

## Study on the influence of various base agents in $K_2TiF_6$ hydrolysis on morphology, structure and photocatalytic activity of $TiO_2$

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### Abstract

$K_2TiF_6$  was hydrolyzed by various base agents including solutions of  $NH_3$ ,  $NaOH$ , and  $KOH$  at the same concentration of 3 M.  $TiO_2$  material was obtained after filtering, washing, drying and calcination at 500 °C of  $Ti(OH)_4$  precipitate. The experimental results showed that there was a significant influence of base agent nature on the morphology, structure, surface area of  $TiO_2$  product. Using  $NH_3$  agent could obtain uniform  $TiO_2$  particles with about 15 nm in size and surface area of  $98.93 \text{ m}^2 \cdot \text{g}^{-1}$ , while using  $NaOH$  or  $KOH$  led to  $TiO_2$  with varying particle sizes (in the range of 15-500 nm), and decreasing surface area (less than  $20 \text{ m}^2 \cdot \text{g}^{-1}$ ). The nature of base agent also significantly influenced photocatalytic activity of  $TiO_2$  product for methylene blue (MB) decomposition. The prepared  $TiO_2$  from  $NH_3$ -using process showed the highest photocatalytic activity in comparison with  $TiO_2$  from  $KOH/NaOH$ -using process or commercial  $TiO_2$  (P25).

**Keywords.**  $K_2TiF_6$ ,  $TiO_2$ ,  $Ti(OH)_4$ , photocatalyst.

### 1. INTRODUCTION

Nanocrystalline titanium dioxide (NTO) is a multifunctional semiconductor photocatalyst. NTO can be used as a catalyst for energy (production hydrogen fuel from water splitting), or for environmental treatment (cleaning air and water), etc. Compared to other available photocatalysts, NTO has many advantages such as high chemical and photochemical durability, environmental friendliness, high activity for decomposition of pollutant organic compounds without any other oxidizers [1, 2].

There are many different methods for the preparation of NTO from ilmenite ore in practice. Ore decomposition method using HF agent to produce  $K_2TiF_6$  followed by hydrolysis of this intermediate compound in base solution to obtain NTO is a method that has many advantages such as reaction at room temperature and simple procedure [3].

Besides, the morphology and structure of NTO depends on prepared methods, titanium-containing precursor, etc. and therefore those changes will affect the photocatalytic activity of NTO [4]. This paper presents some results of study on the influence of various base agents in  $K_2TiF_6$  hydrolysis on

morphology, structure and photocatalytic activity of  $TiO_2$

### 2. EXPERIMENTAL

#### 2.1. Chemicals and equipment

Ilmenite ore (Binh Dinh); HF 40 % (China);  $NH_3$  25 % (China); KCl (China);  $KOH$  (China);  $NaOH$  (China).

The experimental equipment includes: reactor made of plastic (polyethylene); magnetic stirrer (VELP Scientifica); vacuum filtration (Rocker 300); drying oven (Lenton); furnace (Nabertherm); UV-A light (the maximum emission wavelength  $\lambda = 365 \text{ nm}$ ).

#### 2.2. Preparation of materials

Firstly, the Binh Dinh ilmenite ore was decomposed by HF solution to obtain  $K_2TiF_6$  complex salt [3].

Secondly,  $K_2TiF_6$  was hydrolyzed in various base solutions including  $NH_3$ ,  $KOH$ , and  $NaOH$  at the same concentration of  $3 \text{ mol} \cdot \text{L}^{-1}$ . The product of  $Ti(OH)_4$  after hydrolysis has been filtered, washed by distilled water, then dried and calcinated at 500

°C to obtain TiO<sub>2</sub> [5]. The TiO<sub>2</sub> samples obtained from processes using NH<sub>3</sub>, KOH, and NaOH were denoted T1, T2 and T3, respectively.

### 2.3. Characterization of materials

The materials were characterized by physico-chemical methods including X-ray diffraction (XRD) on D8-Advance 5005, scanning electron microscopy (SEM) on Nova NanoSEM 450; adsorption-desorption N<sub>2</sub> at 77 K (BET) on TriStar 3000 Micromeritics.

### 2.4. Photocatalytic activity test

The photocatalytic activity of prepared TiO<sub>2</sub> materials were tested for decomposition reaction of methylene blue (MB) and compared with commercial TiO<sub>2</sub> (P25) in the same condition (MB concentration of 10 mg.L<sup>-1</sup>, 20 mg of catalyst in 40 mL of MB solution, reaction time of 60 minutes, UV irradiation at wavelength of 365 nm). Methylene blue concentration was determined by UV-Vis absorption spectrum method (UV-1800 Shimadzu) at 664 nm.

## 3. RESULTS AND DISCUSSION

### 3.1. X-ray diffraction (XRD) characterization

The XRD patterns of T1, T2 and T3 samples that is corresponding to TiO<sub>2</sub> obtained from processes using NH<sub>3</sub>, KOH, and NaOH, are shown in figure 1. The T1 sample contains only single phase of anatase (tetragonal lattice) which characterized by peaks at diffraction angles 2θ of 25.26; 37.78; 38.56; 48.5 and 53.9° (according to JCPDS 21-1272). These peaks of crystalline anatase TiO<sub>2</sub> still present in XRD patterns of T2 and T3, but less intense than that of the T1. Thus, it can be confirmed that base agents such as NH<sub>3</sub>, KOH, and NaOH can be used for hydrolysis of K<sub>2</sub>TiF<sub>6</sub> to produce anatase TiO<sub>2</sub>.

However, there are other peaks on XRD patterns of T2 and T3 samples, which prove the presence of crystalline impurities along with TiO<sub>2</sub> crystals. Detailed analysis shows that, besides characterized peaks of anatase as the main component, there are peaks of crystalline jepeite phase (K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>) of monoclinic lattice in the XRD pattern of T2 sample, and there are peaks indicating the presence of potassium sodium titanium oxide fluoride (K<sub>2</sub>NaTiOF<sub>5</sub>) crystals in the XRD pattern of T3 sample. During the experiments, double-distilled water was used for filtration and washing of Ti(OH)<sub>4</sub>

and the washing process ended when the pH of washing solution reached neutral values, but the residual of by-products containing potassium and sodium is inevitable for processes using KOH, and NaOH. This may be because KOH and NaOH are the alkaline bases, which can react immediately to Ti(OH)<sub>4</sub> in the hydrolysis. Furthermore, using NaOH can afford NaF as low solubility compound [6] so it exists together with products and will combine with TiO<sub>2</sub> when calcinating to produce K<sub>2</sub>NaTiOF<sub>5</sub>.

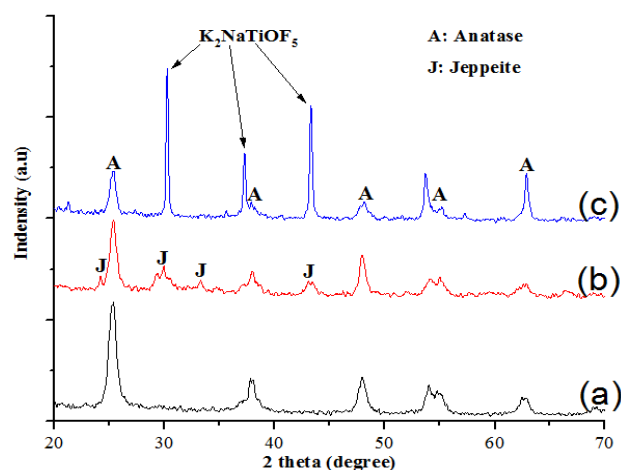


Figure 1: XRD patterns of material samples T1 (a), T2 (b), and T3 (c)

From the value of line broadening at half the maximum intensity in the patterns, applying the Debye-Scherrer formula, the mean size of the crystalline TiO<sub>2</sub> is about 13 nm for T1 sample, and 15 nm for T2, T3 samples. Thus, using the base agents in hydrolysis of K<sub>2</sub>TiF<sub>6</sub> can produces TiO<sub>2</sub> products at nanometer-scale in size.

### 3.2. Scanning electron microscopy (SEM) characterization

The microstructure morphology of prepared TiO<sub>2</sub> materials is characterized by scanning electron microscopy. The SEM images are shown in figure 2. SEM image of T1 sample (figure 2a) shows that TiO<sub>2</sub> are formed by accumulating of about 15 nm in size particles. Meanwhile, the SEM images of samples T2 (figure 2b) and T3 (figure 2c) show that besides the particles with their size of about 15 nm, there are pieces, blocks with their dimensions up to 500 nm, and certain gaps between particles of TiO<sub>2</sub>. This result allowed us to predict that T1 sample will have a larger surface area and so have better photocatalytic activity than T2 and T3 samples.

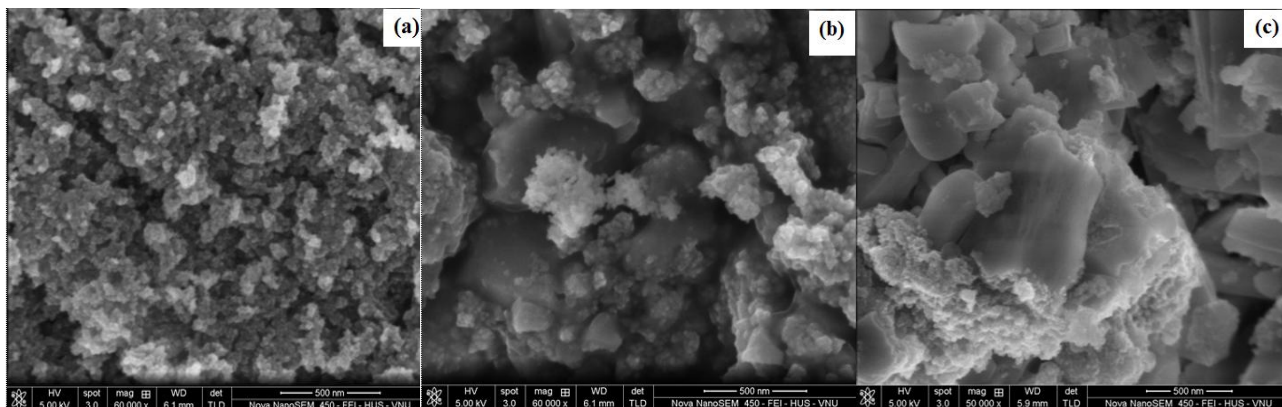


Figure 2: SEM images of T1 (a), T2 (b), and T3 (c) samples

Observing SEM images (figures 2b and 2c) and XRD spectra (figures 1b and 1c) we noticed that particles with size of about 15 nm correspond to TiO<sub>2</sub> crystalline anatase and pieces, blocks correspond to crystals of K<sub>2</sub>Ti<sub>6</sub>O<sub>13</sub>, K<sub>2</sub>NaTiOF<sub>5</sub>.

### 3.3. Porosity characterization

Specific surface area and porous characteristics of material samples were determined by BET method. The N<sub>2</sub> adsorption-desorption isotherms at 77 K and the corresponding BJH pore size distribution curves of T1, T2, T3 samples are shown

in figures 3 and 4.

It can be seen from figure 3 that the nitrogen adsorption-desorption isotherms of prepared materials are of type IV (classified by IUPAC) hysteresis loop (in the relative pressure  $0.74 < p/p_0 < 0.99$ ) that is characteristic of mesoporous material. However, by combining with SEM images (Fig. 2), it is confirmed that the T1, T2 and T3 samples are not mesoporous materials, but actually there are empty gaps between the TiO<sub>2</sub> particles. The BJH pore size distribution curves of the samples also show this. The empty spaces between particles in T2 sample (figure 4b) distributed mainly in the

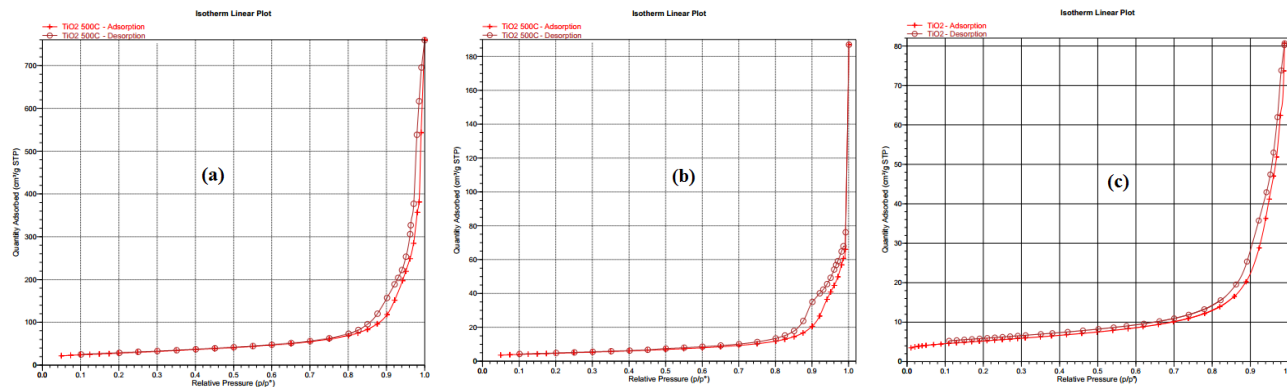


Figure 3: N<sub>2</sub> adsorption-desorption isotherms at 77 K (BET) of T1 (a), T2 (b), and T3 (c) samples

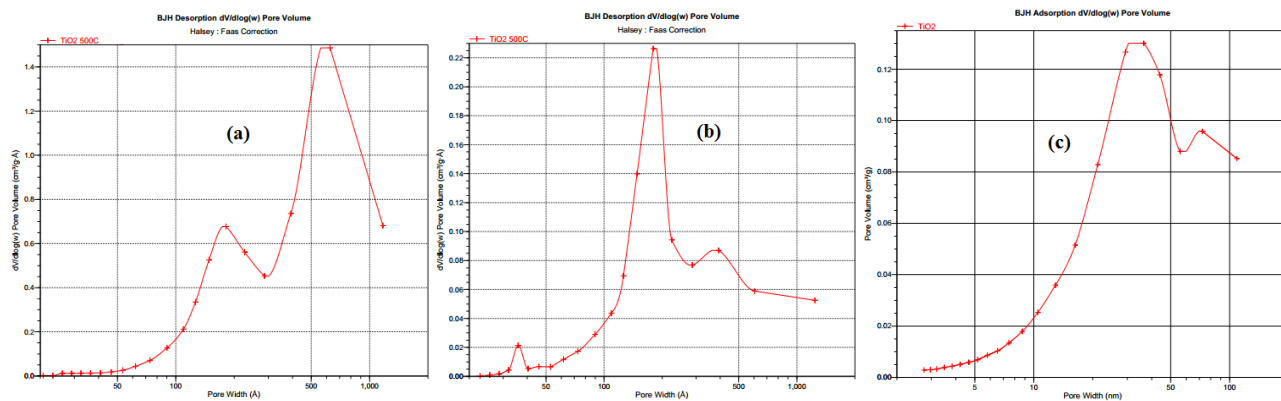


Figure 4: BJH pore size distribution curves of T1 (a), T2 (b) and T3 (c) samples

range of 10 to 20 nm. Meanwhile for T1 and T3 samples (figure 4a and 4c), the distribution of empty spaces between particles concentrated in the region is 30 to 50 nm, and expanded to 100 nm.

From the results of N<sub>2</sub> adsorption-desorption isotherms study, the specific surface areas determined by BET model for T1, T2, and T3 samples are 98.93, 16.51, and 18.48 m<sup>2</sup>.g<sup>-1</sup>, respectively. This result is consistent with the observation of SEM images (figure 2).

### 3.4. Photocatalytic activity tests

The results in Figure 5 show that after 60 minutes irradiation with UV-A light ( $\lambda = 365$  nm), all samples have great decomposing capacity of MB; the descending order in conversion rate of MB on samples is T1, P25, T3, T2.

This can be explained by the larger surface area of T1 than T2 and T3 sample, and the smaller particle size of T1 form than P25 material. These factors can enhance the quantum efficiency, reduce the recombination of electrons and holes [7].

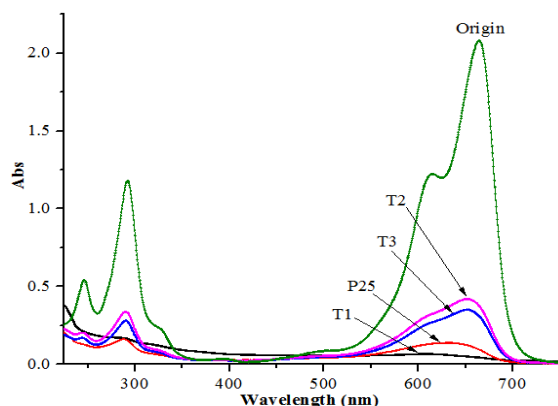


Figure 5: UV-Vis spectrum of MB before and after treatment with T1, T2, T3, and P25 samples

The same photocatalytic activity of T2, T3 samples in decomposing reaction of MB was lower than P25 sample. These results can be explained by the approximal specific surface area of the two samples T2, T3. Also, the presence of impurities in T2, T3 can prevent the absorption of photons from UV irradiation that reduces conversion capacity of MB compared to P25 sample [8].

## 4. CONCLUSIONS

TiO<sub>2</sub> materials were successfully prepared from

K<sub>2</sub>TiF<sub>6</sub> precursors by hydrolysis method with various base solutions including NH<sub>3</sub>, KOH, and NaOH. The TiO<sub>2</sub> sample obtained from processes using NH<sub>3</sub> achieves specific surface area of 98.93 m<sup>2</sup>.g<sup>-1</sup>, including particles with their size of about 15 nm. When replace NH<sub>3</sub> by KOH or NaOH, the specific surface area of obtained TiO<sub>2</sub> decreases significantly. The specific surface area of TiO<sub>2</sub> from processes using KOH and NaOH are 16.51 and 18.48 m<sup>2</sup>.g<sup>-1</sup>, respectively.

The photocatalytic activity of prepared TiO<sub>2</sub> materials has been examined for decomposition reaction of methylene blue. The experimental results showed that, the descending order in conversion rate of methylene blue on samples is TiO<sub>2</sub>-using NH<sub>3</sub>, commercial TiO<sub>2</sub> P25, TiO<sub>2</sub>-using NaOH, TiO<sub>2</sub>-using KOH.

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