Malaysian Journal of Catalysis 2 (2017) 23-27

Malaysian Journal of Catalysis

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MJCat

Effect of calcium and iron doping over MoO_3-PO_4/Al_2O_3 catalyst in oxidative desulfurization of Malaysian diesel

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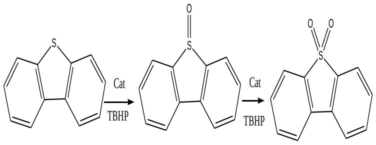
Article history :
Received 11 October 2016
Accepted 22 February 2017

GRAPHICAL ABSTRACT



ABSTRACT

The catalytic oxidative desulfurization (Cat-ODS) process has emerged as a new technology to achieve ultra-low sulfur levels in diesel fuels. The effect of calcium and iron dopant in MoO_3-PO_4/Al_2O_3 catalyst were tested on desulfurization reaction at ambient condition. The oxidizing reagent used was *tert*-butyl hydroperoxide (TBHP) and dimethylformamide (DMF) acted as an extraction solvent. A commercial Petronas diesel with 440 ppmw of total sulfur was employed to evaluate the elimination of sulfur compounds. The result obtained revealed that Fe/MoO_3-PO_4/Al_2O_3 catalyst gave superior performance towards desulfurization. The Fe/MoO_3-PO_4 catalyst was able to reduce the sulfur in commercial diesel from 440 to 79 ppmw with 82% of total sulfur removal while Ca/MoO_3-PO_4/Al_2O_3 catalyst only achieved 76% of sulfur removal. Ammonia temperature programme desorption (TPD) analyses showed that the Fe/MoO_3-PO_4/Al_2O_3 catalyst contained both strong and weak acid sites while field emission scanning electron microscopy (FESEM) micrograph illustrated well-dispersed homogeneous structure. The mechanistic study showed that it was depended on the type of dopant as the Fe/MoO_3-PO_4/Al_2O_3 catalyst tended to form sulfone in the oxidative desulfurization reaction meanwhile, the sulfoxide formation was dominated in the oxidative desulfurization reaction using Ca/MoO_3-PO_4(10:90)/ Al_2O_3 catalyst. The results obtained showed that Fe/MoO_3-PO_4(10:90)/Al_2O_3 catalyst can be used as a potential catalyst for the removal of sulfur in Malaysian diesel to achieve Euro IV diesel.

Keywords: catalyst, catalytic oxidative desulfurization, commercial diesel,*tert*-butyl hydroperoxide

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| eISSN 0128-2581 |

1. INTRODUCTION

Sulfur compounds are the most notorious and undesirable petroleum contaminants and a large portion of these compounds would be transferred to diesel oil during refining process. In general, sulfur presents as hydrogen sulfide, organic sulfides and disulfides, benzothiophene, dibenzothiophene, and their alkylated derivatives [1]. Upon diesel combustion, sulfur compounds are converted to sulfur oxides (SOx) that contribute to acid rain and environmental pollution [2]. In the near future, the requirements for sulfur content in the fuel will become more stringent – with zero sulfur emission from the transport fuel, which calls for the development of advanced technologies for ultra clean fuel. Thus, great efforts have been made todecrease the content of sulfur in diesel oil [3]. Nevertheless, the present technology, hydrodesulfurization (HDS) is incapable in removing sulfur in diesel especially the aromatic dibenzothiophene (DBT) and its derivates in order to achieve ultra-low sulfur diesel (ULSD) [4]. Since then, catalytic oxidative desulfurization (Cat-ODS) has gained their attention and been documented in recent articles [5-8]. However, there is no detailed work to define the appropriate conditions, particularly in selective catalysts. In the present study, the supported bimetallic oxide catalysts made of Fe/MoO_3-PO_4(10:90)/Al_2O_3 and Ca/MoO_3-PO_4(10:90)/Al_2O_3 were prepared. Therefore, the aim of the present investigation is to elucidate the effect of iron, Fe and calcium, Ca toward supported MoO_3-PO_4/Al_2O_3 catalyst on the catalytic activity, structure and physicochemical properties for desulfurization reaction as well as its mechanistic study.

2. EXPERIMENTS

2.1 Materials

All solvents and reactants were purchased and used without further purification. Phosphomolybdic acid hydrate (Across Organic), Iron(III) nitrate nonahydrate (QRëc) and calcium nitrate tetrahydrate (Sigma-Aldrich), λ- Al_2O_3 beads 3-5 mm diameter (Sigma- Aldrich) with 100% purity, *tert*-butyl hydroperoxide, (TBHP) 70 wt.% in water (Across Organic), dimethylformamide, DMF (MERCK) were used in this research. The fuel tested was a commercial diesel fuel from Petronas, Malaysia with 440 ppmw of sulfur content. Dibenzothiophenes, DBT in N-Octane (100 ppmw) was used as model compound.

2.2. Preparation and Characterization of Catalyst

Iron and calcium-doped MoO_3-PO_4/Al_2O_3 were prepared at ratio 10:90 by dissolving phosphomolybdic acid either with iron(III) nitrate nonahydrate or calcium nitrate tetrahydrate in the sufficient volume of water and the solution was used for impregnation of Al_2O_3 (surface area: 292 m^2/g) at room temperature. The wet sample was dried overnight at room temperature before it was calcined at 500ºC temperatures for 5 h in air. The morphology of the catalyst surface was analyzed by field emission scanning electron microscopy (FESEM), using Zeiss Supra 35VP and the acidity of the oxide catalysts was determined by temperature programmed desorption (TPD). A 10% NH_3:90% He gas mixture was introduced into the sample cell. The TCD response was recorded and by quantifying the peak area, the total amount of NH_3 adsorbed onto the sample was calculated.

2.3. Catalytic Oxidative Desulfurization

All oxidative desulfurization (ODS) reactions were conducted in a 100 mL round-bottom flask, equipped with amagnetic stirrer and fitted with condenser. In a typical run, the oil bath was first heated and stabilized at a constant temperature (45°C). Then, 10 mL of commercial diesel (440 ppmw) was added to the flask, followed by the addition of sulfur/TBHP in the ratio of 3 and 0.12 g catalyst. The mixture was refluxed for 30 minutes under vigorous stirring at atmospheric pressure. The oxidized diesel was extracted with DMF at ratio diesel/solvent = 1.0. The extraction process was conducted by vigorous stirring for 30 minutes followed by phase separation between diesel and solvent. The treated diesel was analyzed by gas-chromatography (Agilent 6890N GC) equipped with FPD detector. Dibenzothiophene (DBT) was used as the model compound to study the ODS mechanism of commercial diesel using TBHP. The oxidation steps were performed as previously described for the ODS procedure. Samples were drawn from the flask at regular intervals for analysis. The GC-FPD was used to identify the oxidation products.

3. RESULTS AND DISCUSSION

Fig. 1(a) and (b) show the comparison of the effect of dopant on the molybdena based catalyst. As shown in the micrographs, the catalyst with Fe dopant showed well-dispersed homogeneous structure (Fig. 1(a)) and the particles of each element are distributed uniformly on the alumina surface. However, Ca/MoO_3-PO_4/Al_2O_3 catalyst displayed the scattered particles with undefined shape and size on the catalyst surface (Figure 1b).

Fig. 2 shows the NH_3-TPD curves for MoO_3–PO_4/Al_2O_3, Fe/MoO_3–PO_4/Al_2O_3 and Ca/MoO_3-PO_4/Al_2O_3 catalysts calcined at 500 ºC. As illustrated in the figure, it clearly showed that the Fe dopant significantly altered the acid strength distribution, causing an increase in strong strength acid sites. In this study, the catalyst which was strong acidic is needed in the oxidation process to enhance the interaction between TBHP and active site of the catalyst surface as reported by our previous research [9].

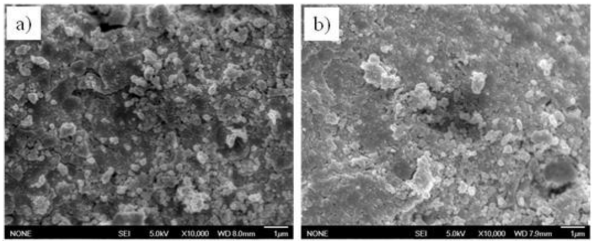

Fig. 1 FESEM micrographs of a) Fe/MoO_3-PO_4/Al_2O_3 and (b) Ca/MoO_3-PO_4/Al_2O_3 catalysts calcined at 500°C with scale bar 1μm, magnification: 10 k.

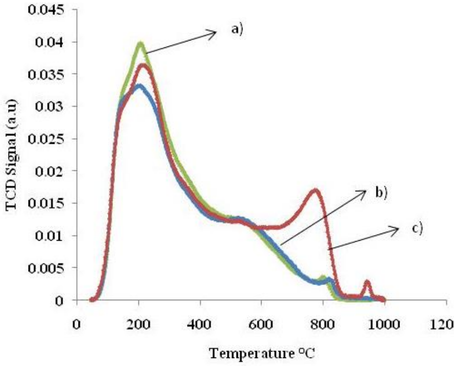

Fig. 2 NH_3-TPD profiles for a) MoO_3-PO_4/Al_2O_3 b) Ca/MoO_3–PO_4/Al_2O_3 c) Fe/MoO_3–PO_4/Al_2O_3 catalysts calcined at 500 °C

According to the previous study [10], transition metal oxide catalysts supported on Al_2O_3 have been reported to be effective in catalyzing the oxidation of sulfur impurities in diesel to the corresponding sulfoxide or sulfone. Meanwhile, Malka and Tatibouet [11] reported that Ca was a promoter of MoO_3/Al_2O_3 catalyst in the oxidation reaction of methanol. Fig 3 shows the effect of dopants on MoO_3-PO_3/Al_2O_3 catalyst calcined at 500ºC on the ODS reaction. The results showed that the catalytic activity of the alumina supported Mo catalyst decreased in the order of: Fe/MoO_3-PO_4/Al_2O_3>Ca/MoO_3-PO_4/ Al_2O_3>MoO_3-PO_4/Al_2O_3. Thus, Fe was regarded as the best dopant for the molybdenum-based catalyst. Fe(III) salts have been reported as a good catalyst for many oxidation reactions at ambient conditions [12]. In comparison with Ca dopant, Fe, as dopant, improved the performance of MoO_3-PO_4/Al_2O_3 most significantly. Therefore, the effect of Fe as dopant was investigated in detailed.

The experiments were further conducted to study the removal of sulfur compounds from commercial diesel with different desulfurization treatments (Table 1). The performance of the ODS process was compared with that Cat-ODS process. It is interesting to note that after employing the catalyst, the sulfur removal performance of the ODS process achieved 82% with a single extraction process. Furthermore, the catalytic oxidative desulfurization with double extraction method had successfully removed 96% of sulfur from oxidized diesel. It was suggested that the single extraction was insufficient to remove sulfones or sulfoxides, and that two successive extractions would be better [3].

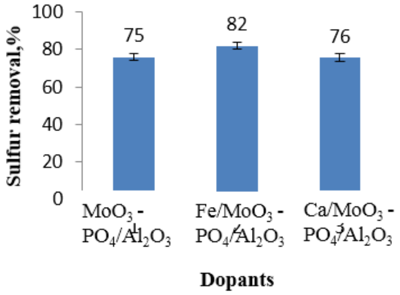

Fig. 3 Effect of the dopants on MoO_3/Al_2O_3 catalyst on the ODS reaction in commercial diesel. Catalytic oxidation = O:S molar ratio = 3:1, solvent DMF, commercial diesel/solvent ratio 1, oxidation T 45 ºC, oxidation time 30 min

Table 1 Catalytic oxidative desulfurization treatment.

Desulfurization Treatment	Sulfur Removal, %
ODS	70
CAT (ODS)	82
CAT (ODS) + 2nd extraction	96

Each experiment was repeated five times to ensure the accuracy of the results. The catalytic activities of these catalysts were tested under similar preparation and experimental conditions. The results of repeatability test over five replicates of $Fe/MoO-PO_4/(10:90)/Al_2O_3$ catalyst are displayed in Figure 4. It can be observed that the catalytic activity reading showed some fluctuations over these five replicates due to the instability of the GC. Based on the results obtained, there were not much different (<5%) on the replicate tests for each commercial diesel samples, indicating the accuracy of the analysis performed.

The reusability of the best catalyst, Fe/MoO_3-PO_4 $(10:90)/Al_2O_3$, was investigated under optimum conditions for further desulfurization of diesel fuel. At the end of the reaction, the catalyst was recovered, washed with methanol to remove the sulfur compound adsorbed on the catalyst and dried in an oven at 80ºC before being subjected to the next ODS process. The presented results in Figure 5 showed that there was no significant decrease in the catalyst activity even after five recycled runs, indicating the superior performance of the fabricated catalyst in this work. Indeed, it explains that Fe/MoO_3-PO_4 $(10:90)/Al_2O_3$ catalyst exhibited high catalytic activity for the ODS of commercial diesel and high resistance to sulfur poisoning.

Different types of catalyst will give different performance on the catalytic activity and the reason for this difference could be observed by studying the oxidation products using GC– FPD (Fig 6). DBT was used as model compound to study the oxidative desulfurization process over TBHP in the presence of $MoO_3–PO_4/Al_2O_3$, $Fe/MoO_3–PO_4/Al_2O_3$ and $Ca/MoO_3–PO_4/Al_2O_3$ catalysts in individual system at a time of interval 5, 15, 30 and 45 min. The results of GC–FPD analysis in the model compound of DBT extracted by DMF in different catalytic system showed that the desulfurization products were DBT sulfoxide and DBT sulfone. The mechanistic study showed that it was depended on the type of dopant as the $Fe/MoO_3-PO_4/Al_2O_3$ catalyst tended to form sulfone (Fig 6 (b)) in the oxidative desulfurization reaction meanwhile, the sulfoxide formation was dominated in the oxidative desulfurization reaction using $Ca/MoO_3-PO_4/ Al_2O_3$ and MoO_3-PO_4/ Al_2O_3 catalyst (Refer Fig. 6 a and c).

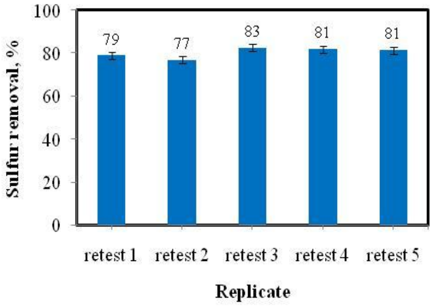

Fig. 4 Repeatability testing over $Fe/MoO_3-PO_4(10:90)/Al_2O_3$ catalyst calcined at 500ºC for 5 h

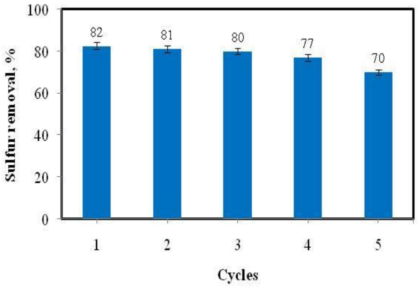

Fig. 5 Reproducibility testing over $Fe/MoO_3-PO_4(10:90)/Al_2O_3$ catalyst calcined at 500ºC for 5 h.

On the basis of above-mentioned results, our proposed peroxidic oxidation mechanism of DBT on $Fe/MoO_3–PO_4(10:90)/Al_2O_3$ catalyst with TBHP is shown in Fig. 7. The reaction pathway proceeded initially through the nucleophilic attack of TBHP on Mo=O which was found to be on catalyst surface to form species (1). The oxidation process must proceed by nucleophilic attack of the sulfur in the DBT (2) on the positively charged peroxometallic complex (1) to form DBT sulfoxide (2) and regenerated polymolybdate species, respectively. Subsequently, the sulfoxide (3) undergoes further oxidation to form DBT sulfone (4). Fe dopant will provide a relatively more positive net charge on the polymolybdate catalyst surface. This property will enhance the reaction of TBHP with the catalyst to form active species. In overall, the activation mechanism of peroxy oxygen is according to Garcia Gutierrez et al [13,14] in which the peroxide reacts with DBT to produce

DBT sulfoxide, and further oxidation produces the corresponding sulfone in presence of Fe/MoO_3–PO_4(10:90)/Al_2O_3 catalyst.

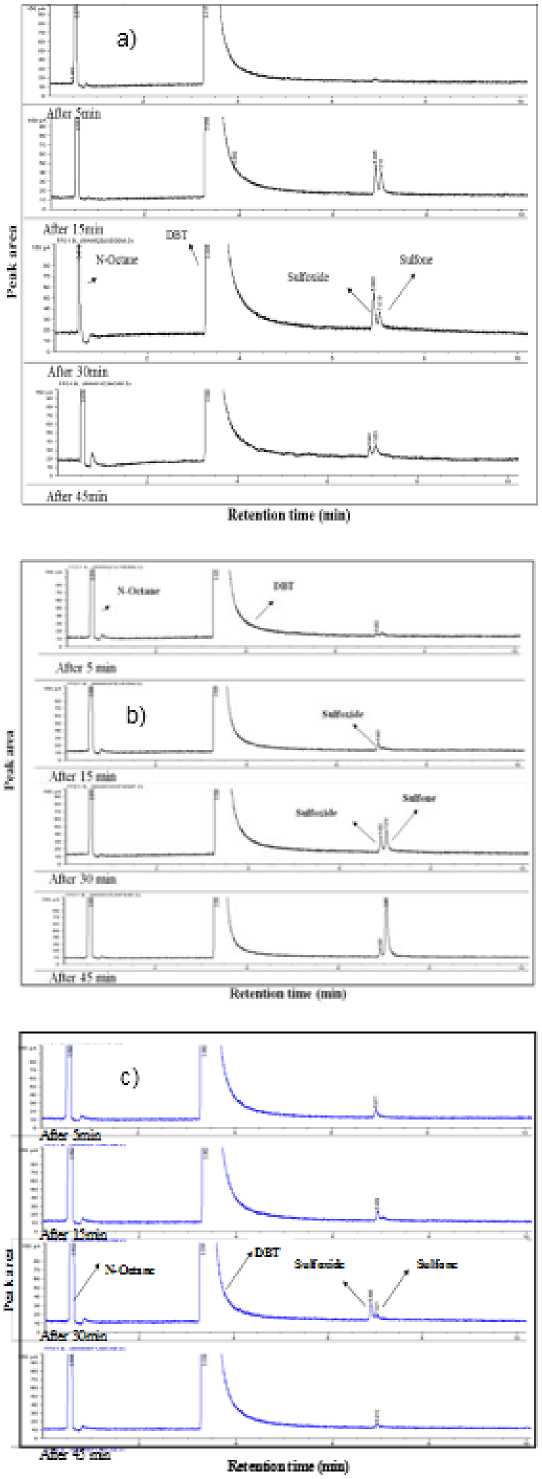

Fig. 6 Chromatograms of GC–FPD analysis for DBT oxidation desulfurization by TBHP after 5 min, 15 min, 30 min and 45 min using a) MoO_3– PO_4/Al_2O_3 b) Fe/MoO_3– PO_4/Al_2O_3 and c) Ca/MoO_3– PO_4/Al_2O_3 calcined at 500 °C.

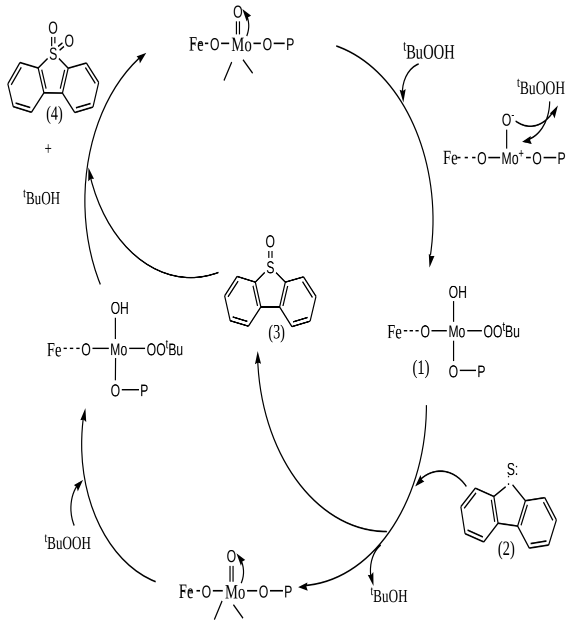

Fig. 7 A proposed cyclic mechanism for the oxidation of dibenzothiophene (DBT) in the presence of Fe/MoO_3-PO_4/Al_2O_3 catalyst

4. CONCLUSION

It was found that the addition of dopant toward MoO_3/Al_2O_3 catalysts increased significantly the selectivity of catalytic performance in the order: MoO_3-PO_4/Al_2O_3<Ca/MoO_3-PO_4/Al_2O_3<Fe/MoO_3-PO_4/Al_2O_3. The addition of iron dopant onto the molybdena based catalyst led to a significant increase in the oxidation activity of the Cat-ODS process. The Fe/MoO_3-PO_4 catalyst was able to reduce the sulfur in commercial diesel from 440 to 79 ppmw with 82% of total sulfur removal while Ca/MoO_3-PO_4 catalyst only achieved 76% of sulfur removal. In addition, >90% of sulfur was removed in commercial diesel after second extraction. These results indicate that Fe/MoO_3–PO_4/(10:90)Al_2O_3 catalyzed on Cat-ODS system has the great potential to be employed in industrial to meet the future regulation of sulfur in diesel fuels.

ACKNOWLEDGEMENTS

The authors would like to acknowledge the Universiti Teknologi Malaysia for the financial support under GUP Grant of 11H99 and FRGS Grant of 4F740.

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