

Photocatalytic oxidative desulfurization of dibenzothiophene catalyzed by amorphous TiO₂ in ionic liquid

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Abstract—Three types of TiO₂ were synthesized by a hydrolysis and calcination method. The catalysts were characterized by X-ray powder diffraction (XRD), diffuse reflectance spectrum (DRS), Raman spectra, and X-ray photoelectron spectroscopy (XPS). The XRD and Raman spectra indicated that amorphous TiO₂ was successfully obtained at 100 °C. The results indicated that amorphous TiO₂ achieved the highest efficiency of desulfurization. The photocatalytic oxidation of dibenzothiophene (DBT), benzothiophene (BT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) and dodecanethiol (RSH) in model oil was studied at room temperature (30 °C) with three catalysts. The system contained amorphous TiO₂, H₂O₂, and [Bmim]BF₄ ionic liquid, ultraviolet (UV), which played vitally important roles in the photocatalytic oxidative desulfurization. Especially, the molar ratio of H₂O₂ and sulfur (O/S) was only 2 : 1, which corresponded to the stoichiometric reaction. The sulfur removal of DBT-containing model oil with amorphous TiO₂ could reach 96.6%, which was apparently superior to a system with anatase TiO₂ (23.6%) or with anatase - rutile TiO₂ (18.2%). The system could be recycled seven times without a significant decrease in photocatalytic activity.

Keywords: Amorphous TiO₂, Photocatalytic Oxidative, Desulfurization

INTRODUCTION

Acid rain is mainly from SO_x by combustion of sulfur-containing compounds. To reduce the emission by SO_x, many developed countries have planned to achieve little-to-no sulfur fuels (S-content <10 ppm) [1]. A traditional desulfurization method, hydrodesulfurization (HDS), requires high hydrogen pressure and temperature, but it is difficult to remove dibenzothiophene (DBT) and its derivatives. During the past few years, to save energy and reduce costs, oxidative desulfurization (ODS) has attracted much attention. As one of the processes, photocatalytic oxidative desulfurization is promising because of safety, high catalytic activity, low energy consumption, recycling [2,3].

As one of semiconductor materials (such as TiO₂, PbS, ZnS, Fe₂O₃), titanium dioxide (TiO₂) is an important photocatalyst based on its high photoactivity, photostability, and inexpensiveness. Anatase or rutile TiO₂ can achieve applications in the decomposition of organic compounds with UV radiation [4]. Especially, TiO₂-based photocatalysts have been used in oxidative desulfurization. Yasuhiro et al. described that anatase TiO₂ with oil/acetonitrile two-phase extraction could achieve deep desulfurization [5]. Titanium (IV) oxide (TiO₂) loaded with multi-walled carbon nanotubes (MWNTs) could also exhibit high photo-chemical activity [6]. With nano-TiO₂ and [Bmim]CuCl₂ ionic liquid, the oxidation of gasoline could reach 98.2% [7]. From these papers, it's known that crystalloid TiO₂ can be used in photocatalytic desulfurization.

So far, many researchers have paid more attention to crystalloid

TiO₂, but little to amorphous TiO₂. Amorphous TiO₂ has the potential feature of high optical absorbance, high dielectric constant and has no primary boundary mechanism for chemical corrosion and optical scattering [8]. Zhang and workers [9] used amorphous TiO₂·nH₂O to generate H₂ gas, and the amorphous TiO₂·nH₂O revealed the high photocatalytic property. Amorphous TiO₂ can be synthesized at low temperature and processed into different shapes and forms. It is easier to be doped with chemical substances, which is compared to crystalline forms. It also exhibits high surface area [10]. However, there is no report about photocatalytic desulfurization by amorphous TiO₂.

Recently, our groups have reported extraction and catalytic oxidative desulfurization (ECODS) in ionic liquids, which exhibited high sulfur removal [11-13]. In this paper, the target is to present a high efficiency photocatalytic desulfurization system containing amorphous TiO₂, ionic liquid and H₂O₂. It was found that DBT could be deep removed by the amorphous TiO₂ combined with only stoichiometric H₂O₂ and conventional [Bmim]BF₄ under UV light. The performance of the recycled catalyst was also detected.

EXPERIMENTAL

1. Preparation of TiO₂

0.00424 mol tetrabutyl titanate (Ti(OBu)₄) was dissolved in 10 mL anhydrous ethanol and 0.9 mL distilled water while being quickly stirred, and then white flocs were formed. Aging occurred for 24 h at room temperature after continuous stirring for 0.5 h. This colloid was kept in the water bath of 40 °C for 6 h, and then heated to 100 °C to get dry precipitate. Afterwards this solid was calcined at 100 °C, 400 °C, 700 °C labeled as Amorphous (Am) TiO₂, Anatase (An) TiO₂, Anatase-Rutile (An-R) TiO₂ [14].

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2. Catalysts Characterization

Ultraviolet-visible (UV-vis) spectrum was performed on UV-2450 spectrophotometer in acetonitrile. X-ray powder diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer with high-intensity Cu K α ($\lambda=1.54$ Å). Raman spectra were taken at room temperature using a Raman microscope with a 532 nm laser source. X-ray photoelectron spectroscopy (XPS) analysis was performed on an ESCA Lab MKII X-ray photo-electron spectrometer using the Mg K α radiation.

3. Photocatalytic Oxidative Desulfurization Procedure of Model Oil

Model oil was prepared by dissolving dibenzothiophene (DBT), benzothiophene (BT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) and dodecanethiol (RSH) in the n-octane, with a corresponding S-content of 500, 250, 250 and 250 ppm, respectively. The four types of model oil were all with 4,000 ppm tetradecane as the internal standard. The photocatalytic reactor consisted of a quartz glass with a circulating water jack and a UV mercury lamp (250 w) with a maximum emission at 365 nm ($\lambda_{max}=365$ nm). The photocatalytic oxidative desulfurization procedure was run as follows: 5 mL of model oil, 0.005 g of catalyst, 1 mL of the conventional IL were added into the reactor and 0.156 mmol H₂O₂ (30 wt%) was injected. The resulting mixture was stirred at 30 °C for 2 h, and after the reaction, the upper clear solution was withdrawn and determined by GC-FID (Agilent 7890A equipped with a capillary column [HP-5, 30 m \times 0.32 mm i.d. \times 0.25 μ m]; FID: Agilent). The conversion of DBT in the model oil was used to calculate the removal of sulfur compounds.

RESULTS AND DISCUSSION

1. Characterization of TiO₂

XRD of Am TiO₂, An TiO₂, An-R TiO₂ is shown in Fig. 1. These three types of TiO₂ were obtained when the calcination temperature was at 100 °C, 400 °C, 700 °C, respectively. No significant diffraction was detected in the sample calcination at 100 °C (Fig. 1(a)). It's con-

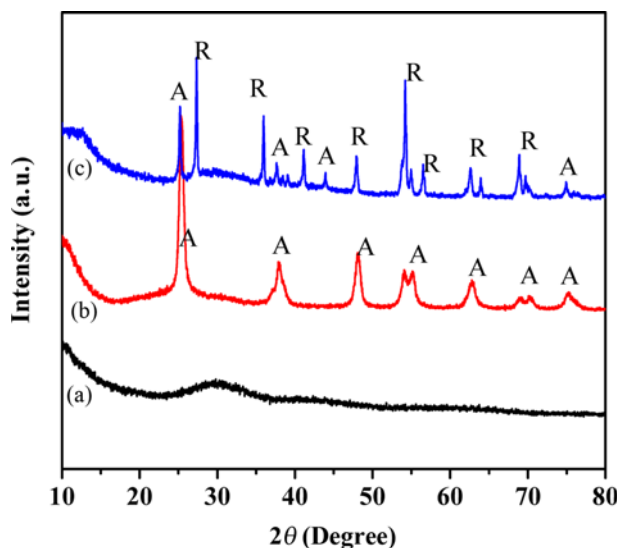


Fig. 1. X-ray powder diffraction patterns of (a) Am TiO₂, (b) An TiO₂, (c) An-R TiO₂.

irmed that the expected Am TiO₂ was prepared. As for the catalyst calcined at 400 °C, the peaks at 25.32° (101), 38.02° (004), 48.18° (200), 54.08° (105), 55.12° (211) (Fig. 1(b)), were clearly representative of the anatase phase. For Fig. 1(c), the catalyst calcined at 700 °C has a mixture of anatase phase and rutile phase. It was indicated that the crystal phase transformation of TiO₂ powder from anatase phase to rutile phase occurred when the temperature was 700 °C [15,16].

The optical properties of TiO₂ were measured by DRS analysis (Fig. 2(I)). The absorption band of the samples (Am TiO₂ \rightarrow An TiO₂ \rightarrow An-R TiO₂) exhibited red-shift. A classical Tauc method is used to calculate E_g value according to the following equation: $\alpha h\nu = B(h\nu - E_g)^n$, where α is the absorption coefficient, B is a constant, $h\nu$ is the energy of excitation and E_g is the band gap energy. Among them, n depends on the transition of a semiconductor (n is 2 for indirect transition and 1/2 for direct transition, in this paper, $n=1/2$) [17]. The energy intercept of a plot of $(\alpha h\nu)^2$ vs. $h\nu$ for a direct transition. As shown in Fig. 2(II), the band gap energies ($h\nu$) of Am TiO₂, An TiO₂, An-R TiO₂ were 3.66 eV, 3.34 eV, 3.16 eV, respectively. With the phase transforming from amorphous to anatase and rutile

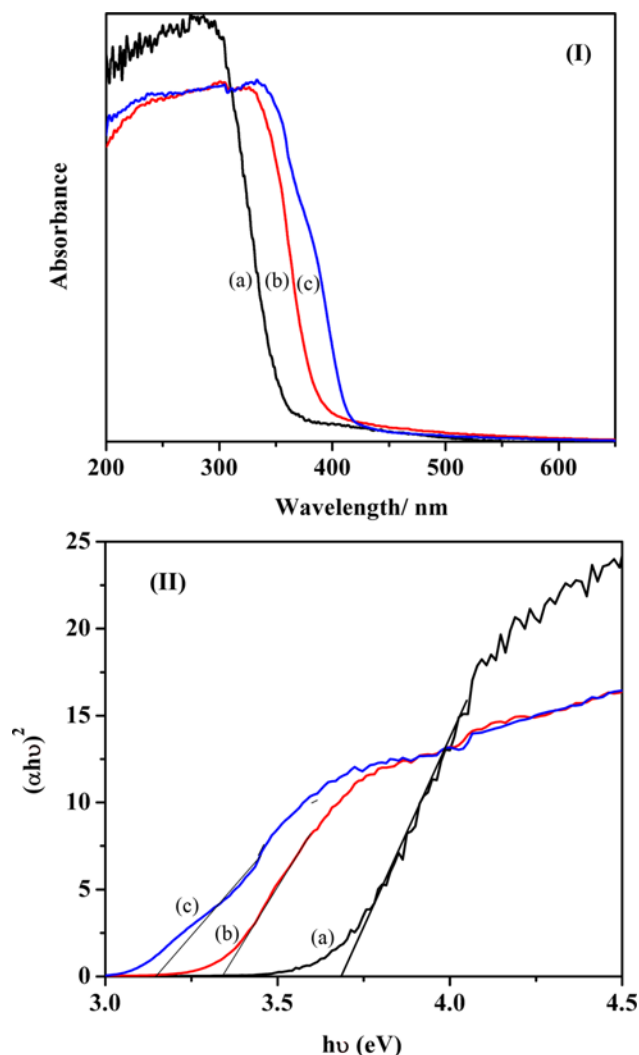


Fig. 2. (I) The diffuse reflectance spectra of (a) Am TiO₂, (b) An TiO₂, (c) An-R TiO₂. (II) $(\alpha h\nu)^2$ vs $h\nu$ curves of (a) Am TiO₂, (b) An TiO₂, (c) An-R TiO₂.

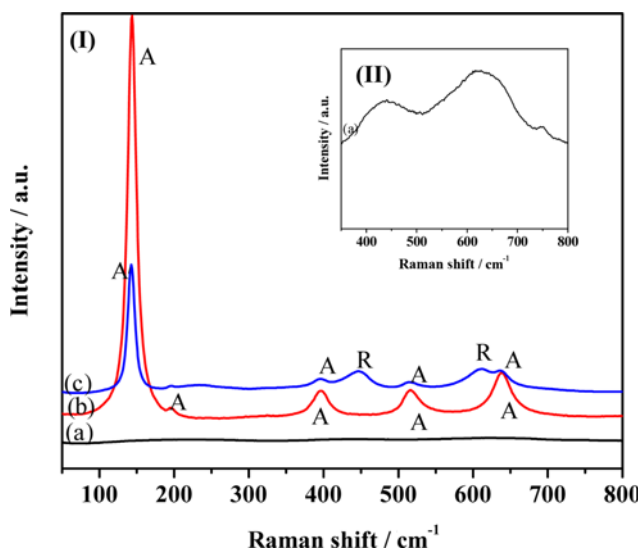


Fig. 3. (I) Raman spectra of (a) Am TiO₂, (b) An TiO₂, (c) An-R TiO₂. (II) Raman spectra of Am TiO₂ in the range 400–800 cm⁻¹ (Inset).

TiO₂, metal oxides typically showed a decreased band gap [18].

Raman analysis for the photocatalysts is shown in Fig. 3. In Fig. 3(I), the spectrum shows a pattern which includes peaks at 146, 199, 399, 517 and 640 cm⁻¹ [19]. This five-peak pattern is called “anatase pattern.” The Raman spectrum of An TiO₂ was composed of a narrow and strong scattering signal and relatively four weak and broad scattering signals. For the An-R TiO₂, the pattern changed into a six-peak spectrum at 148, 399, 447, 515, 611 and 640 cm⁻¹. This was summation of anatase pattern and rutile pattern [20]. The peaks of 148, 399, 515, and 640 cm⁻¹ belonged to anatase pattern and were weakened gradually. The peaks of 447, 611 cm⁻¹ were attributed to rutile pattern and were slowly strengthened. In Fig. 3(II), the bands from 400 to 800 cm⁻¹ are characteristic of the formation of an O-Ti-O lattice [19].

The data of XPS spectrum for Am TiO₂ in Fig. 4 indicated that the expected elements of titanium, oxygen were detected. The spectrum of individual lines of Ti 2p exhibited two peaks of 2p_{3/2} and 2p_{1/2} at 458.61 eV and 464.54 eV. They were attributed to the lattice titanium in titanium oxide. O 1s of Am TiO₂ could be attributed to Ti-OH [21].

In Table 1, the surface area, pore volume, and pore diameters of Am TiO₂, An TiO₂, An-R TiO₂ are listed. The Am TiO₂ exhibits a maximum surface area (53.93 m²/g) and pore volume (0.077 cm³/g). The surface area and pore volume of An TiO₂ (10.75 m²/g, 0.019 cm³/g) and An-R TiO₂ (8.49 m²/g, 0.018 cm³/g) decreased with the rise of calcination temperature. Am TiO₂ with high surface area and large pore volume is great interest for adsorption of DBT, so that it's in favor of the photocatalytic oxidation of DBT.

2. Effect of Different Systems on Sulfur Removal

Different systems on sulfur removal are shown in Table 2. The photocatalytic desulfurization of DBT-containing in model oil only by Am TiO₂ was examined. The sulfur removal was negligible (only 1.8%). When H₂O₂ was added into the model oil, the sulfur removal increased insignificantly, reaching 4.4%. The low sulfur removal lay in water-oil biphasic reaction in this system. H₂O₂ could not make

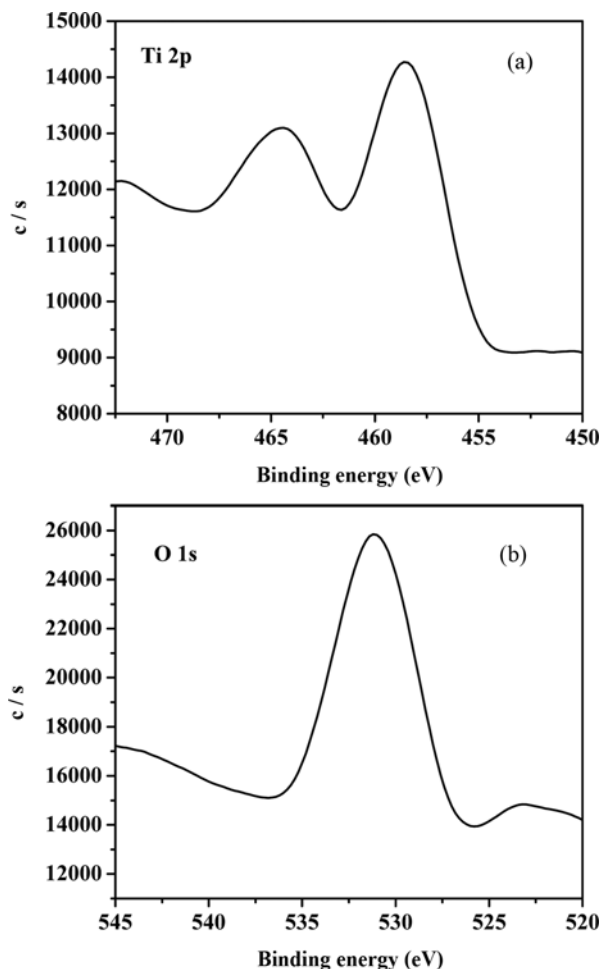


Fig. 4. XPS spectrum of individual lines: (I) Ti 2p; (II) O 1s for Am TiO₂, respectively.

Table 1. The structure properties of three types of TiO₂

Sample	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Am TiO ₂	53.93	0.077	2.43
An TiO ₂	10.75	0.019	3.75
An-R TiO ₂	8.49	0.018	3.75

Table 2. Sulfur removal of different photocatalytic desulfurization systems in model oil

Entry	Condition	Sulfur removal (%)
1	Am TiO ₂ +UV	1.8
2	Am TiO ₂ +H ₂ O ₂ +UV	4.4
3	Am TiO ₂ + [Bmim]BF ₄ +H ₂ O ₂ +UV	96.6
4	Am TiO ₂ + [Bmim]BF ₄ +UV	18.9
5	Am TiO ₂ +H ₂ O+H ₂ O ₂ +UV	1.3
6	[Bmim]BF ₄ +H ₂ O ₂ +UV	25.2

Experimental conditions: V(DBT)=5 mL, m(catalyst)=0.005 g, V(H₂O₂) = 16 μL, V([Bmim]BF₄)=1 mL, T=30 °C, t=2 h, UV

a good contact with DBT. With [Bmim]BF₄ added into the above system, sulfur removal rose sharply, reaching 96.6%. This result

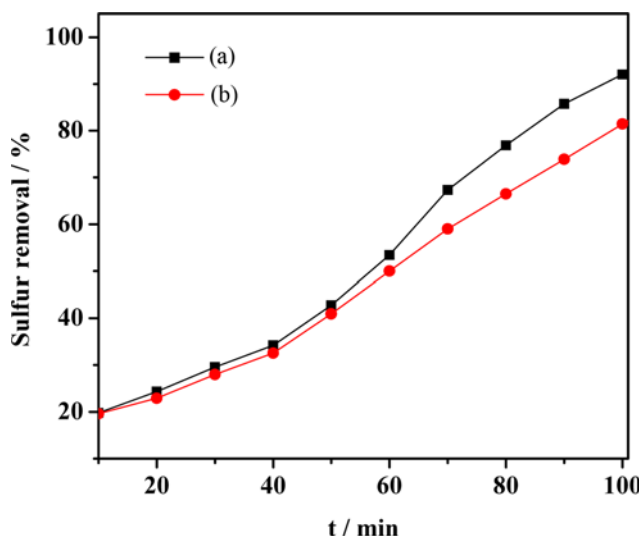


Fig. 5. Effect of Am TiO₂ on DBT removal with or without UV. Experiment conditions: V(DBT)=5 mL, m(catalyst)=0.005 g, V(H₂O₂)=16 μ L, V([Bmim]BF₄)=1 mL, T=30 °C, t=2 h. (a) with UV, (b) without UV.

indicated that the synergistic effect of Am TiO₂, H₂O₂, and [Bmim]BF₄ was very favorable for the improvement of the photocatalytic activity of DBT oxidation. However, without H₂O₂, the sulfur removal decreased to 18.9%. As [Bmim]BF₄ was replaced by H₂O, the sulfur removal decreased to 1.3%. The results indicated that H₂O₂ and [Bmim]BF₄ both played important roles in extraction and photocatalytic oxidative desulfurization. In [Bmim]BF₄ phase, DBT could be successfully oxidized by H₂O₂ under photocatalyst. Without Am TiO₂, sulfur removal of DBT significantly decreased to 25.2%, which indicated that photocatalyst was indispensable in this catalytic oxidative desulfurization system (ECODS).

3. Effect of UV Light on Sulfur Removal

Comparing oxidation of DBT with UV irradiation and without UV, sulfur removal with Am TiO₂ photocatalysts is shown in Fig. 5. With UV irradiation, the sulfur removal was 92.0% in 100 min, while without UV irradiation, the sulfur removal could reach 81.4%. It might lie in isolated titanium oxide species [22] in Am TiO₂ which could react with H₂O₂ to generate peroxy-species to oxidize DBT. With UV irradiation, the sulfur removal increased to 92.0% in 100 min. When Am TiO₂ was irradiated by UV light, the conduction band electron (e⁻) and valence band holes (h⁺) were generated. The e⁻ could react with electron acceptor H₂O₂ to form hydroxyl radicals (HO·) which could oxidize DBT to corresponding sulfones [23]. So the sulfur removal of the system with UV was higher than the system without UV.

4. Effect of Different Catalysts on Sulfur Removal

Sulfur removal for photocatalytic oxidation of DBT with Am TiO₂, An TiO₂, and An-R TiO₂ photocatalysts in [Bmim]BF₄ is shown in Fig. 6. Am TiO₂ catalyst exhibited relatively high activity. The conversion of DBT could reach 96.6%. The high activity of Am TiO₂ might be attributed to higher concentration of isolated titanium oxide species [22] than An TiO₂ and An-R TiO₂. At the same reaction conditions, An TiO₂ and An-R TiO₂ showed very low activities. It was reported that the activity of TiO₂ would be depressed when H₂O₂ was added to An TiO₂ [24]. These results indicated that

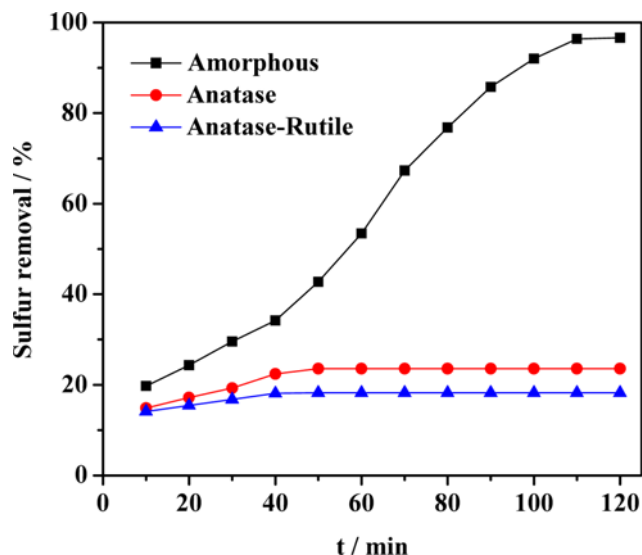


Fig. 6. Effect of different catalysts on DBT removal. Experiment conditions: V(DBT)=5 mL, m(catalyst)=0.005 g, V(H₂O₂)=16 μ L, V([Bmim]BF₄)=1 mL, T=30 °C, t=2 h, UV.

amorphous TiO₂ was a good photocatalyst in ECODS using IL.

5. Effect of the Amount of the Oxidant on Sulfur Removal

To investigate the effect of the amount of the oxidant on the sulfur removal, various H₂O₂/sulfur (O/S) molar ratios at 30 °C with amorphous TiO₂ as the catalyst are shown in Fig. 7. As can be seen, sulfur removal of DBT was 66.3% when the O/S was 1 : 1 in 120 min. With the O/S was increased from 2 : 1 to 4 : 1, the corresponding sulfur removal of DBT was up to 96.6%, 100%, 100% in 120 min, respectively, which was superior to the photooxidative desulfurization systems of H₂O₂/[Bmim]PF₆ [25] and H₂O₂/TS-1 [26]. When the O/S molar ratio was 2 : 1, the sulfur removal of DBT could reach deep desulfurization. So only a stoichiometric ratio of 2 : 1 was chosen as the optimal ratio.

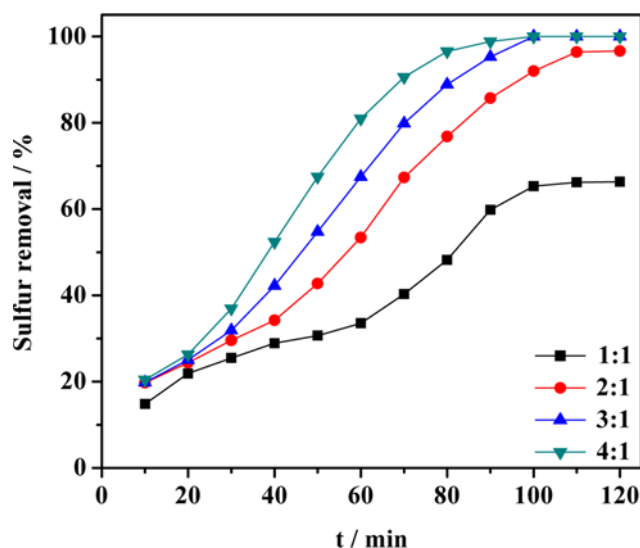


Fig. 7. Effect of different H₂O₂/sulfur (O/S) molar ratios on DBT removal. Experiment conditions: V(DBT)=5 mL, m(Am TiO₂)=0.005 g, V([Bmim]BF₄)=1 mL, T=30 °C, t=2 h, UV.

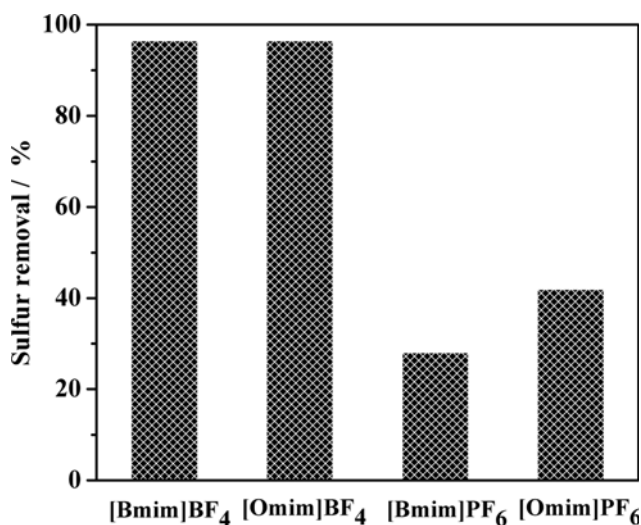


Fig. 8. Effect of different ionic liquids on DBT removal. Experiment conditions: V(DBT)=5 mL, m(Am TiO₂)=0.005 g, V(H₂O₂)=16 μ L, T=30 $^{\circ}$ C, t=2 h, UV.

6. Effect of Different Ionic Liquids on Sulfur Removal

In the desulfurization system, DBT was first extracted into the IL phase and then oxidized in IL phase. Therefore, different ILs may play an important role on sulfur removal. To study the influence and find the optimal solvent, the experiments were done using [Bmim]BF₄, [Omim]BF₄, [Bmim]PF₆, [Omim]PF₆ as solvents, and the results are presented in Fig. 8. As can be seen, [Bmim]BF₄ and [Omim]BF₄ were superior to [Bmim]PF₆ and [Omim]PF₆. Sulfur removal could get to 96.6% and 96.6% in [Bmim]BF₄, [Omim]BF₄, but only 28.2% and 42.0% in [Bmim]PF₆, [Omim]PF₆. The difference of sulfur removal was ascribed to the feature of BF₄⁻ and PF₆⁻ based IL. The results demonstrated that the ILs containing BF₄⁻ anion could enhance the sulfur removal, which was in accordance with the reported catalyst Na₇H₂LnW₁₀O₃₆·32H₂O (LnW₁₀, Ln=Eu, La) [27]. Herein, [Bmim]BF₄ was superior to other ILs in this system with Am TiO₂ as catalyst due to the high desulfurization efficiency and low operation cost.

7. Effect of Different Sulfur Substrates on Sulfur Removal

To investigate the photocatalytic desulfurization performance of the Am TiO₂ on different substrates, BT, DBT, 4,6-DMDBT and RSH were studied. As shown in Fig. 9, the sulfur removal decreased in the order of DBT>BT>RSH>4,6-DMDBT at the same reaction conditions. Among the three aromatic sulfur compounds (BT, DBT, 4,6-DMDBT), the activity was affected mainly by steric hindrance and electron density around the sulfur atom of sulfur compounds. The electron density on the sulfur atoms in DBT, BT, 4,6-DMDBT was 5.758, 5.739, and 5.760, respectively [28]. In the case of DBT and BT, the sulfur conversion increased with the increase of aromatic electron density. Compared with DBT and BT, the conversion of 4,6-DMDBT was lowest due to the domination of the influence of steric hindrance. Therefore, the desulfurization performance of three aromatic sulfur compounds was in the following order: DBT>BT>4,6-DMDBT. RSH as aliphatic compound was more easily oxidized than aromatic sulfur compounds. On the other hand, the steric hindrance of long alkyl chain of RSH was an obstacle for the approach of the sulfur atom to the catalytically active species. For

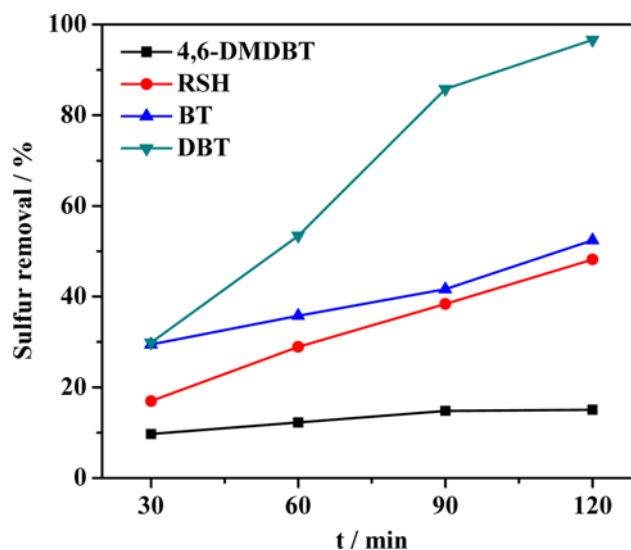


Fig. 9. Effect of different substrates on DBT removal. Experiment conditions: V(DBT)=5 mL, m(Am TiO₂)=0.005 g, V(H₂O₂)=16 μ L, V([Bmim]BF₄)=1 mL, T=30 $^{\circ}$ C, t=2 h, UV.

the above reasons, the catalytic oxidation reactivity of the different substrates was in the following order: DBT>BT>RSH>4,6-DMDBT.

8. Recycling of Catalytic System

The reusability of the catalyst was investigated in the oxidation of DBT. At the end of each run, the upper layer (model oil) was removed by decantation, and then the system was recharged with fresh H₂O₂ and model oil for the next run. Fig. 10 indicates that this desulfurization system could be recycled seven times with a slight decrease in activity. Sulfur removal was 96.6%, 95.6%, 92.9%, 92.7%, 91.5%, 90.7%, 88.0%, respectively.

9. The Process and Mechanism of Reaction

DBT as a representative sulfur compound in fuel was chosen to remove in experiments. The extraction and photocatalytic oxidation desulfurization system contained [Bmim]BF₄, Am TiO₂, hydrogen

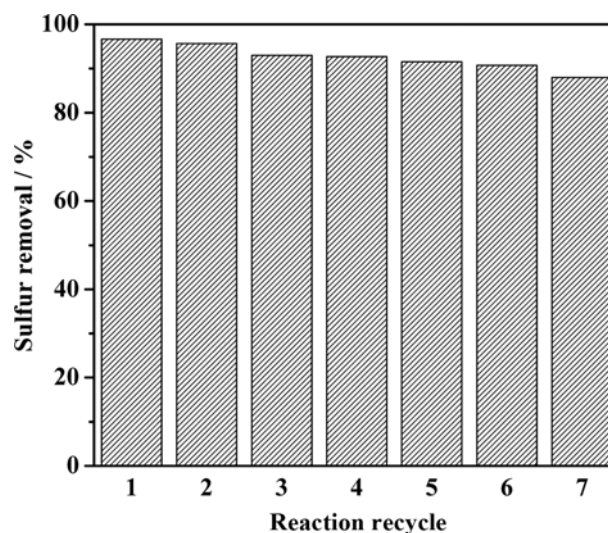


Fig. 10. Effect of recycling of the system. Experiment conditions: V(DBT)=5 mL, m(Am TiO₂)=0.005 g, V(H₂O₂)=16 μ L, V([Bmim]BF₄)=1 mL, T=30 $^{\circ}$ C, t=2 h, UV.

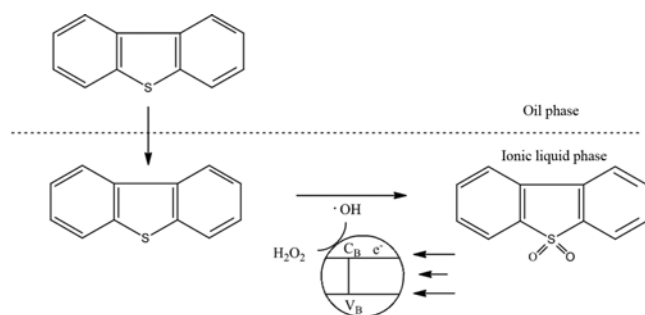


Fig. 11. Suggested extraction and photocatalytic oxidation circle of desulfurization.

peroxide and UV irradiation. In Fig. 11, the sulfur-containing compounds were extracted into the IL phase, and then were selectively oxidized to corresponding sulfones by the strong oxidant HO• radical. The sulfones accumulated in IL and could be separated from IL by centrifugation. Thus, organic sulfur was removed from the model oil. By this means, desulfurization could be achieved [29]. The UV-light source ($\lambda < 300$ nm) is only absorbed by hydrogen peroxide. The addition of hydrogen peroxide to the TiO₂/UV system increased in the HO• concentration. The role of H₂O₂ in generating the HO• was expressed in the following ways: [23]

(i) H₂O₂ traps the photogenerated conduction band electron and prohibits the electron-hole recombination. Molecules of H₂O₂ contribute to the desulfurization by acting as an electron scavenger.



(ii) H₂O₂ may also be as a direct source of UV-irradiated hydroxyl radicals



The high absorption of H₂O₂ was in the range of 212 nm–300 nm. (Eq. (3)). But in this work, the practical application of wavelength was 365 nm at which H₂O₂ has low absorption.

So, in this work, the way (i) played the leading role in the photocatalytic oxidative desulfurization. When Am TiO₂ was irradiated by UV light, electrons in the valence band were promoted into the conduction band. The e[−] could react with H₂O₂ to form hydroxyl radicals (HO•) which could oxidize DBT to corresponding sulfones.

CONCLUSION

Am TiO₂, An TiO₂, An-R TiO₂ were synthesized at 100 °C, 400 °C, 700 °C, respectively. Three types of catalysts were dispersed in ILs to oxidize sulfur-containing compounds with H₂O₂ under UV irradiation at room temperature. The Am TiO₂ photocatalyst had the highest photocatalytic desulfurization efficiency. The system containing Am TiO₂, [Bmim]BF₄, H₂O₂ could oxidize DBT to corresponding sulfone with desulfurization rate of 96.6% under UV irradiation. The photocatalytic reactivity of sulfur substrates decreased in the order of DBT > BT > RSH > 4,6-DMDBT. The photocatalytic reaction could be recycled seven times with a slight decrease in sulfur removal, which might be developed into a promising, green,

reproducible and environment-friendly process of photocatalytic desulfurization.

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