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Photocatalytic oxidative desulfurization of thiophene using $BiVO_4$ catalyst

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Visible-light-induced $BiVO_4$ was prepared by hydrothemal method and characterized by XRD, SEM and UV–vis spectroscopy. The characterization indicated that photocatalyst had better structure. The result indicated that the $BiVO_4$ sample synthesized at 140℃ and 2h was monoclinic phase with a 0.5μm of average particle sizes, and exhibited strong absorption in the visible light region. The photocatalytic properties of the $BiVO_4$ samples were evaluated by removing thiophene in n-octane, the result showed that the $BiVO_4$ sample exhibited higher photocatalytic desulfurization, and the removal of thiophene of the mode compound in the visible light/H_2O_2/$BiVO_4$ system was in three steps.

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Keywords: Photocatalyst, $BiVO_4$, Desulfurization, Thiophene

1. Introduction

With people awareness to environmental pollution strengthening, the desulfurization of fuels has received much attention recently in items of environmental issues. Interests were now focused on oxidative desulfurization (ODS), which could be processed under room conditions [1]. In the ODS process, these sulfur compounds were oxidized into more polar sulfones, which can be removed in the later extraction process.

Recently, many researchers have investigated the desulfurization of aromatic sulfur compounds by photocatalytic techniques [2,3]. Followed the work, a series of photocatalysts was studied, such as Bi_2WO_6 [4], $BiVO_4$ [5], $CaBi_2O_4$ [6], and $InVO_4$[7]. As a new visible-active catalyst, $BiVO_4$ could provide a great surface area, which was beneficial for substrate contact with the active sites of the catalyst [8,9]. However, the limitation of the low photocatalytic efficiency has considerably restricted their applications. In order to overcome the obstacles, the photocatalytic oxidation reaction process was intensified by the addition of H_2O_2 as oxidant [10].

Here, we reported results on photocatalytic oxidation of thiophene in acetonitrile using $BiVO_4$. The results could be used as the reference for evaluating reactions in hydrocarbons, which aimed at the development of the photocatalytic oxidation desulfurization process.

2. Experimental

2.1. Preparation of the photocatalysts

All the reagents were of analytical grade and were used without any further purification. 1mol $Bi(NO_3)_3 \cdot 5H_2O$ and 1mol NH_4VO_3 were added to 4 $mol \cdot L^{-1}$ nitric acid solution and distilled water, respectively. Mixed the resulting solution and stirred 30 min vigorously, adjusted pH value as 7. The solution was reacted at 140℃ for 2h by hydrothemal method. After reaction, the solution were centrifuged and washed with distilled water. Finally the sample was obtained by drying at 80℃ for 4h.

2.2. Characterization

The phase and composition of the as-prepared samples were measured by X-ray diffraction (XRD) using monochromatized Cu K_α radiation under 40 kV and 100 mA and with the 2θ ranging from 10º to 80º (Shimadzu, XRD-7000). The morphologies and microstructures of as-prepared samples were analyzed by the scanning electron microscope (SEM) (JEOL JSM-6700F). UV–vis diffuse reflectance spectra (DRS) of the as-prepared samples were recorded with an UV–vis spectrophotometer (shimadzu UV-2550) using an integrating-sphere accessory.

2.3. Photocatalytic oxidative desulfurization of model oil with $BiVO_4$

The thiophene was dissolved in n-octane to form mode compound of light oil. A 400W metal halide was used as the light source with a 400 nm cut-off filter to provide visible-light irradiation. In each experiment, the $BiVO_4$ catalyst sample at a concentration of 0.5-2.5 g/L, the H_2O_2 catalyst sample at a concentration of 3-15% (10 vol. % of a commercial 30% H_2O_2 solution in a sample solution), 5 mL of acetonitrile as extraction used as extraction agent and 10 mL ofmodel oil were added into quartz tube to form a solution, which prior to illumination under a metal halide lamp was stirred in the dark for 30 min to assure an adsorption-desorption equilibrium between the $BiVO_4$ sample and model oil. Then, the solution was illuminated under the metal halide and stirred magnetically. At a given time interval, the solution was centrifuged for removing the $BiVO_4$ particles. The total sulfur concentration was analyzed in the n-octane phase by a microcoulometer (Jiangsu Jiangfen Electroanalysis Company Limited, WK-2D) and then desulfurization rare was calculated.

3. Results and discussion

3.1. XRD patterns of the $BiVO_4$

Fig. 1 shows the XRD patterns of $BiVO_4$ powders synthesized at different temperatures. It can be seen that the as-prepared sample at low temperature (below 140℃) showed weak crystallization. With increasing synthesized temperature, the diffraction peak intensity of $BiVO_4$ obviously increased and the diffraction peak width became gradually narrower. At 140℃, the diffraction peaks of the samples showed that the sample was well crystallized, could be indexed with the pure monoclinic phase $BiVO_4$ (JCPDS No. 14-0688). It is well known that the crystallization and the surface area of the photocatalyst were of two important factors influencing the photocatalytic reaction activity. However, with the improvement of crystallization, the crystallites became larger, the surface areas of the samples decreased [11]. When the synthesized temperature increased to 160℃, the diffraction peak intensity and width hand a little change.

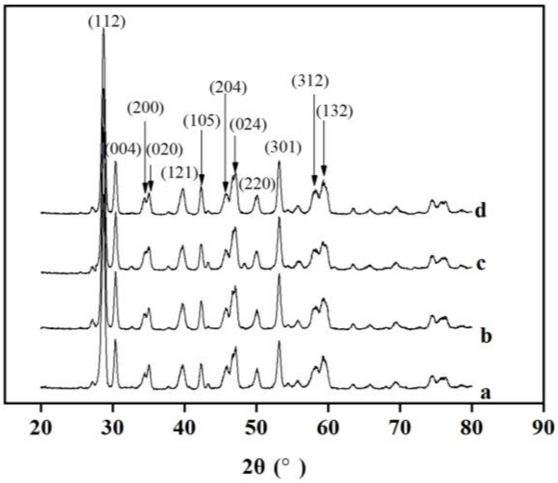

Fig. 1. XRD patterns of as-prepared $BiVO_4$ particles hydrothemal synthesized for (a) 100 ℃, (b) 120 ℃, (c) 140 ℃ and (d) 160 ℃ in 2h.

Fig. 2 showed XRD patterns of $BiVO_4$ powders synthesized at different reaction times. It could be seen that all of the reflections of the starting precipitate obtained at the 0.5 h (Fig. 2a). It could be readily indexed to a pure tetragonal scheelite phase of lattice constants a = 0.7351 nm, b = 0.7351 nm and c = 0.6489 nm, which agreed with the reported values of a = 0.7300 nm, b = 0.7300 nm and c = 0.6457 nm (JCPDS No. 48-0744). No peaks for any other phases or impurities were detected. After 1 hour, as shown in Fig. 2b, part of the peaks in the XRD pattern were indexed to monoclinic $BiVO_4$(JCPDS No. 14-0688), which indicated that the samples were the mixture of monoclinic and tetragonal phases. As the time increased to 1.5h, the peaks corresponding to monoclinic $BiVO_4$ became more and more dominant, and the peaks intensity of the tetragonal $BiVO_4$ gradually weaken. After 2 h, all the diffraction peaks could be indexed to be a pure monoclinic $BiVO_4$. The results demonstrated that a phase transition from the tetragonal to monoclinic phase had taken place during the formation of pure monoclinic $BiVO_4$ by hydrothemal synthesize method.

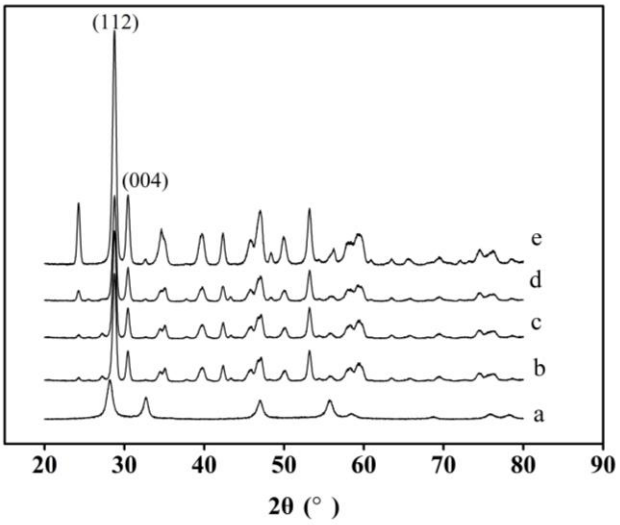

Fig. 2. XRD patterns of as-prepared $BiVO_4$ particles hydrothemal synthesized for (a)0.5h, (b)1h, (c) 1.5h, (d) 2h and (e)3h in 140 ℃.

3.2. UV–vis spectra

Fig. 3 showed the UV–vis DRS of the as-prepared samples. According to the spectra, the $BiVO_4$ powders presented the photoabsorption properties from the UV light region to visible-light region until 550 nm. The band gap energy (eV) could be obtained by the $Eg=hc/\lambda_0$ based on the diffuse reflection spectral data, where $h\nu$ was the photon energy($h\nu$=1240), λ_0 was the absorption edge (λ_0 = 550), and E_g was the band gap energy[12]. Thus, the Eg of $BiVO_4$ was estimated to be 2.30 eV, which indicated that the $BiVO_4$ powders suited for photocatalytic decomposition of organic contaminants under visible-light irradiation.

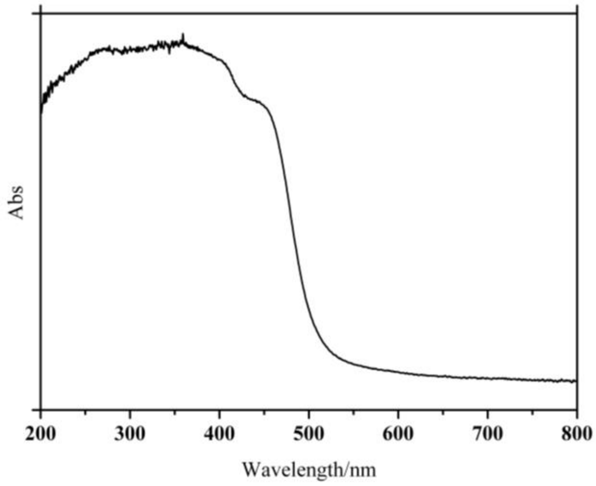

Fig. 3. The UV -Vis spectra of $BiVO_4$ under 140 ℃, 2h.

3.3 Morphology and microstructure

The morphology and microstructure of the samples was revealed by scanning electron microscopy. Fig. 4 was the SEM images of pure $BiVO_4$ powders (140℃, 2h). This showed that they appeared to be high crystallinity and displayed mainly thin particles with borders of several hundred nanometers. The $BiVO_4$ powders consisted of irregular particles and the particles were aggregated as shown in Fig. 4a. Magnified image in Fig. 4b showed a rough surface of the $BiVO_4$ particles with a 0.5μm of average particle sizes.

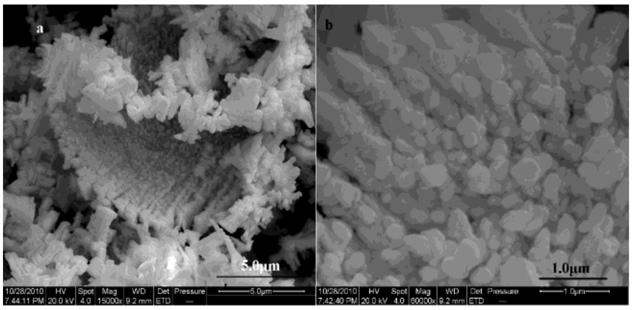

Fig. 4. The SEM of $BiVO_4$ under 140 ℃, 2h.

3.4. Photocatalytic desulfurization performance for model gasoline

3.4.1. Effect of the catalyst amount on photocatalytic desulfurization of thiophene

Fig. 5 showed the effect of the amount of catalyst on photocatalytic desulfurization.. The desulfurization rate increased when the amount of $BiVO_4$ catalyst increased from 0g/L to 1.5g/L. Since in the course of photocatalytic oxidation reaction, the concentration of ·OH species in the reaction mixture was very important to the free radical chain reaction of photocatalytic oxidation, an increase of catalyst amount could enhance the ·OH formation rate in hydrogen peroxide to foster the degradation reaction. The desulfurization rate of model compound with 1.5 g/L of $BiVO_4$ powder could reach 84.5% after being irradiated by visible light for 2h, but on the contrary the degradation efficiency dropped when the photocatalyst amount increased to 2.5 g/L. With regard to the photocatalytic oxidation reaction, the hydroxyl free radicals formed in this system were less and the ·OH radicals could reach a definite concentration to secure the initiation of chain reaction, and further increase of catalyst amount could affect the light transmittance of solution to cause light scattering and reduce absorption of light in the reaction system, resulting in reduction of excited state of reactants and impeding the proceeding of desulfurization reaction.

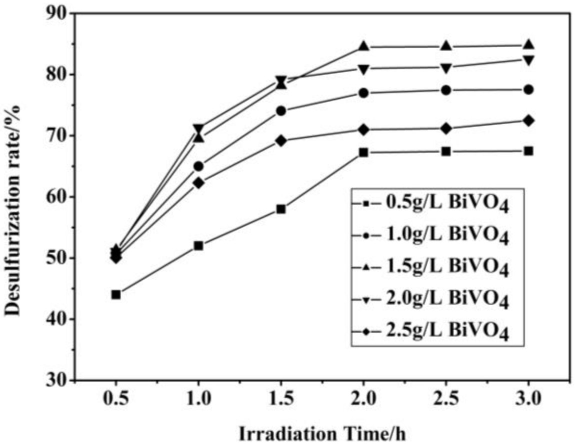

Fig. 5. Effect of the catalyst amount on photocatalytic desulfurization with 10% H_2O_2.

3.4.2. Effect of H_2O_2 on the photodecomposition of thiophene

The addition of other powerful oxidizing species such as hydrogen peroxide (H_2O_2) and potassium peroxydisulfate ($K_2S_2O_8$) to photocatalyse suspensions was a well known procedure and in many cases leaded to an increase in the rate of photooxidation [10]. In our case the photocatalytic oxidation of 0.1% (volume ratio) thiophene in the presence of 1.5g/L $BiVO_4$ has been studied at different H_2O_2 concentrations.

The effect of the amount of H_2O_2 on the desulfurization was shown in Fig. 6. An increase in the concentration of H_2O_2 from 3% to 15% leaded to a twofold increase in the reaction rate. A possible explanation for the $BiVO_4$ concerning the synergetic effect of H_2O_2 on the photocatalytic oxidation could be the extent of adsorption of H_2O_2 onto $BiVO_4$ surface. As a consequence, the photogenerated electrons in $BiVO_4$ suspensions could more easily reduce due to the H_2O_2 molecules leading to a lower e-/h+ recombination rate.

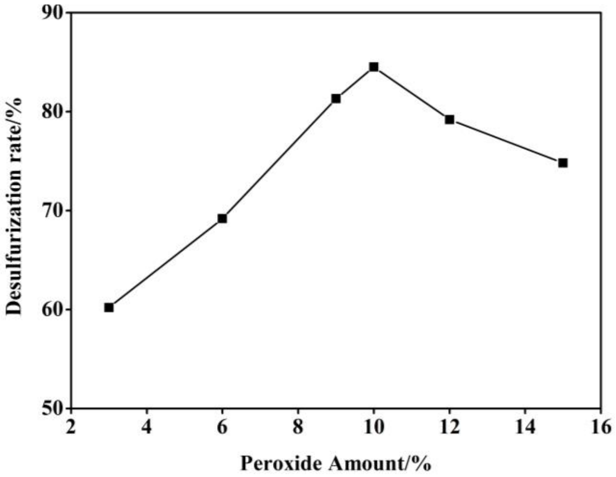

Fig. 6. Effect of the peroxide amount on photocatalytic desulfurization with 1.5g/L $BiVO_4$.

The role of H_2O_2 in the process of photocatalytic oxidation was dual [13]. It accepted a photogenerated electron from the conduction band and thus promoted the charge separation, Eq. (1), and it also formed ·OH radicals via superoxide according to Eq. (2), while a possible reaction of H_2O_2 with the photogenerated intermediates could not be excluded.

$$H_2O_2 + e^- \rightarrow OH^- + \cdot OH \tag{1}$$

$$H_2O_2 + O_2^- \rightarrow OH^- + \cdot OH + O_2 \tag{2}$$

From Fig. 6, a higher concentration of H_2O_2 resulted to a reaction rate reduction. In the presence of excess H_2O_2, it may react with oxidative h^+ on the catalyst surface (Eq(3)) [14], or act as a ·OH scanvenger (Eq(4)) [15], or react with $BiVO_4$ to form peroxo compounds, which were detrimental to the photocatalytic oxidation processes. It could also compete with the organic compound for the adsorption sites on the catalyst surface, resulting in a “chromatographic peaking effect” of the pollutant concentration in the solution during the initial stages of the photocatalytic process [16]. What's more, the HO_2 radicals generated from Eq.(4) could further react with the remaining ·OH to form ineffective oxygen and water, as shown in Eq.(5) [14]. This explained the need for an optimal concentration of H_2O_2 for the maximum effect.

$$H_2O_2 + h^+ \rightarrow O_2 + 2H^+ \tag{3}$$

$$H_2O_2 + \cdot OH \rightarrow H_2O + HO_2 \tag{4}$$

$$HO_2 + \cdot OH \rightarrow H_2O + O_2 \tag{5}$$

3.4.3. Recycling of $BiVO_4$ photocatalyst

To confirm the stability of the high photocatalytic performance of $BiVO_4$, the circulating runs were examined under operation condition as follow: visible light irradiation, 1.5g/L $BiVO_4$, 10% H_2O_2. Table 1 showed the result of the stability and repeatability of $BiVO_4$ photocatalyst. In the four previous recyclings, photocatalyst exhibited strong catalytic ability althrough photocatalytic property was slower than that of the first one indicating photocatalyst did not be corroded in the photocatalytic oxidative process. In the fifth recycling, photocatalytic property decreased obviously, and it could be due to the agglomeration of catalyst particles in the recycling procedure.

Table 1. The stability and repeatability of $BiVO_4$ photocatalyst.

Cycle-index	1	2	3	4	5
desulfurization rate	84.5%	83.93%	83.9%	82.97%	67.33%

3.5. Possible reaction mechanism of Desulfurization over $BiVO_4$

Photocatalytic oxidation desulfurization of light oil involved photochemical reaction and liquid–liquid extraction. However, in the photocatalytic process, photocatalytic oxidation occurred mainly in the extraction phase [17]. Based on the photocatalytic results, the possible photocatalytic mechanism in the visible light/H_2O_2/$BiVO_4$ system was proposed as follows (Fig. 7). The first was diffusion of a fraction of the thiophene from oil phase into the acetonitrile and could be oxidized with the catalyst dissolved in the acetonitrile. As the reaction progressed, thiophene was continuously transferred into the acetonitrile phase, providing a continuous extraction process and achieving deep desulfurization. Secondly, under the irradiation of visible light, the electrons received energy from the photons and were thus excited from the valence band to the conduction band, leaving positively charged holes in the valence band (Eq. (6)). However, the photogenerated charge carriers recombined in the bulk or on the surface of the semiconductor during the migration process, which could decrease the photocatalytic rate of $BiVO_4$ dramatically. H_2O_2 as an efficient electron scavenger could trap the photogenerated electrons (Eq. (7)) and prevented the recombination of electron-hole pairs effectively [18], which was favorable to the enhancement of the photocatalytic activity of $BiVO_4$.

$$BiVO_4 \xrightarrow{hv} e^- + h^+ \tag{6}$$

$$H_2O_2 + BiVO_4(e^-) \xrightarrow{hv} \cdot OH + OH^- \qquad (7)$$

Thirdly, the photo-generated holes could emigrate to the surface of the photocatalyst and react with the adsorbed sulfur compounds directly (Eq. (8)). Meanwhile, the •OH generated from the above reaction has strong oxidizing ability and was available to oxidize thiophene (Eq. (9)).

$$BiVO_4\ (h^+) + \text{thiophene} \rightarrow BiVO_4 + \text{thiophene oxide} \qquad (8)$$

$$\cdot OH + \text{thiophene} \rightarrow \text{thiophene oxide} \qquad (9)$$

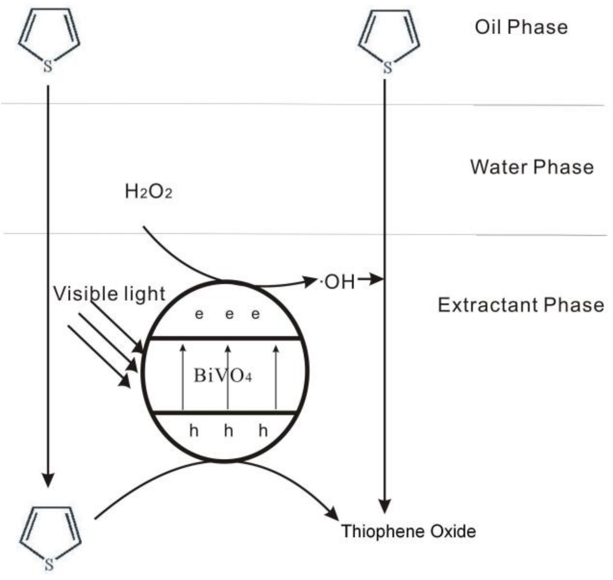

Fig.7. Photocatalysis mechanism of thiophene by $BiVO_4$ under visible light.

4. Conclusions

In summary, $BiVO_4$ photocatalyst with visible-light response was hydrothemal synthesized and characterized by XRD, DRS, SEM. A strong correlation was found among the processing, structure and properties of the samples. The $BiVO_4$ sample synthesized at 140℃ and 2h was monoclinic phase and exhibited strong absorption in the visible light region. The photocatalytic properties of the $BiVO_4$ samples were evaluated by removing thiophene in n-octane, the result showed that the $BiVO_4$ sample exhibited higher photocatalytic desulfurization, its desulfurization rate could be up to 84.5%.

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