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Oxidative-Extractive Deep Desulfurization of Gasoline by Functionalized Heteropoly Acid Catalyst

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A series of functionalized heteropoly acid catalysts with two PEG chains and Anderson-type polyoxoanion $IMo_6O_{24}^{5-}$ have been in situ synthesized, and applied for catalytic oxidative desulfurization coupling with extraction (oxidative-extractive desulfurization, OEDS). Two PEG chains endow the catalyst a good extracting ability for sulfur compounds, particularly, their corresponding oxidative products. The oxidation and extraction can simultaneously be performed. No additional extracting agent is added after oxidation. The mechanism of OEDS is proposed. The effect factors for OEDS of model gasoline with H_2O_2 and O_2 as oxidants are respectively investigated, and the optimum conditions are respectively obtained. The H_2O_2 OEDS system is more efficient, rapid and low energy consumption. It just takes several tens of minutes at the mild conditions to achieve the completely removal of dibenzothiophene (DBT), benzothiophene (BT) and thiophene in model gasoline. The novel H_2O_2 OEDS system has been also applied for the desulfurization of the real gasoline. The vast majority of sulfides in real gasoline are removed after OEDS, and the content of sulfur from 110 ppm can be reduced to 10 ppm. Moreover, the functionalized heteropoly acid catalyst has showed a good recyclability.

1. Introduction

Recently, deep desulfurization of fuel is badly in need of innovative approaches, since sulfur compounds in fuel not only give rise to air pollution and acid rain, but also are irreversibly toxic to the noble metal catalysts in automobiles. To meet with the stringent environmental regulations, it is urgently demanded to expand new techniques to obtain “no sulfur” fuel, namely sulfur content below 10 ppm.[1] Although conventional hydrodesulfurization (HDS) technology is highly efficient to remove mercaptans, thioethers and disulfides, it is exceedingly difficult to reduce benzothiophene (BT), dibenzothiophene (DBT) and their alkylated derivatives to zero because of their large steric hindrance in hydrogenation.[2] Furthermore, owing to the severe operation conditions (high temperature, high pressure, high hydrogen consumption and expensive equipment), the wide use of HDS is restricted. Hence, much attention has recently focused on non-HDS processes, such as adsorptive desulfurization[3], oxidative desulfurization (ODS)[4], extractive desulfurization[5], biodesulfurization[6] and others.

Among these non-HDS techniques, extractive desulfurization should be the easiest process to industrialization. However, the desulfurization efficiency only with simple extraction is relatively low since the difference of polarity between the sulfur compound and fuel is little. To overcome this difficulty, extractive desulfurization coupling with oxidation (oxidative-extractive desulfurization, OEDS) has attracted extensive interest of people and become a hot topic of research.[7] In this method, the refractory sulfur-containing compound is first efficiently oxidized to its corresponding sulfoxide and/or sulfone both which with higher polarities can be more easily removed by extraction. In the most developed OEDS systems, the common flammable/volatile organics as extracting agents are added after the oxidation. Then, the environmental and safe issues caused by these extracting agents turn into one of the primary concerns.[8]

From an environmental perspective, room-temperature ionic liquids (RTILs) are more superior in comparison with the common organic solvents, because they possess excellent characteristics of negligible vapor pressure, non-flammability, high thermal stability, recyclability, especially, higher affinity for sulfur compounds.[9] Therefore, many kinds of ILs as extracting agents have been used for direct extractive desulfurization.[10] Meanwhile, some OEDS systems with different oxidative catalysts and IL extractants have been developed such as CH_3COOH in $[BMIM]BF_4$[11], $Na_2MoO_4{\cdot}2H_2O$ in $[BMIM]BF_4$[12] , $Na_7H_2LaW_{10}O_{36}{\cdot}32H_2O$ in $[BMIM]BF_4$[13], V_2O_5 in $[BMIM]BF_4$[14] and $[(C_8H_{17})_3NCH_3]_2W_6O_{19}$ in $[OMIM]PF_6$[15].

According to the designability of ILs, a large number of task-specific ionic liquids (TSILs) have been developed.16 In our previous work, we have successfully prepared a kind of oxidative and thermoregulated bifunctional ILs with the thermoregulated structural unit (PEG chain) and Keggin-type

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heteropolyanion $PW_{12}O_{40}^{3-}$. The prepared TSILs have been applied for catalyzing H_2O_2 ODS in the thermoregulated system to achieve an integration of homogeneous catalysis and heterogeneous separation.[17] The desulfurization rate for model gasoline can reach 92%. This catalytic system needs the addition of toluene for realizing thermoregulation, and after oxidation the extracting agent DMF is used for sulfur removal. More recently, Keggin-type polyoxometalates as oxidative catalysts have been widely applied to ODS of fuels.[18] However, Anderson-type polyoxometalates have not received much attention as oxidative catalysts. In 2010, Li has first reported Anderson-type polyoxoanion $IMo_6O_{24}^{5-}$ for catalytic ODS of model fuel with O_2 as oxidant.[19] The oxidative reaction can proceed under the mild conditions. However, the reaction time is relatively long, and the recycling performance of the catalyst is not mentioned.

In this paper, a kind of oxidative and extractive bifunctional ionic liquids not only as oxidative catalyst but also as excellent extracting agent for OEDS of fuel has been designed and synthesized. Two PEG chains as functional groups of extraction are introduced into quaternary ammonium cation, and Anderson-type polyoxoanion $IMo_6O_{24}^{5-}$ is used as catalytic oxidation unit. The prepared functionalized ionic liquids have been applied for OEDS of model gasoline and real gasoline with H_2O_2 and O_2 as oxidant, respectively. The oxidation and extraction can be performed simultaneously. The IL catalysts with $IMo_6O_{24}^{5-}$ have exhibited very high catalytic activity in the presence of H_2O_2, and the refractory sulfur compounds DBT, BT and thiophene in model gasoline can be completely oxidized within several tens of minutes. Especially, we find the IL catalysts with two PEG chains simultaneously have an exceptionally high extraction ability for sulfur compounds, particularly, their corresponding oxidative products, sulfones. Recently, PEG as a green solvent for simple extractive desulfurization has been reported.[20] The extraction function of PEG chain for sulfur compounds is achieved mainly by electrostatic effect and hydrogen bond. However, OEDS is more superior to simple extraction as mentioned above. Therefore, a highly efficient deep desulfurization system with oxidative and extractive bifunctional catalyst has been developed. What's more, the catalytic system has showed excellent recyclability. Here, we declare the detail of the study.

2. Experimental

2.1 Materials and product analysis

All chemicals were used as purchased and of reagent grade. Solvents were dried by known procedures and used freshly distilled. The product was analyzed by a Nicolet-510P IR spectrometer. ^1H NMR spectrum was recorded on a Brucker AV 500 MHz spectrometer with tetramethylsilane as the standard. GC spectrum was analyzed by an Agilent 6890 N instrument equipped with a flame photometric detector (FPD) and a capillary column (OV-1701, 50 m×0.25 mm×0.25 μm). The sulfur content of fuel was measured by a WK-2D microcoulometric detector.

2.2 Synthesis of functionalized heteropoly acid catalyst

N-PEG substituted octadecylamine **1** and quaternary ammonium chloride **2** were prepared according to our previous work.[17] $Na_5IMo_6O_{24}$ was prepared according to procedures described elsewhere.[21] Quaternary ammonium chloride **2** (4 mmol) and 20 mL sulfuric acid solution (2 mol/L) were added to a three-neck round-bottomed flask equipped with a thermometer, a reflux condenser and a constant pressure drop funnel. Under stirring, the solution was heated to 60 °C. Then, another 10 mL sulfuric acid solution (2 mol/L) with $Na_5IMo_6O_{24}$ (0.8 mmol) was dropped slowly. After completion of the dropping, the reaction was kept the temperature for 24 h. The blue solution was gradually formed. After that, the reaction mixture was distilled in vacuum to eliminate the water and the produced hydrogen chloride. Then, the blue residue was dissolved into chloroform to remove Na_2SO_4 by filtration. After chloroform was distilled, heteropoly blue **3** was afforded. Finally, 50 μL H_2O_2 (30 wt%) was added to 1.5 g heteropoly blue **3**. Under stirring, the solution was heated to 45 °C. Within tens of minutes, the solution changed into orange indicating the formation of heteropoly acid catalyst **4** with $IMo_6O_{24}^{5-}$. The typical spectra data of **4** (n=108) were listed here. IR (KBr): ν=3429 cm^{-1} (-OH), 2921 cm^{-1} (C-H), 2871 cm^{-1} (C-H), 1112 cm^{-1} (C-O-C), 950 cm^{-1} (Mo-O_t), 885 cm^{-1} (Mo-O_b-Mo), 680 and 629 cm^{-1} (Mo-O_a-I). ^1H NMR (500 MHz, DMSO): δ=0.83 (t, *J*=8.0 Hz, 3H), 1.06 (t, *J*=8.0 Hz, 3H), 1.08~1.18 (m, 36H), 3.34~3.79 (m, 436H).

2.3 Typical procedure of OEDS

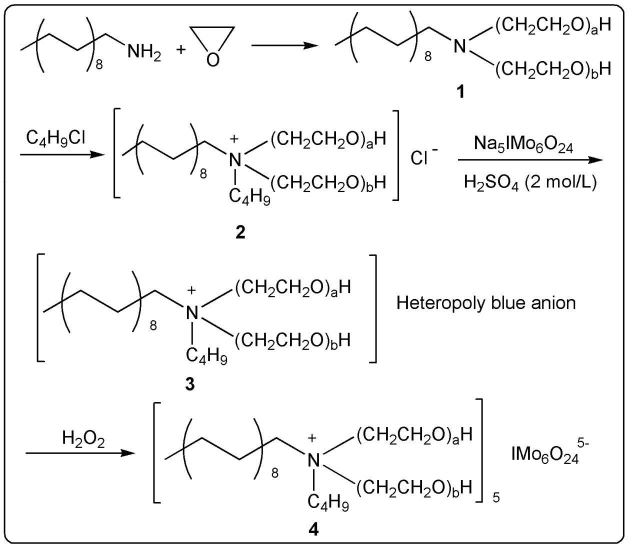
The above synthesized heteropoly blue **3** as a catalyst precursor was directly applied for OEDS. The real catalyst **4** was formed in situ when the oxidant was added in the system. Three kinds of model gasolines were prepared by respectively dissolving the model sulfur compounds containing DBT, BT and thiophene in *n*-octane. The corresponding S-contents were all 200 ppm. A typical H_2O_2 OEDS: 5 mL model gasoline, 1.5 g heteropoly blue **3**, 50 μL H_2O_2 (30 wt%) were added into a three-neck round-bottomed flask equipped with a thermometer and a reflux condenser. The resulting mixture was stirred at 45 °C for 20 min in a water bath. A typical O_2 OEDS: 5 mL model gasoline and 4.0 g heteropoly blue **3** were added into an autoclave equipped with a thermometer and filled with 1 MPa O_2. The resulting mixture was stirred at 105 °C for 120 min in an oil bath. After the reaction, the mixture was cooled to room temperature. The upper oil phase was withdrawn and then analyzed using a microcoulometric detector. The lower heteropoly blue **3** was dried and directly reused by the addition of fresh model oil and the oxidant.

3. Results and discussion

3.1 Synthesis of functionalized heteropoly acid catalyst

A series of oxidative and extractive bifunctional ionic liquids were synthesized. The route of the whole synthesis was outlined in Scheme 1. Briefly, the opening ring reaction of ethylene oxide with *n*-octadecylamine produced the tertiary amine **1** with two PEG chains. The average polymerization degree (n=a+b) of **1** could be calculated by the increasing mass.

Then, the tertiary amine **1** reacted with *n*-chlorobutane to give the ammonium chloride **2**. Afterwards, the ammonium chloride **2** reacted with $Na_5IMo_6O_{24}$ under the condition of strong acid to give the heteropoly blue **3**. Finally, the heteropoly blue **3** was oxidated by H_2O_2 into the heteropoly acid catalyst **4** with $IMo_6O_{24}^{5-}$.



Scheme 1. The synthesis route of functionalized heteropoly acid catalyst.

In the synthesis, when $Na_5IMo_6O_{24}$ was mixed with the ammonium chloride **2**, the direct anion exchange as reported in the literature did not proceed.[19] However, under the condition of strong acid, the heteropoly blue anion with the mixed valence states of Mo was formed. Additionally, the chromogenic reaction of iodine and amylopectin proved the presence of I_2. However, when H_2O_2 was added to the solution of heteropoly blue, the color change from blue to orange indicated the formation of Anderson-type polyoxoanion $IMo_6O_{24}^{5-}$ (See Supplementary information).

The possible mechanism of interconversion between the heteropoly blue anion and $IMo_6O_{24}^{5-}$ is elaborated in Fig. 1. $IMo_6O_{24}^{5-}$ under the acidic condition is decomposed into Mo (VI) and IO_4^-, and then the system undergos a further oxidation-reduction reaction by which the heteropoly blue anion with the mixed valence states of Mo and I_2 are formed. When H_2O_2 is added, Mo (IV) is oxidized to Mo (VI), and I_2 is oxidized to IO_4^-. Finally, Mo (VI) and IO_4^- can recombine to $IMo_6O_{24}^{5-}$.[21]

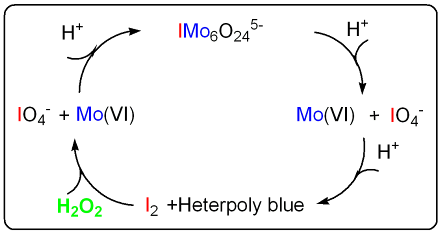


Fig.1 The possible mechanism of interconversion between the heteropoly blue and $IMo_6O_{24}^{5-}$.

According to the reported article[19], there are four characteristic absorption peaks of Anderson structure in the band of 500~1000 cm^{-1}. As shown in Fig. 2, the curve a is the spectrum of heteropoly acid **4** with $IMo_6O_{24}^{5-}$. The antisymmetric stretching vibration of Mo-O_t bond is 950 cm^{-1}. The antisymmetric stretching vibration of Mo-O_b-Mo bond is 885 cm^{-1}. Two kinds of the antisymmetric stretching vibrations of Mo-O_a-I bond are 680 and 629 cm^{-1}, respectively. However, in the spectrum of heteropoly blue **3** (the curve b), the Mo-O_b-Mo bond and Mo-O_a-I bond are absent.

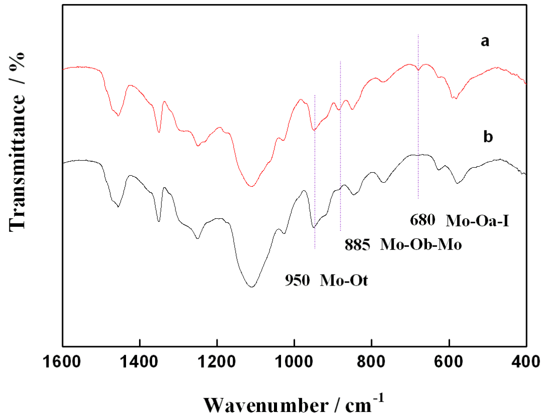


Fig.2 IR spectra of the heteropoly acid **4** (a) and the heteropoly blue **3** (b) (n=108).

3.2 Extraction of heteropoly acid catalyst

Model gasoline is firstly prepared by dissolving the model sulfur-containing compound benzothiophene (BT) in *n*-octane. The extracting ability of the synthesized heteropoly acid catalyst **4** for BT in fuel is tested, and the Nernst distribution coefficients of BT (*K*(BT)) in conventional extractant N,N-dimethylformamide (DMF)/model fuel and the heteropoly acid **4** (n=108)/model fuel at 30 °C are 1.5 and 3.4, respectively. It is obvious that the heteropoly acid **4** has stronger extracting ability for BT. The Nernst distribution coefficients of the oxidation product of BT (BTO_2) are also tested, and the results show that *K*(BTO_2) in DMF/model fuel and the heteropoly acid **4** (n=108)/model fuel at 30 °C are 2.4 and 95, respectively. In comparison with *K*(BT), the significant increase of *K*(BTO_2) shows that the heteropoly acid **4** has more superior extracting ability for the corresponding oxidative product of sulfur compound. Therefore, when the heteropoly acid **4** as catalyst is applied for the OEDS of fuel, the oxidation and extraction can simultaneously be performed. No additional extracting agent is needed to add after oxidation.

3.3 OEDS of model gasoline

It is very pleased that Anderson-type catalyst **4** can be formed in situ when the heteropoly blue **3** is directly applied for OEDS of model gasoline (BT in *n*-octane) with H_2O_2 as oxidant. What's more, we find the heteropoly blue anion can also invert into Anderson-type polyoxoanion $IMo_6O_{24}^{5-}$ under the presence of O_2. Therefore, the heteropoly blue **3** as a catalyst precursor has been applied for OEDS of model gasoline with H_2O_2 and O_2 as the oxidants, respectively. The corresponding blank experiments on simple extraction by the heteropoly blue **3** are also done. The comparative results are listed in Table 1. From Table 1, the desulfurization rate with the simple extraction is just about 40%. The polymerization degree of ammonium cation (n value) has little effect on the simple extraction in our experiments. However, the polymerization degree of ammonium cation gives a large effect on the OEDS. According to Table 1, for H_2O_2 OEDS, with the increase of the polymerization degree, the catalytic activity of the catalyst **4** formed in situ gradually decreases. This is because the viscosity of the catalyst gives a large effect on the catalytic activity. The viscosity increases with the increasing polymerization degree. With the increase of the viscosity, the larger mass transfer resistance results in the lower reaction activity. For O_2 OEDS, because the reaction temperature is high (105 ^{o}C), the viscosity of the catalyst is not the main effect factor for the catalytic activity. With the increase of the polymerization degree, the larger spatial effect of the catalyst means it can not contact well with the reaction substrate. Therefore, the preferable average polymerization degrees for H_2O_2 and O_2 systems are n=108 and n=148, respectively.

Table 1. The comparative results for extractive desulfurization, H_2O_2 OEDS and O_2 OEDS with the heteropoly blue **3**.

Polymerization degree	Viscosity (cp)^{a}	Desulfurization rate (%)		
		Extraction^{b}	O_2 OEDS^{c}	H_2O_2 OEDS^{d}
n=108	408.2	43.3	46.4	100
n=129	425.9	41.5	49.3	81.5
n=148	440.1	41.2	70.0	63.1
n=169	458.5	41.6	54.2	52.1
n=189	470.3	42.0	44.0	45.4

Conditions^{a}: 25 ^{o}C. Conditions^{b}: 45 ^{o}C, 20 min, primary extraction. Conditions^{c}: 105 ^{o}C, 1 MPa O_2 and 120 min. Conditions^{d}: 45 ^{o}C, 50 μL H_2O_2 and 20 min.

The effect factors for H_2O_2 and O_2 OEDS are fully investigated, respectively. For O_2 OEDS system, the selected optimum conditions are as follows: the heteropoly blue **3** (n=148, m=4.0 g), P(O_2)=1.0 MPa, T=105 °C and t=2 h (See Supplementary information). Under the optimum conditions, the desulfurization rate can reach 85%. For H_2O_2 OEDS system, the selected optimal conditions are as follows: the heteropoly blue **3** (n=108, m=1.5 g), V(H_2O_2, 30 wt%)=50 μL, T=45 ^{o}C and t=20 min (See Supplementary information). Under the above conditions, the sulfur compound BT can be completely removed. It is obvious that Anderson-type catalyst **4** can more efficiently catalyze the oxidation of H_2O_2 in contrast to the oxidation of O_2. Owing to the possible influences of the physical state and the solubility, H_2O_2 is more active than O_2. Therefore, the emphasis study is focused on the H_2O_2 OEDS system.

The reactivities of diverse sulfides including DBT, BT, and thiophene in model gasolines have been evaluated in the developed H_2O_2 OEDS system. The new catalytic system has showed high catalytic efficiency for these three substrates. The sulfides can be completely oxidized within several tens of minutes. The results of the desulfurization rate contrast to the reaction time at different temperatures for different sulfides are respectively shown in Fig. 3, Fig. 4 and Fig. 5. The desulfurization rate increases with the increase of temperature. From Fig. 3, for the 100% removal of DBT, 20 min at 25 ^{o}C is reduced to 10 min at 35 ^{o}C. According to Fig. 4, for the removal of BT, the desulfurization rate from 63.2% for 10 min can reach 100% for 60 min at 25 ^{o}C. With the temperature increasing, the 100% removal of BT can be achieved at 45 ^{o}C for 20 min. For the removal of thiophene (Fig. 5), the desulfurization rate is only 67.3% at 25 ^{o}C for 20 min, and the complete removal needs 55 ^{o}C for 60 min. The results have showed the reactivity of three sulfur-containing compounds follows the order of DBT>BT>thiophene, which is consistent with the literature.[22] However, though the reactivity of thiophene is comparatively low, it also can be efficiently oxidized and removed within one hour in the new H_2O_2 OEDS system.

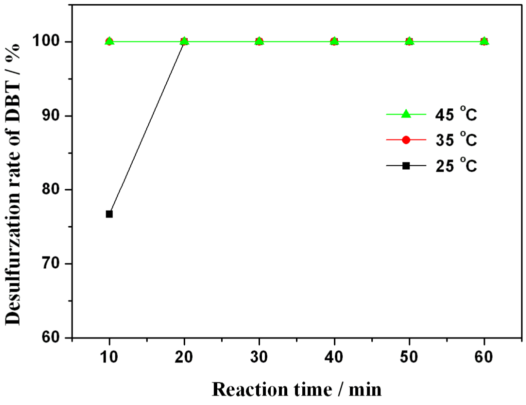


Fig. 3 Desulfurization rate of DBT *vs.* reaction time at different reaction temperatures.

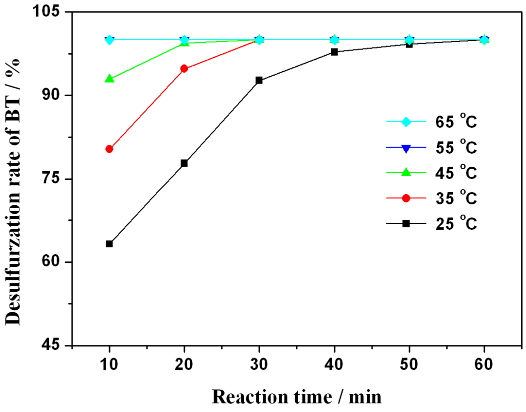


Fig. 4 Desulfurization rate of BT *vs.* reaction time at different reaction temperatures.

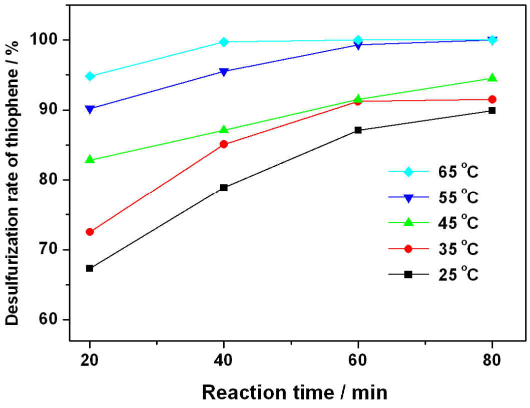


Fig. 5 Desulfurization rate of thiophene *vs.* reaction time at different reaction temperatures.

3.4 OEDS of real gasoline

The novel H_2O_2 OEDS system has been applied to the desulfurization of real gasoline with the total sulfur content of 110 ppm. Fig. 6 shows that the desulfurization rate increases with the increasing temperature from 25 °C to 65 °C. At 65 °C for 30 min, the content of sulfur from 110 ppm can be reduced to 10 ppm. Sulfur-specific GC-FPD chromatograms of the real gasoline before and after OEDS are shown in Fig. 7. From the curve a, there are diverse sulfides with different contents in the untreated real gasoline. However, from the curve b, it is clearly observed that the vast majority of sulfides are removed after OEDS. The results show that the novel H_2O_2 OEDS system is highly efficient for the desulfurization of real gasoline, and the new system is applicable to the removal of both thiophenic sulfurs and other diverse sulfides.

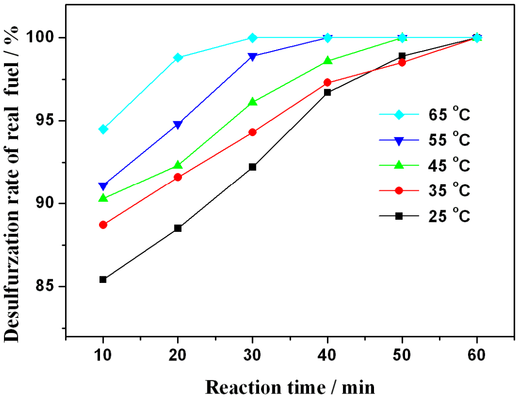


Fig. 6 Desulfurization rate of real gasoline *vs.* reaction time at different reaction temperatures.

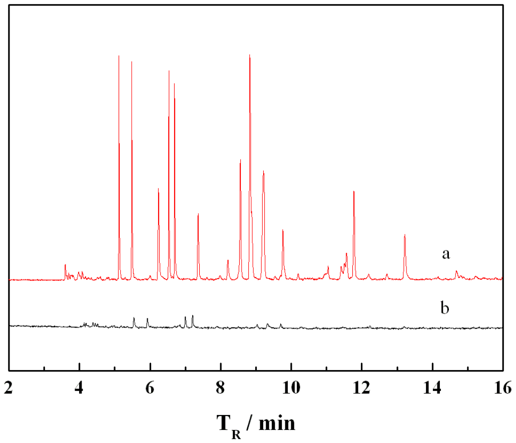


Fig. 7 Sulfur-specific GC-FPD chromatograms of the real gasoline before (a) and after (b) OEDS.

3.5 Proposed mechanism of OEDS

The possible mechanism of H_2O_2 OEDS in the new catalytic system is proposed as shown in Fig. 8. When H_2O_2 solution is added, the heteropoly blue is first oxidized to $IMo_6O_{24}^{5-}$ accompanying with the color change from blue to orange. The sulfur compound is first extracted into the catalyst phase, and then oxidized by $IMo_6O_{24}^{5-}$. The corresponding oxidative product sulfone is afforded, and simultaneously $IMo_6O_{24}^{5-}$ is reduced to the heteropoly blue again. The mechanism of OEDS system is comparable to those delivered by others so far. [23]

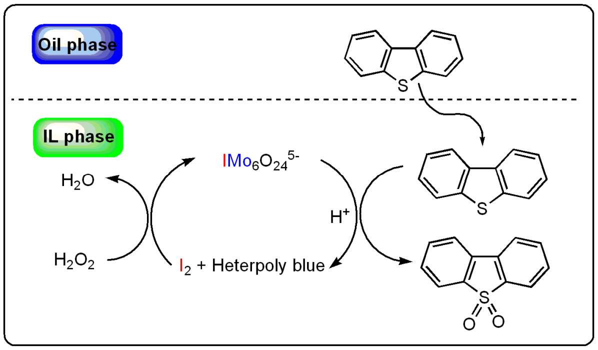


Fig. 8 Proposed mechanisms of H_2O_2 OEDS system.

3.6 Recycle of the catalyst

After the reaction, the upper oil phase was withdrawn and then analyzed. The lower heteropoly blue was dried and directly reused by the addition of fresh fuel and H_2O_2.

The recycling efficiencies for H_2O_2 OEDS of DBT, BT and thiophene have been shown in Fig. 9. From Fig. 9, the desulfurization rates of DBT, BT and thiophene are all slowly declined during the recycles, since the extraction of the catalyst is gradually saturated by sulfides. After 8 times recycles, the lower heteropoly blue solution is regenerated by back-extraction with water to remove the sulfides.[24] Afterwards, the regenerated heteropoly blue is again used for H_2O_2 OEDS of model fuel (the 9th recycle). From Fig. 9, the desulfurization rate is comparable with that afforded by the first used catalyst. What's more, the regenerated heteropoly blue is characterized by IR. The comparative result with the fresh heteropoly blue has showed that the structure of the heteropoly blue doesn't change (See Supplementary information). Therefore, the catalyst in the new system has a good recyclability.

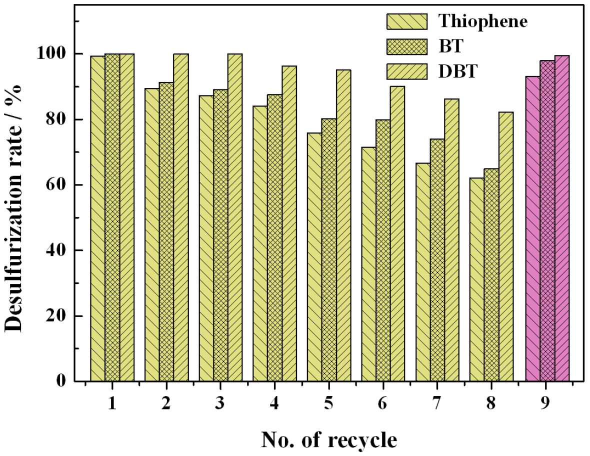


Fig. 9 The recycle of the catalyst for H_2O_2 OEDS of DBT, BT and thiophene (DBT: 35 °C, 10 min; BT: 45 °C, 20 min; thiophene: 55 °C, 60 min).

4. Conclusion

A highly efficient OEDS system with H_2O_2 as oxidant has been developed by using the functionalized heteropoly acid catalyst with two PEG chains and Anderson-type polyoxoanion $IMo_6O_{24}^{5-}$. The catalyst can be formed in situ by the oxidation of heteropoly blue with H_2O_2. The functionalized heteropoly acid acts as not only the catalyst but also the excellent extracting agent. The oxidation and extraction are simultaneously performed. The refractory sulfur compounds DBT, BT and thiophene in model gasolines can be completely removal under the mild conditions in a few tens of minutes. The developed H_2O_2 OEDS system is also applicable to the removal of other diverse sulfides and is highly efficient for the real gasoline. The vast majority of sulfides in real gasoline are removed after OEDS, and the total content of sulfur from 110 ppm can be reduced to 10 ppm. What's more, the catalyst shows a good recyclability, and the regenerated catalyst is comparable with the new catalyst. In all, the study provides a fast, mild and highly efficient desulfurization method.

Acknowledgements

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Graphical abstract

Anderson-type heteropoly acid catalyst with $IMo_6O_{24}^{5-}$ is applied for oxidative-extractive desulfurization, and the oxidation and the extraction are simultaneously performed.