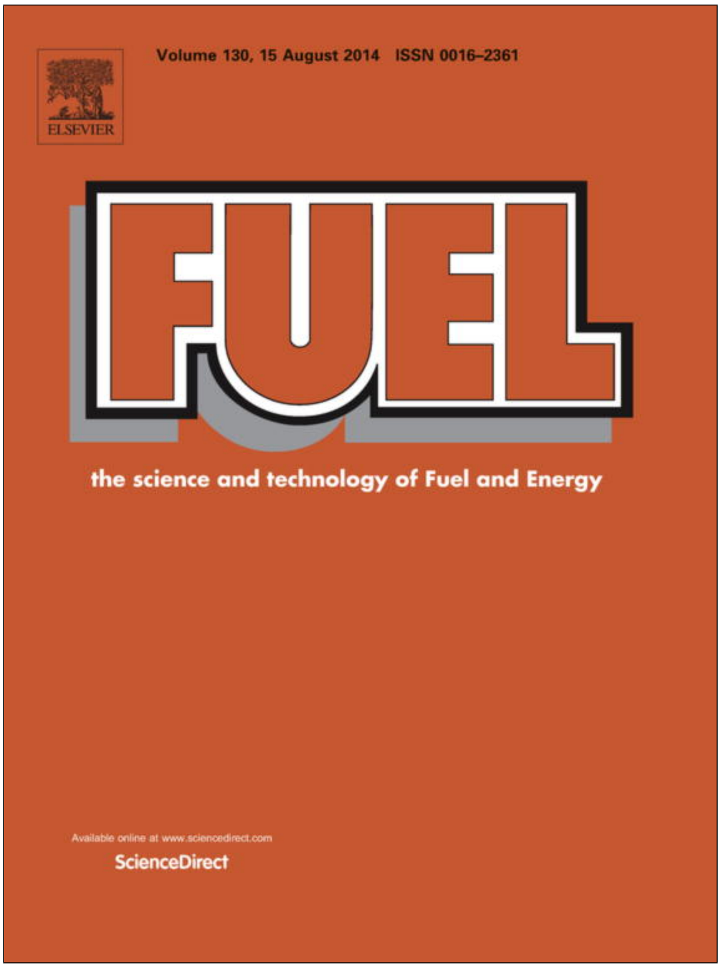

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Catalytic oxidative desulfurization of dibenzothiophene using catalyst of tungsten supported on resin D152

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HIGHLIGHTS

- Catalyst W/D152 was prepared and characterized.
- Sulfur level in gasoline was reduced from 400 to 3.52 ppm under optimal conditions.
- Catalyst W/D152 could be reused for 7 times.
- Mechanisms and kinetics of catalytic oxidation of DBT in gasoline were examined.

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ABSTRACT

In this paper, the performance of catalytic oxidative desulfurization (ODS) were studied using catalyst W/D152 which was prepared by depositing tungsten on resin D152, a macroporous polyacrylic cationic resin. Dibenzothiophene (DBT) was selected as the target compound, and oil-soluble cyclohexanone peroxide (CYHPO) as an oxidant. The effect of different reaction parameters, including reaction temperature, reaction time, the weight of catalyst W/D152 and the molar ratio of CYHPO/DBT were investigated, and the oxidation mechanisms as well as the kinetics were also examined individually. The conversion of DBT and the sulfur content reached 99.1% and 3.52 ppm, respectively at the optimal catalytic conditions of 100 °C, mass ratio of model gasoline to catalyst W/D152 of 100, molar ratio of CYHPO/DBT of 2.5 and reaction time of 40 min. The catalyst could be reused for 7 times before the total sulfur content of treated model gasoline was higher than 10 ppm. The catalytic oxidation of DBT fitted the first-order kinetic model pretty well. The catalyst W/D152 was analyzed by the scanning electron microscopy (SEM) and Fourier Transform Infrared Spectroscopy (FTIR), and the data show that a thin layer of active components was covered on the catalyst surface which helps explain the satisfactory catalytic performance.

1. Introduction

In order to produce ultra clean fuels to protect the environment and to meet government regulations worldwide, more advanced refinery and purification technologies are always pursued in the oil refinery industry [1]. Sulfur is poisonous to the environment, catalytic converter and engine of vehicles. Therefore, clean fuel with low sulfur content is crucial not only for reducing vehicle emissions, but also for prolonging the life span of the exhausting gas treatment system. Consequently, research on methods for cost-effective removal of sulfur from fuel has been paid close attention [2].

Sulfur-containing compounds in petroleum include polysulfides, mercaptans, disulfides, thiophene, DBT, benzothiophene, 4,6-dimethyldibenzothiophene and their alkylated derivatives. These compounds are very difficult to be removed from fuel. The technologies of sulfur removal consist of hydrodesulfurization (HDS) and other technologies. As a conventional approach, HDS is facing a huge challenge in meeting new stringent regulations and legislations. HDS consumes hydrogen, and was carried out at relatively harsh reaction conditions such as high operating temperature and pressure [3]. Side reactions during hydrogenation in HDS also reduce the octane number [4–6]. Moreover, HDS is less effective for aromatic sulfur compounds removal due to their steric

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hindrance [3,7,8]. Other technologies include oxidative desulfurization (ODS), biodesulfurization, adsorption desulfurization, extractive desulfurization and alkylation desulfurization. ODS is a complementary or alternative technology to HDS [7,8], and is one of the most important and effective method for ultra-deep desulfurization in petroleum refining. ODS consists of two steps, the first step is oxidation of sulfur to sulfones, and the next is the removal of these compounds [9]. Catalysts for ODS play a key role which are mainly composed of precious metals such as iridium, nickel, palladium, molybdenum, rhodium, platinum and tungsten, and tungsten has attracted more interests [10–14]. Tungsten has received considerable attention in catalysis because of its unique physical-chemical properties [12]. Tungsten-containing catalyst is highly reactive [10,11,13–15], and is effective for desulfurization of DBT [10,11]. Sattler and Parkin [14] reported the desulfurization of thiophene by molecular tungsten compounds, investigated the carbon-sulfur bond cleavage of thiophene and achieved a high conversion of thiophene.

However, tungsten-containing catalysts for ODS usually exists two drawbacks. One is the choice of supporter. When tungsten-containing powders are applied directly to the catalytic oxidative reactions, it is difficult to separate them from the organic phase. Supporters considerably improve activities of catalysts and facilitate the separation. Therefore, a series of supporters have been studied, such as silica, activated carbon, alumina [9], kaolin and zeolite [16]. Due to complex preparation processes, and high energy consumption for the catalysts mentioned above, investigations on new supporters are needed [17]. Recently, resin as supporter has attracted more interests [17,18]. The surface area and particle size of resin D152 is 540–580 $m^2\,g^{-1}$ and 0.315–1.25 mm respectively. Therefore, resin D152 could present enough supporting spots, which could act as a new mesoporous material.

The other drawback is the choice of oxidant. In most ODS systems, H_2O_2 is used as oxidant which is immiscible with the n-octane, so the intersolubility of H_2O_2 and DBT is not well [18–20]. Cyclohexanone peroxide (CYHPO) as an oil-soluble oxidant was selected due to it could be complete contacted with DBT and has good oxidative performance.

To improve the existing ODS process, tungsten was selected as catalyst, resin D152 as the supporter, and CYHPO as the oxidant in this study. The effects of temperature, reaction time, mass ratio of CYHPO/DBT and the weight of catalyst on DBT removal were investigated, and the catalytic mechanisms and kinetics were also examined. The results from this study could help to demonstrate the feasibility of the catalytic system for DBT removal from gasoline.

2. Experimental

2.1. Materials

DBT (>98%, analytical-grade reagent, AR) was the product of Acros Organics Co. Ltd. (USA); n-octane (AR) was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. (China); D152 resin was obtained from Anhui Sanxing Resin Technology Co. Ltd. (China) whose properties were shown in Table 1; Ammonium tungstate hydrate (AR) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China); Model gasoline with 400 ppm (wt.) of sulfur content was prepared by dissolving DBT in n-octane. All solvents and reagents were used without any further purification.

2.2. Catalyst preparation and characterization

Table 1
Some basic characteristics of resin D152.

Property	Date
Exchange equivalent (mmol g^{-1})	⩾8.0
Particle size (mm)	0.315–1.25
Density (g ml^{-1})	0.70–0.75
Surface area ($m^2\,g^{-1}$)	540–580
Average pore diameter (nm)	24
Maximum temperature (°C)	100

The catalyst was prepared by the incipient wetness impregnation [21]. The preparation procedure was as follows: firstly, 5.0 g of resin D152 was macerated with 400 ml deionized water at pH 2.5 for 24 h. Water was discharged, and the resin was added to aqueous solution of ammonium tungstate hydrate with the mass volume concentration of 2.5 wt.% at 30 °C. The mixture was stirred for 4 h. During this processing, the pH value of the tungstate solution was maintained constantly at 2.5 using 0.1 M HCl. Then, the resin was filtered, and washed with deionized water and diethyl ether for 10 min, respectively. At last, the catalyst was dried in a vacuum dryer at 50 °C to reach a constant weight. The catalyst was denoted as catalyst W/D152 in this study.

The surface morphology of catalyst W/D152 was analyzed using scanning electron microscopy (SEM) (QUANTA 200, FEI, USA) with acceleration voltages of 20.0 kV and at 1000 × magnification. The catalyst samples were coated with Au to reduce charge problems. The Fourier Transform Infrared Spectroscopy (FTIR) of the catalyst, diluted with KBr and pressed into a pellet, was performed on a FTIR spectrometer (VARIAN 3100, Shimadzu, Japan) at resolution of 4 cm^{-1} over the range of 400–4500 cm^{-1}. All FTIR spectra were collected at room temperature.

2.3. Procedures for catalytic oxidation of DBT

Experiments of catalytic oxidation were carried out in an Erlenmeyer flask (250 ml) at an atmospheric pressure. The reactor was placed in an oil bath at different constant temperature (40–120 °C), and applied with magnetic stirring. The typical catalytic oxidation procedure was as follows: 30 g of model gasoline with sulfur contents of 400 ppm was added into the reactor, then 0.3 g of catalyst W/D152 (mass ratio of model gasoline/catalyst W/D152 of 100) and 0.03 g of CYHPO (molar ratio of CYHPO/DBT of 2.5) were also added respectively. After 40 min of reaction, the resulted mixtures were cooled down to ambient temperature and transferred to a separation funnel (250 ml). The mixtures in the separation funnel were washed with 30 ml deionized water for 10 min, then held for 15 min. After separation, the gasoline was washed with 30 ml of N,N-Dimethylformamide for 10 min and held for 15 min. Subsequently, the supernatant was separated and washed with 20 ml N,N-Dimethylformamide for 10 min to make sure that sulfur compounds were completely removed. At last, the supernatant was washed with 20 ml deionized water again. Thus the refined gasoline was obtained. This experimental procedure consists of oxidation and separation, which was modified from the procedure established by Abdalla et al. [9]. N,N-Dimethylformamide was reused after regeneration. All experiments were repeated three times to secure reproducibility of results.

2.4. Catalyst regeneration

The regeneration and subsequent recycling of catalytic oxidation of catalyst are important for the industry application [15]. In this study, catalyst W/D152 was regenerated using the solvent elution technique. Catalyst W/D152 was separated from the reaction mixture by filtration, and then washed with diethyl ether for

10 min. Subsequently, the catalyst was drip-rinsed with 95% ethanol for 15 min to remove residual DBT and sulfones on the resin surface at room temperature. At last, it was filtered and dried in a vacuum drier at 60 °C. In experiments, regenerated catalyst and fresh one were used under the same reaction conditions.

2.5. Analysis

DBT concentration in samples was analyzed using gas chromatography (GC) (Agilent 6890 N, USA). The GC was equipped with a flame ionization detector (FID, HP6890) and HP-5 capillary column (30 m × 0.32 mm × 0.25 μm film thickness). Highly purified nitrogen (mass concentration ⩾99.9999%) was used as carrier gas.

The conversion of DBT was calculated to evaluate the activity of the catalyst W/D152. Reaction rates equations for oxidative desulfurization was calculated using Eq. (1), in which η is the conversion rate, and C_0 and C_t stand for the initial and final concentration of DBT in the model gasoline, respectively.

$$\eta = [(C_0 - C_t)/C_0] \times 100\% \qquad (1)$$

Yield rate of model gasoline equation is shown in Eq. (2), where λ is the yield rate, and m_0 and m_t are the initial and final weight of model gasoline, respectively.

$$\lambda = [(m_0 - m_t)/m_0] \times 100\% \qquad (2)$$

3. Results and discussion

3.1. Characterization of catalyst W/D152

In order to understand the effect of the morphology on the catalyst W/D152 activity, SEM has been used to exam the morphology difference between resin D152 (Fig. 1a) and catalyst W/D152 (Fig. 1b). Fig. 1b shows that agglomerates with particle size of 5–10 μm deposited on the surface of catalyst W/D152. This result is in accordance with previous results published from the other studies [22,23]. The SEM images of catalyst W/D152 indicate that tungsten had been successfully immobilized on resin D152.

The FTIR spectra of catalyst W/D152 and resin D152 were shown in Fig. 1c. It can be seen from Fig. 1c that the C–Cl stretch at 621 cm^{-1} dominated in all of the samples (resin D152 and catalyst W/D152). The FTIR spectrum of catalyst W/D152 shows that W–O band could be observed around 983 cm^{-1}. Therefore, the signal broadening around 983 cm^{-1} could be ascribed to that the tungsten had been immobilized on resin D152, which is in accordance with the previous report [24]. This conclusion is consistent with the observation from SEM images (Fig. 1a and b). According to the literature [25], the FTIR bands at 3415 cm^{-1} correspond to the stretching vibrations of adsorbed H_2O molecules. Furthermore, band at 1622 cm^{-1} is associated with the phenyl group from resin D152.

3.2. Effects of reaction conditions on the conversion of DBT

3.2.1. Effect of reaction temperature

Reaction temperature is an important parameter for the catalytic oxidation of DBT [16]. In order to investigate the effect of temperature on catalytic oxidation of DBT by W/D152, experiments were carried out at the following temperatures: 40 °C, 60 °C, 80 °C, 100 °C, 105 °C and 120 °C. The reaction duration was kept at 40 min, molar ratio of CYHPO/DBT of 2.5, and mass of the catalyst and model gasoline was 0.3 and 30 g, respectively. The conversions of DBT at different reaction temperature, as shown in Fig. 2a, were increased dramatically from 48.2% to 86.0% with the increase of reaction temperature from 50 to 80 °C. When temperature was further increased to 100 °C, the highest conversion of DBT of 99.1% was observed. However, when temperature was increased from 105 to 120 °C, the conversion of DBT decreased sharply from 99.1% to 72.5% and the sulfur content in the final product was also increased sharply from 3.52 to 112 ppm. Although CYHPO may be decomposed at temperatures less than 100 °C [18], the decomposition rate of CYHPO was increased significantly, and the catalyst would be destroyed at 120 °C. In addition, it is interesting to notice that the conversion exceeded 99% at temperature of 100 °C and 105 °C.

The yield rate of model gasoline was also influenced by reaction temperature (Fig. 2a). From Fig. 2a, the yield rate of the model gasoline decreased slightly when the reaction temperature increased from 40 °C to 100 °C. While the yield rate of model gasoline decreased sharply from 93.9% to 87.2% when the temperature was further increased to 120 °C. In consideration of these results, the reaction temperature was set at 100 °C in the consequent experiments.

3.2.2. Effect of reaction time

The effect of reaction time on the conversion of DBT was evaluated at the following reaction conditions: temperature of 100 °C, molar ratio of CYHPO/DBT of 2.5, and mass of the catalyst and model gasoline was 0.3 and 30 g, respectively. The results are plotted in Fig. 2b. As the reaction time increased, the conversion of DBT first increased fast and then gradually increased to the maximized at 99.1% at 40 min. It can also be seen from Fig. 2b that the yield rate of the model gasoline did not changed significantly in the first 20 min. As time was further increased to 60 min, the conversion of DBT did not increase any more, and the yield rate decreased from 93.8% to 90.7%. These were possibly due to the occurrence of volatilization of the model gasoline. However, the effect of volatilization on the conversion of DBT was not so significant at a shorter reaction time of 40 min. Therefore, the optimum reaction time was about 40 min. Hulea et al. [26] report that required reaction time ranged from 30 to 40 min when tungsten catalyst supported on MgAl–NO_3 was used for DBT removal.

3.2.3. Effect of molar ratio of CYHPO/DBT

The effect of the molar ratio of CYHPO/DBT on the conversion of DBT was studied under the same conditions mentioned above, and five different molar ratios of CYHPO/DBT were evaluated. When the CYHPO/DBT molar ratio increased from 0.50 to 2.0, the conversion of DBT increased from 41.7% to 91.0% (Fig. 2c). At the molar ratio of 2.5, the conversion of DBT maximized 99.1% at 40 min. Further increase of the molar ratio led to stable DBT removal rate of 99%. The optimal molar ratio of 2.5 is larger than the theoretical stoichiometric molar ratio of 2, which is probably because of thermal decomposition of CYHPO during the reaction process. Zhou et al. [18] reported that the reaction of CYHPO synthesis is reversible, and Zang et al. [27] found that the CYHPO decomposition was observed at 100 °C. The yield rate did not change appreciably at the various molar ratios. In consideration of the cost of CYHPO in the reaction system, the appropriate mass ratio employed for the next studies was set at 2.5.

3.2.4. Effect of catalytic weight

Catalytic oxidation experiments were carried out under various mass of fresh catalyst W/D152 in the range of from 0.15 to 0.40 g. The effect of catalyst weight on the conversion for DBT is shown in Fig. 2d. When the catalyst weight was increased from 0.15 to 0.25 g, the conversion of DBT rose considerably from 91.3% to 96.2%, and the corresponding sulfur content decreased from 34.8 to 15.2 ppm. Further increase of the weight of the catalyst to 0.3 g led to 99.1% of DBT conversion and the corresponding sulfur

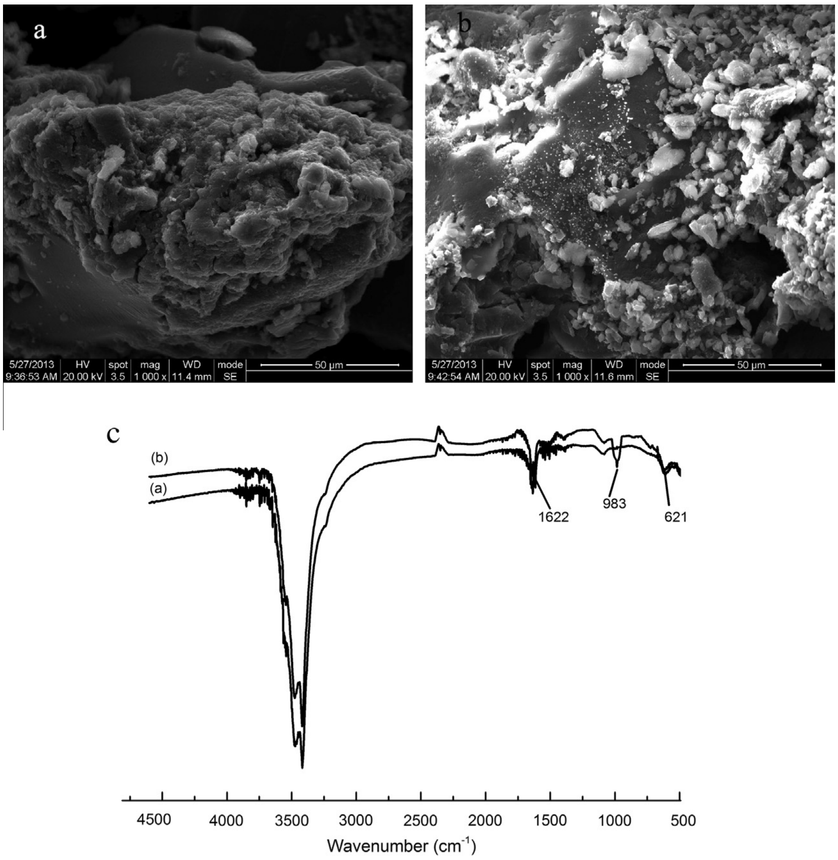


Fig. 1. Characterization: (a) SEM of resin D152; (b) SEM of catalyst W/D152 and (c) FTIR of resin D152 (a) and catalyst W/D152 (b).

contents of 3.52 ppm. While the catalyst weight was increased from 0.3 to 0.4 g, the conversion of DBT did not change appreciably because most DBT was oxidized. The yield rate changed little at the various catalyst weights evaluated (Fig. 2d). Therefore, the catalyst weight of 0.3 g was preferable. Similar data was also observed in removal of thiophene by TiO_2/Ni-ZSM-5 [16].

3.3. Comparison experiments and catalyst reuse

Comparison experiments were carried out when the catalyst was absent in the system. DBT was oxidized by CYHPO at 100 °C for 40 min without the catalyst. The results show that only 86.5% DBT removal was achieved, and the corresponding residue sulfur concentration was 54.2 ppm. However, the conversion was 45.3%, and the corresponding residue sulfur concentration was 218.8 ppm for the reaction system without CYHPO. Therefore, CYHPO played an important role though the residue sulfur was more than 10 ppm. When the catalyst was added, the conversion of DBT was increased to 99.1%, and the corresponding sulfur content decreased to 3.52 ppm. Compared with the reaction without the catalyst, the conversion of DBT with the catalyst was increased by 12.6%, and the sulfur content was decreased by 50.68 ppm, which indicate that it is the catalyst which result in the sulfur content of lower than 10 ppm. The SEM images and FTIR spectrums have revealed that tungsten was successfully immobilized on resin D152, which helps explain the high sulfur removal efficiency of the catalyst (Fig. 1). These results demonstrate that catalyst W/D152 contributed to the ODS reaction significantly. Similar results were reported in literatures in which high removal rate of DBT is resulted from the catalytic activity of other catalysts containing tungsten [10,11,15].

Performance of regenerated catalyst is important for industrial applications. The catalytic oxidation ability of catalyst W/D152 decreased from 99.1% to 97.5% after the catalyst was regenerated seven times possible due to the unstability of the catalyst. The data of the regenerated catalyst indicates that the catalyst performed well after regeneration.

3.4. Mechanisms and kinetics for catalytic oxidation

The products of the oxidation were analyzed by GC-MS, and sulfones and cyclohexanone were detected. Lü et al. [28] and Abdalla et al. [9] reported similar intermediate products. A possible pathway for the catalytic oxidative desulfurization of DBT by the W/D152-CYHPO system was proposed (Scheme 1). First, DBT reacted with CYHPO, and sulfones as well as cyclohexanone were produced [18]. Then, the products were extracted from the model gasoline with deionized water and N,N-Dimethylformamide.

The role of tungstate in the catalyst was to activate CYHPO molecule, so DBT could be rapidly oxidized to sulfones at the presence of catalyst W/D152. Yang et al. [29] explain the reaction mechanisms from the atomic orbitals for adsorption desulfurization, and suggest that sorbents binds thiophenic compounds selectively by π complexation.

Reaction kinetics was also examined to better understand the catalytic oxidation of DBT. The kinetic profiles of the oxidation reaction of catalyst W/D152 are presented in Fig. 3, which shows that this catalyst exhibits remarkably higher activity in the conversion of DBT. The constant rate for the apparent consumption of DBT was gained from the first-order kinetic model (Eq. (3)) as follows:

$$-\frac{dc}{dt} = kc \tag{3}$$

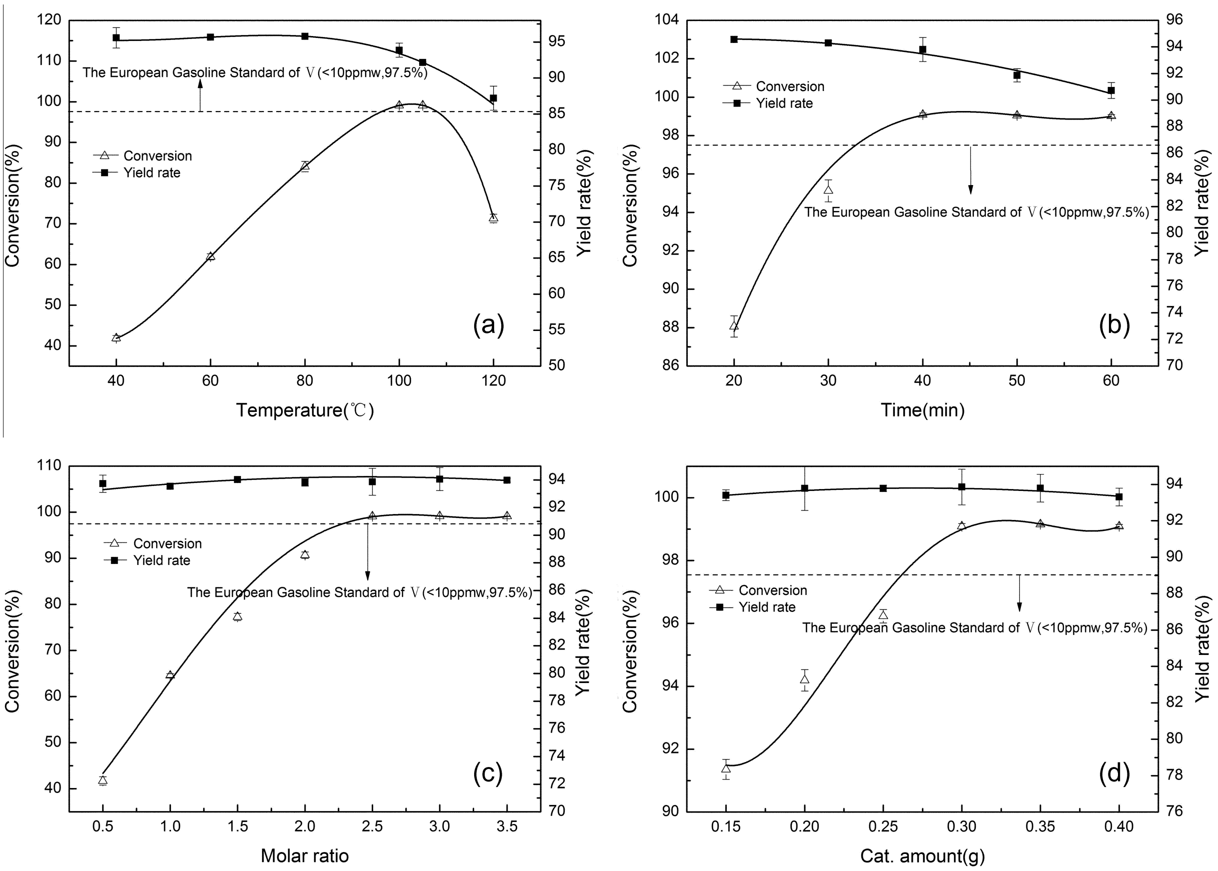
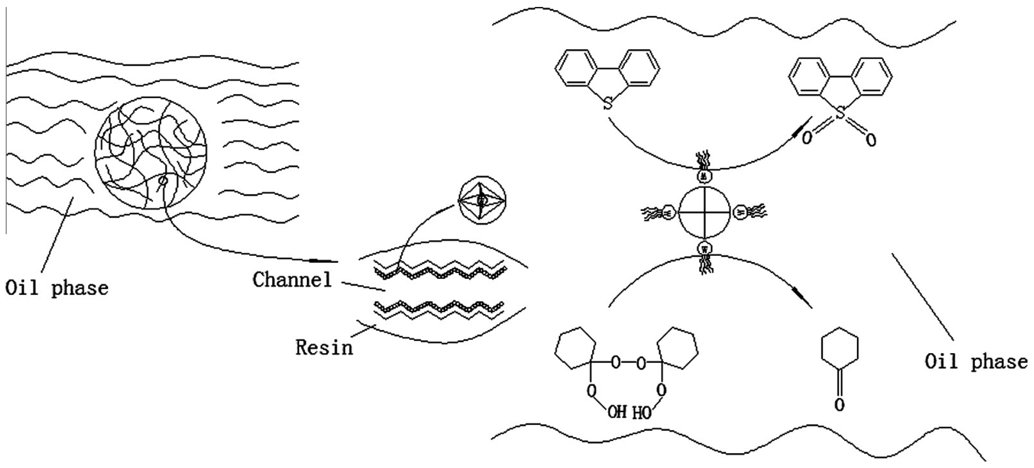


Fig. 2. Influence of reaction conditions: (a) effect of reaction temperature on the conversion of DBT. Conditions: $M_{catalyst}$ = 0.3 g, CYHPO/DBT = 2.5, $M_{model\ gasoline}$ = 30 g, t = 40 min; (b): effect of the reaction time on the conversion of DBT. Conditions: $M_{catalyst}$ = 0.3 g, CYHPO/DBT = 2.5, $M_{model\ gasoline}$ = 30 g, T = 100 °C; (c) influence of the molar ratio of CYHPO/DBT on the conversion of DBT. Conditions: $M_{catalyst}$ = 0.3 g, $M_{model\ gasoline}$ = 30 g, t = 40 min, T = 100 °C and (d) effect of catalyst W/D152 amount on the conversion of DBT. Conditions: CYHPO/DBT = 2.5, $M_{model\ gasoline}$ = 30 g, t = 40 min, T = 100 °C.



Scheme 1. Schematic representation for catalytic oxidation desulfurization system of removal DBT.

Integral on both sides of Eq. (3):

$$-\int_{C_0}^{C_t}\frac{dc}{c}=\ln\frac{C_t}{C_0}=kt \tag{4}$$

$$C_t=C_0e^{-kt} \tag{5}$$

The plot of $\ln(C_0/C_t)$ against t, a straight line with slope k was gained (Fig. 3). Eq. (6) was derived from Eq. (4) by replacing C_t with $C_0/2$:

$$t_{1/2}=\frac{\ln 2}{k}=\frac{0.693}{0.1091}=6.35 \tag{6}$$

The rate constant k of DBT was 0.109 min^{-1}, and the half-life was 6.35 min. The conversion of DBT at reaction time of 40 min was 45.3% for the system without the catalyst, which was equivalent to that at reaction time of 6 min for the system with the catalyst. The particle size of the catalyst was 0.315–1.25 mm, the conversion of DBT changed not significantly in the first seven times of the test, and the mass ratio of model gasoline to catalyst was

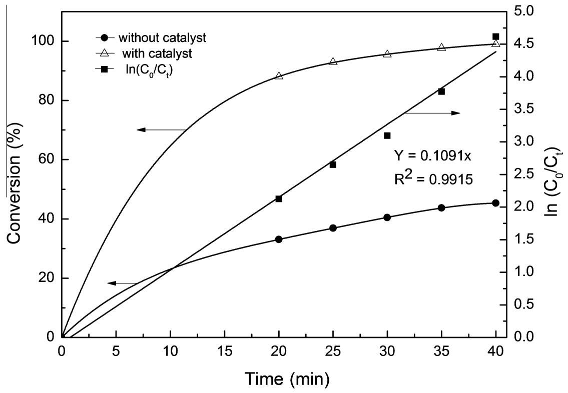


Fig. 3. Dynamics fitting curve of the DBT.

100/1. Therefore, the effect of diffusion and adsorption on kinetic was not taken into account in this paper. Zhou et al [18] and Zhu et al [30] did not take the effects of diffusion and adsorption into consideration as well. Eqs. (3)–(6) indicated that the reaction kinetics for catalytic oxidation of DBT fitted the first-order kinetic model pretty well. Dhir et al [19] applied the Langmuir–Hinshelwood and Eley–Rideal mechanisms to model the kinetics of oxidative desulfurization with tungsten-containing catalyst. Zhu et al. [30] reported that the reaction kinetics of oxidative DBT with ionic liquids follows the first-order kinetic rate.

4. Conclusions

The characterization and performances of catalyst W/D152 show that tungsten have been successfully immobilized on resin D152.

The conversion of DBT increased from 48.2% to 99.1% with increased reaction temperature from 40 to 100 °C, and decreased when temperature exceeded 105 °C. The conversion of DBT increased with reaction time when below 40 min, and stabilized when more than 40 min. In addition, the conversion of DBT increased when the molar ratio of CYHPO/DBT was less than 2.5 and the weight of catalyst W/D152 was 0.3 g for 30 g of model gasoline.

Sulfur content in the model gasoline could be reduced from 400 to 3.52 ppm with 99.1% conversion of DBT at the following optimal reaction conditions: temperature of 100 °C, mass ratio of model gasoline/catalyst of 100, and molar ratio of CYHPO/DBT of 2.5 within 40 min. The catalyst could be reused for 7 times before the total sulfur content of treated model gasoline was higher than 10 ppm.

A possible pathway for the catalytic oxidative desulfurization of DBT by the W/D152-CYHPO system was proposed, and the kinetics follows the first-order equation.

The W/D152-CYHPO reaction system which shows high catalytic oxidative activity could overcome the disadvantages of existing technologies and possesses potential for industrial applications.

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