

# The effect of calcination temperature on the structure and activity of TiO<sub>2</sub>/SiO<sub>2</sub> composite catalysts derived from titanium sulfate and fly ash acid sludge

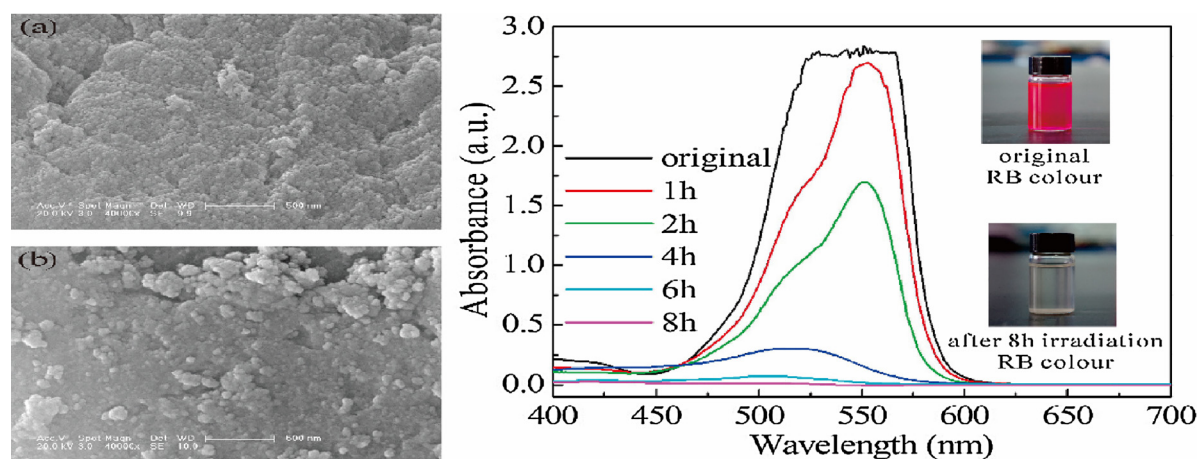
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## GRAPHICAL ABSTRACT



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## ABSTRACT

The composite catalysts of TiO<sub>2</sub>/SiO<sub>2</sub> were prepared through a sol-gel process followed by the calcination crystallization process. The inexpensive precursors, titanium sulfate and fly ash acid sludge, were used as providing titania and silica sources, respectively. The decomposition of fly ash acid sludge was digested with NaOH to extract silica, and the obtained sodium silicate was used to prepare TiO<sub>2</sub>/SiO<sub>2</sub> composite. The effect of calcination temperature on the structure of TiO<sub>2</sub>/SiO<sub>2</sub> composites was studied by means of XRD, BET, FTIR, SEM, photocatalysis and adsorption test. It was found that the anatase-to-rutile phase transition temperature of TiO<sub>2</sub>/SiO<sub>2</sub> composite powders was significantly higher than that of pure TiO<sub>2</sub>. The presence of the Ti–O–Si bond was confirmed in the final products when the incorporation of titania into silica were performed. The photocatalytic performance of TiO<sub>2</sub>/SiO<sub>2</sub> composite annealed at different temperatures was evaluated by Rhodamine B (RhB) as the target pollutant under visible-light irradiation. Results indicated that the sample exhibited the highest photocatalytic activity when the calcination temperature is up to 600 °C. After 4 h visible-light irradiation, about 90% of RhB was removed by this type of photocatalysts.

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## 1. Introduction

Titanium dioxide (TiO<sub>2</sub>) is recognized as one of the most promising photocatalysts for removing organic dye pollutants from textile wastewater, owing to its low cost, strong oxidability, nontoxicity, biological and chemical inertness [1–8]. However, the small-sized particles share a high level of surface energy. TiO<sub>2</sub> nano-particles are easy to form agglomerates, which degrades activity and significantly limits the practical application for pure TiO<sub>2</sub> in view of wastewater treatment [9–14]. To solve these problems, some researches have focused on study and modify the surface of TiO<sub>2</sub> to prepare the composite catalysts with excellent properties, such as TiO<sub>2</sub>/SiO<sub>2</sub>, TiO<sub>2</sub>/ZrO<sub>2</sub>, TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, TiO<sub>2</sub>/ZrO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [15–19].

Fly ash acid sludge (FAAS) is a kind of industrial waste residue, which derived from circulating fluidized bed fly ash extracted alumina by acid leaching process. The main component of FAAS is amorphous silica. The high silica content of FAAS makes it an ideal raw material for preparing silico-based products, such as white carbon black, 4A molecular sieve, silica aerogel [20–22], which could not only perfect and extend the industrial chain of comprehensive utilization of fly ash, but also solve a series of negative issues brought about by FAAS. Nevertheless, the preparation of TiO<sub>2</sub>/SiO<sub>2</sub> composite catalysts using FAAS as silica source and titanium sulfate as titanium source has rarely been reported.

In the present study, TiO<sub>2</sub>/SiO<sub>2</sub> composite catalysts were prepared using cheap FAAS and titanium sulfate as precursors via a sol-gel process followed by the calcination crystallization process. The silica in FAAS was extracted by alkali dissolution process to form sodium silicate solution as silicon precursor. The TiO<sub>2</sub>/SiO<sub>2</sub> composite catalysts prepared under different calcination temperatures were characterized and the comparative photocatalytic and adsorption activity studies were also carried out.

## 2. Experimental methods

### 2.1. Raw material and chemical reagents

Fly ash was hydrothermally reacted with HCl solution and then the obtained mixture was filtered using a vacuum filter. The resulting residue was FAAS. The FAAS consists mostly of SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, as well as smaller amounts of TiO<sub>2</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub> and K<sub>2</sub>O. Deionized (DI) water was used in all experiments. Titanium sulfate (Ti(SO<sub>4</sub>)<sub>2</sub>), sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), sodium hydroxide (NaOH) and Rhodamine B (RhB) used in the experiments were analytical grade reagents and supplied by Beijing Chemical Reagent Research Institute.

### 2.2. Synthesis process

#### 2.2.1. Silica extraction

Firstly, FAAS (10 g) was mixed with NaOH solution (15 wt.%, 45 g), and then the mixture added to a reaction kettle heated and stirred at 90 °C for 2 h. Then, the mixture was filtered and washed. The filtrate was the Na<sub>2</sub>SiO<sub>3</sub> solution, which would be used as silicon precursor to prepare TiO<sub>2</sub>/SiO<sub>2</sub> composite catalysts.

#### 2.2.2. Synthesis of TiO<sub>2</sub>/SiO<sub>2</sub> composite catalysts

The above resulting Na<sub>2</sub>SiO<sub>3</sub> solution was adjusted to pH = 2–3 with 2 mol/L H<sub>2</sub>SO<sub>4</sub> solution, and then the solution was adjusted to pH to pH = 5–6 using the 1.0 mol/L NaOH solution. A portion of 3 mol/L Ti(SO<sub>4</sub>)<sub>2</sub> solution was added into the adjusted Na<sub>2</sub>SiO<sub>3</sub> solution (Ti/Si molar ratio = 0.5) under stirring for 60 min, obtaining TiO<sub>2</sub>/SiO<sub>2</sub> composite sol. The temperature was set at 80 °C for gelation. Afterwards, the TiO<sub>2</sub>/SiO<sub>2</sub> composite gel was aged at 80 °C for 2 h. The obtained gel was washed with DI water and then dried at 120 °C (labeled TSC). Finally, the dried sample was calcined at different temperatures for 2 h (dubbed TSC-calcination temperature, for example,

the sample calcined at 300 °C was named TSC-300). For comparison, pure TiO<sub>2</sub> was obtained in the absence of Na<sub>2</sub>SiO<sub>3</sub> solution, which was replaced by DI water. Ti(SO<sub>4</sub>)<sub>2</sub> solution was added into the adjusted DI water under stirring for 60 min. The mixture solution was aged at 80 °C. The product was collected by filtration and dried at 120 °C (labeled TT). The dried sample was calcined at different temperatures for 2 h (denoted TT-calcination temperature, for example, the sample calcined at 300 °C was named TT-300).

### 2.3. Characterization

The crystal structure of the samples was characterized by X-ray diffraction analysis (XRD, DX-2700, China). The light absorption behaviors of the samples were investigated by a UV–vis diffuse reflectance spectrometer (UV–vis DSR, TU-1901, China). The chemical bonding state of the samples was confirmed with Fourier transform infrared spectroscopy (FTIR, Nicolet 380, US). Brunauer-Emmett-Teller (BET) method on the nitrogen adsorption apparatus (ASAP 2010, USA) was applied to determine the specific surface area of the samples. The microstructure of the samples was investigated by field emission scanning electron microscopy (FE-SEM, FEI, XL30, US).

### 2.4. Photocatalytic and adsorption test

Rhodamine B (RhB) was chosen as a model organic pollutant to evaluate the photocatalytic activity, and the experiments were performed under a 250 W high-pressure mercury lamp (Philips). The light beam was passed through optical filter to cut-off wavelengths shorter than 400 nm. Briefly, 0.040 g of the composite photocatalyst was dispersed in 10 mL RhB solution (30 mg/l), while the amount of pure TiO<sub>2</sub> (0.010 g) equivalent to that present in the composite catalyst was used. The solution was irradiated regularly by visible light source. Prior to the measurement step, the catalyst was separated from the solution by centrifugation. The supernatant was analyzed using an UV–vis spectrophotometer and record the maximum absorption peak of RhB at 554 nm. The adsorption behavior of the photocatalysts was assessed in the adsorption of RhB solution. The experiment was the same as the photocatalytic experiment, except that there was no light source.

The decolorization percentage ( $\eta$ ) of RhB can be calculated by the following equation:

$$\eta = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

where  $C_0$  and  $C_t$  are the concentrations of RhB at initial time and at time  $t$ , respectively.

## 3. Results and discussion

The crystal phase of TiO<sub>2</sub> can have a significant effect on the photocatalytic performance, and the crystalline phase and crystallinity of TiO<sub>2</sub> depend strongly on the calcination temperature [23]. The XRD patterns of TSC and TT catalyst calcined at different temperatures are shown in Fig. 1. As displayed in Fig. 1(a), the XRD pattern of TSC catalyst without calcination exhibited the weaker diffraction peaks for anatase TiO<sub>2</sub>. As calcination temperature increased, the characteristic peaks of anatase TiO<sub>2</sub> became more and more sharp. This finding implied the enhancement in degree of crystallinity. When the calcination temperature reached 1300 °C, a small diffraction peaks corresponding to rutile TiO<sub>2</sub> appeared. According to the reports [24,25], rutile TiO<sub>2</sub> has less photocatalytic activity than anatase TiO<sub>2</sub>. Compared with TSC catalyst, it was easier to transform from anatase phase into rutile phase for TT catalyst and transition temperature was around 800 °C (Fig. 1(b)). These results illustrate that the TSC powders synthesized in this paper can inhibit the crystalline phase transformation from anatase to rutile up to 1200 °C, that is, anatase TiO<sub>2</sub> with the higher crystallinity and less surface defects can be obtained. It will be beneficial to enhance the photocatalytic performance.

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