-ray powder diffraction (Philips PW1830 instrument with CuKα radiation) were used. The surface areas of TiO_2 particles were observed with Brunauer-Emmett-Teller (Philips, XL 30 cp).

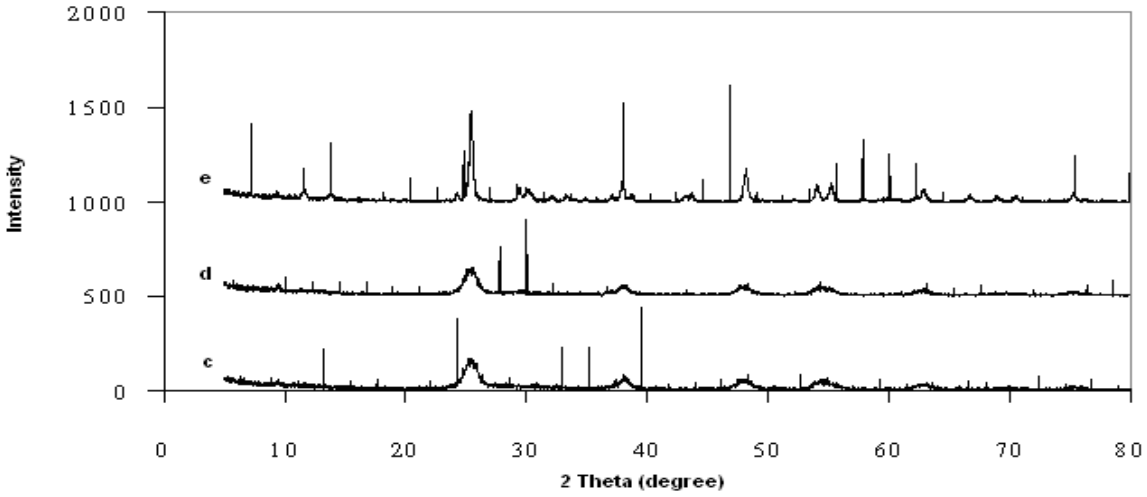

Figure 1 XRD patterns of prepared TiO_2 paricles calcined at 400°C for 2 h and obtained from different concentrations of (a) 0.3 (b) 0.5 and (c) 0.7 mol L^{-1} precursor solution.

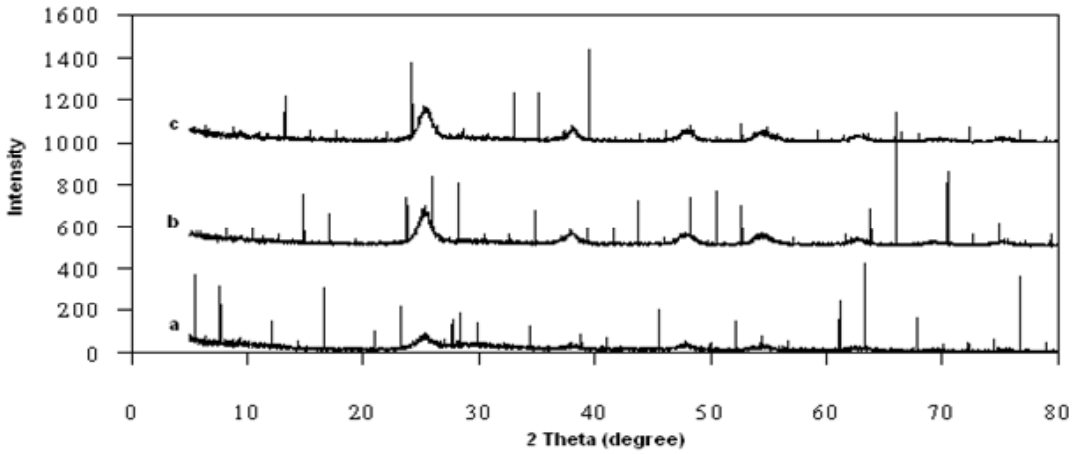

Figure 2 XRD patterns of TiO_2 prepared from 0.7 mol L^{-1}precursor solution by calcination at different temperature (c) 400°C; (d) 500°C and (e) 700°C

3. Results and Discussion

The white precipitates of TiO_2 were characterized by X-ray diffraction to confirm the TiO_2 phase. Fig. 1 showed XRD patterns of TiO_2 particles from different precursor concentrations without CMC at the calcination temperature of 400°C for 2h. From XRD patterns, only anatase phase was obtained. The degree of crystallinity

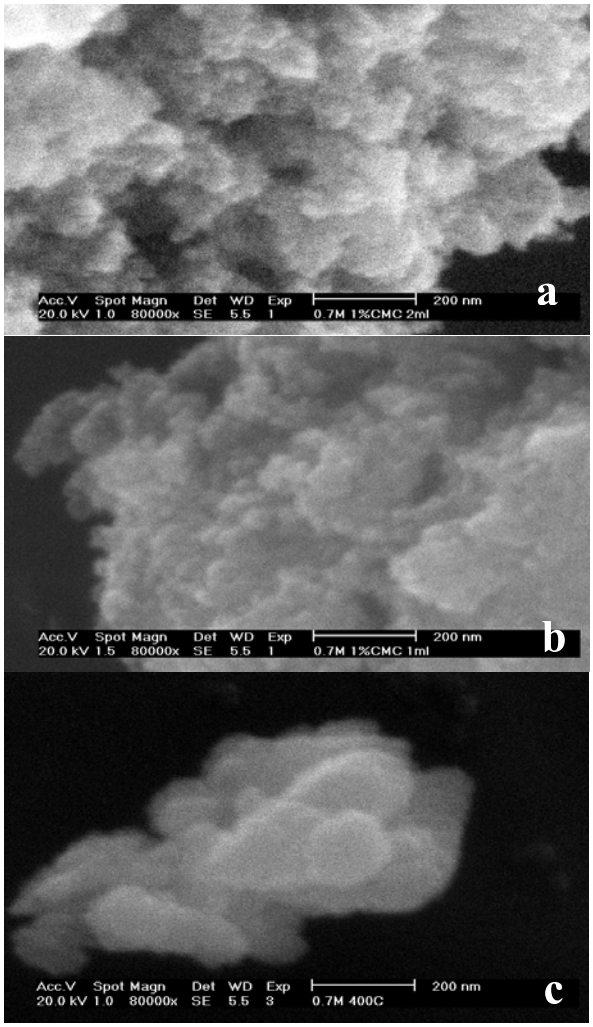

Figure 3 SEM images of TiO_2 particles prepared from 0.7 mol L^{-1} precursor solution and annealed at 400°C for 2 h: with the addition of (a) 1 mL of 1%w/v CMC (b) 2 mL of 1%w/v CMC and (c) and without the addition of CMC.

was increased with increasingly concentration of precursor solution. The effect of precursor concentration on TiO_2 particle size by using different precursor concentration and calcined at 400°C for 2h was studied. At higher concentration, more precursors dissolved in toluene solvent therefore higher opportunity for obtaining large crystal. On the other hand, at the lower concentration of precursor in the solvent, the small crystal occurred. The small TiO_2 particles that formed from the lowest concentration of precursor solution gave the highest surface area when compared to the others which was confirmed by BET. As calcination temperature was one of variables that affected particle size and pore volume. TiO_2 particles from the 0.7 mol L^{-1} of precursor solution calcined at different temperatures of 400, 500 and 700°C were studied and the XRD spectra were compared as shown in fig. 2. At 700°C, high intensity XRD patterns were (figure 2e) which implied that the free energy on surface of TiO_2 decreased. Consequently, agglomerated form with large crystals of TiO_2 occurred at higher calcination temperature. This result agreed with BET surface area analysis as the prepared TiO_2 annealing at 700°C showed the lowest surface area, compared to those annealing at 400 and 500°C, respectively. The effect of CMC on physical properties of TiO_2 particles was extensively studied. Various amounts of 1%w/v CMC solution were added to 0.7 mol L^{-1} precursor solution and calcined at 400 °C for 2h. Increasing surface area measured by BET method was observed when concentration of added CMC solution was increased. By adding 1 mL and 2 mL of 1%w/v, the surface area of resulted TiO_2 was found to be 188.53 m^2/g and 196.31 m^2/g, respectively, while that without mixing CMC was 111.45 m^2/g. Figure. 3 showed SEM images of obtained TiO_2 particles. As shown in figure 3 (a) and (b), the morphology appeared to aggregates of very fine particles resulting in higher surface area compared to the

one without the addition of CMC (figure 3(c)). Normally, CMC is well known as high viscosity polymer additive when dissolved in water. This property led to the interest of using TiO_2 as photocatalyst materials in the further study.

4. Conclusion

With sol-gel technique, white powder of TiO_2 particles was synthesized. As increasing the concentration of precursor solution, the crystal size of TiO_2 particle tended to increase leading to the lower surface area. For the effect of the calcination temperature on the particle size, it was found that as increasing the temperature to 700°C, the particle size became larger resulting from the decrease of free energy on surface. With the addition of 2 mL of 1%w/v CMC to 0.7 mol L^{-1} of precursor solution and annealed at 400°C for 2 h, the surface area of 196.31 m^2/g was obtained which compared to its of 111.45 m^2/g for the one without CMC addition.

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References

[1] Wauthoz, P., Ruwet, M., Machej, T. and Grange, P., "Influence of the preparation method on the $V_2O_5/TiO_2/SiO_2$ catalysts in selective catalytic reduction of nitric oxide with ammonia," Appl. Catal., Vol. 69, 1991, pp.149-169.

[2] Towata, A., Uwamino, Y., Sando, M., Iseda, K. and Taoda, H., "Synthesis of titania photocatalysts dispersed with nickel nanosized particles,". Nanostructured Materials, Vol. 10, 1998, pp. 1033-1042.

[3] Rivera, A. P., Tanaka, K. and Hisanaga, T., "Photocatalytic degradation of pollutant over TiO_2 in different crystal structures," Applied Catalysis B: Environmental, Vol. 3, 1993, pp. 37-44.

[4] Wen-Ti, W., McEvoy, A. J. and Grätzel, M., "Chronoamperometric evidence for fractality in porous TiO_2 films," Journal of Electroanalytical Chemistry, Vol. 291, 1990, pp. 235-242.

[5] Reddy, C. V., Cao, W., Tan, O. K., Zhu, W. and Akbar, S. A., "Selective detection of ethanol vapor using $xTiO_2$–$(1 - x)WO_3$ based sensor," Sensors and Actuators B: Chemical, Vol. 94, 2003, pp. 99-102.

[6] Nagase, K., Nakajima, S., Ohshima, E., Watanabe, A., Kikuchi, M. and Syono, Y., "Structural changes of TI oxide system on non-isothermal thermogravimetry with slow heating rates," Physica C: Superconductivity, Vol. 235, 1994, pp. 969-970.

[7] Barringer, E. A., Novich, B. E. and Ring, T.A., "Determination of colloid stability using photon correlation spectroscopy," Journal of Colloid and Interface Science, Vol. 100, 1984, pp. 584-586.

[8] Iino, K., Kitano, M., Takeuchi, M., Matsuoka, M. and Anpo, M., "Design and development of second-generation titanium oxide photocatalyst materials operating under visible light irradiation by applying advanced ion-engineering techniques," Current Applied Physics, Vol. 6, 2006, pp. 982-986.

[9] Lin, H., Kozuka, H. and Yoko, T., "Preparation of TiO_2 films on self-assembled monolayers by sol–gel method," Thin Solid Films, Vol. 315, 1998, pp. 111-117.

[10] Fukushima, M., Yanagi, H., Hayashi, S., Sun, H. and Kawata, S., "Microfabrication of gold dots in SiO_2/TiO_2 glass films by two-photon absorption," Physica E: Low-dimensional Systems and Nanostructures, Vol. 21, 2004, pp. 456-459

[11] Habazaki, H., Fushimi, K., Shimizu, K., Skeldon, P. and Thompson, G.E.,"Fast migration of fluoride ions

in growing anodic titanium oxide," Electrochemistry Communications, Vol. 9, 2007, pp. 1222-1227.

[12] Singh, R. and Prakash, S., "Phonons in nanocrystalline fcc nickel," Surface Science, Vol. 532, 2003, pp. 272-275.

[13] Takahashi, R.,Yonezawa, Y., Ohtani, M., Kawasaki, M., Matsumoto, Y. and Koinuma, H., "Combinatorial exploration of flux material for $Bi_4Ti_3O_{12}$ single crystal film growth," Applied Surface Science, Vol. 252, 2006, pp. 2477-2481.

[14] Kure, S., Chujo, Y. and Saegusa, T.," An organic-inorganic hybrid polymer derived from polyoxazoline," Reactive Polymers, Vol. 39, 1990, pp. 241-242.

[15] Xie, L., Liu, Y., Wang, Y. T., Zheng, J. and Li, X. G.,"Superior hydrogen storage kinetics of MgH_2 nanoparticles doped with TiF_3," Acta Materialia, Vol. 55, 2007, pp. 4585-4591.

[16] Sookman, C. and Kongkachuichay, P., "Effect of calcined temperature on sol-gel synthesized NiO properties," Advance in Technology of Material And Material Process Journal, Vol. 8, 2006, pp. 73-76.