



## Study on the behavior of sulfur in hydrolysis process of titanyl sulfate solution



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### ABSTRACT

The existing forms of sulfur in hydrolysis process of titanyl sulfate solution were studied. Also the effects of sulfur on crystal structure, crystallite size and crystal phase transition of the hydrated titanium dioxide ( $\text{TiO}_2 \cdot \text{H}_2\text{O}$ ) and titanium dioxide ( $\text{TiO}_2$ ) were conducted. The analysis and methods of thermogravimetric-differential scanning calorimetry (TG-DSC), energy dispersive spectrometer (EDS), Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), UV–Vis diffuse reflectance spectra and Raman spectroscopy were employed to characterize. The results indicated that the sulfur was present in the form of  $\text{SO}_4^{2-}$  ions in the hydrolysate of titanyl sulfate solution, and a portion of  $\text{SO}_4^{2-}$  ions were combined on the surface of hydrated titanium dioxide by chemical adsorption in the forms of inorganic chelating bidentate coordination and covalent sulfate coordination, the residual  $\text{SO}_4^{2-}$  ions were adsorbed on the surface of hydrated titanium dioxide by physical adsorption. The chemical adsorption of  $\text{SO}_4^{2-}$  ions were conducive to the formation and stabilization of anatase, which changed the crystal structure, and hindered the transformation of the anatase into rutile. The results of Raman spectroscopy showed that the sulfur was dissociated in the forms of  $\text{SO}_4^{2-}$  and  $\text{HSO}_4^-$  ions during the hydrolysis of titanyl sulfate solution. The characteristic peak at  $1004 \text{ cm}^{-1}$  corresponding to a new complex has been observed, which was composed of  $\text{SO}_4^{2-}$  and hydrated titanium complex ions through the bonding on the surface. In basis of the above experimental results, the hydrolysis process of titanyl sulfate solution was illustrated from the microstructure with 3D atlas.

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### 1. Introduction

Titanium dioxide, because of its optical properties, plays a significant role in the chemical industry, particularly in the form of anatase pigment powders. Precipitation by thermal hydrolysis in sulphuric medium of titanyl sulphate solution is the usual process for the production of anatase. In the process, hydrolysis is one of the key steps [1–3]. Some simple ions are present in the hydrolysis process, such as  $\text{TiO}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{HSO}_4^-$ ,  $\text{H}^+$ ,  $\text{OH}^-$ , but some complex ions may also exist because of the complexity of the process. Among them the ions containing sulfur will directly influence the formation of hydrated titanium dioxide particles and at last influence the crystal structure and properties of titanium dioxide [4,5]. Therefore, it is necessary to study the behavior of sulfur in hydrolysis process and hydrolysate of titanyl sulfate solution.

Some researchers have done much work to study the behavior

of sulfur in hydrolysis process and hydrolysate of titanyl sulfate solution. Lijuan Zheng [6] investigated the effects of the concentrations of impurities in ilmenite on hydrolytic conversion and morphology of the hydrolysates. In basis of the sulfur content in hydrolysate detected by EDS and TG analysis, she speculated that  $\text{SO}_4^{2-}$  was not involved in formation of titanium hydrate complex in the hydrolysis process. The primary particles will further aggregate and form secondary aggregates via sulfate bridge bonds. Takaaki Sakai [7] studied the electrical conductivity and electrochemical properties of hydrous sulfated nano-titania. He found that the physical adsorption of  $\text{SO}_4^{2-}$  would bond with  $\text{TiO}_2$  on the surface of hydrolysate after heat treatment at  $350 \text{ }^\circ\text{C}$ , and the bonding sulfonic acid groups promoted the proton conduction on the surface of the titania nanoparticles. Some relevant studies also have been done. Mingjun Zhang [8,9] prepared  $\text{SO}_4^{2-}/\text{TiO}_2$  superacid catalyst with titanyl sulfate as titanium source and put forward that  $\text{SO}_4^{2-}$  bonded with  $\text{TiO}_2$  in the form of chelating bidentate coordination on the surface of hydrolysate after calcinating at  $300 \text{ }^\circ\text{C}$ . Fabien Baillon [10] investigated FT-Raman spectrometry of the addition of titanium(IV) to aqueous solutions of sulphuric acid, solutions

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containing 0 M–4.01 M of titanium(IV) and 1.98 M–6.17 M of sulphuric acid. From mass balance it was deduced that two complexes were present in the solution:  $[\text{Ti}(\text{OH})_2\text{SO}_4(\text{H}_2\text{O})_3]$  and  $[\text{Ti}(\text{OH})_2(\text{SO}_4)_2(\text{H}_2\text{O})_2]^{2-}$ . In order to prepare  $\text{TiO}_2$  photocatalytic material with excellent properties, some researchers investigated the titania nanocatalyst doped with sulphur and studied the effects of different valence states of sulfur on the crystal structure and electronic structure of anatase. They found that the sulfur was either doped as an anion and replaced the lattice oxygen or incorporated as cation and replaced Ti ions in the S doped  $\text{TiO}_2$ . The lattice deformed and band gap decreased after doping sulfur in  $\text{TiO}_2$  [11–15].

Although many investigations have been conducted on the behavior of sulfur in hydrolysis process and hydrolysate of titanyl sulfate solution to some extents, it appears that their researches are not systematic enough. Their work has mainly focused on the effect of the composition of the precipitate liquors and operating conditions on hydrolytic conversion, crystal structure and particle size of the hydrolysates, or focused on the preparation of  $\text{SO}_4^{2-}/\text{TiO}_2$  superacid to change photocatalytic activity of  $\text{TiO}_2$  nanocatalyst etc. Actually, the behavior of sulfur in hydrolysis process of titanyl sulfate solution is unclear, and hydrolysis mechanism need to be further clarified.

In this paper, titanyl sulfate was used as hydrolysis raw material to prepare hydrated titanium dioxide particles by self generated seed method. We focused on the study of the existing forms of sulfur in hydrolysate, the effects of sulfur on crystal structure, crystallite size and crystal phase transition of the hydrated titanium dioxide and titanium dioxide. On the basis of the above results, analysis of the behavior of sulfur during hydrolysis was done. It is beneficial to clarifying the hydrolysis mechanism of titanyl sulfate solution, providing a reference for the process and quality control of product during producing titanium dioxide by sulfuric acid method.

## 2. Experimental

### 2.1. Sample preparation

250 g titanyl sulfate solid (CP, 98wt%, Xiya Reagent) was dissolved in 500 ml deionized water under the ultrasonic condition for 30 min, and stirred under normal circumstance until the titanyl sulfate thoroughly dissolved. Then the solution was concentrated

under vacuum to adjust the  $\text{TiO}_2$  concentration in the solution to  $103 \text{ g L}^{-1}$ ,  $156 \text{ g L}^{-1}$ ,  $195 \text{ g L}^{-1}$  and a certain amount of sulfuric acid was added to adjust the F value [ $m(\text{effective H}_2\text{SO}_4)/m(\text{TiO}_2)$ ] to 1.9, respectively.

The reactor with 50 ml titanyl sulfate solution with  $\text{TiO}_2$  concentration of  $103 \text{ g L}^{-1}$  and 10 ml pre-adding deionized water were warmed up to  $96 \text{ }^\circ\text{C}$  in a thermostat water bath respectively, then the heated titanyl sulfate solution was dropped into the pre-adding deionized water at a constant speed during 20 s under stirring condition. After feeding off, 200 ml boiled deionized water was added to the titanyl sulfate solution system immediately. Thus the temperature was about  $96 \text{ }^\circ\text{C}$  and remained constant. Keep stirring and heating in magnetic stirring water bath until the reaction time was 90 min. Change the amount of washing water during filtering and washing to obtain hydrolysis product hydrated titanium dioxide ( $\text{TiO}_2 \cdot \text{H}_2\text{O}$ ). All the  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  particles were dried at  $110 \text{ }^\circ\text{C}$  for 2 h to obtain different  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  samples. The amount of washing water was 0 L, 1.6 L, 4.5 L, and the obtained samples were labeled as A, B and C, respectively. Then the  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  sample A was calcined at  $500 \text{ }^\circ\text{C}$ ,  $600 \text{ }^\circ\text{C}$ ,  $700 \text{ }^\circ\text{C}$ ,  $800 \text{ }^\circ\text{C}$  and  $900 \text{ }^\circ\text{C}$  for 2 h in muffle furnace at heating rate of  $10 \text{ }^\circ\text{C min}^{-1}$  to prepare titanium dioxide ( $\text{TiO}_2$ ), and the obtained samples were labeled as  $\text{A}_1$ ,  $\text{A}_2$ ,  $\text{A}_3$ ,  $\text{A}_4$  and  $\text{A}_5$ , respectively.

Maintain the other experimental conditions constant and change the  $\text{TiO}_2$  concentration of titanyl sulfate solution. 2 ml reaction solution with different  $\text{TiO}_2$  concentrations was taken to be examined by Raman spectrometer after hydrolysis 30 min.

### 2.2. Characterization

The weight loss of samples was determined by thermogravimetric-differential scanning calorimet (TG-DSC, Netzsch, STA449C, Germany). The content of sulfur in the samples was determined by JSM-5900LV scanning electron microscope equipped with energy dispersive spectrometer (EDS, INCA, Japan). FTIR spectra (Spectrum Two, L1600300, Perkin Elmer, USA) was employed to investigate ionic bonds in  $\text{TiO}_2 \cdot \text{H}_2\text{O}$ . Sample powder was mixed with KBr and subsequently pressured into thin disks to be measured in a Pyrex cell. The energy gap value of samples were calculated through the analysis of UV-Vis diffuse reflectance spectra (UV2100, SHIMADZU, Japan). XRD experiments of samples were performed with a DX-2007 X-ray diffraction spectrometer (Danton, China) to investigate the effect of chemical adsorption of

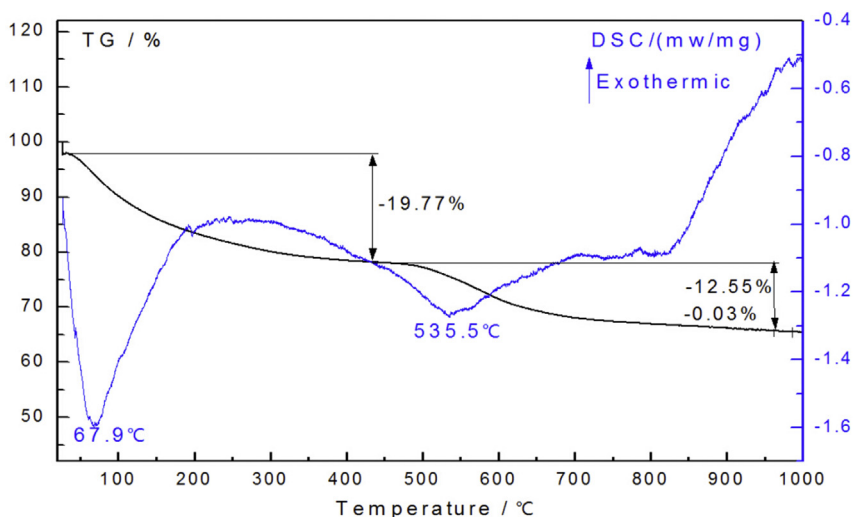


Fig. 1. Thermogravimetric-differential scanning calorimet curve of the  $\text{TiO}_2 \cdot \text{H}_2\text{O}$  sample A.

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