

Thermostability of TiO₂ nanoparticle and its Photocatalytic Reactivity at Different Anatase/Rutile Ratio

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ABSTRACT

Thermostability study of commercial P25 TiO₂ nanoparticles was carried out by ascending annealing temperature from 400 to 1100 °C. The thermostability of TiO₂ structure was measured by X-ray diffraction (XRD). Anatase-Rutile phase transition occurred only when temperature exceeds 600°C. Rutile weight fraction increased from 25 to 100 % between 400 to 840 °C. Phase transition activation energy was calculated by using Arrhenius plot to be 27 kJ/mol. Transmission electron microscope (TEM), Brunauer-Emmett-Teller (BET), and dynamic light scattering (DLS) techniques were applied to determine the size of grown particles. Results of particle size analysis using TEM imaging method were the same as those using BET instruments up to 840 °C. BET measurements tend to overestimate the particle size at temperature greater than 840 °C. In contrast, DLS overestimate the size of TiO₂ particles due to agglomeration in solution. Mean TiO₂ particle sizes grew from 25 to 450 nm when temperature increased from 400 to 1100 °C. Furthermore, the photocatalytic reactivity in the degradation of dye decreased with the increase of particle size and rutile fraction.

Keywords: photocatalyst, thermostability, methylene blue

INTRODUCTION

Since the discovery of the photoelectrochemical splitting of water on titanium dioxide electrodes [1], the semiconductor-based photocatalysis has been extensively studied. Titanium dioxide has become one of the most popular photocatalysts due to its non-toxicity, low cost, strong redox ability and wide applications, such as air purification, water treatment, deodorization, self-cleaning, and antibacterial coating [2]. The TiO₂ absorbs photons, and evolves active oxygen species, such as OH radical and O₂⁻ ion, by reaction with H₂O and O₂ that are adsorbed on the TiO₂ surface. The high oxidation potential of active oxygen species is responsible for the decomposition of many pollutants [1,2].

Much has been reported on the photocatalytic reactions of TiO₂. Majority of the research on the photocatalysis of

TiO₂ focus on the bandgap modifications and effect of physical properties such as particle size and crystal structures on photocatalysis [2]. No information is available on the thermostability and its effect on the photocatalysis. In this present study, we investigated the thermostability of P25 nanoparticle and its photocatalytic activity. The degree of phase transformation was observed using XRD and the activated energy of Anatase-Rutile phase transition was determined by the Arrhenius equation accordingly. The particle size of TiO₂ photocatalyst was characterized by TEM, specific surface area by the BET, and DLS techniques. The anatase-rutile fraction ratio was determined as a function of temperature.

EXPERIMENTAL

Preparation and characterization of TiO₂

Degussa P25 TiO₂ was heat-treated in a conventional muffle furnace at 773, 873, 933, 1053, 1113, 1243, and 1373 K for four hours. The crystal phase and surface area were measured with a powder X-ray diffraction (Rigaku D max B) with a CuK radiation source and a N₂-gas adsorption analyzer (NOVA 2000), respectively. The particle size was determined using the TEM (Jeol 2000) and DLS (Malvern 3000HS) in distilled water medium. This is necessary as to minimize the degree of aggregation.

Photocatalytic decoloration of methylene blue

A volume of 100 mL of the aqueous solution of methylene blue (Co = 6.25 nM) was introduced into a batch reactor with 10 mg of TiO₂, which was pre-dispersed with a 100-W ultrasonic tip for 2 minutes. The decoloration reaction was carried out at 288 K under UVA irradiation provided by two 20-W black lamps. The distance between the solution and the lamp was 10 cm. After centrifugation at 10000 rpm for 15 minutes, the absorbance of the methylene blue solution at 660 nm was measured using a UV/VIS spectrometer (HP 8452A) to determine the residual concentration.

RESULTS AND DISCUSSION

Characterization of TiO₂

In this work, the anatase-rutile phase composition was determined by XRD. Based on the XRD data it is possible to calculate the distribution of anatase and rutile using the following empirical equation [3]:

$$W_R = I_R/I_0 = I_R/(0.88I_A + I_R) \quad (1)$$

where W_R is the rutile weight fraction in percent, I_A and I_R are integrated diffraction peak intensity from anatase (101) and rutile (110), respectively. I_0 is the total integrated (101) and (110) peak intensity. The variation of anatase-rutile weight fraction (in percent) is shown in the Table 1. The obvious phase transition only occurred about 873 K. The anatase phase decreased with increase of temperature, and disappeared at temperature above 1113 K. Assuming that the phase transformation is a first-order reaction [4], the activation energy can be calculated by the Arrhenius equation as shown in Figure 2. The activation energy was 27.0 kJ/mol with a correlation coefficient value of 0.968, which indicated that mass transfer was the limiting step for the phase transition reaction.

Table 1. The effect of annealing temperature on the anatase-rutile weight fraction, specific surface area, and apparent reaction rate constant

Temp. (K)	W_R (%)	d_{DLS}/d_{TEM}	Surface area (m ² /g)	k_{app} (10 ³ min ⁻¹)
P25*	27	7.26	53.1	-
773	28	7.30	52.2	53.0
873	47	6.26	44.5	45.2
933	51	6.84	32.9	34.4
1053	89	4.63	15.0	21.8
1113	100	4.33	9.8	16.9
1243	100	2.96	3.4	11.8
1373	100	2.29	2.4	10.9

k_{app} : methyl blue degradation rate constant

*: original TiO₂ (P25)

Figures 3 and 4 show the particle size distribution of the TiO₂ particles determined by TEM, DLS, and BET surface area techniques. Rapid grain growth and formation of rutile phase appeared at temperature above 1053 K. The particle size can be calculated from the specific surface area by using the following equation with the assumption of spherical and nonporous particles [5]:

$$d_{BET} = 6000/\rho A \quad (2)$$

where d_{BET} is the calculated particle size (nm), ρ is the density of TiO₂ (g/cm³), and A is the specific surface area

(m²/g). Results from TEM and BET measurements were consistent with each other in the temperature range of ambient to 1113 K. The plausible reason is that there was significant aggregation of TiO₂ at high surface energy at elevated temperature [6]. As a result, the specific surface area was underestimated at the temperature above 1053 K. In contrast, DLS overestimates the size of TiO₂ particles due to agglomeration in the solution. The degree of aggregation (d_{DLS}/d_{TEM}) increased with decrease in particle size due to the high surface energy of small particles.

Photocatalytic activity

Figure 5 shows the conversion of methylene blue in the presence of various TiO₂ photocatalysts. The decoloration reaction did not proceed in the absence of both TiO₂ and UV light. The decoloration reaction followed a pseudo-first order rate law, which was consistent with previous literatures [7].

Figure 4 also shows the effect of annealing temperature on the apparent decoloration rate. The reaction rate decreased with increase in the annealing temperature due to grain growth of TiO₂. Several reports have indicated that anatase phase has greater photocatalytic activity than the rutile phase due to the difference in band-gap energy ($E_{g,A} = 3.2 > E_{g,R} = 3.0$) and electron-hole recombination rate ($r_{rec,R} > r_{rec,A}$) [8]. Results of this present work show that the surface area and the aggregation effect also play important roles on the photocatalytic characteristics. The samples prepared at 873 K and 933 K had similar anatase fraction, but the reaction rate at 873 K was larger than at 933 K because of the difference in specific surface area. Moreover, both the anatase fraction and the surface area of TiO₂ at 773 K are much larger than those at 1373 K, but the reaction rate of TiO₂ at 773 K was only five times that of TiO₂ prepared at 1373 K. It may be in part attributed to the fact the secondary particle of TiO₂ at 1373 K was only four times that at 773 K.

Maira and coworkers also reported that the photoactivity of TiO₂ in term of trichloroethylene degradation was strongly dependent on the degree of aggregation of TiO₂ [9]. Therefore, the anatase fraction is not the most important factor affecting the photocatalytic decoloration of methylene blue. The decoloration reaction is only related to decomposing the chromophores group of the dye; rutile phase alone is sufficient to decolorize the dye through its oxidation activity. The large surface area (small primary particle size) and small secondary particle size are more important than the anatase fraction of TiO₂ in determining the decoloration rate.

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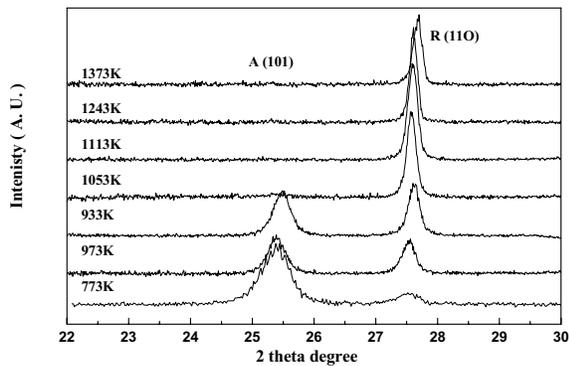


Figure 1 The XRD patterns of phase transition of TiO_2 particle

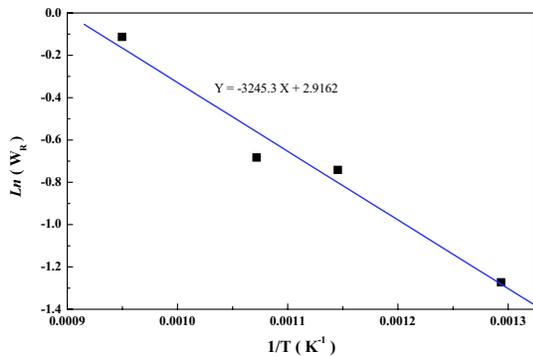


Figure 2 The Arrhenius plot of phase transition of TiO_2 particle

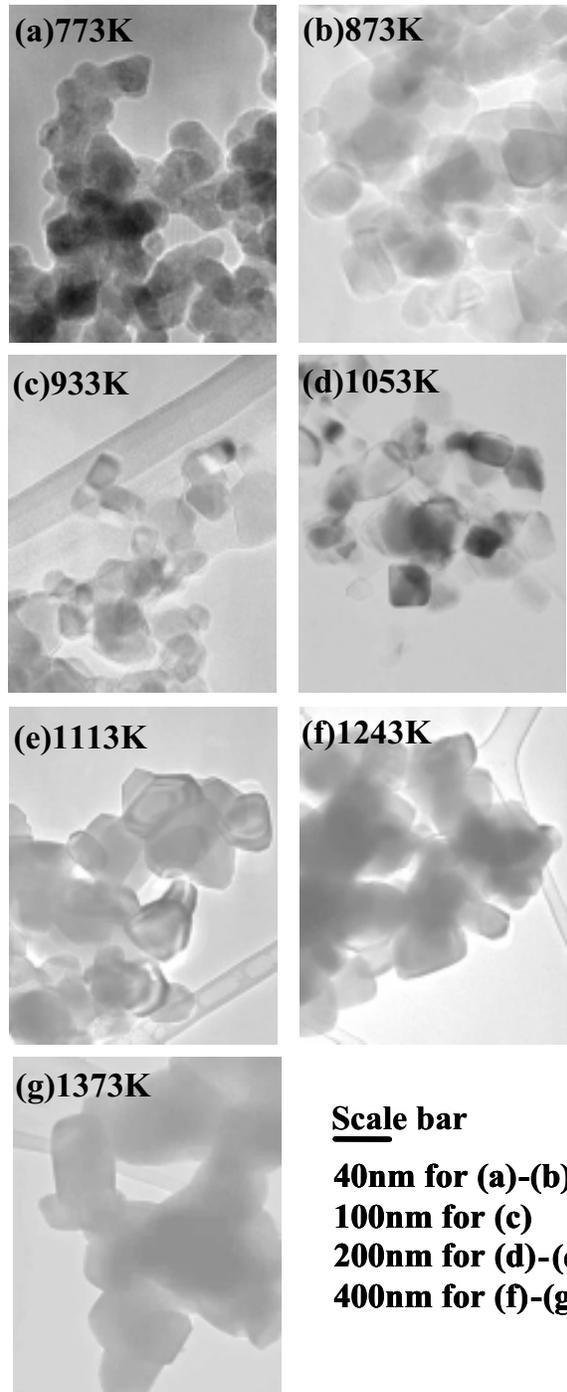


Figure 3 TEM images of variant TiO_2 particles

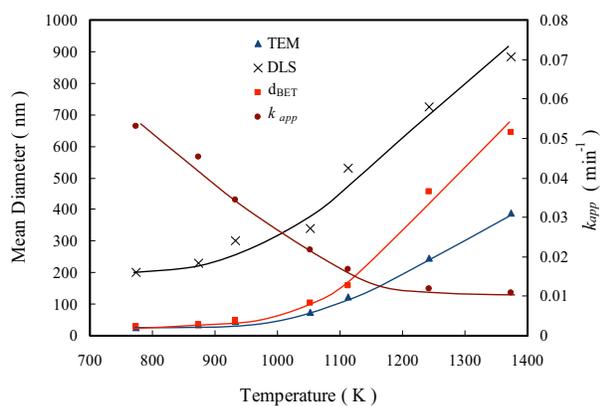


Figure 4 The effect of annealing temperature on the and particle size apparent rate

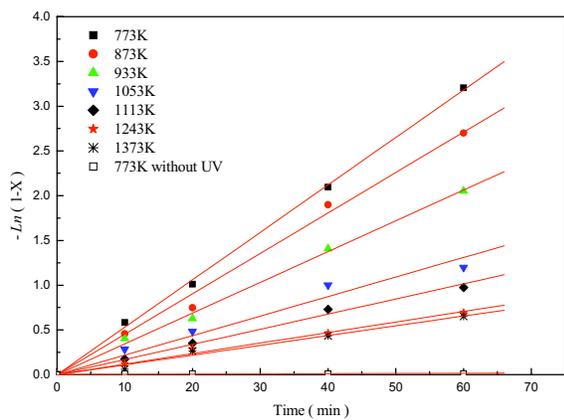


Figure 5 Conversions of methylene blue vs. time with variant TiO_2 catalysts; 100 mL of 6.25 nM methylene blue, 10 mg of TiO_2 , 15°C, 2 sets of 20 W black lamp