



Study of the effects of surface modification by thermal shock method on photocatalytic activity of TiO₂ P25



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ABSTRACT

In this study, we have modified TiO₂ P25 photocatalyst by thermal shock method at different temperatures in order to study the effects of thermal shock process on the crystal structure, surface properties and photocatalytic activity. The thermal-shock-modified catalysts were respectively characterized by X ray diffraction (XRD), scanning electronic microscopy (SEM), X ray photoelectron spectroscopy (XPS) and UV–vis diffuse reflectance spectra and compared with thermal-shock-fluorinated TiO₂ catalysts. The photocatalytic activity was evaluated via the degradation of methylene blue under UV and visible light irradiation. The results show that the deficiency of oxygen on the surface of catalysts created by thermal shock at 500 °C can enhance the photocatalysis under both UV and visible light. Moreover, when the thermal shock was combined with the fluorination of TiO₂, the photocatalytic performance was further improved. However, the thermal shock from 700 °C promoted the growth of particles and the phase transition from anatase to rutile, which resulted in two different effects: inhibit the photocatalysis under UV irradiation but improve it under visible irradiation.

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1. Introduction

During the past decade, a great deal of effort has been devoted to improve the photocatalytic activity of TiO₂ by doping this oxide with transition metals or non metal ions. It was generally observed that the presence of these dopants on substituted or interstitial sites of TiO₂ lattice could induce the formation of defects on the surface and in the bulk of TiO₂ such as dislocation defect, oxygen vacancies and titanium vacancies. However, the effect of these defects on the photocatalytic activity is still under debate. Some studies demonstrated that the defects can increase the photocatalytic performance and extend it into the visible light region [1–5] whereas the others found a decrease of TiO₂ activity with the increase of defects [6–8]. It should be noted that there always exist structural defects on the surface and inside TiO₂ bulk [9]. The defects formed in the bulk might lower its activity since they provide sites for the recombination of photogenerated charge carriers, while the presence of defects on the surface of semiconductors is beneficial for the photocatalysis [1,6,10,11]. The surface defects may act as electron capture centers, retarding the recombination of charge carriers [12,13].

Moreover, the surface oxygen vacancies can promote the adsorption of O₂ molecules [14,15], which can capture photogenerated electrons to produce high oxidative species such as O₂^{•−} radical groups. Therefore, introducing defects on the surface of photocatalysts can be a feasible way to improve the photocatalytic activity.

In our previous studies, fluorinated TiO₂ was successfully prepared by a simple thermal shock method [16,17]. This is the method which allowed us to carry out solid phase reactions at high temperatures during a short time. The results showed that the fluorination by thermal shock method in determined conditions could only affect the surface of TiO₂ without modifying the bulk structure and the morphology. Although TiO₂ fluorination was carried out by many previous study which indicated that the surface fluorination or insertion of F atoms into TiO₂ lattice only improve the UV light induced photocatalytic activity, our fluorinated catalysts demonstrated better activities under both UV and visible light illumination than naked TiO₂ P25 due to the formation of surface adsorbed fluoride ions and surface defects. This result indicated that the effect of thermal shock process play a very important role in photocatalytic activity of TiO₂.

However, the role of thermal shock method without fluorination in the photocatalytic performance of TiO₂ was not elucidated. R.G. Nair et al. [18] studied the influence of thermal treatment at various temperatures, from 600 to 850 °C during 1 h on the properties

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of TiO₂ but the thermal treatment used in their study is totally different from our thermal shock method. Therefore, in this work, we investigated the effects of thermal shock process at different temperatures on crystal structure, particle size, surface composition and then evaluated the photocatalytic activity of modified catalysts under both UV and visible light irradiation. Then the properties of modified TiO₂ by thermal shock method were compared with that of fluorinated TiO₂ to study the synergic effects of thermal shock and fluorination process. It should be noted that the photocatalytic tests for fluorinated TiO₂ catalysts in [16] was only carried out under visible light. Thus we also evaluated their photocatalytic performance under UV irradiation for a better overall comparison with thermal shock modified TiO₂ in this work.

2. Experimental

2.1. Thermal shock process

TiO₂ P25 (Evonik Aeroxide), a mixture of anatase and rutile with a primary particle size of 20–50 nm, was used as the target catalyst to modify by thermal shock method because it is so far the best commercial photocatalyst. TiO₂ was washed and dried at 150 °C. Then this powder was placed in an alumina crucible and rapidly put into a furnace for thermal shock (TS) sequences of 5 min at different temperatures: 500, 700, 950 °C and at normal atmospheric pressure. After 5 min, the samples were directly removed from the furnace, cooled down to the room temperature and grounded to obtain the final powder products. These samples were labeled as P25-X (with X the TS temperature).

For comparison, fluorinated TiO₂ samples were also prepared by TS method as described in our previous study [16]. Briefly, TiO₂ P25 nanoparticles were suspended in 10 mL of a KF solution (0.625 mol L⁻¹) with the molar ratio of fluorine to titanium of 1:1. The obtained white suspension was dried at 150 °C for 3 h and underwent a TS process at 500, 700 and 950 °C during 5 min. These fluorinated samples were labeled as FTO-X (with X the temperature of thermal shock process).

2.2. Characterization

The powder X ray diffraction (XRD) patterns of catalysts were measured on a SIEMENS D5000 X ray diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in order to investigate the crystal structure and phase composition. The acceleration voltage and the applied current were 40 kV and 20 mA, respectively. Data was collected from 20° to 80° (2θ) with a scan rate of 0.03° 2θ s⁻¹. The Rietveld refinement was carried out using the Fullprof 2009 structure refinement software [19].

Scanning electron microscopy (SEM) images were taken using a scanning electron microscope Hitachi S-4800 operating at the accelerating voltage of 30 keV and the probe current of 10⁻¹⁰ A. The surface area was measured by N₂ adsorption at 77 K using a Quantachrome NOVA 1000 Surface Area and Pore Size Analyzer. A five-point nitrogen adsorption isotherm was used to determine the BET surface area of catalysts.

The surface atomic composition and the chemical environment of elements on sample surface were analyzed by X ray photoelectron spectra (XPS) obtained on a Thermo K-alpha system with a hemispherical analyzer and a microfocussed (analysis area was ca. 200 μm^2) monochromatized radiation Al K α (1486.6 eV) operating at 75 W under the residual pressure of 1×10^{-7} mBar. Surface charging was minimized by a neutralizer gun, which sprays the low energy electrons and Ar⁺ ions over the sample surface. All the binding energy values are calibrated by using the standard binding energy of contamination carbon (C 1s = 285.0 eV) as a reference. The

treatment of core peaks was carried out using a nonlinear Shirley-type background [20]. The quantification of surface composition was based on Scofield's relative sensitivity factors [21].

UV-vis absorption spectra of catalysts were obtained using a UV-vis spectrophotometer with an integrating sphere (JASCO V-550). They were recorded at room temperature in steps of 2 nm, in the range 200–900 nm with a bandwidth of 2 nm and were referenced to BaSO₄. The band gap energy E_g can be evaluated from a plot of $(\alpha)^{1/2}$ versus photon energy ($h\nu$) where α is the absorption coefficient [22].

2.3. Photocatalytic study

The photocatalytic activities of TiO₂ P25 and modified samples by TS method as well as fluorinated samples were evaluated through the degradation of methylene blue (MB). The tests were performed in a reactor which consists of a glass beaker containing 250 mL of aqueous MB solution (10⁻⁵ mol L⁻¹) with catalyst (0.5 g L⁻¹), cooled by continuous water flow and stirred continuously by magnetic agitator in the dark for 30 min to ensure the adsorption/desorption equilibrium. The reaction solution was then irradiated by an 8-W UV light lamp (350 nm) or an 8-W visible light lamp (420 nm) placed about 15 cm above the solution surface. The initial pH of prepared suspensions was seven and did not considerably change during all the experiments (pH = 6.8 \pm 0.2). During the illumination, 10 mL of dispersions were sampled every 30 min, centrifuged and analyzed by SP-300 Optima spectrophotometer.

3. Results and discussions

3.1. Crystal structure and morphology

X ray diffraction was used to investigate the effect of TS process on the crystal structure and phase composition of TiO₂ P25. Fig. 1 shows the X ray diffractograms of TiO₂ P25 and TS-modified catalysts at different temperatures. The phase composition of these samples was summarized and compared with those of fluorinated catalysts obtained in our previous study [16] in Table 1. TiO₂ P25 consists of a mixed phase of anatase (space group I4₁/amd, JCPDS No. 21-1272) and rutile (space group P4₂/mnm, JCPDS No. 21-1276) in the ratio of 90:10. When TiO₂ P25 was modified with TS process at 500 °C, no modification of phase composition was observed. The width of peaks of P25-500 sample also remains unchanged in comparison with TiO₂ P25. This is similar to XRD results of FTO-500 sample, indicating that the TS process at this temperature does not change the phase composition and the oxide crystallite size. However, when TS temperature reaches at 700 °C, the rutile amount slightly increases (about 15%) whereas the anatase amount decreases (about 85%). This is in good agreement with the phase transition from anatase to rutile which generally occurs at 700 °C [23]. At TS temperature of 950 °C, XRD pattern shows that all anatase phase was completely transformed into rutile phase. The average diameter of anatase and rutile crystallites were respectively calculated from the full width of half maximum (FWHM) of diffraction peaks by using the Debye-Scherrer formula:

$$D_{hkl} = \frac{k\lambda}{\beta \cos \theta}$$

where D_{hkl} is the crystallite size, k is the constant dependent on crystallite shape (0.9), λ is the wavelength of copper K α X-ray radiation (1.5406 \AA), β is the FWHM of the most intense diffraction lines for anatase (1 0 1) and rutile (1 1 0) and θ is their diffraction angle (Table 1). The crystallite sizes are found to be in nanoscale and about 20–50 nm for both anatase and rutile phases in TiO₂ P25, PTO-500 and PTO-700 samples. The average rutile crystallite size only increased to 69.5 nm when TiO₂ P25 was TS-modified at 950 °C.

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