

Catalytic Oxidative Desulfurization (ODS) by Using HPA supported Alumina Catalyst

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Abstract- The existing process for desulfurization of liquid fuels is Hydro desulfurization (HDS) which requires very high operating conditions and very high cost to remove refractory sulfur compounds such as BT, DBT, 4,6-DMDBT and other derivatives of dibenzothiophene from the liquid fuels. This limitation of existing technology motivates research to find out alternate way to remove these refractory sulfur compounds. Oxidative desulfurization (ODS) is very effective and economic process to removal of these sulfur compounds. In this work ODS was improved by using heterogeneous catalyst. An ammonium salt of molybdenum heteropoly acid was prepared and loaded on modified alumina support. This catalyst is applied on oxidative desulfurization process for removal of benzothiophene (BT), dibenzothiophene (DBT) or 4,6-dimethyldibenzothiophene (4,6 DMDBT) in model oil under mild operating conditions. This heterogeneous catalyst improve the ODS process and work efficiently for 98.8% removal of organo sulfur compounds from model oil. This catalyst recycled easily and reused for several times without a significant decreasing in the activity.

Key Words: Heteropoly acid, DBT, BT, 4,6-DMDBT, Alumina

1. INTRODUCTION

Emission of sulfur from transportation fuels are a major source of air pollution. The deep desulfurization of fuels is needed urgently, because of increased stringent fuel specifications and environment pollution. The sulfur content of the diesel oil will be decreased to 10 mg/kg in many countries by 2010 [1,2]. The existing technology for removing sulfur in industry is catalytic hydrodesulfurization (HDS) process, but is limited for treating some refractory sulfur compounds such as

dibenzothiophene (DBT) or its derivatives with one which are abundant in liquid fuels especially in diesel [3,4].

Dibenzothiophene derivatives (DBTs) are the most difficult sulfur compounds to eliminate from transport fuels due to its low reactivity [5]. Thus, alternative deep desulfurization process like adsorption [6], biodesulfurization [7], extraction [8], oxidation [9], and photo-oxidation [10] are used to eliminate remained sulfur compounds of hydrodesulfurized oil. Among these techniques, the catalytic ultra-deep oxidative desulfurization has been widely studied because of its mild operation conditions (atmospheric pressure and temperatures less than 100°C) and high sulfur removal efficiency. Different catalytic systems, such as organic acid [11], heteropolyoxometalates [12], ionic liquid [13,14], molecular sieve [15,16] and Photocatalysts [17], have been reported for oxidative desulfurization processes (ODS).

To improve the ODS process, a heteropoly acid were synthesized and supported on alumina were studied in this work. The catalyst were systematically characterized by several techniques and applied on oxidative desulfurization process for removal of BT, DBT and 4,6-DMDBT under mild condition.

2. EXPERIMENT

2.1. Preparation of the Catalyst

2.1.1. Preparation of carbamated alumina

Phenyl isocyanate is prepared by the reaction of sodium azide with benzoyl chloride for 8 hours in presence of dry benzene at 0°C [18]. Sodium azide is taken in a flat-bottomed flask with dry benzene and kept in an ice bath. Benzoyl chloride is added drop wise with stirring. The reaction mixture is vacuum filtered and permeate obtained is collected. Dried alumina is reacted with phenyl isocyanate for four hours at ambient conditions. The isocyanate reacts with the OH present on alumina giving O-C-NH groups on its surface. This is further reacted with 1,

2-dichloroethane for further modification of alumina as follows.

Modification of carbamated alumina by reacting with 1, 2-dichloroethane: Carbamated alumina is reacted with 50ml dichloroethane in presence of $ZnCl_2$ at $80^\circ C$ for two hours. The product is then washed with dichloroethane and dried. The ethylene chloride reacts at the phenyl end of the carbamate alumina, thereby giving a chlorine group on alumina which can then be made to react with the complex molecule.

2.1.2. Preparation of HPA Catalyst

An ammonium salt of molybdenum heteropoly acid was prepared according to the procedure reported in literature [19]. Aqueous solution of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ (4.24g, 0.0034 moles) was prepared by dissolving it in 40 ml of water at 373 K. Similarly an aqueous solution of diammonium hydrogen orthophosphate, $(NH_4)_2HPO_4$ (0.27g, 0.002moles) was prepared in 20 ml of water. Then they were mixed and its pH was adjusted to 1.0 by addition of nitric acid. The yellow precipitate obtained was the ammonium salt of molybdenum heteropoly acid, $(NH_4)_3PMo_{12}O_{40}$ (denoted by HPA). This suspension was directly used for the preparation of the heterogeneous catalyst. Instead of separating it by filtration and drying, this suspension is used to modify the acidity of the Al_2O_3 catalyst. The modified (with phenyl isocyanate) Al_2O_3 (50g) was added to 30g of HPA solution. This was then kept under reflux conditions at $70^\circ C$ for 8h in. The solid material which was filtered and dried was the final catalyst having 5% of the HPA. This final catalyst is denoted by Al_2O_3 -HPA.

3. CATALYST TEST

3.1 Oxidative desulfurization test

Three model oils were prepared by dissolving benzothiophene (BT), dibenzothiophene (DBT), or 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) separately into toluene to give a desired sulfur content (sulfur-containing compounds concentration of 0.2 wt.%). In a typical run, 20 mL of model oil was placed in a three-neck flask. The reaction temperature was stabilized by oil bath. The catalyst and 30 wt.% H_2O_2 were added to the flask successively to run the reaction. The samples were collected at an interval of 20 min. The feeds and products were analyzed by nucon gas chromatograph equipped with a FID detector and HP-5 capillary column (Limit of detection was 10₋₆ mg/kg). The conversions of sulfur-containing compound in the sample were used as a measure of the catalytic performance. The experiment was repeated for three times, and the average value was used for the conversion. For the case of diesel oil, 10 mL diesel

oil (sulfur-content: 500 mg/L) was used. The catalyst was separated by centrifugation and the oxidized diesel oil was extracted.

4. RESULT AND DISCUSSION

4.1 FTIR Analysis of Catalyst

The loading of the HPA on the support has been confirmed by the FTIR of the catalyst. The spectrum of carbamated alumina synthesized shows the NH group at 3337 cm^{-1} , C=O at 1650 cm^{-1} and -OH at 3466 cm^{-1} (given in Figure 1). The carbamated alumina is then reacted with 1,2-dichloroethane and its FTIR confirms the reaction by showing the chlorine group (-Cl) at 694 cm^{-1} and the carbamate group -CONH- at 2341 cm^{-1} (shown in Figure 2). The FTIR of the final catalyst prepared by covalent bonding of the HPA modified alumina shows the bonding of the complex at the Cl group, where the peak for -Cl has disappeared (shown in Figure 3).

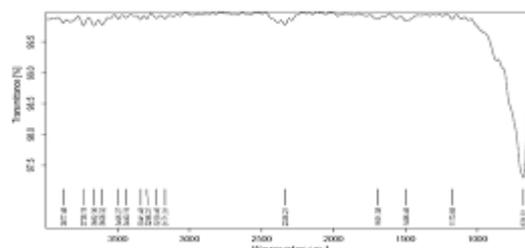


Fig -1: FTIR Spectrum of Neat Alumina

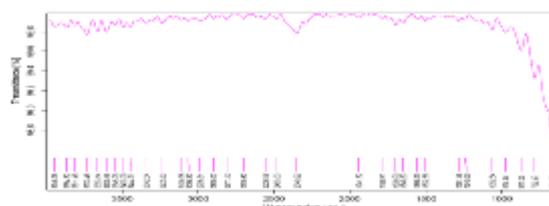


Fig -2: FTIR Spectrum of Modified Alumina Reacted with 1, 2 Dichloroethane formed

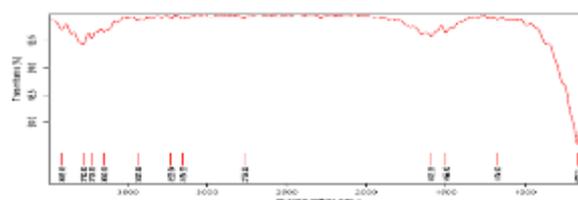


Fig -3: FTIR Spectrum of Covalently bonded with HPA Catalyst

4.2 Scanning Electron Microscopy of the catalyst

SEM of final catalyst and used HPA-Al₂O₃ has been shown in fig. 4 and fig. 5 show the image of the fresh and used catalyst respectively which shows no alteration in the catalyst.

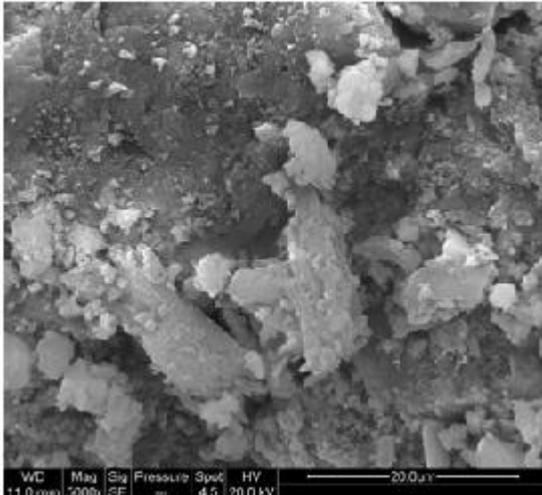


Fig -4: SEM Photographs of the Fresh HPA-Al₂O₃ Catalyst

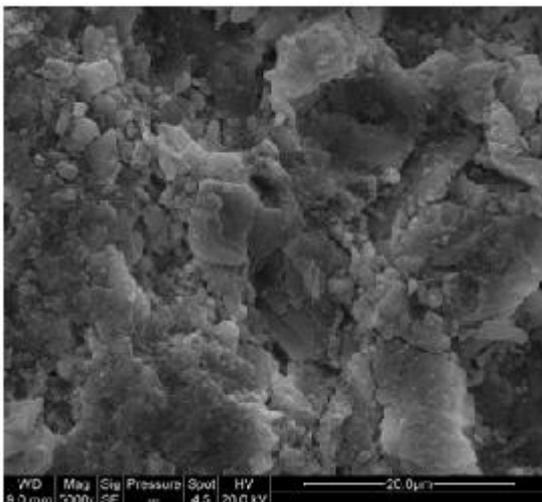


Fig -5: SEM Photographs of the Used HPA-Al₂O₃ Complex Catalyst

4.3 Thermogravimetric analysis (TGA) of HPA-Al₂O₃

The TGA analysis of the complex catalyst was carried out using a Perkin –Elemer instrument in N₂ atmosphere. The TGA graphs of HPA-Al₂O₃ catalysts are given in figure 6. About 10-15 mg of the sample (HPA-Al₂O₃) was taken and heated from 40° C to 950°C at the rate of 10°C/min and the weight loss was measured in this temperature range. Table 1 gives the temperature until which the catalyst

(HPA-Al₂O₃) is thermally stable. The catalyst showed considerable weight loss (more than 35%) on heating till 250°C while the corresponding complex catalysts were found to be stable till 500 °C.

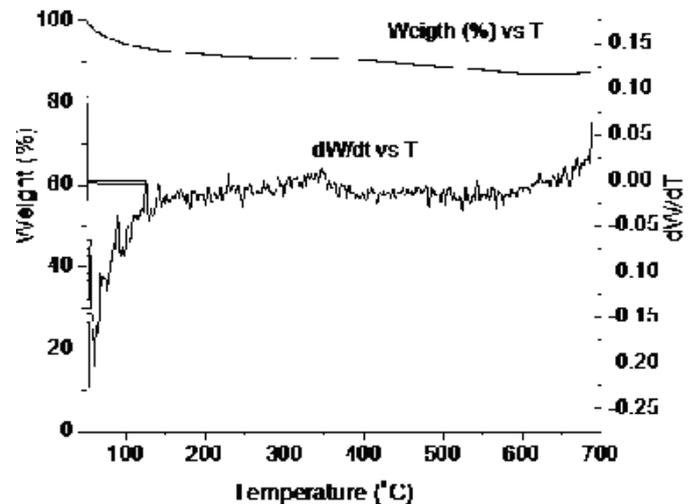


Fig -6: Thermogravimetric Analysis of the HPA-Al₂O₃

4.4 Surface area Analysis

The surface area (SA) of the catalyst at various stages of the catalyst preparation has been measured on a Coulter SA 2100 instrument and is analyzed by the BET method. The surface area of the modified alumina with HPA was found to be 226m²g⁻¹.

4.5 CHN analysis of the HPA-Al₂O₃

The CHN analysis of the HPA-Al₂O₃ was carried out on a CE-440 elemental analyzer (Leeman Labs Inc., USA). About 3-5 mg of the powdered sample is taken and first homogenized at 80°C. Helium gas was used as a carrier and O₂ as oxidant and the sample was heated up to 950°C. The percentage of Carbon, Hydrogen, and Nitrogen present in the complex were determined experimentally as: C, 45.231%; H, 4.720%; N, 8.895%.

Table -1: Reaction conditions: 0.1 g [HPA/Al₂O₃, 10 mL diesel fuel (S-content: 500 mg/L)

Entry	Reaction temperature (°C)	O/S Molar ratio	Reaction time (min)	Sulfur removal(%)
1	50	5	20	86.1
2	60	5	20	98.3
3	70	5	20	97.3
4	80	5	20	98.2

5	50	3	20	82.8
6	60	3	20	98.8
7	70	3	20	92.2

5. CONCLUSIONS

In this work, HPA/Al₂O₃ was used to catalyze the oxidation of sulfur-containing compounds in model oil using H₂O₂ as the oxidant under mild condition. 4,6-DMDBT was oxidized completely in 60 min at 60°C, atmospheric pressure and O/S molar ratio of 3.0. The catalytic oxidation activity for sulfur-containing compounds decreased in the order DBT > 4,6-DMDBT > BT. The solid catalyst was separated easily from the oxidation system by centrifugation and could be recycled for several times without obvious decreasing in oxidation activity. The HPA/Al₂O₃ oxidation system was effective to remove aromatic sulfur-containing compounds from hydrotreated diesel oil, the sulfur content decrease up to 98.8% at mild operating conditions.

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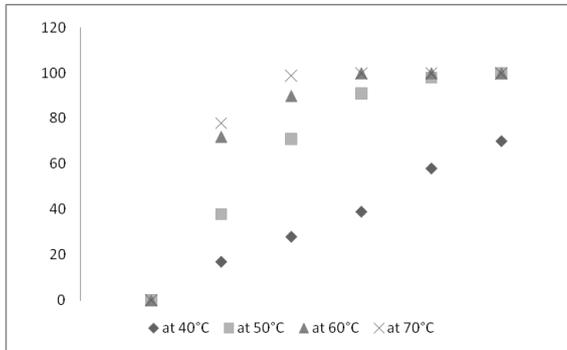


Fig -7: Influence of reaction temperature on the catalytic performance of HPA/Al₂O₃ on the ODS of 4,6-DMDBT with a O/S molar ratio of 3.0.

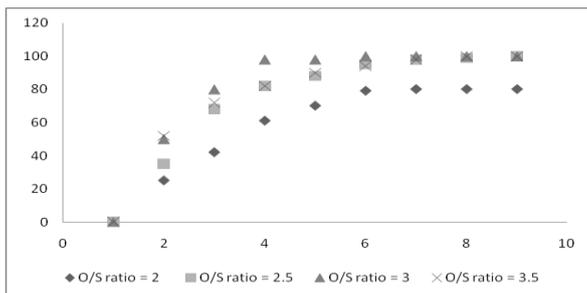


Fig -8: Influence of different O/S molar ratio on the ODS performance of 4,6-DMDBT over HPA/Al₂O₃

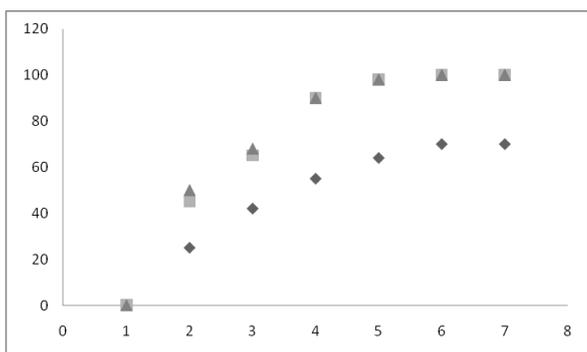


Fig -9: Influence of different sulfur-containing compound on the ODS performance over HPA/Al₂O₃ (reaction conditions: (a) 50°C, (b) 60°C, O/S molar ratio of 3.0, and 0.2 wt.% BT, DBT or 4,6-DMDBT in toluene).

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BIOGRAPHIES



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