

Preparation of heteropoly acid quaternary ammonium salt eco-friendly catalyst for diesel oil deep oxidative desulfurization

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Hydrodesulfurization (HDS) is the most widely used method for fuel oil desulfurization, which can easily remove mercaptan and thiophene from diesel oil, but the removal rate of dibenzothiophene (DBT) and its alkylated derivatives is low. Compared with traditional HDS technology, oxidative desulfurization (ODS) technology has the advantages of less investment, mild reaction conditions, and high ODS activity for DBT and its derivatives. Heteropoly acid (salt)/H₂O₂ system is highly efficient and the oxidation product of hydrogen peroxide is water, making them green catalysts. A new type of polyoxometalates phase transfer catalyst, [(C₁₆H₃₃(CH₃)₃)N]₃-HPW₁₁VO₄₀, was synthesized through ion exchange method. It was applied to the catalytic oxidative desulfurization of model diesel oil using H₂O₂ as oxidant. The influencing factors of reaction were investigated in detail. The catalyst exhibits the dibenzothiophene conversion rate of 100% and excellent reusability and retrievability with 99.97% conversion after five times reaction in mild reaction conditions of n(catalyst)/n(DBT)=1/80, n(H₂O₂)/n(DBT)=8/1, 50 °C, and atmospheric pressure in 3 h. The catalyst could be quickly separated and recycled by centrifugation after reaction and hence be promising in the low-sulfur fuel production.

Keywords: oxidative desulfurization, vanadium-substituted phosphotungstic acid, phase transfer catalyst, dibenzothiophene.

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Получение экологичного катализатора на основе четвертичной аммониевой соли гетерополикислоты для глубокой окислительной десульфуризации дизельного топлива

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Процесс гидродесульфуризации – наиболее широко используемый метод, позволяющий легко удалить из дизельного топлива меркаптан и тиофен, но скорость удаления дибензотиофена (ДБТ) и его алкилированных производных низка. В сравнении с вышесказанным, технология окислительной десульфурации (ОДС) имеет преимущества в виде меньших инвестиций, мягких условий реакции и высокой активности в отношении ДБТ и его производных. Система гетерополикислота (соль)/H₂O₂ высокоэффективна, а продуктом окисления пероксида водорода является вода, что делает её экологически чистым катализатором. Методом ионного обмена синтезирован новый тип катализатора фазового переноса полиоксометаллатов [(C₁₆H₃₃(CH₃)₃)N]₃-HPW₁₁VO₄₀, который был применён для каталитической окислительной десульфуризации модельного дизельного топлива с использованием пероксида водорода в качестве окислителя. Подробно исследованы факторы, влияющие на ход реакции. Катализатор демонстрирует степень конверсии дибензотиофена 100% и отличную пригодность для повторного использования и восстановления после пятикратной реакции в мягких условиях: n(катализатор)/n(DBT)=1/80, n(H₂O₂)/n(DBT)=8/1, 50 °C и атмосферном давлении в течение 3 ч. Катализатор может быть быстро отделён и утилизирован центрифугированием после реакции и перспективен для производства топлива с низким содержанием серы.

Ключевые слова: окислительная десульфурация, ванадий-замещённая фосфотунгстовая кислота, катализатор фазового переноса, дибензотиофен.

After the combustion of sulfur-containing compounds in diesel oil, sulfur oxide compounds (SO_x) formed is an important reason of acid rain and haze. So ultra-low-sulfur diesel, with sulfur content lower than 10 or 15 ppmw, is applicable in China, Europe and North America [1–3]. Hydrodesulfurization (HDS) is the most widely used method for fuel oil desulfurization, which can easily remove mercaptan and thiophene from diesel oil, but the removal rate of dibenzothiophene (DBT) and its alkylated derivatives is low. Compared with traditional HDS technology, oxidative desulfurization (ODS) technology has the advantages of less investment, mild reaction conditions, and high ODS activity for DBT and its derivatives [1, 2].

Heteropoly acid (salt) catalysts are dual-function catalysts that are both acidic and redox in nature, with unique hexagonal cage-like structures and pseudo-liquid-like behavior characteristics. The catalytic performance can be modulated by changing the central atom and coordination atom, which is beneficial for catalyst design. Heteropoly acid (salt)/ H_2O_2 system have attracted more attention of many researchers because they are highly efficient and the oxidation product of hydrogen peroxide is water, making them green catalysts [3–6]. However, the heteropoly acid / H_2O_2 system is carried out in a two-phase system, and the aqueous H_2O_2 and sulfur-containing compounds in fuel have high interphase resistance and low mass transfer rate, which affects the oxidation reaction rate and desulfurization effect. The application of quaternary ammonium salt phase transfer catalyst can help transfer the reactants from one phase to another, reduce the reaction resistance, and accelerate the reaction rate of the hetero-phase system [2, 4].

Objects and methods of research

Different heteropoly acid (salt) catalysts have different oxidative ability [7, 8]. Similarly, different quaternary ammonium salts have different phase transfer abilities [4]. Our purpose is to prepare a new type of polyoxometalate phase transfer catalyst with good amphiphilic and oxidizing properties. In this study, vanadium-substituted ternary heteropolyacid ($\text{H}_4[\text{PW}_{11}\text{VO}_{40}]$) was first synthesized and then reacted with different proportions of cetyltrimethyl ammonium bromide (CTAB) by ion exchange method to obtain a series of phase transfer catalysts with different compositions. The ODS activity and reusability of catalysts, optimum catalyst composition and reaction conditions were investigated.

$\text{H}_4[\text{PW}_{11}\text{VO}_{40}]$ was synthesized according to the literature [5]. The phase transfer catalysts with different composition were prepared by ion exchange method. Taking $(\text{CTAB})_n\text{H}_{4-n}[\text{PW}_{11}\text{VO}_{40}]$ for example. 0.8, 0.6, 0.4 and 0.2 mmol CTAB were dissolved in 20 mL distilled water to form solution A, respectively. 0.55 g (0.2 mmol) of $\text{H}_4[\text{PW}_{11}\text{VO}_{40}]$ was dissolved in 30 mL distilled water to form solution B, which was added dropwise to solution A and stirred at 50 °C for 5 h, producing milky precipitate. After cooling at room temperature, it was filtered and washed with deionized water until Br was not present. The powder solids were dried at 110 °C to obtain different compositions catalysts, which were denoted as $(\text{CTAB})_4[\text{PW}_{11}\text{VO}_{40}]$, $(\text{CTAB})_3\text{H}[\text{PW}_{11}\text{VO}_{40}]$, $(\text{CTAB})_2\text{H}_2[\text{PW}_{11}\text{VO}_{40}]$, $(\text{CTAB})\text{H}_3[\text{PW}_{11}\text{VO}_{40}]$, respectively.

In a typical DBT oxidation experiment, 40 mL of model fuel (1.0 wt.% DBT in n-octane) was added to a three-neck flask with a magnetic stirring device, and then a certain amount of catalyst and H_2O_2 . The reaction was carried out in a constant temperature water bath at 50 °C for 1–3 h. Evaluation of catalyst activity was measured by DBT conversion. Both raw material and products were analyzed on Agilent 6890N gas chromatograph, equipped with HP-5 capillary column (30 m×0.32 mm×0.25 μm), and FID detector. Infrared spectra of catalysts were measured by Beijing Beifen-Ruili WQF-510A FT/IR spectrometer during the wavenumber range 400–4000 cm^{-1} using KBr pellet.

Results and discussion

Figure 1 shows FT-IR spectra of $\text{H}_4[\text{PW}_{11}\text{VO}_{40}]$, CTAB, $(\text{CTAB})_3\text{H}[\text{PW}_{11}\text{VO}_{40}]$ before and after reaction. In the infrared spectra of fresh $\text{H}_4[\text{PW}_{11}\text{VO}_{40}]$, there are four characteristic vibrational bands at 804, 893, 982 and 1080 cm^{-1} , which are assigned to $\nu_{\text{as}}(\text{P}-\text{O}_a)$, $\nu_{\text{as}}(\text{M}=\text{O}_d)$, $\nu_{\text{as}}(\text{M}-\text{O}_b-\text{M})$ and $\nu_{\text{as}}(\text{M}-\text{O}_c-\text{M})$ ($\text{M}=\text{W}, \text{V}$), respectively. Those four well-known characteristic bands prove the presence of Keggin-type heteropoly anion (HPA) [5]. In the infrared spectra of CTAB, the absorption peaks at 2920 cm^{-1} and 2849 cm^{-1} are attributed to the stretching vibration of $-\text{CH}_2$ and $-\text{CH}_3$, respectively, while 1475 cm^{-1} and 720 cm^{-1} are due to the deformation vibration peaks of $-\text{CH}$ [4]. Moreover the characteristic peaks of Keggin-type heteropoly acid and alkyl can be seen from the IR-spectra of $(\text{CTAB})_3\text{H}[\text{PW}_{11}\text{VO}_{40}]$, indicating that the existence of quaternary ammonium cation group and heteropoly anion groups in the obtained phase

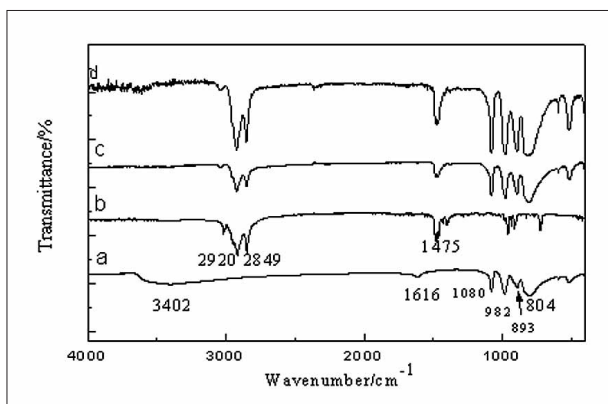


Fig. 1. FT-IR spectra of the samples: a – $H_4[PW_{11}VO_{40}]$, b – CTAB, c – fresh $(CTAB)_3H[PW_{11}VO_{40}]$, d – spent $(CTAB)_3H[PW_{11}VO_{40}]$

transfer catalyst. Compared with fresh catalyst, the IR spectra of spent catalyst remained almost unchanged after the fivefold reaction, indicating good catalyst stability.

The oxidative desulfurization performance of different catalysts were evaluated and shown in Table 1. The conversion rate of DBT in the absence of catalyst is 3.37%, indicating that the reaction rate is very slow (Table 1). The DBT conversions of $H_3PW_{12}O_{40}$ and $H_4PW_{11}VO_{40}$ catalysts were 24.38% and 36.15%, respectively. The low conversions were mainly attributed to the high mass transfer resistance in the oil-water two-phase system, which affected the reaction

rate and desulfurization efficiency. Under the same conditions, the DBT removal rates of $(CTAB)_3PW_{12}O_{40}$ and $(CTAB)_3HPW_{11}VO_{40}$ catalysts were 2.96 times and 2.39 times higher than those of $H_3PW_{12}O_{40}$ and $H_4PW_{11}VO_{40}$ catalysts, respectively, indicating that the phase transfer catalysts reduced the mass transfer resistance of oil-water two-phase system, and the desulfurization efficiency is significantly improved.

Different composition of catalysts also affects the oxidative desulfurization activity of DBT, which is probably due to the fact that different composition leads to different mass transfer rates (Table 1). The appropriate $n(CTAB)/n(PW_{11}VO_{40})$ ratio is conducive to the formation of stable emulsion drops and full contact of reactants, reducing mass transfer resistance. $(CTAB)_3HPW_{11}VO_{40}$ has the best catalytic performance.

Table 1 also shows the influence of different oxygen-sulfur ratio ($n(H_2O_2)/n(S)$) on DBT conversion rate. When oxygen-sulfur ratio is 2, DBT conversion rate is 82.67%. When the ratio of oxygen to sulfur was 4:1, the conversion rate of DBT increased, but not significantly. When the ratio of oxygen to sulfur is 8:1, the desulfurization rate can reach 99.96% after 3 h, which is close to the complete reaction.

The influence of catalyst dosage (calculated by molar ratio of $n(catalyst)/n(S)$) on DBT conversion is shown in Table 1. In addition to the catalyst with a molar ratio of 1/100, the other

Table 1

Comparison of catalytic efficiency for ODS of DBT on different catalysts

No.	Catalyst	T, °C	t, h	$n(catalyst)/n(s)$	$n(H_2O_2):n(S)$	DBT conversion, %
1	without catalyst	50	3	0	4 : 1	3.37
2	$H_3PW_{12}O_{40}$	50	3	1/20	4 : 1	24.38
3	$H_4PW_{11}VO_{40}$	50	31	1/20	4 : 1	26.15
4	$(CTAB)_3PW_{12}O_{40}$	50	3	1/20	4 : 1	72.26
5	$(CTAB)H_3PW_{11}VO_{40}$	50	3	1/20	4 : 1	62.15
6	$(CTAB)_2H_2PW_{11}VO_{40}$	50	3	1/20	4 : 1	83.22
7	$(CTAB)_3HPW_{11}VO_{40}$	50	3	1/20	4 : 1	86.41
8	$(CTAB)_4PW_{11}VO_{40}$	50	3	1/20	4 : 1	77.68
9	$(CTAB)_3HPW_{11}VO_{40}$	50	3	1/20	2 : 1	82.67
10	$(CTAB)_3HPW_{11}VO_{40}$	50	3	1/20	8 : 1	99.96
11	$(CTAB)_3HPW_{11}VO_{40}$	50	3	1/40	8 : 1	100
12	$(CTAB)_3HPW_{11}VO_{40}$	50	3	1/80	8 : 1	100
13	$(CTAB)_3HPW_{11}VO_{40}$	50	3	1/100	8 : 1	96.63
14	$(CTAB)_3HPW_{11}VO_{40}$	50	2	1/80	8 : 1	97.86
15	$(CTAB)_3HPW_{11}VO_{40}$	40	2	1/80	8 : 1	91.12
16	$(CTAB)_3HPW_{11}VO_{40}$	30	2	1/80	8 : 1	45.66

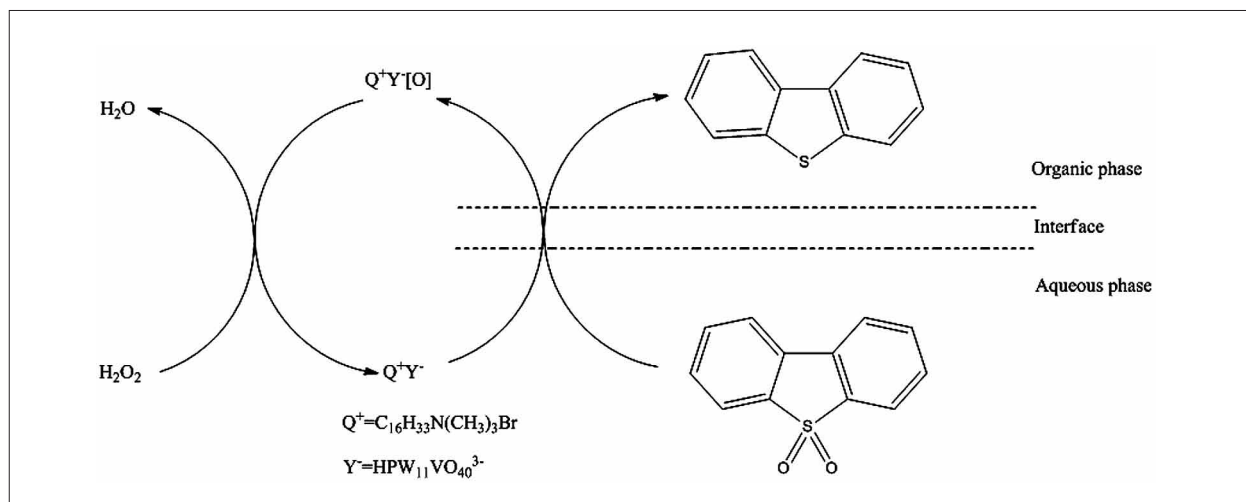


Fig. 2. ODS mechanism of DBT using $(C_{16}H_{33}N(CH_3)_3)HPW_{11}VO_{40}$ catalyst

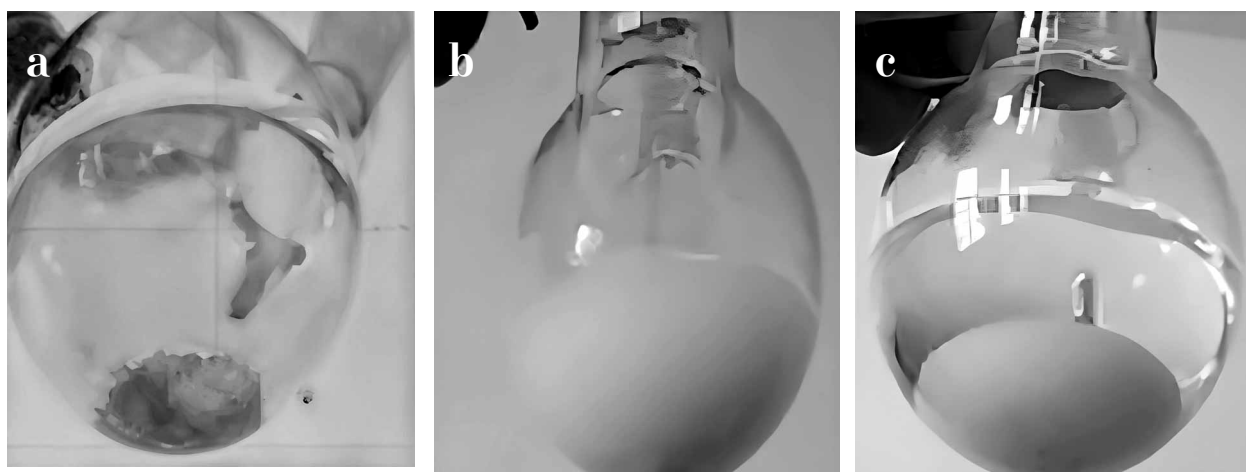


Fig. 3. Diagram of catalytic oxidative desulfurization process of DBT: a, b, c – before, during, and at the end of the reaction, respectively

catalysts can achieve more than 99% desulfurization after 3 h, so the catalyst with a molar ratio of 1/80 is selected as the best dosage.

As can be seen from Table 1, temperature is the key factor affecting the conversion rate of DBT. The conversion rate of DBT at 30 °C in 2h is 45.66%. When the reaction temperature was increased to 40 and 50 °C, the conversion rate of DBT increased significantly, reaching 91.12% and 97.86%, respectively. When the reaction time was increased from 2 to 3 h, the conversion rate of DBT reached 100%, indicating that the thermodynamic equilibrium was reached after 3 h. Therefore, 50 °C and 3 h are the best reaction temperature and reaction time from the perspective of reaction equilibrium time and DBT conversion.

The mechanism of the phase transfer catalytic oxidative desulfurization reaction can be explained by Figure 2. Heteropolyacid

anion Y^- and quaternary ammonium cation Q^+ exist in the reaction system in the form of ion pairs. Heteropolyacid anion Y^- is a hydrophilic group, which is oxidized by H_2O_2 in the aqueous phase to become an active peroxy heteropolyacid anion $Y^-[O]$. Quaternary ammonium cation Q^+ is a lipophilic group, which can bring the oxidized heteropolyacid anion $Y^-[O]$ into the oil phase. The sulfur compound DBT in the oil was catalyzed to become the more polar dibenzothiophene sulfone, and the peroxy heteropoly anion was reduced to heteropoly anion and re-entered the water phase, finishing a catalytic cycle.

It is assumed that heteropoly acid (HPA) anion provided catalytic activity, while quaternary ammonium cation provided phase transfer ability, which not only improved catalytic activity, but also facilitated the recovery of catalysts. The oxidative desulphurization process

of DBT over the phase transfer catalyst was shown from Figure 3. At the beginning of the reaction, the catalyst was solid at the bottom of the reactor and forms a heterogeneous system (Fig. 3a). When the reaction temperature was raised to 50 °C under stirring, the catalyst and reactants formed a microemulsion system and behave like homogeneous mixture during reaction (Fig. 3b). At the end of the reaction, the catalyst was cooled and settled at the bottom of the reactor (Fig. 3c). The catalyst could be quickly separated and recycled by centrifugation. It was proved that the conversion rate of DBT hardly changes after five runs, indicating that the catalyst has good reusability.

Conclusion

$[(C_{16}H_{33}(CH_3)_3N)_3HPW_{11}VO_{40}]$ with amphiphilic and oxidizing properties was synthesized through ion exchange method. It was proved to be efficient and reusable phase transfer catalyst for ODS of DBT. The catalyst exhibits DBT conversion rate of 100% and excellent reusability with 99.97% conversion after five times reaction under mild reaction conditions of $n(\text{catalyst})/n(\text{DBT})=1/80$, $n(H_2O_2)/n(\text{DBT})=8/1$, 50 °C, and atmospheric pressure in 3 h. The catalyst could be quickly separated and recycled by centrifugation after reaction and hence be promising in the low-sulfur fuel production.

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