

SYNTHESIS AND CHARACTERIZATION OF Co-Mo/ γ -Al₂O₃ NEW CATALYST FOR OXIDATIVE DESULFURIZATION (ODS) OF MODEL DIESEL FUEL

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Abstract

A series of γ -alumina-supported cobalt–molybdenum mesoporous catalysts have been provided with various ratios of Co/Mo (0.0, 0.1, 0.3 and 0.5). Cobalt and molybdenum were loaded on a support via an incipient wetness impregnation method. Samples of the catalysts were characterized using XRD, BET and BJH. Then Oxidative desulfurization (ODS) of Benzothiophene (BT) and Dibenzothiophene (DBT) with H₂O₂ as oxidant was studied. The catalyst with Co/Mo mole ratio 0.1 and Cat/oil ratio 0.03 (g/mL) showed high performance to oxidation of BT and DBT, which has led to about 19% conversion increase for BT and 17% of DBT comparing catalysts without cobalt (Co/Mo 0.0). The various sulfur compounds reactivity was studied which followed the order of DBT >>BT.

Keywords: Oxidative Desulfurization; Co-Mo/ γ -Al₂O₃ catalysts; Co/Mo mole ratio; Benzothiophene (BT); Dibenzothiophene (DBT).

1. Introduction

It is well known that sulfur elimination from petroleum derivatives is essential for both environmental and industrial reasons. In processing the petroleum products sulfur present poisons the catalysts in refinery and corrodes parts of internal combustion engines by forming acidic product [1].

Legislative regulation trends have been increased strictly on sulfur content in fuels in most countries for past two decades. As an example, the U.S. EPA has reduced the sulfur content of most diesel fuels to 15 ppm in 2006. In Europe, sulfur content reductions to 10 ppm by 2009, and in Japan imposed a decrease to 15 ppm [2].

Sulfur in most diesel fuel is present in organic form as BT, DBT and alkylated derivatives. The traditional process of reducing sulfur in petroleum is hydrodesulfurization (HDS), which is carried out under high hydrogen pressure and temperature over a suitable catalyst. Consequently, it is difficult or very costly to use the existing HDS technology to meet the need of new sulfur content regulation, it is necessary to develop new approaches to ultra-deep desulfurization of liquid fuel.

One of the promising approaches, which has a noticeable advantage over HDS is oxidative desulfurization (ODS), which is the removal refractory sulfur component such as DBT and its alkylated derivatives under mild condition and without hydrogen. This process is used as a complementary to HDS process for deep desulfurization of diesel fuel.

In previous studies various oxidant have been used in ODS process such as Oxygen [3], *tert*-butyl hydroperoxide [4-5], cyclohexanone peroxide [6], hydrogen peroxide [7-10], ozone [11]. However, the most widely used oxidant is hydrogen peroxide due to the superior selectivity, low cost and safety.

To reach the oxidation activity of the oxidant, several homogenous and heterogeneous catalysts including organic acids [12-13], polyoxometalates [14-15], methyltrioxorhenium [16], or various supported catalysts, i.e. MoO₃, CrO₃ and WO₃ supported on alumina [17] are used in different ODS systems.

Abdalla *et al.* [18] used $(\text{Bu}_4\text{N})_4\text{H}_3(\text{PW}_{11}\text{O}_{39})$ supported on MCM-41 as catalyst and H_2O_2 as oxidant for elimination of sulfur from FCC cycle oil, the sulfur removal of 97.2% was achieved.

Farhan *et al.* [19] used Na_2WO_4 and H_2O_2 as oxidant to treat commercial diesel, sulfur content is reduced from 1100 to 40 ppmw. Sujit Mondal *et al.* [7] managed to desulfurize diesel fuel containing 345 ppmw to 75% in 3 hours using Fe-TAML as catalyst and H_2O_2 as oxidant.

Trakarnpruk *et al.* [14] used polyoxometalate including $\text{Na}_2\text{HPM}_{12}\text{O}_{40}$, $\text{H}_3\text{PM}_{12}\text{O}_{40}$ and $\text{Na}_2\text{HPM}_{12}\text{O}_{40}$ (M=Mo, W) as catalyst and H_2O_2 /Acetic acid as oxidant for desulfurization of model diesel, they reported in mild condition, sulfur elimination is reached to 98%. The trend of the ODS reactivity in this system is as follow: 4, 6-DMDBT >DBT>BT. The sulfur containing compounds in fuel oil can be oxidized into sulfones and sulfoxides by hydrogen peroxide over active carbon [13]. Chica *et al.* [20] used tert-butyl hydroperoxide as oxidant and $\text{Mo}_x/\text{Al}_2\text{O}_3$ as catalyst in fixed bed reactor.

Hongying Lu *et al.* [8] reported an oxidation of many kinds of sulfur compounds in synthetic diesel over $[\text{C}_{18}\text{H}_{37}\text{N}(\text{CH}_3)_3]_4\text{-}[\text{H}_2\text{NaPW}_{10}\text{O}_{36}]$ based catalyst with H_2O_2 as oxidant, The sulfur level of diesel fuel can be reduced from about 500 to less than 0.1 ppmw under mild condition.

According to previous studies, using of heterogeneous catalyst has high performance efficiency then homogenous catalyst.

The present work describes the preparation and characterization of the new mesoporous Co-Mo/ $\gamma\text{-Al}_2\text{O}_3$ catalyst and its application in ODS of BT and DBT as the model sulfur compounds of diesel fuel with H_2O_2 as the oxidant. Also effect of adding of cobalt to molybdenum on catalyst characterization and performance and Cat/Oil ratio has been investigated.

2. Experimental

2.1 Materials

All the materials were used without further treatment. A $\gamma\text{-Al}_2\text{O}_3$ with a surface area of 120-190 m^2/g , Ammonium hepta molybdate tetra hydrate $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$, cobalt (II) nitrate hexahydrate $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$, Benzothiophene (BT), Dibenzothiophene (DBT), n-octane (was used as model fuel) and Hydrogen peroxide (30%w aqueous solution) were supplied by Merck company.

2.2 Catalyst preparation

Series of cobalt-molybdate catalysts were prepared by co-impregnation of $\gamma\text{-Al}_2\text{O}_3$ with solutions containing appropriate amounts of cobalt nitrate and ammonium hepta molybdate. Appropriate amount of salts in a specific volume of distilled water were dissolved and then added to support slowly. A series of catalysts was prepared in which the mass ratio of (Co+Mo)/support was kept constant at 0.18 with different Co/Mo mole ratios of 0.0, 0.1, 0.3, and 0.5.

The mixture was dried in a dryer at 120°C for 12 h then calcined at 500°C in air for 8 h.

2.3 Catalyst characterization

The synthesized catalysts was characterized by X-ray diffraction (XRD) patterns, which were recorded on a BRUKER D8 ADVANCE diffractometer using Cu K α radiation (1.5406 Å, 40 kV, 30 mA). The used scan speed and step size were 1 sec/step and 0.02°, respectively. The step scan technique is in 2 θ range of 4 to 85°.

The specific surface area and pore volume was measured according to the Brunauer, Emmett and Teller (BET) method by means of BELSorp, Japan, Inc. The Barrett, Joyner and Halenda (BJH) method was used to determine pore size distribution.

2.4 Oxidative desulfurization (ODS)

The equimolar Benzothiophene (BT) and Dibenzothiophene (DBT) were dissolved in n-octane to act as the model fuel, in which the concentration of the substrates was 650 ppmw of sulfur.

The catalytic experiments were carried out in a 100 ml glass batch reactor equipped with a condenser, mechanical stirrer and water bath for temperature control at atmospheric pressure.

In a typical run, 1.5 g catalyst and 50ml model fuel (catalyst/oil=0.03g/mL) were stirred vigorously and then a certain amount of Oxidant, H_2O_2 (molar ratio of $\text{H}_2\text{O}_2/\text{S}=3$) were added to the reactor. The reaction was carried out at 313 K for 1 hour.

Achieved oil phase samples are analyzed by a 3420A gas chromatograph. A flame ionization detector (GC-FID) is used in this process. For separation, A DB-5 capillary column having 32 m length and 0.25 mm inner diameter was used.

Conversion rate of sulfur components were calculated as follow:

$$Y = (1 - C_f / C_0) \times 100 \%$$

where C_0 is the initial concentration of sulfur components in the n-octane solution; C_f is the final sulfur components concentration of the oil phase after desired reaction time.

3. Results and Discussion

3. 1 Catalyst characterization

The XRD patterns of γ - Al_2O_3 and catalyst samples with different Co/Mo mole ratio (0.0, 0.1, 0.3 and 0.5) are shown in Fig.1.

All peaks related to molybdenum oxide are observable in $2\theta = 23.4^\circ$, 27.3° and 49.3° , which indicate orthorhombic molybdenum oxide crystals. Also, peak related to cobalt- molybdenum oxide is observable in $2\theta = 26.4^\circ$, which indicates monoclinic cobalt- molybdenum oxide crystal. As we can see, when cobalt to molybdenum ratio increases, peak heights related to molybdenum oxide decreases while, cobalt- molybdenum oxide peak height increases which indicates added cobalt participation in cobalt cobalt-molybdenum crystal. In addition, no cobalt oxide crystals were observed, that is similar to Ali *et al.* works [21].

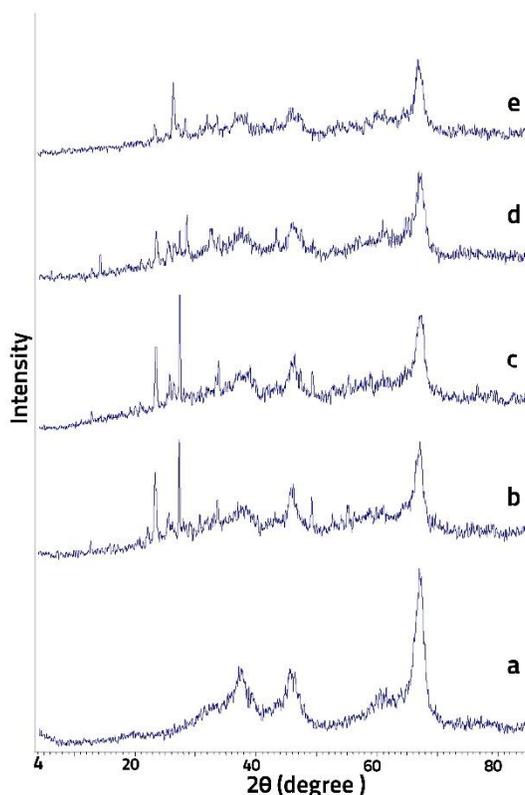


Fig.1 XRD patterns of γ - Al_2O_3 (a), CoMo/ γ - Al_2O_3 catalysts, Co/Mo: 0.0 (b), Co/Mo: 0.1 (c), Co/Mo: 0.3 (d) and Co/Mo: 0.5 (e)

For catalyst with Co/Mo=0.1, BET analysis was done to determine pore volume and surface area. BET results show that the pore volume and surface area of catalyst are $0.17\text{cm}^3/\text{g}$ and $90\text{m}^2/\text{g}$.

Results were shown in Fig.2 which indicate a uniform mesoporous structure with an average pore diameter of 8.6 nm (peak pore diameter=5.48nm).

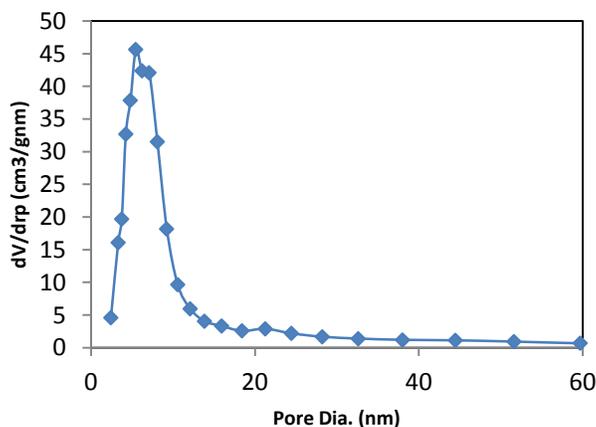


Fig. 2 Pore size distribution Co-Mo/ γ -Al₂O₃ (Co/Mo mole ratio 0.1)

3.2 Effect of Co/Mo mole ratio on ODS

For optimizing of mesoporous catalyst for desulfurization of sulfur component with ODS process using H₂O₂ as oxidant, Co/Mo ratio effect is shown in figure 3. In this case, catalysts are provided in various Co/Mo molar ratios, 0, 0.1, 0.3, 0.5 and are used in ODS process with below followed conditions. Initial value of sulfur is 650 ppmw in model fuel, 40°C temperature, oxidant/sulfur molar ratio considered as 3 and reaction time is one hour. As it is specified in fig. 3, by adding cobalt to molybdenum, conversion amount increases. However, adding to much cobalt will decrease this conversion amount. Therefore, catalyst with Co/Mo ratio 0.1 is select as optimum catalyst.

Adding cobalt to molybdenum (Co/Mo 0.1) has increased the conversion value for BT from 11 to 30 % and DBT from 73 to 90 approximately comparing to catalyst without cobalt (Co/Mo 0.0).

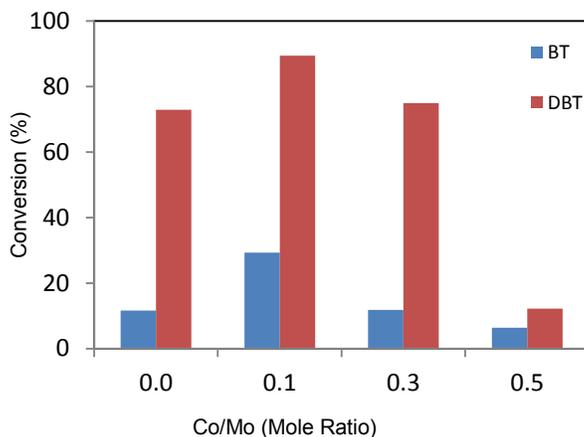


Fig 3: Effect of Co/Mo ratio on BT and DBT removal

3.3 Effect of catalyst/oil ratio (g/mL) on ODS

In order to reach the optimize catalyst amount to get maximum conversion by using minimum quantity of catalyst, figure 4 illustrates the effect of catalyst ratio on the oil. As it is observed, by adding catalyst, the amount of removal of DBT increases and reaches the maximum quantity in 0.03 g/ml ratio. Increasing the active sites of Mo and Co oxide due to enhancement of DBT oxidation by increasing the catalyst amount up to 0.03 g/mL

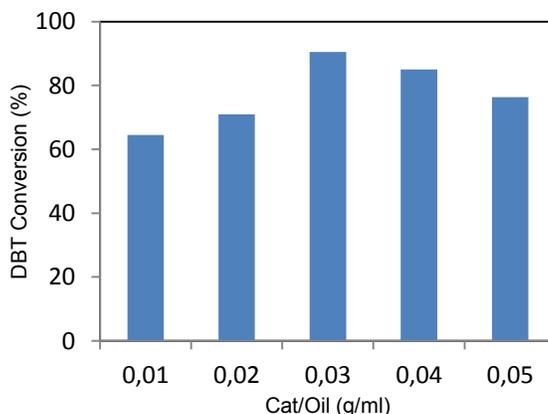


Fig. 4 Effect of cat/oil (g/ml) ratio on DBT oxidation in temp. 40°C, oxidant/S=3, sulfur initial value=500 ppmw

However, oxidation of DBT decreases by adding further amount of the catalyst containing a hydrophilic surface. This is possibly due to the hydroxyl groups present in catalyst acting as physical adsorbent of H_2O_2 thus reducing the formation of molybdenum or cobalt peroxide species [22]. A proper selection of catalyst amount which has a good dispersion of catalyst particles in reaction media without any deposition or agglomeration was an important point. This condition was observed in catalyst concentration of 0.03 (g/mL).

3.4 Catalyst stability

After three times using of catalyst for ODS without any washing, only around 10% decreasing in DBT conversion is observed. The reason for this is reaction product and impurities accumulation on the catalyst surface and reduction of catalyst active surface.

4. Conclusion

In this study, an oxidative desulfurization (ODS) for model diesel fuel has been achieved over the Co-Mo/ γ - Al_2O_3 catalyst and H_2O_2 as oxidant.

The mesoporous Co-Mo/ γ - Al_2O_3 catalyst with Co/Mo ration 0.1 and Cat/Oil 0.03 (g/mL) is highly efficient for oxidation of BT and DBT which are present in model diesel fuel as refractory sulfur compounds in conventional HDS process. Using the catalyst with Co/Mo ratio 0.1 increased the conversion of BT by 19 % and DBT by 17 % in compare with catalyst without cobalt. Also the synthesized catalyst has good stability after three times using without any washing.

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