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Chemical Engineering Science

Mechanism and kinetics of titanium hydrolysis in concentrated titanyl sulfate solution based on infrared and Raman spectra

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HIGHLIGHTS

- Bridging bidentate SO_4^{2-} ligands were found in solution using FTIR spectra.
- Quantization of concentrations of SO_{4free}^{2-}, $SO_{4complex}^{2-}$, HSO_{4pair}^{-} and HSO_{4free}^{-}.
- Transformation from SO_4^{2-} ligand to free HSO_4^{-} are detected by Raman spectra.
- A chemical kinetic model was established to fit the titanium hydrolysis.

ARTICLE INFO

ABSTRACT

The titanium hydrolysis in the concentrated titanyl sulfate solution is essential to the TiO_2 production by using the new NaOH roasting method proposed by authors, which is undergoing to scale up. The experimental titanium hydrolysis was detected by the infrared and Raman spectra for the first time to reveal the significant role of SO_4^{2-} ions. The bridging bidentate SO_4^{2-} ligands arrange the Ti–O octahedra of hydrated titanium dioxide (HTD) in zigzag chains along the crystal face (221) to form anatase structure and are changed into unidentate SO_4^{2-} ligands and free bisulfate ions step by step with increasing hydrolysis time. This proposed mechanism of titanium hydrolysis in titanyl sulfate solution

was applied to establish a new kinetic model $x = 1 - \frac{k_n e^{-k_n \left(\frac{1}{2k_m C_{Ti}^0} + t \right)}}{2k_m C_{Ti}^0} \left[Ei\left(k_n t + \frac{k_n}{2k_m C_{Ti}^0}\right) - Ei\left(\frac{k_n}{2k_m C_{Ti}^0}\right) \right] - e^{-k_n t}$,

which indicates the important effect of initial concentrations of titanium, sulfuric acid, and water on the titanium hydrolysis. The hydrolysis kinetic model is capable of describing the behavior of the system and can provide basic knowledge for scale-up of TiO_2 production.

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1. Introduction

Titanium dioxide (TiO_2) has been widely used as pigment in paper, textiles, leather, and porcelain, as photocatalyst in water treatment, and as sensor in environmental monitoring (Barksdale, 1966; Almquist and Biswas, 2001; Gokhale et al., 2009). There are two main commercial manufacture methods: sulfate (Hixson and Plechner, 1933) and chloride (Cheng et al., 1995) route. In the chloride process, synthetic rutile or high titanium slag ($>90\%$ TiO_2) are chloridized and then oxidized at 1000–1700 °C to produce high quality TiO_2. However, the chloride method is energy intensive and generates toxic dioxines to cause serious environmental problem

(Yang and Hlavacek, 2000). In China, 98% of the pigment TiO_2 in 2012 was produced by the sulfate process (Zhao, 2012) where low-grade ilmenite and acid-soluble titanium slag are mainly employed as the feed materials. In the sulfate process, more serious environmental problems occurred because 8 t of dilute sulfuric acid and 3–4 t of copperas are simultaneously discarded (Liang et al., 2005). For these reasons, a novel process (Xue et al., 2009; Wang et al., 2010), namely the NaOH roasting method, was recently proposed with higher titanium extraction up 98% by use of natural rutile ore and titanium slag. This new process includes four key steps: (1) Roasting. The titanium slag blended with NaOH is roasted at 500 °C and titanium is converted to α-Na_2TiO_3. (2) Leaching. The roasted solids are leached by pure water and diluted sulfuric acid to obtain the $Na_mH_{2-m}TiO_3$ filter cake by filtration. (3) Dissolution. The $Na_mH_{2-m}TiO_3$ is dissolved by sulfuric acid to generate concentrated titanyl sulfate solution. (4) Hydrolysis. Hydrated titanium dioxide is precipitated by heating titanyl sulfate solution to boiling point.

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Similar to the sulfate process, hydrolysis is an essential step to control the structure of the precipitates (hydrated titanium dioxide) (Jalava et al., 2000; Grzmil et al., 2008) in this new process, and further decides the TiO_2 pigment quality. Most of studies in hydrolysis mechanism and kinetics were carried out for lower concentration of the titanyl sulfate solution involved in the sulfate process. However, the information of its hydrolysis in concentrated solution is rarely reported in literature and is very significant for the development of this new process. Many researchers proposed the mechanisms of the hydrolysis over the low range concentration of titanium. Ligorio and Work (1937) found that in the titanyl sulfate solution, hydrolysis of the initial complex $Ti(OH_2)_8^{4+}$ is considered to occur in a number of successive steps such as dehydrogenation, olation, and oxolation, repeatedly. Duncan and Richards (1976) used the ultraviolet (UV) spectrum data at 220 nm to study the kinetic hydrolysis and the results show that the initial complex $Ti(OH)_3(OH_2)_2HSO_4$ (Beukenkamp and Herrington, 1960) was hydrolyzed into hydrated titanium dioxide via the intermediate $Ti(OH)_3^+$. Matijević et al. (1977) investigated the chemical mechanism of the hydrolysis based on light scattering measurements. The strong titano-sulfate complexes were gradually decomposed to yield hydrated titanium dioxide. On the basis of assumption that the hydrolytic reaction occurred in the active center on the surface of crystal nuclei, Wang et al. (1991) established a model of hydrolysis rate with considering the effect of the concentrations of titanium and sulfuric acid. Sathyamoorthy et al. (2001a, 2001b) concluded that the formation of hydrate TiO_2 evolves a series of ionic reaction and polymerization. The olation and oxolation firstly give birth to nucleate, and then continue to grow and aggregate to the final form. In addition to investigate the mechanism and the structure, many researchers wanted to simulate the hydrolysis process by semi-empirical models. The Avrami nucleation-growth model (Charbonneau et al., 2009) and Boltzmann growth model (Wang et al., 2013) were used to describe the S-shaped kinetic curve in the hydrolysis of titanyl solution.

In addition to the UV spectrum analysis, X-ray absorption near-edge structure and Raman spectrum were applied to investigate the structure of the titanyl sulfate solution. Miyanaga et al. (1990) studied the mixed-valence complex (Ti^{III}–Ti^{IV}) and found that the zigzag chain structure (Ti–O–Ti–O–Ti) disappears when Ti^{III} ions appear in titanyl sulfate solution because Ti^{III} ions prevent the formation of Ti–O–Ti chains. Baillon et al. (2008) examined the concentrated titanyl sulfate solution by use of Raman spectrum and they found that the titano-sulfate complex appears at 1010 cm^{-1} with the presence of two Ti^{IV} complexes $[Ti(OH)_2SO_4]$ (aq) and $[Ti(OH)_2(SO_4)_2]^{2-}$(aq). Furthermore, two Raman bands (995 and 1009 cm^{-1}) were also identified by Szilágyi et al. (2009). As mentioned above, Raman spectrum with a high detection concentration is recently considered to be a useful method to analyze the structure of the concentrated titanyl sulfate solution.

In present study, hydrolysis mechanism in concentrated titanyl sulfate solution for the new process is investigated. To be concrete, the titanium hydrolysis mechanism in concentrated solution was analyzed by the Fourier transform infrared and Raman spectra. The effect of the concentrations of titanium and sulfuric acid on the titanium hydrolysis was experimentally measured. A new hydrolysis kinetic model with empirical parameters is established on the basis of experimental data, which can meaningfully provide the basic knowledge for scale-up of this new process of TiO_2 production.

2. Experimental section

2.1. Materials

The precursor $Na_mH_{2-m}TiO_3$ was prepared by leaching α-Na_2TiO_3 with pure water and diluted sulfuric acid at 40 °C (Xue et al., 2009).

The detailed structure of $Na_mH_{2-m}TiO_3$ prepared was examined by X-ray powder diffraction (XRD, X'Pert PRO MPD, PANalytical, Netherlands) as shown in Fig. 1.

The results illustrated that the solid precursor is mainly amorphous while the layered $Na_2Ti_2O(OH)_4$ (Liu et al., 2012) and Brookite TiO_2 with the weak and broad peak at 9.5° and 26.0° also exist. Compared with titanyl sulfate monohydrate (Gatehouse et al., 1993) generated from the reaction between sulfuric acid and ilmenite, this kind of poor crystalline precursor $Na_mH_{2-m}TiO_3$ is more soluble in the diluted sulfuric acid at ambient temperature, from which the obtained solutions contain fewer impurities (Na, Fe, Mg, etc.) (Wang et al., 2013) to effectively collect accurate spectral signal.

2.2. Experimental procedure

During the preparation of stock titanyl sulfate solutions by dissolving the precursor $Na_mH_{2-m}TiO_3$ in diluted sulfuric acid (17–67%) at 50 °C, a small amount of iron powder was added to retain the reductive atmosphere. The different titanyl sulfate solutions (Tb-F, 'b' is the concentration of titanium; 'F' is the sulfate–titanium ratio), with Ti 0.75–2.69 mol/L and sulfuric acid 1.24–4.65 mol/L, were prepared by adjusting the ratios of the $Na_mH_{2-m}TiO_3$ mass (g) to the volume (dm^3) of the diluted sulfuric acid listed in Table S1. As shown in Table S1, the sodium ion is the main impurity. The effect of sodium ion concentration in the hydrolysis process in Fig. S1 illustrates that hydrolysis curves changed slightly at lower sodium ion concentration (< 10 g/L). In our study, the sodium concentration is lower enough to be neglected for hydrolysis kinetics.

A four-necked round-bottomed flask with volume of 0.5 dm^3 was used to test the hydrolysis experiments at boiling point. The stirring device installed in the center neck of the flask assures the steady mixing while the water-cooled condenser is used to avoid the evaporation. Sample of 4 mL is withdrawn by 5 mL microcentrifuge tubes and immediately cooled in ice-water for FTIR and Raman spectrum analysis. After that the sample solution is filtered with a membrane filter to obtain filtrate and filter cake (hydrated titanium dioxide). The concentration of titanium (C_{Ti}^t) in the filtrate was titrated by volumetric method, while the volume (V^t) was measured with pipette. The mass of hydrated titanium dioxide (m^t) in the filter cake was quantified by balance, and then 0.2–0.4 g cake was dissolved in concentrated sulfuric acid (20 mL) to obtain the mass fraction of titanium dioxide ($W_{TiO_2}^t$) by titrated method. The hydrolysis ratio (x) is calculate in the following equation,

$$x = (W_{TiO_2}^t m^t)/(V^t C_{Ti}^t + W_{TiO_2}^t m^t) \qquad (1)$$

where C_{Ti}^t is the concentration of titanium at time t (mol/L), C_{Ti}^0 is the initial concentration of titanium (mol/L) at the time $t=0$. During the hydrolysis
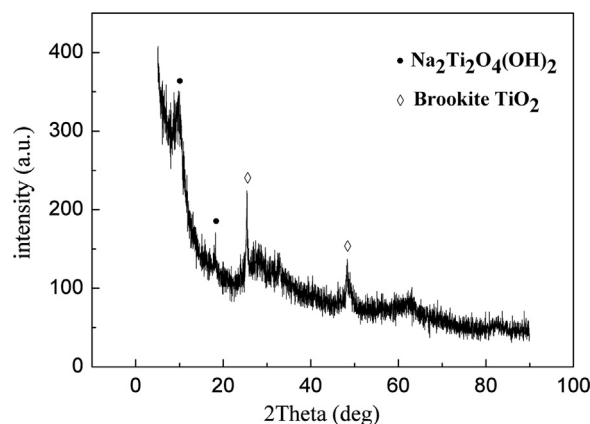

Fig. 1. The XRD spectrum of the precursor $Na_mH_{2-m}TiO_3$.