Preparation and Characterization of MoO_3/Al_2O_3 Catalyst for Oxidative Desulfurization of Diesel using H_2O_2: Effect of Drying Method and Mo Loading

Azam Akbari, Mohammadreza Omidkhah, Jafar Toufighi Darian

Abstract—The mesoporous $MoO_3/\gamma-Al_2O_3$ catalyst was prepared by incipient wetness impregnation method aiming to investigate the effect of drying method and molybdenum content on the catalyst property and performance towards the oxidation of benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyle dibenzothiophene (4,6-DMDBT) with H_2O_2 for deep oxidative desulfurization of diesel fuel. The catalyst was characterized by XRD, BET, BJH and SEM method. The catalyst with 10wt.% and 15wt.% Mo content represent same optimum performance for DBT and 4,6-DMDBT removal, but a catalyst with 10wt.% Mo has higher efficiency than 15wt.% Mo for BT conversion. The SEM images show that use of rotary evaporator in drying step reaches a more homogenous impregnation. The oxidation reactivity of different sulfur compounds was studied which followed the order of DBT>4,6-DMDBT>>BT.

Keywords—desulfurization, oxidation, MoO_3/Al_2O_3 catalyst

I. INTRODUCTION

THE new environmental legislations increase the demand for ultra low sulfur diesel fuel with less than 10 ppmw sulfur [1]. Different organosulfur compounds present in diesel fuel contribute to the air pollution and acid rain as well as the failure of pollution control devices. Most organosulsur compounds in diesel fuel are BT, DBT and its alkylated derivatives. The conventional hydrodesulfurization process (HDS) has operation problems with DBT and its alkylated derivatives due to the steric hindrance of these compounds on the catalyst surface [2]. Therefore, complete elimination of these compounds by HDS requires severe operating conditions as high H_2 pressure and temperature as well as larger reactors and high active catalysts making it a costly process. From the economical point of view, catalytic oxidative desulfurization (ODS) is a most promising alternative or complementary process after HDS to obtain the ultra low sulfur fuel. This process can potentially be used after HDS particularly for deep desulfurization of diesel fuel. In this process using an oxidizing agent and catalyst the organosulfur compounds are oxidized to their corresponding polar sulfones which are easily removed by extraction. The main advantage of ODS is the removal of refractory organosulfur compounds such as DBT and its derivatives under atmospheric pressure and mild temperature without the use of expensive hydrogen.

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Various oxidant agents such as hydrogen peroxide [3,4], oxygen [5], tert-butyl hydroperoxide (t-BuOOH) [6,7] have been used in the previous studies. However hydrogen peroxide is reported as more promising oxidant due to the high selectivity, safety, environmental friendliness and process economics. To enhance the oxidation activity of the oxidizing reagent, several homogenous and heterogeneous catalysts including organic acids [3,4,8], polyoxometalates [2,9], Ti-containing zeolites [10], mesoporous molecular sieves [10-13] or metal oxide supported on alumina or silica [14-18] are evaluated in different ODS systems. It is seem that the separation and recycling of the homogenous catalysts can be difficult [18]. Therefore use of advanced solid catalysts in a fine operating condition is desirable. In this context, good reported results for high performance of molybdenum oxides supported catalysts can be found in the literature. Wang et al. [6] reported high performance efficiency of $MoO_3/\gamma-Al_2O_3$ compared to various metal oxides supported on alumina, MoO_3 supported on titania and silica alumina, which were examined for oxidation of DBT in kerosene (with sulfur content of 55 ppm). Ishihara et al. [7] used 16%w $MoO_3/\gamma-Al_2O_3$ to treat light gas oil containing 39 ppm sulfur. Both studies evaluated the catalyst in ODS of the low sulfur fuels with t-BuOOH as oxidant. Prasad et al. [14] reported that Bi-Mo/silica-alumina exhibited the best catalytic activity for ODS of 4,6-DMDBT as well as light cycle oil using t-BuOOH. G-Gutierrez et al. [17, 18] presented ODS of model sulfur compounds and diesel fuel using satable polymolybdate supported on alumina and H_2O_2 as oxidant with a large amount of acetonitrile as the extraction solvent. They reduced sulfur content from 320 ppmw to less than 10 ppmw at 75 min. Jia et al. [19] explored an efficient ODS process with $MoO_3/\gamma-Al_2O_3$ and H_2O_2 in a solvent free system for low sulfur fuels (with sulfur content of 50 to 150 ppmw). However, literature confirms that there is insufficient investigation about the efficient ODS of diesel fuel with higher sulfur contents without any solvent.

The present work describes the preparation and characterization of the mesoporous $MoO_3/\gamma-Al_2O_3$ catalyst and then its application in ODS of BT, DBT and 4,6-DMDBT as the model sulfur compounds of diesel fuel with H_2O_2 as the oxidant. The effect of molybdenum oxide content and drying as well as the reactivity of sulfur compounds are considered.

II. EXPERIMENTAL

A. Materials

All chemical agents were used without further treatment.

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The γ-Al$_2$O$_3$, ammonium hepta molybdate tetra hydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$.4H$_2$O), benzothiophene (BT), dibenzothiophene (DBT), hydrogen peroxide (30%w aqueous solution) were supplied by Merck company, Germany. 4,6-dimethyle dibenzothiophene (4,6-DMDBT, 97%) was supplied by Haohua Industry company Ltd., china.

B. Catalyst preparation

MoO$_3$/γ-Al$_2$O$_3$ catalyst was prepared by incipient wetness impregnation (IWI) method. According to required weight percent of MoO3, appropriate amount of ammonium hepta molybdate in a specific volume of distilled water was dissolved and then added slowly to the support at ambient temperature. The mixture was dried in a vacuumed rotary evaporator and then calcined at 500°C in air for 6 h.

C. Characterization techniques

The X-Ray diffraction (XRD) patterns of the synthesized catalyst was observed with a STOE/STADI MP diffractometer with Cu/kα radiation (1.5406 °A; 40 kv; 30 mA) and step scan technique in 2θ range of 5 to 85 °.

The specific surface area and pore volume was measured according to the BET method by means of Accelerated Surface Area and Porosity (ASAP 2010, Micromeritics). The Barrett, Joyner and Halenda (BJH) method was used to determine pore size distribution.

The surface morphology of the catalyst was observed using scanning electron microscopy (SEM) by Hitachi.

D. Oxidative desulfurization method

The catalytic experiments were carried out in a 100 ml glass batch reactor equipped with a condenser, magnetic stirrer and recirculation water bath for temperature control at atmospheric pressure. An equimolar solution of BT, DBT and 4,6-DMDBT in n-hexane was prepared as the model diesel fuel. In a typical run, the prepared solid catalyst was suspended slowly under vigorous stirring speed in a mixture containing model diesel (catalyst/oil=0.03 g/mL) and H2O2 in the reactor at a constant temperature. After a desired reaction time, the oil phase samples were withdrawn and analyzed by a 3420A gas chromatograph using a flame ionization detector (GC-FID). A DB-5 capillary column having 32 m length and 0.25 mm inner diameter was used for the separation.

III. RESULTS AND DISCUSSION

A. Catalyst characterization

The XRD patterns of catalyst samples with different molybdenum oxide content (0%, 5wt%, 10wt% and 20wt%) are shown in Fig. 1. The results reveal the absence of molybdenum oxide crystals in 5wt% and 10wt% molybdenum, suggesting the amorphous nature of MoO3 on the support. Increase of molybdenum content up to 20wt% leads to apparent the crystalline MoO3 with broad reflection centering at 2θ of 20-30°.

BET results indicate that the pore volume and surface area of MoO$_3$

(10wt.%)/Al$_2$O$_3$ catalyst are 0.20 cm^3/g and 110 m^2/g. Fig. 2 shows the pore size distribution of the sample measured according to BJH method. It can be seen that the catalyst shows a uniform mesoporous structure with an average pore diameter of 7.7 nm (Peak pore diameter=6.1 nm).
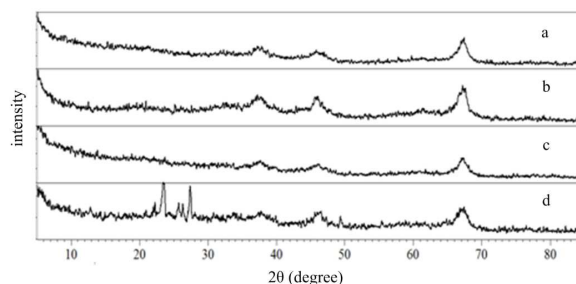

Fig. 1 XRD patterns of γ-Al$_2$O$_3$ (a) and MoO$_3$/γ-Al$_2$O$_3$ catalyst involved Mo content of 5wt.% (b), 10wt.% (c) and 20wt.% (d)
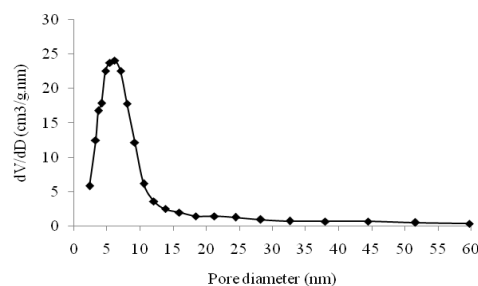
Fig. 2 Pore size distribution of MoO$_3$ (10wt.%)/γ-Al$_2$O$_3$ catalyst

B. Effect of drying method

During evaporation of the solvent form catalyst sample, redistribution of the active phase may be taken place. Fig. 3 shows the SEM images of two MoO$_3$ (10wt%)/γ-Al$_2$O$_3$ catalyst samples after calcination. Sample 1 was dried in an oven at 120°C for 12 h and sample 2 was dried in a vacuum rotary evaporator. It seems that use of rotary evaporator enhances the dispersion of active phase over the support bodies avoiding the agglomeration of impregnation solution. Therefore a more homogenous impregnation than the previous researches [6, 14, 17, 19] is available using rotary evaporator. Furthermore, this approach causes production of a catalyst with a uniform particle size distribution.
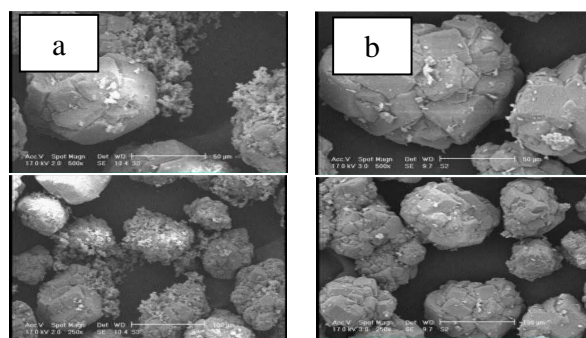

Fig. 3 Scanning electron micrographs of catalyst samples dried at 120 °C for 12h in an oven (a) and by rotary evaporator (b)

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C. Effect of molybdenum content

To find the optimum mesoporous catalyst for ODS with H_2O_2, the effect of Mo loading was evaluated which is shown in Fig. 4. To this purpose, the catalysts with 0%, 5wt%, 10wt%, 15wt% and 20wt% Mo content were prepared and evaluated in ODS reaction at a feed sulfur concentration of 575.0 ppmw, H_2O_2/sulfur ratio of 3.0 mol/mol and temperature of 35 °C, at 30 min reaction. Fig. 4 illustrates that the reaction is not carried out without Mo loading on the catalyst. Once Mo is dispersed, the conversion of sulfur compounds increases with increasing Mo content and then decreases. For DBT and 4,6-DMDBT, a catalyst with 10wt.% and 15wt.% yields a similar optimum conversions, but higher conversion of BT is related to the catalyst with 10wt.% Mo. Therefore, the catalyst with 10wt% Mo is selected as optimum. According to the previous investigations, a catalyst with 14-16% Mo loading presented highest activity for DBT oxidation using t-BuOOH or H_2O_2 [6, 19]. Probably, more polymerization of Mo spaces was produced by increasing Mo loading; leading to decrease of the catalyst activity especially in ODS of BT [19].
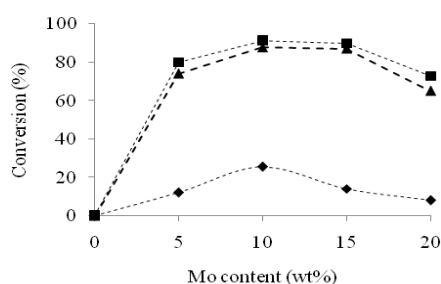

Fig. 4 influence of molybdenum content in the MoO_3/γ-Al_2O_3 on the catalyst performance to oxidize BT (♦), DBT (■) and 4,6-DMDBT (▲)

D. Reactivity of different model sulfur compounds

The experimental results represent 91.0%, 87.7% and 25.5% for DBT, 4,6-DMDBT and BT conversion, respectively, using the catalyst with 10wt% Mo content after 30 min reaction (Fig. 4). Therefore the oxidative reactivity of different compounds follows the order of DBT>4,6-DMDBT>>BT in our experimental oxidation domain using mesoporous MoO_3 (10wt.%)/γ-Al_2O_3 catalyst and H_2O_2 as oxidant reagent, after 30 min reaction. As a result, both the electron density and steric hindrance of the methyl groups affect the reactivity. Accordingly, the low electron density of BT leads to the lowest oxidation reactivity comparing to two other compounds. The electron density of DBT and 4,6-DMDBT are almost same (5.758 and 5.760 respectively), and here the steric hindrance has determined the reactivity. This trend is in agreement with Wang et al. [7] results obtained for the ODS system using MoO_3/γ-Al_2O_3 catalyst and t-BuOOH as oxidizing agent. However, the result is different from G-Gutierrez et al. [17].

The oxidation reaction of model sulfur compounds using mesoporous MoO_3/γ-Al_2O_3 catalyst and H_2O_2 produces the corresponding sulfones and no sulfoxide is detected, same to the ODS result of caero et al. [15] and Jia et al. [18].

To complete the removal of sulfur compounds, more reaction time is needed. After 1 hr reaction, 97.0%, 95.0% and 55.0% conversion is reached for DBT, 4,6-DMDBT and BT respectively for a fuel feed with 575.0 ppmw sulfur concentration.

IV. CONCLUSION

The mesoporous MoO_3/γ-Al_2O_3 catalyst with 10wt.% Mo content is high efficient for oxidation of BT, DBT and 4,6-DMDBT which are present in diesel fuel as refractory sulfur compounds after HDS. The use of rotary evaporator during drying of the catalyst sample enhances dispersion of active sites and then the catalyst performance. The most oxidation reactivity is attributed to DBT which is reached 91.0% after a short time as 30 min for a fuel with 575.0 ppmw sulfur content.

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