



Catalytic Performance of Ammonium Salt of Molybdenum Heteropoly Acid Supported Silica for Oxidative Desulfurization of Benzothiophene, Dibenzothiophene and 4,6-Dimethyldibenzothiophene in Model Oil

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An ammonium salt of molybdenum heteropoly acid was loaded on silica support (HPA-SiO₂), used as catalyst in oxidative desulfurization for removing benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) from model oil. The structural properties of prepared catalyst were studied by using various analytical techniques; Fourier transforms infrared spectroscopy, X-ray diffraction, scanning electron microscopy and thermogravimetric analysis. The results showed that the ammonium salt of molybdenum heteropoly acid highly dispersed on SiO₂. The final catalyst exhibits good catalytic activity of oxidative desulfurization. The 94.6 % of thiophene compounds of the model oil were removed under optimal conditions; temperature at 80 °C, reaction time 100 min. The oxidation is decreased in order of DBT > 4,6-DMDBT > BT.

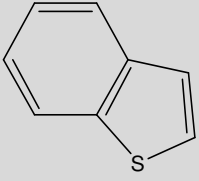
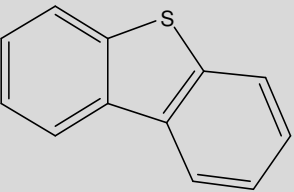
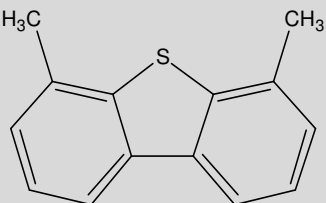
Keywords: Benzothiophene, Dibenzothiophene, 4,6-Dimethyldibenzothiophene, Heteropoly acid, Model oil.

INTRODUCTION

Environmental regulations for sulfur emission limit for liquid fuels became more strict in last 20 years and more stringent legislation on the specification of sulfur content in liquid fuel have been issued over word wide. Production of ultra low sulfur liquid fuel is a challenge for petroleum industry because existing hydro desulfurization processes (HDS) for reducing sulfur in gasoline and diesel require critical operating conditions (high temperature and high pressure) for deep desulfurization. Hydro desulfurization processes is most common industrial process used in petroleum industry to reduce sulphur content of liquid fuels and has received extensive attention since its discovery in 1930's, It is a process in which light oils is heated, mixed with hydrogen and charged in to a reactor packed with a catalyst. At this temperature, some or all of the feed is convert in to vapour, depending on the boiling range of the feed and the pressure is the unit [1,2]. Liquid fuels contain sulfur in form of mercaptans, sulphides, disulfides and thiophenes. It is undesirable compound because it forms sulphur dioxide (SO₂) during fuel oil combustion [3]. The HDS has been fail to removing aromatic organo sulfur compounds, such as benzothiophene (BT), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene due to their stearic hindrance [4-6]. The electron density of BT, DBT, 4,6-DMDBT shown in Table-1.

Therefore, many alternative non-hydrodesulfurization technologies, such as oxidation [7-9], adsorption [10-12], extraction [13], biodesulfurization [14], have been widely investigated. Among these, oxidative desulfurization, which operates under mild conditions without requiring hydrogen, is regarded as the promising and economical process [15]. This process is used to convert thiophene, benzenethiophene, dibenzothiophene and 4,6-dimethyldibenzothiophene into sulfones and sulfoxides in presence of oxidizing agent and sulfones and sulfoxides are easily separated by extraction with polar solvent [16-19]. The ODS process widely studied in various systems, such as organic acid [20], heteropolyoxo-metalates [21], ionic liquid [22,23], molecular sieve [24,25] and photocatalysts [26], heteropoly acid (HPA) catalysts [27-29], HPA catalysts, especially those having the keggin structure, have been determined to be very effective for the oxidation of sulfur containing compounds in a liquid-liquid two phase system. Li *et al.* [30] reported mesoporous silica pillared clay incorporated with phosphotungstic acid. Chamack *et al.* [31] reported a series of cesium salts of tungsten substituted molybdo-phosphoric acid, Cs_xH_{3-x}[PMo_{12-y}WyO₄₀], (x = 1-3, y = 2-1) supported on platelet SBA-15). Wu *et al.* [32] reported metal-modified [PW₁₁O₃₉(H₂O)M]⁵⁻ (M = Ni²⁺ or Co²⁺) were incorporated into the mesoporous silica pillared clays (MSPC) which shows excellent performance in ODS. These catalysts showed the

good performance in ODS system. In this work, an ammonium salt of molybdenum heteropoly acid (HPA) was synthesized and loaded on silica support. The porosity and large surface area of silica combine with heteropoly acid which have good redox properties and strong acidity. 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.

TABLE-1 ELECTRON DENSITY OF BT, DBT, 4,6-DMDBT [Ref. 33]		
Sulfur compounds	Structure	Electron density
BT		5.716
DBT		5.756
4,6-DMDBT		5.760

EXPERIMENTAL

All the chemicals including hydroperoxide analytical reagent grade benzothiophene (BT), dibenzothiophene (DBT), 4,6-dimethyl-dibenzothiophene (4,6-DMDBT), ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (4.24 g, 0.0034 mol), diammonium hydrogen orthophosphate, $(\text{NH}_4)_2\text{HPO}_4$ (0.27 g, 0.002 mol), iso-octane, nitric acid, SiO_2 purchased from Molychem company.

Preparation of model oil: Three model oils were prepared by dissolving benzothiophene, dibenzothiophene and 4,6-dimethyl-dibenzothiophene separately into iso-octane to give a desired sulfur content (sulfur-containing compounds concentration of 0.2 wt. %).

Preparation of catalyst

Preparation of $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ heteropoly acid (HPA): An ammonium salt of molybdenum heteropoly acid was prepared

according to the literature [34]. Aqueous solution of ammonium heptamolybdate, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ (4.24 g, 0.0034 mol) was prepared by dissolving it in 40 mL of water at 373 K. Similarly an aqueous solution of diammonium hydrogen orthophosphate, $(\text{NH}_4)_2\text{HPO}_4$ (0.27 g, 0.002 mol) 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, $(\text{NH}_4)_3\text{PMo}_{12}\text{O}_{40}$ (denoted by HPA). This suspension was directly used for the preparation of the heterogeneous catalyst.

Preparation of final catalyst: The silica (50 g) was added to 30 g of HPA solution. This was then kept under reflux conditions at 70 °C for 8 h. The solid material which was filtered and dried was the final catalyst having 5 % of the HPA. This final catalyst is denoted by HPA- SiO_2 .

Catalyst test

Reaction: Three model oils were prepared by dissolving benzothiophene (BT), dibenzothiophene (DBT) or 4,6-dimethyl-dibenzothiophene (4,6-DMDBT) separately into iso-octane 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. Dibenzothiophene oxidize to form corresponding sulfoxides and sulfones in presence of oxidizing agent and catalyst is shown in Fig. 1.

Mechanism for sulfur removal from oil in the presence of ammonium salt of molybdophosphoric acid (HPA)- SiO_2 catalyst by ODS process shown in Fig. 2 [32]. (1) Firstly,

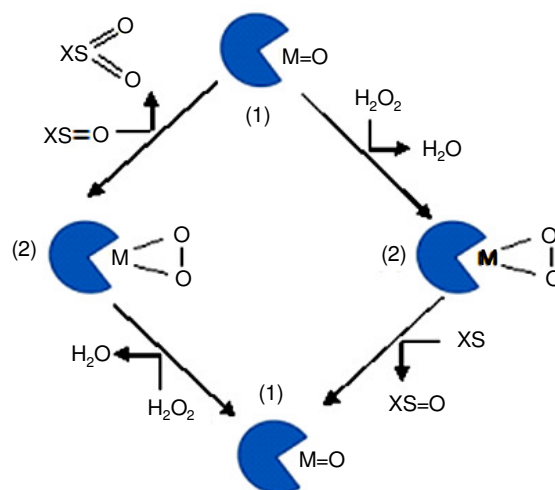


Fig. 2. Mechanism for the oxidation of organosulfur compound by H_2O_2 (oxidant) and HPA- SiO_2 (catalyst) [31]

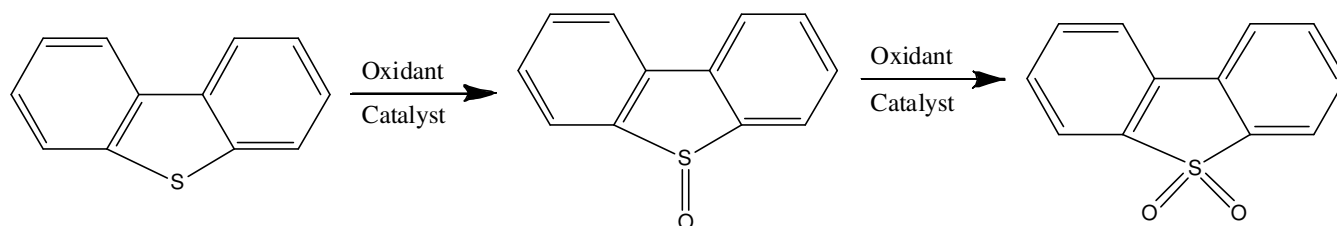


Fig. 1. Reaction of DBT in the catalytic oxidation

addenda atom of POM take the oxygen from oxidant and forms peroxy species (2), the peroxy species donate an oxygen to organosulfur compound and oxidise it to organo sulfoxide and recovered as POM (1).

Reaction monitoring: To determine the concentration of the selected sulfur compound in the organic phase, approximately 0.5 mL of sample were withdrawn from the reactor at fixed time intervals and after phase separation the organic phase was analyzed by gas chromatography. GC equipped with a flame ionization detector, using a 30 m. i.d. 0.32 mm HP-5 column. The main parameters were the following: carrier gas, nitrogen with a flow of 2 mL/min; injector temperature, 250 °C; detector temperature, 260 °C; temperature program, 40 °C or the first 5 min, 40-100 °C at 10 °C/min, 100-200 °C at 15 °C/min, 200 °C for 5 min, 200-250 °C for 15 min [35].

RESULTS AND DISCUSSION

Catalyst characterization

Scanning electron microscope (SEM) of HPA/SiO₂: The SEM analysis of catalyst has been taken on a JEOL JSM-840A. The powder sample is gold coated under vacuum to make it conducting for electrons. The SEM image (Fig. 3) confirms the dispersion of ammonium salt of molybdophosphoric acid (HPA) over silica surface and shows porous surface of the catalyst with high surface area.

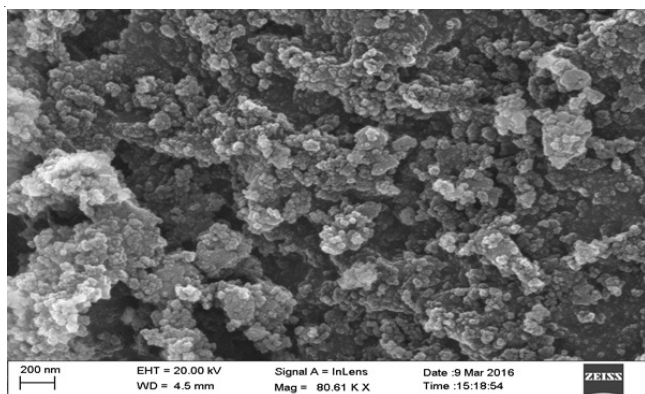


Fig. 3. SEM image of HPA-SiO₂ catalyst

FTIR analysis of the HPA/SiO₂ catalyst: The FTIR analysis was carried out on a Bruker Vector 22 instrument in the 4000-400 cm⁻¹ wave number range. The FTIR spectrum of the final heterogeneous catalyst is shown in Fig. 4. The deposition of molybdenum heteropoly acid on the surface of the support was shown by the bands at 1401, 1024 and 930 cm⁻¹ which represent the stretching vibrations of NH₄⁺ ion, P-O and Mo-O, respectively and the band at 780 cm⁻¹ is attributed to stretching vibration of Mo=O=Mo.

X-ray diffraction of HPA/SiO₂: X-ray diffraction measurements of the catalyst were carried out on a Sietronics XRD diffractometer equipped with Cu-K_α (λ = 1.54 nm) radiation. The voltage and current applied to the X-ray tube were 40 kV and 20 mA, respectively and the sampling step was set at 0.05° with scanning speed as 3 °/min (2θ = 10° to 80°). The XRD pattern of the final catalyst, HPA/SiO₂ is shown in Fig. 5. X-ray diffraction measurements of the catalyst were carried out on a Sietronics XRD diffractometer equipped with Cu-K_α (λ = 1.54

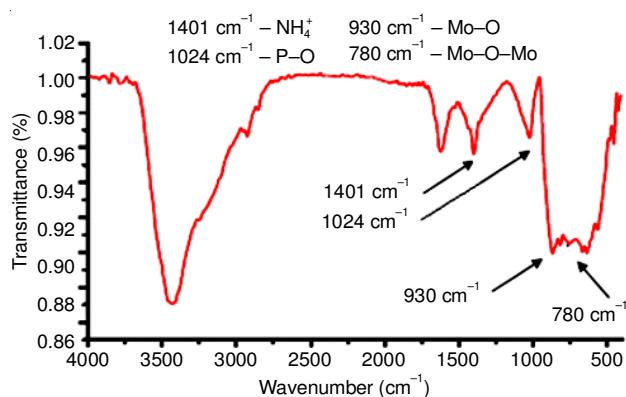


Fig. 4. FTIR of HPA-SiO₂ catalyst

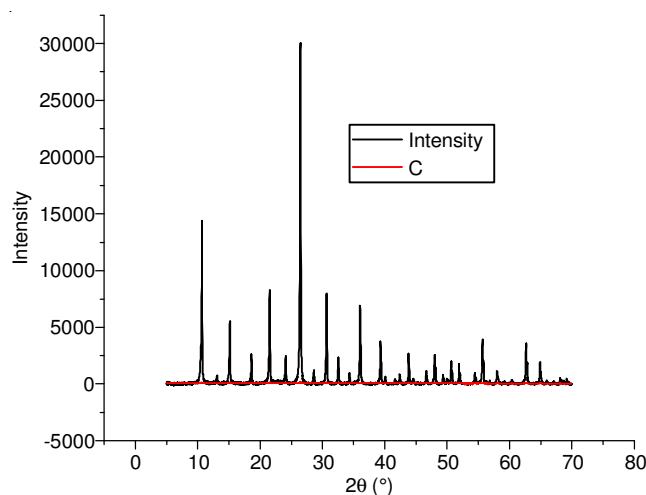


Fig. 5. X-ray diffraction of HPA-SiO₂

nm) radiation. The voltage and current applied to the X-ray tube were 40 kV and 20 mA, respectively and the sampling step was set at 0.05° with scanning speed as 3 °/min (2θ = 10° to 80°). 2θ = 10-20 and 25-30 correspond to the deposition of molybdenum heteropoly acid (HPA) [34].

Thermogravimetric analysis: The TGA analysis of the complex catalyst was carried out using a Perkin-Elmer instrument in N₂ atmosphere. The TGA graph of HPA/SiO₂ catalyst is given in Fig. 6. The catalyst showed a considerable weight loss on heating till 250 °C while the corresponding catalyst were found to be stable till 500 °C.

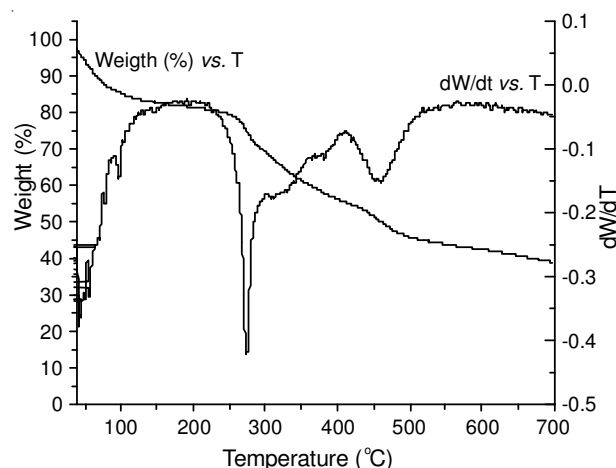


Fig. 6. TGA of HPA-SiO₂

Influence of reaction temperature on the catalytic performance of HPA/SiO₂ on ODS of BT: The influence of reaction parameters, such as the reaction temperature and O/S molar ratio with reaction time were studied by using HPA/SiO₂ catalyst shown in Fig. 7.

Fig. 7 (a), (c), (e) shows the effect of temperature and O/S molar ratio on oxidation of sulfur compounds under the experimental conditions at different molar ratio of 2, 3, 4, 5, with time at 80 °C. With increasing the ratio from 2 to 3, the sulfur removal increase up to 91.2, 94.3 and 92.1 in 100 min for oil containing BT, DBT and 4,6-DMDBT, respectively. Further increase in molar ratio up to 5 leads to decreasing the sulfur removal. The phenomenon may be attributed to the fact that there is a competition between the decomposition of H₂O₂ and the oxidation of sulfur compounds by H₂O₂ [15]. When the O/S molar ratio was increased from 4 to 5, the decrease of desulfurization activity was attributed to the water produced from oxidation reaction and thermal decomposition of H₂O₂, which inhibited the oxidation reaction. Therefore, the optimized H₂O₂/BT mole ratio as selected as 3.

Fig. 7, (b) (d) (f) shows the effect of the amount of H₂O₂ on oxidation of sulfur compounds under the experimental conditions at 40, 60, 80 and 100 °C with time. With increasing the temperature from 60 to 80, the sulfur removal increases up to 91.5, 94.6 and 92.5 for oil containing BT, DBT, 4,6-DMDBT, respectively. It was indicated that the sulfur removal of BT increased with increasing time at different temperatures. At beginning of reaction, the less H₂O₂ decomposed. It was known that the higher the reaction temperature was, the faster

reaction rate was. Therefore, the sulfur removal followed order of 40 °C < 60 °C < 80 °C. After 100 °C the sulfur removal decreased. The phenomenon attributed to decomposition of H₂O₂. As the reaction progressed, the higher temperature could lead to more decomposition of H₂O₂ and worse utilization of H₂O₂. On the basis of results, the reaction for 100 min at 80 °C is chosen as an optimal condition for the desulfurization process. The maximum sulfur removal at optimal condition in presence of HPA/SiO₂ catalyst is shown in Table-2.

TABLE-2
SULFUR REMOVAL AT OPTIMAL CONDITIONS

Compounds	Conversion (%)
Benzothiophene (BT)	91.5
Dibenzothiophene (DBT)	94.6
4,6-Dimethyldibenzothiophene (4,6-DMDBT)	92.5

Conclusion

As oxidative desulfurization ammonium salt of molybdenum heteropoly acid were successfully impregnated on silica. FTIR spectra and SEM confirms the deposition of HPA over silica support. TGA shows high thermal stability of catalyst. After 100 min the sulfur compounds BT, DBT and 4,6-DMDBT are oxidized up to 91.5, 94.6 and 92.5, respectively. The oxidation reactivity decreased in order of DBT > 4,6-DMDBT > BT. The solid catalyst was separated easily from the oxidation system by centrifugation and could be recycled for seven times without obvious decreasing in oxidation activity. The HPA/SiO₂ oxidation system was effective to remove aromatic sulfur-

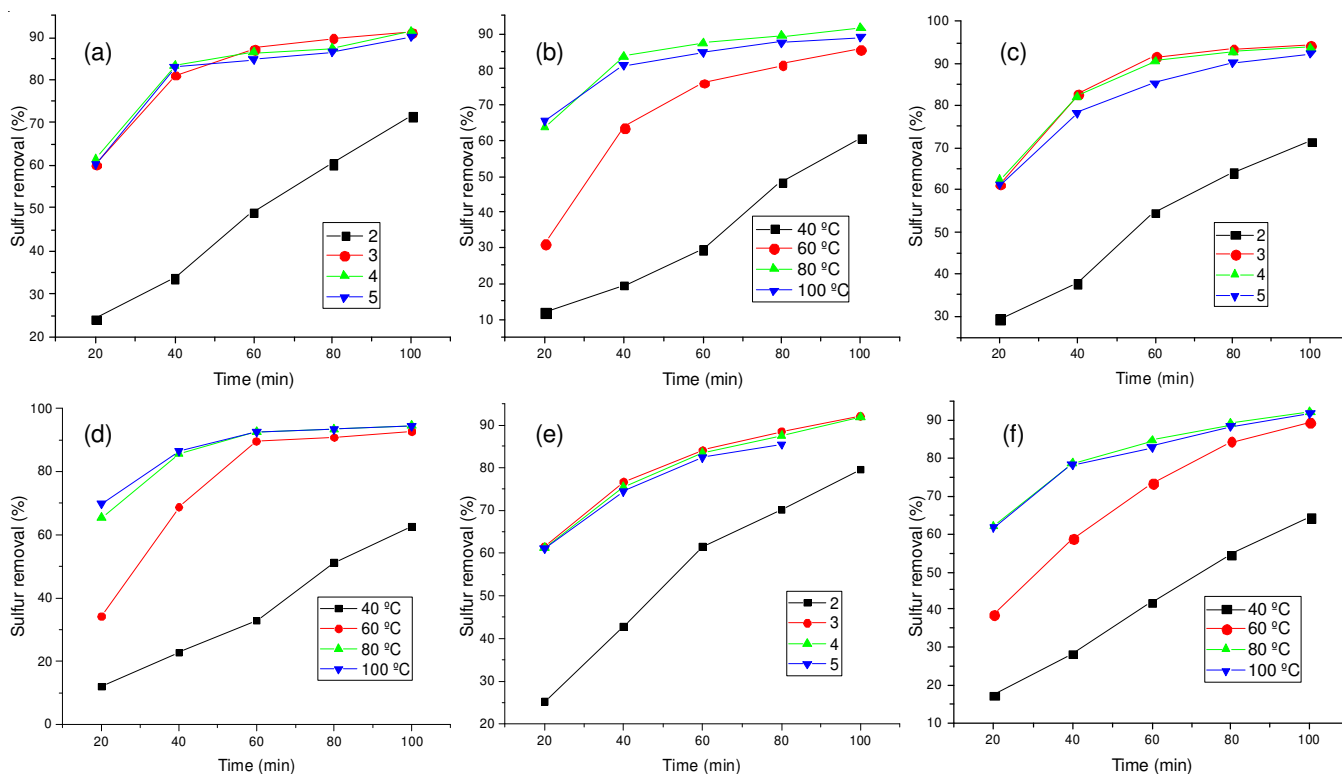


Fig. 7. (a) Influence of O/S molar ratio on performance of catalyst (HPA-SiO₂) in ODS of BT at temperature 80 °C (b) Influence of temperature at O/S molar ratio 3 on performance of catalyst in ODS of BT (c) Influence of O/S molar ratio on performance of catalyst in ODS of DBT at temperature 80 °C (d) Influence of temperature at O/S molar ratio 3 on performance of catalyst in ODS of DBT (e) Influence of O/S molar ratio on performance of catalyst in ODS of 4,6-DMDBT BT at temperature 80 °C (f) Influence of temperature at O/S molar ratio 3 on performance of catalyst in ODS of 4,6-DMDBT

containing compounds from hydro treated diesel oil, the sulfur content decrease up to 96 % at mild operating conditions.

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