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# Catalytic oxidative desulfurization of BT and DBT from *n*-octane using cyclohexanone peroxide and catalyst of molybdenum supported on 4A molecular sieve

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ABSTRACT

In this paper, the performance of catalytic oxidative desulfurization (ODS) was studied using catalyst $MoO_3$/4A which was prepared by depositing molybdenum on 4A molecular sieve, a microporous material. Dibenzothiophene (DBT) and benzothiophene (BT) were selected as the target compounds, and oil-soluble cyclohexanone peroxide (CYHPO) as an oxidant. The effects of relevant parameters on ODS including molybdenum loading, reaction temperature, reaction time, the molar ratio of CYHPO/DBT and the weight of catalyst $MoO_3$/4A were investigated, and the oxidation mechanisms as well as the kinetics were also examined individually. The catalytic oxidative removal of DBT and the residual sulfur content reached 99.0% and 5 ppmw, respectively, at an optimal catalytic condition of Mo loading of 6 wt.%, molar ratio of CYHPO/DBT of 2.5 and volume mass ratio of model gasoline to catalyst $MoO_3$/4A of 100 at 373 K over 30 min. The optimal design of experiments using Box–Behnken method was employed to evaluate the effects of individual process variables such as, reaction temperature, reaction time and molar ratio of CYHPO/DBT and their optimum values were found to be 340 K, 38 min and 3.8, respectively, to achieve a conversion of 100%. The catalyst could be reused for 4 times before the total DBT content of treated model gasoline was higher than 10 ppmw, and the activity of the desulfurization system was above 95% after regenerating for 9 times. The catalytic oxidation of DBT and BT fitted the pseudo-first order kinetic model pretty well. The catalyst $MoO_3$/4A was characterized by the scanning electron microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR) and X-ray photoelectron spectrum (XPS), and the data showed that a thin layer of active components was covered on the catalyst surface which helped to explain the satisfactory catalytic performance.

## 1. Introduction

Sulfur in transportation fuels is a major source of air pollution. Ultra-low sulfur fuel is of great demand in today's world and most of the countries impose a strict regulation in lowering the sulfur content in petroleum oils. According to the United States guidelines the sulfur level in diesel fuel should not be more than 15 ppmw since 2006 [1,2]. Additionally, the environmental regulations have limited the level of sulfur in diesel less than 10 ppmw since 2005 in Europe, and less than 50 ppmw since 2008 in China [2].

Trace amounts of organic sulfur existed in liquid fuels, especially diesel and gasoline, are sufficient to fairly poison the environment, engine of vehicles and catalytic converter. Thus, clean fuel with low sulfur content is important not only for reducing vehicle emissions, but also for prolonging the life span of the exhausting gas treatment system [3].

Sulfur-containing compounds in petroleum consist of disulfides, mercaptans, polysulfides, thiophene, BT, DBT, 4,6-dimethyldibenzothiophene and their alkylated derivatives. The sulfur removal technologies include hydrodesulfurization (HDS) and others. HDS as a conventional approach is facing a great challenge in confronting new stringent legislations and regulations. Severe operating conditions with high temperatures, high pressures, and high hydrogen consumption are required for HDS to

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achieve ultra-deep desulfurization of diesel with *S* concentration <10 ppmw [2]. Among other technologies such as ODS, adsorption desulfurization, extractive desulfurization, biodesulfurization and alkylation desulfurization, ODS has attracted much attention owing to its advantages of no consumption of $H_2$ and mild operating conditions. At the same time, ODS is an alternative or complementary technology to HDS [4,5], and is one of the most important and effective method for ultra-deep desulfurization in petroleum refining. During ODS procedure, sulfur compounds are oxidized into their corresponding sulfones, which can be removed by extraction with polar solvent easily [6,7].

The catalysts which primarily consist of precious metals such as nickel, iridium, tungsten, palladium, platinum, rhodium, and molybdenum play a vital role in ODS. Moreover, molybdenum has obtained considerable attention in catalysis due to its unique physicalchemical properties [4,5,8,9]. Meanwhile, molybdenum-containing catalyst is extremely reactive, and is highly effective for desulfurization of DBT [5,9].

Nevertheless, molybdenum-containing catalysts cannot be applied directly to the catalytic oxidative reactions on account of their difficulty to be separated from the organic phase. Supports play a crucial part in determining the number and the nature of active sites, and consequently affect the catalytic activity of catalyst. Xun et al. [10] have studied the metal-based ionic liquid embedded on silica gel, which had a high catalytic performance in desulfurization. Zhou et al. [9] reported that resin-supported molybdenum showed a high catalytic activity in the oxidation of DBT. Recently, molecular sieve as a support has received more interests as a result of its inherent characteristics and environmental friendliness [11,12]. In consideration of the fact that the surface area and particle size of 4A molecular sieve is 600–800 $m^2/g$ and 3.0–5.0 mm respectively, it could provide enough support surface area. Besides, 4A molecular sieve has several advantages such as its economy and non-toxicity (which proved to be highly efficient in soil amelioration).

In most ODS systems, $H_2O_2$ is utilized as the oxidant which is immiscible with the *n*-octane, so the intersolubility of $H_2O_2$ and DBT is not satisfactory [13–15]. Cyclohexanone peroxide (CYHPO) as an oil-soluble oxidant was selected because of its complete contact with DBT and good oxidative performance [15].

To enhance the existing ODS procedure, molybdenum was selected as catalyst, 4A molecular sieve as the support, and CYHPO as the oxidant in this work. The effects of catalyst loading, temperature, reaction time, molar ratio of CYHPO/DBT and the weight of catalyst on DBT removal were investigated, and the catalytic mechanisms and kinetics were also examined. A Box–Behnken design was applied to determine the optimum DBT conversion, and also to explain the relations between DBT removal and three pertinent parameters namely, reaction temperature, reaction time and molar ratio of CYHPO/DBT.

## 2. Experimental

### 2.1. Materials

All the chemicals were of analytical grade and used as received. DBT (>98%) was the product of Beijing Bailingwei Technology Co. Ltd. (China); BT (>98%) was the product of Beijing Bailingwei Technology Co. Ltd (China); *n*-octane was purchased from Tianjin Kemiou Chemical Reagent Co. Ltd. (China); 4A molecular sieve was obtained from Tianjin Kemiou Chemical Reagent Co. Ltd. (China) whose properties were shown in Table 1; Ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$) was purchased from Sinopharm Chemical Reagent Co. Ltd. (China); CYHPO was purchased from Aladdin Reagent Co. Ltd. (China); DMAC was purchased from Tianjin Fuyu Fine Chemistry Co. Ltd. (China).

**Table 1**
Properties of 4A molecular sieve.

| Property | Data |
|---|---|
| Particle size (mm) | 3.0–5.0 |
| Bulk density (g $mL^{-1}$) | ⩾0.6 |
| Surface area ($m^2/g$) | 600–800 |
| Average pore diameter (nm) | 0.4 |
| Static water adsorption (wt.%) | ⩾20.5 |

### 2.2. Catalyst preparation and characterization

The catalysts with Mo loading ranging from 2 to 8 wt.% were prepared via the incipient wetness impregnation [16]. According to the weight percent requirement of $MoO_3$, 10 g of ammonium heptamolybdate was dissolved in 50 mL of distilled water to prepare an aqueous solution of ammonium heptamolybdate with a mass volume concentration of 20 wt.% at 305 K. Three steps were included in the preparation procedure. Firstly, 5 g of 4A molecular sieve was washed with deionized water for several times and then dried at 373 K. Then, the molecular sieve mentioned above was macerated with 250 mL deionized water at pH 3.0 in continuous stirring with the stirring speed of 200 rpm overnight. Water was filtered, and the molecular sieve was dried at 373 K in an oven and then calcined at 773 K for 5 h under air. At last, the molecular sieve was added to aqueous solution of ammonium heptamolybdate at the temperature of 305 K. The mass volume ratio of molecular sieve to aqueous solution of ammonium heptamolybdate was 1:10. After 24 h, the catalyst was filtered, dried in a vacuum rotary evaporator and then calcined at 773 K to reach a constant weight. The catalyst was then sieved through 100 mesh screen. The catalyst was denoted as catalyst $MoO_3$/4A in this study.

Scanning electron microscope (SEM) images were obtained on a JEOL JSM-6700. The Fourier Transform Infrared Spectroscopy (FTIR) of the catalyst, diluted with KBr and pressed into a pellet, was recorded 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. The X-ray photoelectron spectrum (XPS) measurements were performed using an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher, USA).

### 2.3. Procedures for catalytic oxidation of DBT

DBT or BT was dissolved in *n*-octane to prepare a model solution of about 500 ppmw sulfur. Experiments of catalytic oxidation were carried out in an Erlenmeyer flask (100 mL) at an atmospheric pressure. The reactor was placed in an oil bath at different constant temperature (313–393 K), and stirred magnetically. The typical catalytic oxidation process was as follows: 20 mL of model gasoline was added into the reactor, then 0.2 g of catalyst $MoO_3$/4A and a certain amount of CYHPO (molar ratio of CYHPO/DBT of 2.5) were also added respectively. After 30 min of reaction, the resulting mixture was cooled down to ambient temperature and then centrifuged for catalyst separation at a speed of 10,000 rpm. Subsequently, the oxidized product was extracted from the resulted mixture where the catalyst was absent with 10 ml of N, N-Dimethylacetamide for 10 min and held for 15 min, and this procedure was repeated two times to make sure that sulfur compounds were completely removed. Thus the refined gasoline was obtained. This experimental procedure was comprised of oxidation and separation, which was modified from the procedures established by Long et al. [3] and Abdalla et al. [17]. N,N-Dimethylacetamide could be reused after being regenerated. All experiments were repeated in triple to ensure the reproducibility of results.