

DEEP DESULFURIZATION OF DIESEL OIL BY ULTRASOUND-ASSISTED CATALYTIC OZONATION COMBINED WITH EXTRACTION PROCESS

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Received January 30, 2013, Accepted March 15, 2013

Abstract

Ultrasonic-assisted catalytic ozonation combined with extraction process was employed to the removal of dibenzothiophene with acetonitrile as extractant. Keggin-type heteropoly compounds, including $H_3PW_{12}O_{40}$, $H_5BW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Ce_{0.8}H_{0.6}PW_{12}O_{40}$ were used as catalysts, and the prepared catalysts $H_5BW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ and $Ce_{0.8}H_{0.6}PW_{12}O_{40}$ were confirmed by FT-IR. Ultrasonic-assisted catalytic ozonation combined with extraction process was found to be effective for desulfurization. The catalytic performance of $H_3PW_{12}O_{40}$ was superior to that of $H_5BW_{12}O_{40}$, and $Ce_{0.8}H_{0.6}PW_{12}O_{40}$ exhibited the best catalytic activity. Moreover, the reused $Ce_{0.8}H_{0.6}PW_{12}O_{40}$ catalyst was recoverable and demonstrated quite close catalytic activity to that of the fresh.

Keywords: heteropoly compounds; ultrasound; extraction; catalytic ozonation desulfurization.

1. Introduction

Sulfur-containing compounds are one of the main contaminants in transportation fuels because through combustion they are converted to sulfur oxides (SO_x) that poison the noble-metal catalysts used in automobiles and contribute to acid rain and environmental pollution. Therefore, environmental regulations have become more and more stringent worldwide to limit the sulfur levels in transportation fuels [1].

In the conventional catalytic hydrodesulfurization (HDS) process, aliphatic and acyclic thiols, sulfides, and disulfides, are easily removed. However, the removal of refractory sulfur-containing compounds, such as dibenzothiophene (DBT) and its derivatives especially 4,6-dimethyldibenzothiophene (4,6-DMDBT), requires severe operating conditions such as high temperatures, high pressures and high hydrogen consumption, which leads to high capital investment and operational costs [2]. Thus, more attention has been paid to develop alternative ultra-deep desulfurization processes. Oxidative desulfurization (ODS) combined with extraction, has been considered one of the most promising desulfurization processes since mild conditions such as ambient temperature and atmospheric pressure are employed and the refractory sulfur-containing compounds can be readily removed in ODS [3,4].

Hydrogen peroxide (H₂O₂) in aqueous solution is the commonly used oxidant in ODS [3,5-7], but the use of H₂O₂ suffers from some shortcomings, such as emulsion-separation with fuels and the low utilization efficiency of H₂O₂ [8,9]. Ozone (O₃) may be an alternative oxidant in ODS since it has a very high oxidation potential, 2.07 V in acid solution [10], and is low cost

and environmentally friendly. For example, Wang *et al.* [11] found that total efficiency of desulfurization from thiophene with ozone near to 100% can be obtained with the $\text{SO}_4^{2-}/\text{ZrO}_2$ catalytic oxidation reaction at room temperature and atmospheric pressure. Here, we reported desulfurization from DBT in catalytic ozonation combined with extraction process under ultrasound wave. Keggin-type heteropoly compounds (HPCs), which are potentially effective catalysts in the ODS process with hydrogen peroxide (H_2O_2) as oxidants [3,6,7], were used as catalysts and acetonitrile (AcN) was used as extractant. Through experimental evaluations, ultrasound-assisted catalytic ozonation combined with extraction was found to be very effective for the oxidative removal of DBT under mild conditions, and a desulfurization efficiency of up to 93.2% was obtained by excellent catalyst $\text{Ce}_{0.8}\text{H}_{0.6}\text{PW}_{12}\text{O}_{40}$ in 60 min. The recovered catalyst demonstrated quite close catalytic activity to that of the fresh.

2. Materials and method

2.1. Materials

All reagents and solvents used were available commercially and were used without further purification unless indicated otherwise. DBT ($\text{C}_{12}\text{H}_8\text{S}$, 99%) was purchased from Sigma-Aldrich. AR-grade phosphotungstic acid ($\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$) was purchased from the National Drug and Chemical Group Co., Ltd. The solution of DBT in normal octane was used as simulated diesel oil, in which the sulfur content was set by fixing the dosage of DBT. Ozone was produced from pure oxygen using an ozone generator.

2.2. Catalyst preparation

$\text{H}_5\text{BW}_{12}\text{O}_{40}$ (HBW) was prepared according to Fu's method [12] as follows: 25 g of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ and 20 g of boric acid (H_3BO_3) were added successively to 125 mL of water with vigorous stirring, then the solution was acidified by 1:1 HCl to pH 5.5. After stirring at 60 °C for 2 h, the solution was acidified to pH 3.8 and then stirred, and the temperature was kept constant at 90 °C for 6 h. After it was kept still for 8 h, the precipitation was filtrated, then 210 mL of 1:2 H_2SO_4 and 70 mL of ether were added, and the required substance was extracted.

$\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot x\text{H}_2\text{O}$ was pretreated according to the literature [13] to obtain $\text{H}_3\text{PW}_{12}\text{O}_{40}\cdot 6\text{H}_2\text{O}$ (HPW). $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ (CsPW) and $\text{Ce}_{0.8}\text{H}_{0.6}\text{PW}_{12}\text{O}_{40}$ (CePW) were prepared and modified following a previously reported procedure [14]. An aqueous solution containing $\text{H}_3\text{PW}_{12}\text{O}_{40}$ was added dropwise to an ethanol solution containing predetermined amounts of metal salts (Cs_2CO_3 and $\text{Ce}(\text{NO}_3)_3$) with stirring at room temperature. The mixture was continuously stirred for about 30 min and then was laid overnight. The precipitates were obtained by evaporating the above mixture to dryness and then calcining at 300 °C for 6 h. This preparation method assured the composition of the metal salts of $\text{PW}_{12}\text{O}_{40}^{3-}$ as $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ and $\text{Ce}_{0.8}\text{H}_{0.6}\text{PW}_{12}\text{O}_{40}$.

2.3. Catalyst characterization

Fourier transform infrared (FT-IR) spectra were recorded on a 5DXC IR spectrometer in the wave number interval between 4000 and 400 cm^{-1} with a 2 cm^{-1} resolution, and samples were diluted into KBr and pressed in the form of a pellet (diameter 13 mm).

2.4. Experimental method

The Desulfurization experiments were carried out in a three-necked 250 mL round-bottomed flask immersed in an ultrasonic generator which supplied ultrasonic irradiation for desulfurization reaction. The middle neck of the flask connected with a gas disperser through which ozone was introduced into the reaction solution at a constant rate, one of the

two side necks connected with a water-cooled reflux condenser to prevent reaction solution loss and serve as a gas outlet, and the other was closed with glass stopper. After 60 mL of simulated diesel oil and 60 mL of AcN were added to the flask, catalyst was added to the above mixture, then ozone was bubbled into the mixture, and at the same time ultrasound was performed. During the reactions, temperature was maintained at 35°C through a temperature control system. The upper oil phase was periodically withdrawn and analyzed for sulfur content using a Model WK-2E microcoulometric integrated analyzer.

3. Results and discussion

3.1. Characterizations of the catalysts

The IR spectra of HBW, CsPW and CePW were shown in Figure 1. In Figure 1a, four main absorption bands were observed at 959, 909, 809 and 700 cm^{-1} , corresponding respectively to the asymmetric vibrations W-Od (terminal O bonded to W), B-Oa (internal O atom connecting B and W), W-Ob (edge-sharing O connecting W), and W-Oc (corner-sharing O connecting W_3O_{13} units) [15]. These bands confirmed Keggin-type $\text{H}_5\text{BW}_{12}\text{O}_{40}$.

Four characteristic peaks reflecting the different vibrations of oxygen atoms of the Keggin-type structure HPW were observed in Figure 1b and 1c, and the peaks at 1080, 983, 889, and 802 cm^{-1} were attributed respectively to the asymmetric vibrations P-Oa (internal O atom connecting P and W), W-Od (terminal O bonded to W), W-Ob (edge-sharing O connecting W), and W-Oc (corner-sharing O connecting W_3O_{13} units) [16]. The results indicated that heteropolyanions retained their original Keggin-type molecular structures in CsPW and CePW.

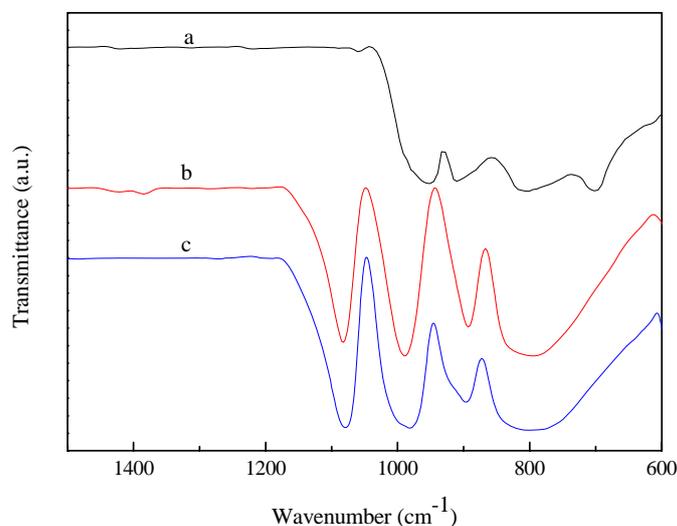


Figure 1. IR spectra of samples. (a) HBW, (b) CsPW and (c) CePW.

3.2 Performance of ultrasonic-assisted catalytic ozonation combined with extraction process

Three different kinds of desulfurization systems, including UAE, UAE+ O_3 and UAE+ O_3 +Ca, where UAE stands for ultrasound-assisted extraction and Ca stands for catalysts, were examined. The results are listed in Table 1.

When AcN was used as the extractant for the simulated diesel oil with ultrasound wave, 60.8% DBT can be removed in 60 min. After the addition of O_3 , the sulfur removal was increased to 73.8%. Then with adding of different HPCs to the reaction system, the removal of DBT was further enhanced.

Table 1. DBT removal in different desulfurization systems^a

Entry	Desulfurization system	Sulfur removal (%)
1	AcN + U ^b	60.8
2	AcN + O ₃ + U	73.8
3 ^c	AcN + O ₃ + HBW + U	79.2
	AcN + O ₃ + HPW + U	89.3
	AcN + O ₃ + CsPW + U	86.7
	AcN + O ₃ + CePW + U	93.2

^a Experimental conditions: initial sulfur concentration, 500 ppm; temperature, 35 °C; ozone dosage, 0.1 g h⁻¹; reaction time, 60 min. ^b Ultrasound. ^c Catalyst dosage, equivalent to 2.5% of the feed mass of *n*-octane.

As shown in Table 1, the catalytic performance of HPW was superior to that of HBW. This result may be related to the oxidative ability of HPAs that the oxidation potential of HPW is higher than that of HBW [17]. At the same time, it was obvious in Table 1 that the introduction of metal ions into HPW changed the catalytic effect. CePW exhibited higher catalytic activity than HPW, with the removal of DBT reaching 93.2% in 60 min. However, CsPW exhibited lower catalytic activity with a desulfurization efficiency of 86.7%. This result was similar to the result found by Wang et al. [6] that the transformation of phosphotungstic acid to its cesium salt, CsPW, weakened the catalytic effect in catalytic oxidative desulfurization combined with extraction with H₂O₂ as oxidant.

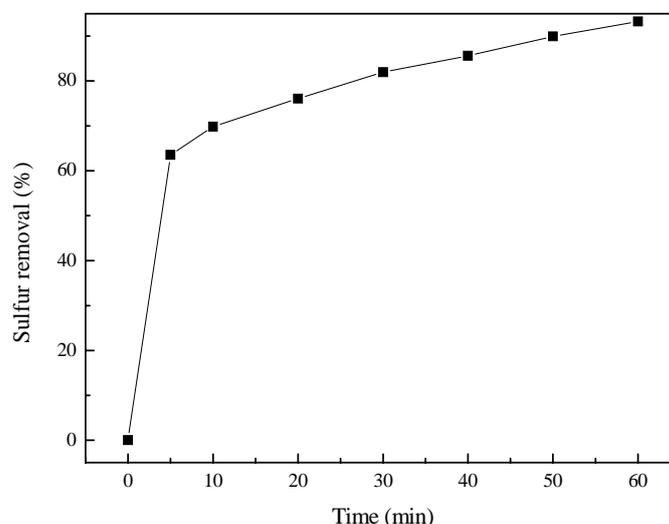


Figure 2. The removal of dibenzothiophene in ultrasound-assisted catalytic ozonation combined with extraction by Ce_{0.8}H_{0.6}PW₁₂O₄₀. Experimental conditions: temperature, 35 °C; initial sulfur concentration, 500 ppm; catalyst dosage, 2.5% of the feed mass of *n*-octane; ozone dosage, 0.1 g h⁻¹; reaction time, 60 min.

Figure 2 showed the typically DBT removal in ultrasound-assisted catalytic ozonation combined with extraction process. It can be found in Figure 2 that DBT was removed rapidly with CePW as catalyst. In the beginning, the removal of DBT from the oil phase was very fast and desulfurization efficiency increased to 63.5% within first 5 min because AcN extraction played an important role in desulfurization for this stage. Then, the desulfurization reaction gradually proceeded, and after 60 min, the removal of DBT reached 93.2%. Hence,

CePW was a quite effective ODS catalyst and ultrasound-assisted catalytic ozonation combined with extraction was highly efficient for desulfurization.

3.3. Catalyst Reuse

The catalytic effect of the used CePW catalyst was explored and recovering process was performed according to the method reported by Wang *et al.* [3]. When the reaction was finished, the reaction mixture was kept still for 20 min. Then, the AcN phase including catalyst was separated and distilled to recover AcN by cooling at the top of the distillation column. After a further treatment by calcination of the residue in the evaporator at 300°C for 6 h, the catalyst can be reused. Using the recovered CePW for the same experiment as

that mentioned above, desulfurization efficiencies of 92.1% and 91.3% were achieved

respectively in two cycles of successive reuse, which was quite close to that obtained using the fresh catalyst as shown in Figure 3.

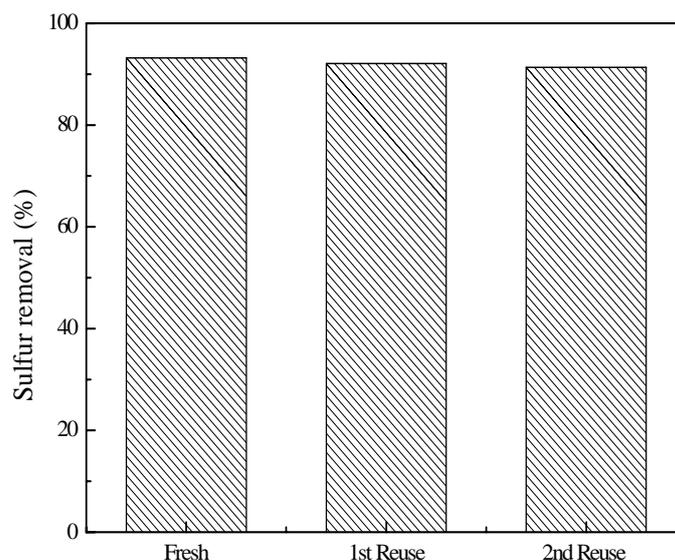


Figure 3. Performance of the recovered catalyst. Experimental conditions: temperature, 35 °C; initial sulfur concentration, 500 ppm; catalyst dosage, 2.5% of the feed mass of n-octane; ozone dosage, 0.1 g h⁻¹; reaction time, 60 min.

4. Conclusions

Ultrasonic-assisted catalytic ozonation combined with extraction process exhibited high catalytic efficiency for the removal of DBT from simulated diesel oil. The catalytic performance of HPW was superior to that of HBW, and the transformation of HPW to its cerium salt, CePW, strengthened the catalytic effect, while the transformation of HPW to its cesium salt, CsPW, weakened the catalytic effect. Moreover, the recovered CePW exhibited quite close catalytic activity as the fresh. As a whole, ultrasonic-assisted catalytic ozonation process combined

with extraction is promising for deep desulfurization of diesel oil.

Acknowledgments

Financial support from the National Natural Science Foundation of China (20976097; 21076116), PetroChina Innovation Foundation (2010D-5006-0405) and Shandong Provincial Natural Science Foundation (ZR2011BM023) is gratefully acknowledged.

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