



# Effect of calcination temperature on the physicochemical properties of highly active sulfated titania photocatalysts



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## ARTICLE INFO

### Article history:

Received 27 November 2012  
Received in revised form 9 October 2013  
Accepted 20 October 2013  
Available online 28 October 2013

### Keywords:

Sulfated titania  
Photocatalysis  
Environmental pollution  
Calcination temperature  
Surface property

## ABSTRACT

Highly active sulfated titania photocatalysts ( $\text{SO}_4^{2-}/\text{TiO}_2$ ) were prepared using  $\text{Ti}(\text{SO}_4)_2$  as precursor via a precipitation and peptization process. Precipitates obtained through adding NaOH solution into  $\text{Ti}(\text{SO}_4)_2$  were peptized with  $\text{HNO}_3$ , followed by calcination at varying temperatures to form  $\text{SO}_4^{2-}/\text{TiO}_2$ . The objective of the present work is to clarify the effect of calcination temperature on the structure and surface properties of  $\text{SO}_4^{2-}/\text{TiO}_2$ . A variety of characterization techniques, involving X-ray diffraction (XRD), Brunauer–Emmett–Teller analysis (BET), X-ray photoelectron spectroscopy (XPS), surface photovoltage spectroscopy (SPS), and electron spin resonance (ESR), were employed in this study. XRD revealed that well-crystallized titania was formed upon calcination at  $300^\circ\text{C}$  ( $\text{SO}_4^{2-}/\text{TiO}_2$ -300). Owing to the stabilization effect of sulfate,  $\text{SO}_4^{2-}/\text{TiO}_2$ -300 exhibited small crystalline size and high surface area, which can account for its superior photocatalytic performance. Catalyst calcination at  $600^\circ\text{C}$  ( $\text{SO}_4^{2-}/\text{TiO}_2$ -600) rendered rapid growth of crystalline size and drop of surface area. Meanwhile, such high-temperature calcination treatment gave rise to  $\text{Ti}^{3+}$  defects and oxygen vacancies. Although the photoactivity of  $\text{SO}_4^{2-}/\text{TiO}_2$ -600 was remarkably reduced as compared with  $\text{SO}_4^{2-}/\text{TiO}_2$ -300, it was still higher than that of Degussa P25 due very likely to the formation of  $\text{Ti}^{3+}$ -oxygen vacancies- $\text{Ti}^{3+}$  sites that are beneficial for the separation of photoinduced electrons and holes.

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## 1. Introduction

As promising materials for environmental pollution treatments, nanosized titania photocatalysts have drawn considerable attention because of their potential application in photocatalytic degradation of various organic pollutants to nontoxic  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [1–3]. One of the prerequisites for the practical applications of this technology is to further enhance the photocatalysis efficiency of titania. Consequently, a great number of studies focusing on titania modification by various methods have been carried out to achieve this goal [4–10]. For example, it was reported that  $\text{Eu}^{3+}$ -doped titania nanoparticles exhibited extraordinary photoactivity because of the incorporation of  $\text{Eu}^{3+}$  ions into bulk titania network, leading to improved physicochemical properties such as pronounced lattice expansion and abundant surface defects [11,12]. Moreover, adding an appropriate amount of silica has also been proved an effective way to enhance the photoactivity of titania. The promotion effect of silica is largely attributed to the fact that silica addition is capable of improving the thermal stability of titania, resulting in smaller crystalline size and larger surface area [13–18]. Especially, Hu et al.

carried out a pioneer study regarding ternary titania/silica, such as Pt-modified titania/silica, and reported that this approach is very promising for considerably enhancing the photocatalysis efficiency of titania [4–6].

In addition to the aforementioned strategies, sulfation of titania has been considered as an effective way to improve the photocatalytic performance of titania as well [7,8]. So far, numerous studies have been published in this field concentrating on the preparation, characterization, and photocatalytic activity of sulfated titania [7–10,13,14,19,20]. Several research groups have made remarkable progress in this research area and reported a series of important findings regarding the physicochemical properties and photocatalytic performance of sulfated titania [7–10,13,14,19–22]. Many studies have attributed the exceptional photoactivity of sulfated titania to the fact that the sulfation treatment can effectively stabilize titania, and maintain its crystalline structure and surface area upon high-temperature calcination treatment [7–9]. Furthermore, this approach has also been widely used to improve the activity of miscellaneous photocatalytic materials such as titania nanotubes and films [23–25]. Zhang et al. [23] synthesized sulfated titania nanotubes using sulfuric acid through a hydrothermal treatment and impregnation method. The authors reported that the photocatalytic performance of as-prepared sulfated titania nanotubes was substantially enhanced, which was found to be strongly

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related with the sulfuric acid concentration and the degree of crystallinity.

Traditionally, sulfated titania photocatalysts are prepared by impregnation of sulfuric acid onto titania [7,8,10,23]. As a consequence, titania with large surface area and porous structure is necessary for effective sulfate immobilization onto titania surfaces. This means that expensive and complicated preparation techniques are usually required for obtaining porous titania with high surface area. As such, it is desirable to develop an efficient and simple preparation method that can overcome the aforementioned obstacle for sulfated titania photocatalysts. In this study, highly active sulfated titania was prepared using  $\text{Ti}(\text{SO}_4)_2$  as the precursor via a precipitation and peptization process, i.e., the precipitates obtained by adding NaOH solution into  $\text{Ti}(\text{SO}_4)_2$  were peptized with  $\text{HNO}_3$ , followed by calcination treatment at varying temperatures. One of major advantages for this method is that it combines the formation of titania network and titania sulfation into one step. As a result, sulfate can be homogeneously distributed throughout the bulk of titania, leading to much more effective sulfate modification. A variety of characterization techniques, involving X-ray diffraction (XRD), Brunauer–Emmett–Teller analysis (BET), X-ray photoelectron spectroscopy (XPS), surface photovoltage spectroscopy (SPS), and electron spin resonance (ESR), were employed in this work to clarify the effect of calcination temperature on the structure and surface properties of sulfated titania.

## 2. Experimental

### 2.1. Catalyst preparation

All chemicals in this study were used as received without further purification. Firstly, white precipitate A was obtained by slowly adding 1.1 M NaOH solution (the mol ratio of NaOH to  $\text{Ti}(\text{SO}_4)_2$  is 4.2:1) into  $\text{Ti}(\text{SO}_4)_2$  solution (analytical grade) under vigorous stirring at ambient temperature. After centrifuged and washed by distilled water until the supernatant liquid was neutral, the precipitate A was dissolved in 70 wt%  $\text{HNO}_3$  to form colloid, and then heated in a water-bath to form precipitate B. Following that, the precipitate B was aged for 24 h at ambient temperature, and then centrifuged and washed by distilled water until the supernatant liquid was neutral. Finally the precipitate B was dried, and calcined at 300 and 600 °C for 2 h, respectively. The samples were labeled as  $\text{SO}_4^{2-}/\text{TiO}_2\text{-}T$ , where  $T$  stands for the calcination temperature.

### 2.2. Catalyst characterization

The crystalline phase of sulfated titania was characterized by a Bruker D8 GADDS X-ray diffractometer using  $\text{Cu K}\alpha$  radiation ( $\lambda = 1.54056 \text{ \AA}$ ). The crystalline size  $D$  was calculated based on the width of lines in the X-ray pattern with the aid of the Scherrer formula:  $D = K\lambda/(\beta \cos \theta)$ , where  $\lambda$  is the wavelength of the X-ray used,  $\beta$  is the width of the line at the half-maximum intensity, and  $K$  is a constant. The second strain root-mean-square values (SS) of sulfated titania catalysts were calculated by X-ray line profile refine method, through which titania phase crystal planes of (1 1 0), (1 0 1) and (1 1 1) were calculated. Surface area measurements were conducted on Micromeritics ASAP 2010 using nitrogen as the adsorbent. Brunauer–Emmett–Teller (BET) equation was used to calculate the surface area from the adsorption branch. The pore size distribution was calculated by analyzing the adsorption branch of the nitrogen sorption isotherm using Barret–Joyner–Halenda (BJH) method. X-ray photoelectron spectroscopy (XPS) was performed in a VG ESCALAB MKII X-ray photoelectron spectrometer. The X-ray source emitted  $\text{Mg K}\alpha$  radiation (1253.6 eV). The pressure for all the

XPS experiments was maintained at  $6.3 \times 10^{-7} \text{ Pa}$ . Binding energies were calibrated with respect to the signal of adventitious carbon (binding energy = 284.6 eV). XPS quantitative analysis was done by normalizing peak areas to the elemental sensitivity factor data supplied with the instrument. Surface photovoltage spectroscopy (SPS) was carried out with a surface photovoltage spectrometer. Monochromatic light was obtained by passing light from a 500 W xenon lamp (CHF XQ500W, Global xenon lamp power made in China) through a double-prism monochromator (Hilger and Watts, D300 made in England). The slit width of entrance and exit was set as 1 mm. A lock-in amplifier (SR830-DSP, made in USA), synchronized with a light chopper (SR540, made in USA), was employed to amplify the photovoltage signal. The range of modulating frequency was from 20 to 70 Hz with the spectral resolution being 1 nm. The raw SPS data was normalized using the illuminometer (Zolix UOM-1S, made in China). The contact between sample and indium-tin-oxide (ITO) electrode is not ohmic contact. The structure of the photovoltaic cell is a sandwich structure, which ensured that the light penetrating depth is much less than the samples' thickness. The signal of photovoltage is attributed to the changes of surface potential barriers before and after illumination. Electron spin resonance (ESR) measurements (Bruker ER200D/SRC, 9.56 GHz) were carried out at 120 K to investigate the generation of paramagnetic species for the sulfated titania photocatalysts calcined at different temperatures. UV–vis spectra were recorded on a Perkin-Elmer Lambda 20 spectrometer.

### 2.3. Photocatalytic reaction system

Photocatalytic activity tests for the degradation of cyclohexene were carried out at ambient temperature using a 300 ml cylindrical quartz tube (4.4 cm i.d. and 20 cm length). In an experiment, 0.1 g catalyst was spread uniformly over the internal surface of the reactor. After this, the reactor was vacuum-packed and then certain amounts of cyclohexene (0.1%, v/v) and oxygen (20%, v/v) were injected into the reactor. Finally ultrapure nitrogen was mixed with the reactant in the reactor to reach atmospheric pressure. In order to reach adsorption equilibrium of gas-phase reactants over the catalyst surfaces, the reactor filled with the mixture of reactant gases was kept in dark for at least 30 min. The concentration of cyclohexene was measured by Gas Chromatography (GC) till it became stable to ensure that the reaction system reached the point of adsorption equilibrium. The photocatalytic reactions were initialized by turning on a 350 W Xe lamp that produces light illumination with a strong peak centered at 450 nm. Subsequently, the reactant concentration in the reactor was monitored by a HP4890 GC with a flame ionization detector (FID). For comparison, the photoactivity of Degussa P25 (a benchmark catalyst in the photocatalysis field) was also measured as a reference. The yields of  $\text{CO}_2$  in the photocatalytic reactions were determined by GC equipped with a thermal conductivity detector (TCD) and a Porapak QS stainless-steel column. Our analyses showed that the generation of  $\text{CO}_2$  in the reactions was stoichiometric with respect to the conversion of cyclohexene, and no other gas-phase intermediates were detected. This fact demonstrates that cyclohexene was mineralized into harmless species such as  $\text{CO}_2$  in the photocatalytic reactions over sulfated titania catalysts.

## 3. Results and discussion

### 3.1. Crystalline structure and BET surface area

The crystalline phase of titania is such a factor that can remarkably influence its photocatalytic performance [1–3]. Therefore, we

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