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Development of bimetallic and trimetallic oxides doped on molybdenum oxide based material on oxidative desulfurization of diesel

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Abstract Catalytic oxidative desulfurization (Cat-ODS) activities of thiophenic sulfur were compared using alumina supported of mono-, bi- and trimetallic oxide molybdena based catalysts, prepared by incipient wetness impregnation. The aim of this study was to inquire on the possibility of supported trimetallic oxide catalysts for deep Cat-ODS process. The prepared catalysts were characterized by nitrogen adsorption, X-ray diffraction, field emission scanning electron microscopy and transmission electron microscopy, and tested in the ODS of model thiophene, dibenzothiophene and 4,6-dimethyldibenzothiphene, as well as on commercial and crude diesel. It was found that the addition of dopant and co-dopant toward MoO_3/Al_2O_3 catalysts increased significantly the selectivity of catalytic performance in the order: mono- < bi- < trimetallic oxide. Under these optimum conditions: TBHP/sulfur ratio of 3, 2.13%V/4.08%W/16.07%MoO_3/Al_2O_3 (0.2 g), temperature of 60 °C, 30 min of reaction, and complete removal of model organosulfur compounds were obtained. In addition, >90% of sulfur was removed in both commercial and crude diesel under similar reaction conditions. Reproducibility test showed that the catalyst has higher catalytic activity and could be repeatedly used with little change after five cycles.

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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 (Song and Ma, 2003). Upon diesel combustion, sulfur compounds are converted to sulfur oxides (SO_x) that contribute to acid rain and environmental pollution (Jose et al., 2011). Although environmental regulation has been

applied in many countries to reduce the sulfur levels in diesel and other fuels (Babich and Mouljin, 2003), ''sulfur removal'' still represents a major operational and economic challenge for petroleum refining industry (Zhu et al., 2015a,b). The conventional catalytic hydrodesulfurization (HDS) process, operated at elevated temperature (> 300 °C) and pressures (20–100 atm H_2) over either Ni–Mo/Al_2O_3 or Co–Mo/Al_2O_3 catalyst, is highly efficient in removing low molecular weight of thiols, sulfides, disulfides and mercaptans. However, thiophenes and multi-ring aromatic compounds such as 4,6-dimethyldibenzothiophene and other alkyl-substituted derivatives of dibenzothiophene are relatively inert to HDS due to their steric hindrance that makes extremely difficult to achieve deep desulfurization by HDS process (Kedra-Krolik et al., 2011; Song, 2003). Thus, HDS causes an inappropriate process to produce diesel fuel that meets the current environmental regulations. Since then, catalytic oxidative desulfurization (Cat-ODS) has gained their attention and been documented in recent articles (Zhu et al., 2015a,b, 2014; Nava et al.; 2009; Cedeño-Caero et al., 2005). It is an excellent option after HDS since thiophene and its derivatives are easily oxidized at low temperature and pressure conditions in the presence of an oxidant, to their corresponding sulfones.

The use of molybdenum based catalysts was widely reported to be applicable in Cat-ODS systems using either H_2O_2 or organic hydroperoxide as the oxidizing agents. As example, Wang et al. (2003) reported that MoO$_3$/Al$_2$O$_3$-TBHP performed the highest ODS activity as compared to other metal oxides. Garcia-Gutierrez et al. (2008) claimed 97.8% of model sulfur was removed utilizing Mo/Al$_2$O$_3$ and H_2O_2 oxidant under mild conditions. Ishihara et al. (2005) applied Mo and TBHP to treat light gas oil with a sulfone adsorption step while Jia et al. (2011) used Mo as both catalyst and adsorbent to process a low sulfur model diesel. A modification on Mo was done by Prasad et al. (2008), where Bi promoter was doped with Mo to increase the catalytic activity in desulfurization of light cycle oil. In addition, Chang et al. (2010) introduced a series of alkaline earth metal dopant on Mo and found out that Ca/Mo/Al$_2$O$_3$ showed the best catalyst toward sulfur removal. Han et al. (2013) modified MoO$_3$/SiO$_2$ with phosphorus to enhance the ODS activity using cumene hydroperoxide as oxidant. Meanwhile, Qiu et al. (2015) synthesized phosphomolybdic acid to remove benzothiophene and dibenzothiophene at 70 °C for 60 min of reaction conditions. However, regarding supported trimetallic oxide catalysts, there was no report done by the researchers.

On the basis of previous studies, we report results from a comparison study of MoO$_3$/Al$_2$O$_3$ catalysts with various dopants and co-dopants such as V, Ti, and W to improve the removal of sulfur compounds from diesel oil under mild reaction conditions. Bimetallic and trimetallic oxide catalysts were characterized and tested in model diesel containing thiophene, dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT). The potential catalyst was further investigated using commercial and crude diesel. The reusability of the catalyst was also studied.

2. Experimental

2.1. Materials

All materials that are purchased from Sigma–Aldrich were used without further purification. *Tert*-butyl hydroperoxide (aqueous, 70 wt.% TBHP) and *N,N*-dimethylformamide (99%, DMF) were used as oxidizing agent and extraction solvent. *N*-octane (99%) was used as solvent for sulfur compounds of thiophene (Th, 99%), dibenzothiophene (DBT, 97%) and 4,6-dimethyldibenzothiophene (4,6-DMDBT, 95%). Model diesel was prepared with 600 ppmw of sulfur; Th (200 ppmw), DBT (200 ppmw) and 4,6-DMDBT (200 ppmw), respectively. Commercial and crude diesels were obtained from Petronas, Malaysia.

2.2. Preparation of catalysts

Incipient wetness impregnation (IWI) method was used in the production of all catalysts referring to the previous works (Bakar et al., 2012, 2015). MoO$_3$/Al$_2$O$_3$ catalyst was initially prepared as reference. Alumina beads were dipped into aqueous solution containing the desired amount of ammonium heptamolybdatetetrahydrate (99%) for 30 min, aging at 80 °C for 24 h followed by calcination process at 600 °C for 5 h under air atmosphere with a ramp of 5 °C min^{-1}. Then, bimetallic oxides catalysts were prepared using three different dopants. Vanadium-, tungsten- and titanium-doped MoO$_3$/Al$_2$O$_3$ catalysts were prepared by dissolving (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O with different precursors of ammonium metavanadate (NH$_4$VO$_3$, 99.9%), ammonium metatungstate ((NH$_4$)$_6$H$_2$W$_{12}$O$_{40}$·H$_2$O, 99.9%) and ammonium titanyl oxalate monohydrate ((NH$_4$)$_2$-TiO(C$_2$O$_4$)$_2$·H$_2$O, 99.9%) with deionized water. For trimetallic oxide catalyst, three types of precursors were used to fabricate the solutions which were, ammonium metatungstate as dopant and ammonium metavanadate or titanyl oxalate as co-dopant. Further preparation steps were similar to monometallic oxide catalysts with different ratio of dopants and co-dopants.

2.3. Characterization of catalyst

The morphology of the surface catalyst was analyzed by field emission scanning electron microscopy (FESEM), using Zeiss Supra 35VP and transmission electron microscopy (TEM) using JEOL-JEM 2100. The XRD patterns of the powder samples were recorded at 2θ between 10° and 80° using a Bruker Advance D8 with Siemens 5000 diffractometer. The Cu Kα radiation operates at 40 kV and 40 mA with $\lambda = 1.5418$ Å. Textural properties were obtained by N_2 adsorption/desorption isotherms, using Micromeritics ASAP 2010 volumetric adsorption analyzer at −196 °C and degassed the catalyst at 200 °C for an hour while elemental composition was determined by energy dispersive X-ray spectroscopy (EDX).

2.4. Catalytic experiments

In a typical reactive cycle, the oil bath was first heated up and stabilized to 60 °C. After that, 20 mL of simulated diesel, commercial diesel or crude diesel, TBHP oxidant (O/S = 3) and catalyst (0.2 g) were introduced into round-bottom flask and refluxed under atmospheric pressure with vigorous stirring (1000 rpm) for 30 min. After the reaction, the oxidized diesel fuel was extracted by solvent extraction (DMF) with DMF to diesel ratio of 1.0 for 30 min at temperature of 30 °C. The mixture of diesel and solvent extraction was vigorously stirred (1000 rpm) followed by phase separation in a separating funnel, and left until two separate layers of diesel and solvent formed (Mokhtar et al., 2015). The reaction progress was monitored for sulfur concentration measurement using Gas Chromatography-Flame Photometric Detector (GC-FPD). A 50 m × 0.25 mm inner diameter × 0.25 lm film thickness HP-1 capillary column was used for separation. High purity helium and hydrogen were used as carrier and fuel for FPD, respectively. Both injection and detection temperatures were maintained at 250 °C. Sample volume of 1.0 mL was injected without any solvent dilution. The removal percentage of sulfur compounds was calculated as follows:

$$Y = \frac{(C_o - C_t)}{C_o} \times 100\%$$

where C_o is the initial concentration of total sulfur in the diesel solution, and C_t is the total sulfur concentration in the treated diesel after reaction t min.

3. Results and discussion

3.1. Catalyst characterization

X-ray diffraction patterns of bimetallic and trimetallic oxides of MoO_3/Al_2O_3 catalysts are shown in Fig. 1. The diffraction patterns of bimetallic oxide catalyst of MoO_3/Al_2O_3 with tungsten (Fig. 1(b)) and vanadium (Fig. 1(c)) as dopants showed similar trend but higher degree of amorphous property than the undoped MoO_3/Al_2O_3 catalyst (Fig. 1(a)). The amorphous structure was shown by a marked decrease and broader intensity of MoO_3 (orthorombic) peaks observed for bimetallic oxide catalysts compared to undoped MoO_3/Al_2O_3 catalyst. Compared to $W/MoO_3/Al_2O_3$ and $V/MoO_3/Al_2O_3$ catalysts, the $Ti/MoO_3/Al_2O_3$ showed a different diffraction patterns since the reflection of MoO_3 phase almost undetected. Some MoO_3 peaks in XRD pattern were disappeared possibly due to the incorporation of Mo species into the bulk matrixes in the presence of titanium as dopant towardMoO_3/Al_2O_3 (Said, 1994). No reflections belonging to W, V or Ti oxides were observed in the XRD patterns emphasized the good dispersion of the deposited metal oxide species on the catalyst surface. Similar situation was observed on $Ti/W/MoO_3/Al_2O_3$ and $V/W/MoO_3/Al_2O_3$ where the catalysts were dominated by the alumina support. This result suggested that the addition of tungsten and vanadium as dopants and co-dopants into alumina supported molybdena catalyst contributes to the remarkable effect of Mo dispersion on the alumina support.

Fig. 2(a)–(c) shows the comparison of the effect of tungsten loading on the molybdena based catalyst. As shown in the micrographs, molybdena catalyst with 4.26 wt.% tungsten species obtained from 15:85 of W:Mo ratio showed well-dispersed homogeneous structure (Fig. 2(b)) and the particles of each element are distributed uniformly on the alumina surface. Fig. 2(d) and (e) shows the comparison of the co-dopants as the trimetallic molybdena based catalysts which are titanium (Fig. 2(d)) and vanadium (Fig. 2(e)) prepared from 5:15:80 of Ti/V:W:Mo ratios after calcination of the precursor at 600 °C.

$W/MoO_3/Al_2O_3$ catalyst with vanadium species as co-dopants showed some degree of dispersion with homogeneous structure. Meanwhile, for $W/MoO_3/Al_2O_3$ catalyst with titanium species as co-dopants, the particles formed agglomeration probably due to the incorporation of Mo species into the bulk matrixes, which lowered the surface contact area of active sites on the surface catalyst. This result was in parallel with XRD analysis obtained, which showed that the addition of titanium toward $W/MoO_3/Al_2O_3$ caused the reflection of MoO_3 species almost undetectable due to the incorporation of Mo species into the bulk matrixes.

Fig. 3 shows the TEM images of the $Ti/W/Mo/Al_2O_3$ and $V/W/Mo/Al_2O_3$ catalysts and calcined at 600 °C for 5 h. The polycrystalline structure could be correlated with γ-Al_2O_3. $Ti/W/Mo/Al_2O_3$ catalyst with molybdenum content of 16.07 wt.% has large crystalline particles with spherical struc-
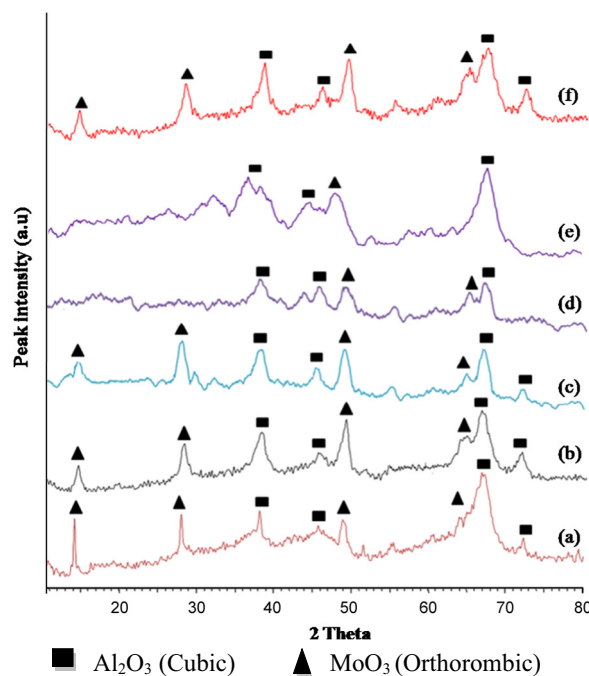


Figure 1 XRD diffractogram patterns of mono-, bi- and trimetallic oxide catalysts of (a) MoO_3/Al_2O_3, (b) WO_3/MoO_3 (15:85)/Al_2O_3, (c) V_2O_5/MoO_3 (15:85)/Al_2O_3, (d) TiO_2/MoO_3 (15:85)/Al_2O_3, (e) $Ti/WO_3/MoO_3$ (5:15:80)/Al_2O_3 and (b) $V/WO_3/MoO_3$ (5:15:80)/Al_2O_3 calcined at 600 °C for 5 h.

ture and composition appeared with size off the dark crystal was approximately 11–12 nm. Meanwhile, for the $V/W/Mo/Al_2O_3$ catalyst, smaller particles with spherical structure were also appeared with approximately 4–5 nm.

Results from textural characterization of MoO_3/Al_2O_3 and prepared bi- and trimetallic oxide catalysts are summarized in Table 1. Meanwhile, nitrogen adsorption/desorption isotherms of the catalysts can be seen in Fig. 4. From the isotherm plots, results showed that $V/W/MoO_3/Al_2O_3$ catalyst possessed higher surface area compared to $W/MoO_3/Al_2O_3$ and MoO_3/Al_2O_3 catalysts. It was clearly explained that by promoting the vanadium in MoO_3/Al_2O_3 catalyst gave a significant effect, where the catalyst led to the production of new active sites (refer Fig. 2). On the other hand, the degree of mesoporosity of Mo based catalysts decreased in the order of monometallic > bimetallic > trimetallic oxide catalysts, indicated by the type of hysteresis loop. Monometallic catalyst (MoO_3/Al_2O_3) showed isotherm characteristic of Type IV with an H2 hysteresis loop, indicating the bottle neck shape with narrow necks and wide body. However, the presence of dopants and co-dopants on the Mo catalyst exhibited similar isotherm characteristic, but in type H3 hysteresis loop with the presence of slit shape pores.

3.2. Catalytic evaluation in diesel fuel

In this section, the MoO_3-based bimetallic/trimetallic catalysts were investigated using different transition metal dopants/co-dopants (e.g., tungsten, vanadium and titanium) and dopant/co-dopant loadings in the Cat-ODS.
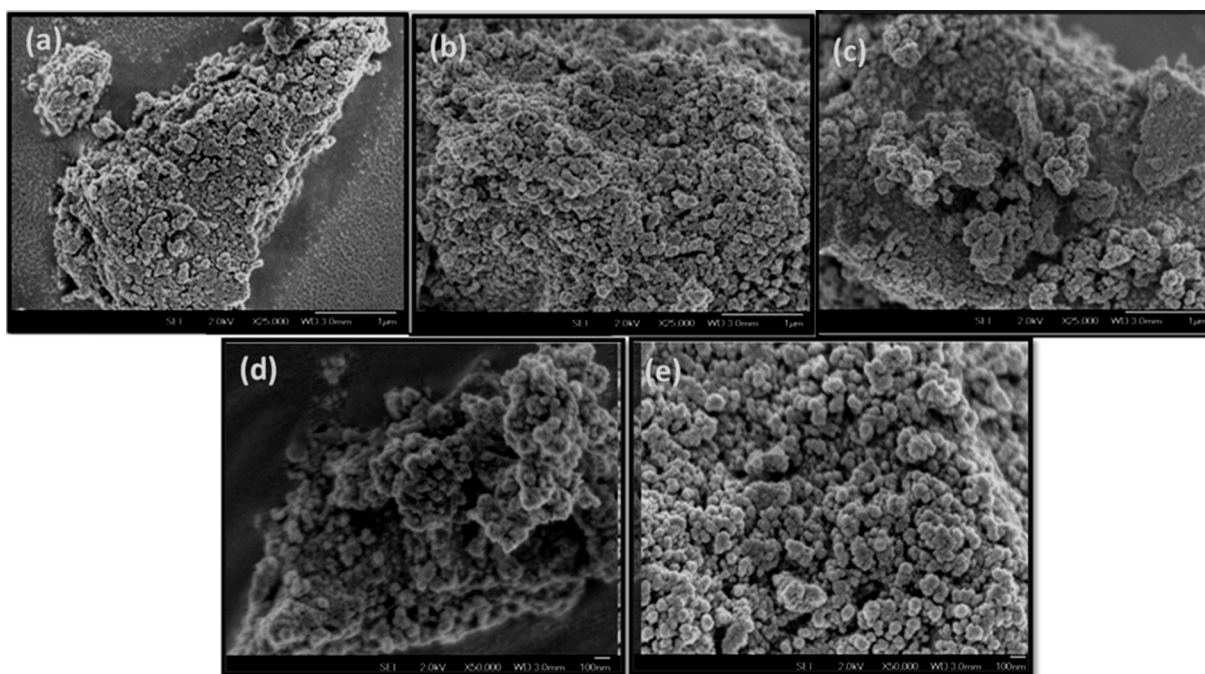
Figure 2 FESEM micrographs of (a) W/MoO$_3$ (5:95)/Al$_2$O$_3$, (b) W/MoO$_3$ (15:85)/Al$_2$O$_3$, (c) W/MoO$_3$ (25:75)/Al$_2$O$_3$, (d) Ti/WO$_3$/MoO$_3$ (5:15:80)/Al$_2$O$_3$ and (e) V/WO$_3$/MoO$_3$ (5:15:80)/Al$_2$O$_3$ calcined at 600 °C for 5 h.
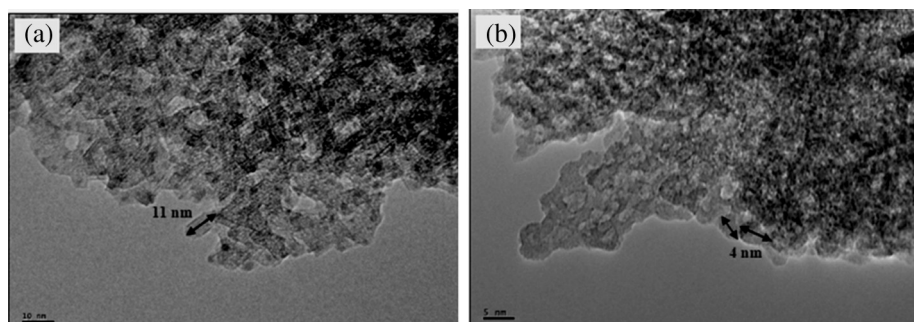
Figure 3 TEM micrographs of (a) Ti/WO$_3$/MoO$_3$ (5:15:80)/Al$_2$O$_3$ and (b) V/WO$_3$/MoO$_3$ (5:15:80)/Al$_2$O$_3$ calcined at 600 °C for 5 h.

**Table 1** Textural properties and elemental composition of alumina supported Mo based catalysts.

Catalyst/Al$_2$O$_3$	Catalyst ratio (wt.%)	S_{BET}[a] (m^2 g^{-1})	V_{Total}[a] (cm^3 g^{-1})	W_d[a] (nm)	Loading (wt.%)				
					V	W	Mo	Al	O
Mo	–	209	0.30	5.76	–	–	16.14	39.92	43.92
W/Mo	5:95	223	0.35	6.33	–	2.71	16.63	39.12	41.53
	15:85	216	0.33	6.35	–	4.26	16.12	38.87	40.75
	25:75	209	0.32	6.38	–	5.87	15.96	37.63	40.30
V/W/Mo	5:15:80	238	0.36	6.63	2.13	4.08	16.07	37.58	40.14
	10:15:75	230	0.34	6.66	3.37	4.11	16.13	37.29	39.12
	15:15:70	228	0.31	6.67	4.16	3.95	15.88	36.82	39.20

[a] S_{BET}: BET surface area, V_{total}: Total pore volume, W_d: Pore diameter.

3.2.1. Effect of dopant on MoO$_3$/Al$_2$O$_3$

Fig. 5 shows the effect of different dopants on Mo/Al$_2$O$_3$ catalyst in desulfurization of diesel fuel. Three types of dopants with the ratio of 15 wt.% have been investigated and the results (Fig. 5) demonstrate that the catalyst reactivity decreased in the order: W/Mo > V/Mo > Ti/
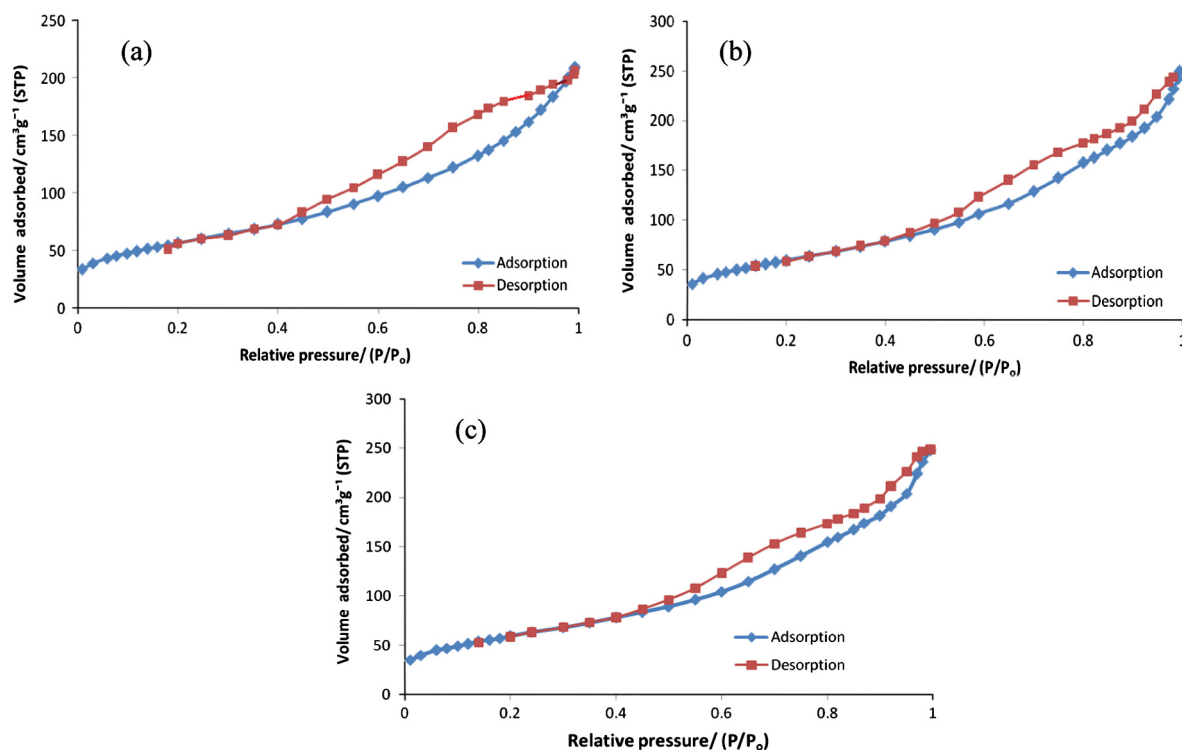
Figure 4 Isotherm plots of (a) MoO_3/Al_2O_3, (b) W/MoO_3 (15:85)/Al_2O_3 and (c) $V/W/MoO_3$ (5:15:80)/Al_2O_3 after calcined at 600 °C for 5 h.

Mo > Mo > without catalyst. As displayed in Fig. 5, W/ MoO_3/Al_2O_3 catalyst showed a highest conversion of sulfur removal: 88.7% (Th), 95.6% (DBT) and 94.2% (4,6-DMDBT) respectively. The addition of W is believed to increase the porosity of the catalyst structure, which could enhance the reaction of the substrate contact area and enhance the catalytic efficiency. This finding is in agreement with Dieterle et al. (2001) who stated that tungsten acts as a promoter and potentially stabilizes the intermediate Mo oxide by forming M–O bonds. On the contrary, $V/MoO_3/Al_2O_3$ catalyst has a slight decrease in the desulfurization yield. This result is in contradiction with Juniora et al. (2005) who reported that V was a promising dopant for catalyst which mainly acted as a textural promoter which can provide higher specific area and thus favoring the successive oxidation due to large substrate contact area. However, the introduction of Ti in MoO_3/Al_2O_3 led to significant decrease in catalytic activity. According to Cheng et al. (2006), the hydrophilic character of Ti-based catalyst caused water to absorb strongly on the catalyst surface, which inhibited the adsorption, and hence resulted in a remarkable decrease in the oxidation activity. On the other hand, alumina support showed a similar trend of desulfurization performance with the oxidative reaction in the absence of catalyst.
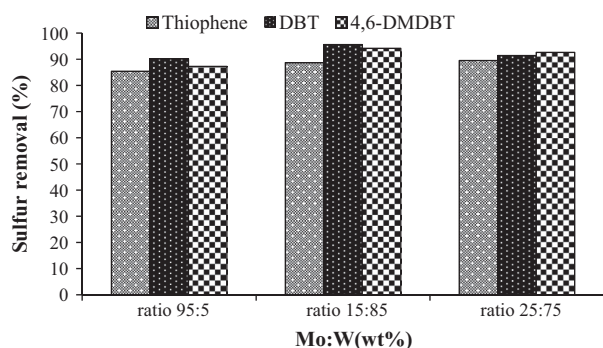
3.2.2. Effect of dopant ratio

The potential $W/MoO_3/Al_2O_3$ catalyst was further investigated on different W ratio and its catalytic performance is shown in Fig. 6. Result showed that 4.26%W/16.12%MoO_3/ Al_2O_3 catalyst prepared in the ratio of 15:85 (W/Mo) contributed to the highest removal of DBT (95.6%), 4,6-DMDBT (94.2%) and thiophene (88.7%), respectively. The
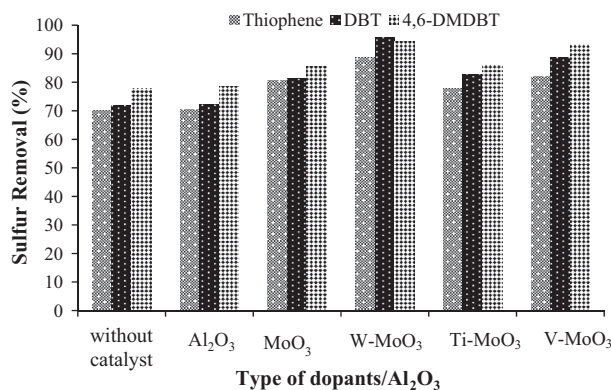
Figure 5 The effect of different dopants on MoO_3/Al_2O_3 catalyst on the performance of sulfur removal in Cat-ODS process.

addition of tungsten (4.26 wt.%) to the catalyst increased the conversion percentage and further increment of tungsten loading has no additional advantage on the catalytic activities. These results suggested that tungsten, which acts as promoter was unnecessary required in large quantity. Furthermore, this finding can be supported by FESEM micrograph (Fig. 2), where an excessive of tungsten in the catalyst caused the agglomeration of molybdenum oxide on the catalyst surface which lowered the degree of dispersion of molybdenum, decreased the number of coordinatively unsaturated sites, and thus possess weak catalytic activity. In view of these results, it can be concluded that the presence of tungsten at 4.26 wt.% is sufficient to serve as good structural promoter

Figure 6 Effect of tungsten dopant ratios on MoO_3/Al_2O_3 catalyst toward catalytic performance of sulfur removal in Cat-ODS process.

Figure 7 Effect of catalyst dosage on Cat-ODS reaction (reaction conditions: Oxidant = TBHP, T = 60 °C, time = 30 min, solvent = DMF, extraction T = 30 °C, mixing time = 30 min and no. of extraction stage = 1).

Table 2 Catalytic oxidative desulfurization of thiophene, DBT and 4,6-DMDBT over trimetallic catalyst by different co-dopants and co-dopant ratios.

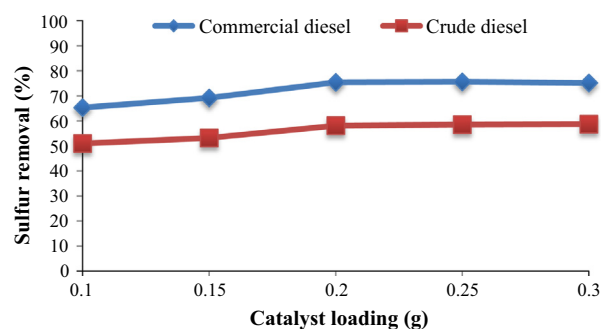| Catalyst/Al_2O_3	Catalyst ratio	Sulfur removal (%)		
		Th	DBT	4,6-DMDBT
MoO_3	–	81.3	84.7	86.6
W/MoO_3	15:85	88.7	95.6	94.2
$Ti/W/MoO_3$	5:15:80	89.7	94.2	93.2
$V/W/MoO_3$	5:15:80	94.5	100	100
$V/W/MoO_3$	10:15:75	92.9	97.8	95.7
$V/W/MoO_3$	15:15:70	89.5	92.2	91.4

which could significantly enhance the catalytic activity and selectivity of the catalyst.

3.2.3. Effect of co-dopant

Table 2 summarizes the catalytic oxidative desulfurization of thiophene, DBT and 4,6-DMDBT over trimetallic catalyst by different co-dopants and co-dopant ratios. From the results obtained, it can be seen that the $V/W/MoO_3/Al_2O_3$ performed a complete removal of DBT and 4,6-DMDBT, while for thiophene 94.5% was removed. Nevertheless, the elimination of thiophene, DBT and 4,6-DMDBT was slightly lower with 89.7%, 94.2% and 93.2% respectively when utilizing $Ti/W/MoO_3/Al_2O_3$ catalyst. The potential $V/W/MoO_3/Al_2O_3$ catalyst was then further investigated on different co-dopants ratios and the result showed that increase in the amount of vanadium toward $W/MoO_3/Al_2O_3$ decreased the efficiency of the sulfur removal.

3.2.4. Effect of catalyst dosage

Fig. 7 represents the effect of the dosage of 2.13%V/4.08% W/16.07%MoO_3/Al_2O_3 catalyst on the oxidative desulfurization of commercial diesel and crude diesel. A set of five different dosages of catalysts 0.10, 0.15, 0.20, 0.25 and 0.30 g were tested to determine the optimum amount of catalyst for oxidation reaction. Based on the results obtained, the catalyst dosage of 0.20 g has the highest sulfur removal compared to other catalyst loadings for both types of diesels. Interestingly,

when the catalyst dosage was increased up to 0.3 g, there was no significant difference in sulfur removal for both types of diesels. This was probably due to the catalyst reached its maximum catalyst loadings for the reaction and agglomeration of the catalyst particles, which led to decrease in the contact area between catalyst and diesel phase. Therefore, the sulfur removal of the diesel exhibited almost similar results even though the catalyst loadings were increased.

3.2.5. The series of oxidative desulfurization treatment on real diesel

Fig. 8 shows the series of oxidative desulfurization on real diesel comprising crude diesel and commercial diesel which contain 8269 ppmw and 550 ppmw of sulfur respectively. After a series of Cat-ODS process under optimum condition reaction, the sulfur content for both diesels achieved up to Green Diesel (10 ppmw) for commercial diesel fuel and Euro IV (<500 ppmw) standard for crude diesel fuel according to International Standard Diesel Fuel. In case of commercial diesel, there was about 75% of sulfur removal after single Cat-ODS process. In order to achieve Green Diesel (10 ppmw), second extraction has been conducted to remove the remaining sulfur in the diesel using other fresh solvent. With this second extraction, another 22.4% of sulfur was diminished which showed that Cat-ODS was a successful method to produce Green Diesel with 10 ppmw of sulfur content. Meanwhile using similar approach, crude diesel was treated up to four cycles of extraction with double oxidation process in order to achieve Euro IV (<500 ppmw) standard. It is because the sulfur content in the crude diesel was very high with various types of sulfur content which led to difficulties in removing most sulfur compound in the diesel fuel.

3.2.6. Reproducibility test of Cat-ODS process

The reusability of 2.13%V/4.08%W/16.07%MoO_3/Al_2O_3 catalyst was tested for five consecutive Cat-ODS cycles and is presented in Fig. 9. The catalyst was tested in a series of oxidation of commercial diesel by similar aforementioned conditions. For each run (30 min), more than 75% of the sulfur compounds were oxidized, and revealed the higher activity and selectivity of the catalyst toward sulfur compounds in diesel fuel. After each used, the catalyst was rinsed with methanol to remove any adsorbed sulfur compounds, followed by drying
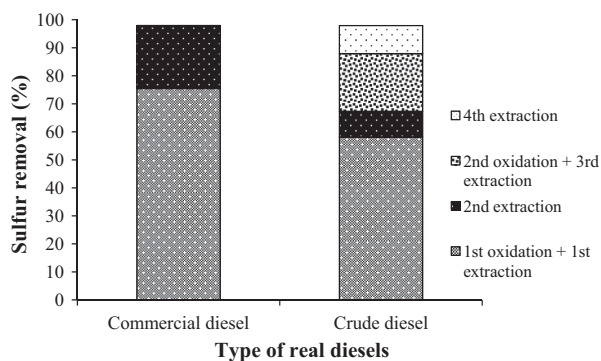
Figure 8 The series of oxidative desulfurization on real diesel (DMF to diesel volume ratio: 1.0 on each batch).
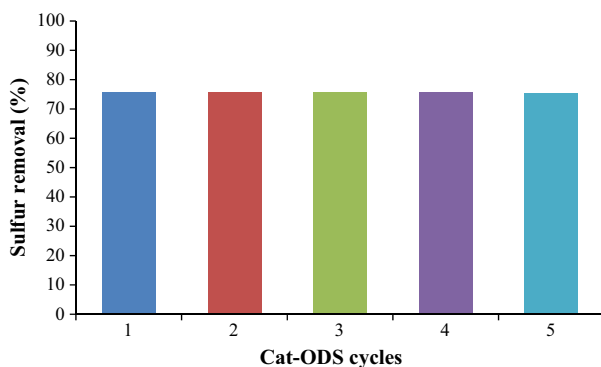
Figure 9 Reproducibility test of Cat-ODS process over 2.13%V/ 4.08%W/16.07%MoO$_3$/Al$_2$O$_3$ catalyst using commercial diesel. (Reaction conditions: Oxidant = TBHP, T = 60 °C, time = 30 - min, catalyst dosage = 0.1 g, solvent = DMF, extraction T = 30 °C, mixing time = 30 min and No. of extraction stage = 1).

at 80 °C and re-used for other reactions. The removal of sulfur during the reaction appeared to little changes through usage of five cycles. Results from EDX analysis over the used 2.13% V/4.08%/16.07%MoO$_3$/Al$_2$O$_3$ catalyst, proved the high reusable ability of the catalyst due to little change in elemental composition presented after usage of five cycles of the catalyst in Cat-ODS compared to fresh catalyst.

4. Conclusion

Trimetallic oxide catalyst of molybdena based on alumina support showed a great performance in desulfurization of model diesel and commercial diesel and also for crude diesel. The addition of tungsten and vanadium in an appropriate ratio onto the molybdena based catalyst led to a significant increase in the oxidation activity of the Cat-ODS process. These results indicate that 2.13%V/4.08%W/16.07% MoO$_3$/Al$_2$O$_3$ catalyzed on Cat-ODS system has the great potential to be employed in industrial to meet the future regulation of sulfur in diesel fuels.

Acknowledgments

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