The Preparation of FeMo/γ-Al₂O₃ Extruded Catalyst and Optimization of the Operating Conditions of the ODS of Light Oil Naphtha

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Preparation of the $5\%Fe10\%Mo/\gamma\text{-}Al_2O_3$ oxidative desulfurization (ODS) catalyst and optimization the ODS operating conditions (the effect of oxidant and catalyst amount, different time and temperature of the ODS activity test) of light oil naphtha are the main targets of this research. At first, the $5\%Fe10\%Mo/\gamma\text{-}Al_2O_3$ extruded catalyst was prepared by incipient wetness impregnation technique. The FeMo/γ-Al₂O₃ extruded catalyst was analyzed by N_2-adsorption/desorption (BET), X-Ray Diffraction Inductively (XRD), Scanning Electron Microscopy (SEM), NH_3-Temperature Programmed Desorption (NH_3-TPD), and Inductively Coupled Plasma-Mass Spectrometry (ICP-MS). The ODS activity tests of the FeMo/γ-Al₂O₃ extruded catalyst were investigated by the ODS setup with light oil naphtha as feed with 250 ppm total sulfur. In order to reach the desired ODS operating conditions, different quantities of oxidant, catalyst, time, and temperature of the ODS tests were examined with the ODS setup and the total sulfur of each test was recorded by the Rigaku apparatus. The best ODS operating conditions were 1 ml H_2O_2 as an oxidant, 1 g FeMo/γ-Al₂O₃ extruded catalyst, 100 min, and 50 °C. The total sulfur of light oil naphtha reached 45 from 250 ppm by this catalyst and ODS process.

Keywords: Catalytic oxidative desulfurization process, FeMo/γ-Al₂O₃ Extruded catalyst, Oxidative desulfurization of light oil naphtha

INTRODUCTION

The hydrodesulfurization process is the ordinary process of sulfur removal of the light oil naphtha. This process is the most applied process for sulfur removal of some thiophene spices and aliphatic sulfur compounds. This process is accomplished under high pressure and temperature in the presence of specific catalysts [1,2]. Although the advantages, the existing hydrodesulfurization could not meet the extremely low sulfur standard because of the limitations in the treatment of benzothiophenes (BTs) and dibenzothiophenes (DBTs) [3]. In comparison with the hydrodesulfurization process, the oxidative desulfurization (ODS) process is the best choice to remove sulfur from the light oil naphtha. As a result, the organic refractory of sulfur spices is oxidized to their related spices. These products can be removed by adsorption, extraction, decomposition, and distillation [4]. In the ODS process, hydrogen peroxide is commonly consumed as an oxidizing agent because it is low price and nonpolluting. In addition, it is commercially accessible, a weak oxidizing, and not a corrosive agent. Some researchers have described the consumption of polyoxometalate acids, organic acids, and their salts in the aqueous solution, as catalysts in the oxidation by hydrogen peroxide. It is hard to apart these homogeneous catalysts from the reaction products. But, the most favorable progression in the ODS process is synthesized the new catalysts [5-7].

ODS process is done in two parts. Firstly, as a result of a chemical reaction between an oxidizing agent and sulfur component, sulfur compounds oxidized to sulfone. Heavy sulfur compounds are oxidized to sulfone and sulfoxide by receiving one and two oxygen atoms, respectively. The oxidizing agents that are used in this step are organic and inorganic acid, catalyzed hydroperoxies, peroxides, peroxy salts, ozone dioxide, and nitrogen [8-11]. Hydrogen

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peroxide with low environmental pollution is the best oxidizing agent in the ODS process [4]. Finally, the oxidized sulfur is separated from oil due to use the polar solvent [12-14]. In this process, after converting sulfur components to sulfone, they are separated by extraction, distillation, and adsorption. Oxidation of thiophene spices to sulfonates increases their molecular weight and polarity that facilitates separation by adsorption, extraction, and distillation. Equation (1) shows the ODS process of 4,6-dimethyl dibenzothiophene (DBT) under low operating conditions and in the presence of a catalyst [15].

(1)
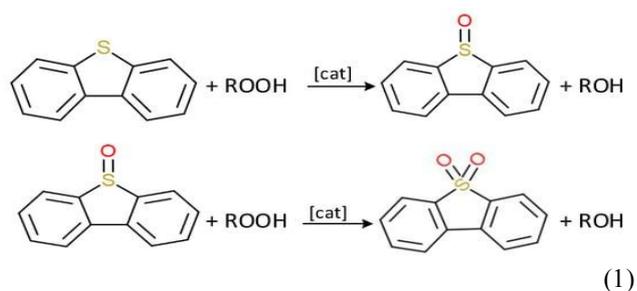
The ODS process of DBT reactions with catalyst

In refineries, sulphones are separated with high polarity solvents such as methanol, dimethylformamide, acetonitrile, and dimethyl sulfoxide [16]. In the ODS process, sulfur removal is mostly done by using polar solvents that can be regenerated and recycled by distillation [10]. Using suitable adsorbents such as silica gel, silica-alumina and zeolites is another way to remove sulfones [17-19]. The Unipure and Sulphu techniques are two new ODS processes that have been commercialized for sulfur removal. The two ODS processes vary in the mechanism and the type of oxidizing agent [19-22].

Most physical chemistry specifications of the ODS catalysts are similar. Although, differences in the synthesized process influenced their performance, mechanical strength, and activity [23]. One of the best catalyst support is gamma alumina. Because it has high specific surface area (170-270 m^2 g^{-1}), pore volume (0.5-0.8 cm^3 g^{-1}) and low price [22].

Beshkoofeh *et al*. (2021) [24,25] studied the influence of the pH, molybdenum amount, and some of the transition metals on the catalyst activity of the ODS process. The ODS activity was analyzed with ODS setup and synthesized catalysts. The catalyst with 10wt%Mo (as an active metal) and 5wt%Co content (as a promoter) at pH = 4 was selected as the best ODS catalyst. Tireli *et al.* (2020) [26] prepared three novel catalysts with an iron and molybdenum mixed oxide (Fe/Mo) on an aluminum pillared clay (Al-PILC) support. These materials were characterized by scanning electron microscopy/energy dispersive spectroscopy (SEM/EDS), X-ray diffraction (XRD), temperature programed reduction (TPR), and nitrogen (N2) physisorption at 77 K. Characterizations indicated that the metal particles were dispersed on the surface of the three catalysts. The catalytic tests showed good results for DBT oxidation using the synthesized catalysts, with high turnover frequency (TOF) values, particularly for the material with 5.0wt.%Fe/Mo. Syakila *et al.,* (2022) [27] studied ultra-low sulfur removal of diesel with low-cost technology under mild conditions. The CoFe/Al$_2$O$_3$ catalyst was prepared through the wet impregnation method. This catalyst was used as the catalyst for sulfur removal of diesel. Lopez Lona *et al.* (2021) [28] prepared New WFe oxides based catalysts by successive or simultaneous impregnation method on pseudo-boehmite in order to understand the role of Fe and evaluate the influence of the preparation method, W loading, and partial reduction of supported species, on the oxidative desulfurization (ODS) performance of dibenzothiophene compounds (DBTs).

This work represents the synthesized, characterized of the γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalysts. Furthermore**,** all the synthesized catalysts were characterized by N$_2$-adsorption/desorption, X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM), NH$_3$-Temperature Programmed Desorption (NH$_3$-TPD), and Inductively Coupled Plasma Mass Spectrometry (ICP-MS). The FeMo/γ-Al$_2$O$_3$ extruded catalyst is used for the ODS activity test of light oil naphtha with 250 ppm sulfur. The operating conditions of ODS are investigated in different quantities of oxidant, FeMo/γ-Al$_2$O$_3$ extruded catalyst, time, and temperature. According to the results, the best ODS activity test was selected.

EXPERIMENTAL

Materials

Table 1 shows the specifications of all raw materials

Table 1. Specifications of all the Raw Materials which are Used to Prepare FeMo/γ-Al$_2$O$_3$ Extruded Catalyst and ODS Activity Tests

No.	Chemical name	Purity	Company
1	Hydroxyethyl cellulose	Industrial grade	Iran
2	Ammonium hepta molybdate tetra hydrate	99%	Merck, Germany
3	Iron(III) chloride hexahydrate	99%	Merck, Germany
4	Distilled water	Industrial grade	Iran
5	Hydrogen peroxide	Industrial grade	Iran
6	Acetonitrile	Industrial grade	Iran
7	Methanol	Industrial grade	Iran
8	Phosphoric acid	Industrial grade	Iran
9	Ammonia	Industrial grade	Iran

which are used to prepare FeMo/γ-Al$_2$O$_3$ extruded catalyst and for ODS activity tests. The main raw material that was used as the precursor is boehmite powder with the Surface Area (SA) > 205 m^2 g^{-1}, Total Pore Volume (TPV) = 0.47 cm^3 g^{-1}, Average Pore Diameter (APD) = 8.08 nm, 100 mesh.

Analysis Equipment

The specific surface area (SSA), total pore volume (TPV), and average pore diameter (APD) of FeMo/γ-Al$_2$O$_3$ extruded catalyst were analyzed by using BET (Belsorp mini II, BEL JAPAN). All γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalysts were treated at the temperature of 300 ℃ for 3 h under vacuum before analysis in order to remove water and impurities (Belprep vac II, BEL JAPAN). This analysis was done in liquid nitrogen (N$_2$) at -196 ℃. The BET isotherms are used to determine the Brunauer-Emmett-Teller (BET). SSA, TPV, and APD distributions were specified by using the Barrett-Joyner-Halenda (BJH) method of the isotherm. The TPV was evaluated from the N$_2$ uptake value at P/P$_0$ = 0.98 (ISO 15901-2-2006, ISO 15901-3-2007). The XRD wide-angle patterns of the FeMo/γ-Al$_2$O$_3$ extruded catalysts were done with a P analytical X' Pert Pro model with a CuKα anti cathode (λ = 1.54 Å; 40 kV; 40 mA) between 10°-90° for 2θ. It uses a 0.1° step with an integration time of 4 s. The surface morphology of the FeMo/γ-Al$_2$O$_3$ extruded catalysts was accomplished by using SEM by ZEISS (Germany) SIGMA VP. NH$_3$-TPD analysis was accomplished with

Micromeritics ChemiSorb 2750 device. ICP-MS was accomplished with PerklinElmer, Optima 7300 model (U.S.A.). Furthermore, the catalytic oxidative desulfurization activity test is tested under the special feed (light oil naphtha) with 250 ppm of sulfur. The total sulfur of each ODS activity test was specified by Rigaku apparatus (U.S.A.) with a semiconductor Silicone PIN diode detector pursuant to ASTMD: 4294.

Oxidative Desulfurization Activity Test

ODS activity test was accomplished in a 100 ml jacketed round-bottom flask with a condenser and magnetic stirrer and recirculation water bath to control temperature and pressure. The 50 ml of light oil naphtha (250 ppm total sulfur) was used as feed in the bottom flask. In a common test, the FeMo/γ-Al$_2$O$_3$ extruded catalyst and H$_2$O$_2$ were mixed under strong stirring speed. At that time, the mixtures were maintained at 30 ℃. Then, the oil portion of the samples was decanted with the suitable solvent three times. The total sulfur was specified by the Rigaku apparatus. The specification of the light oil naphtha is shown in Table 2.

The Synthesized FeMo/γ-Al$_2$O$_3$ Extruded Catalyst

Boehmite powder as the precursor was mixed with 5% hydroxyethyl cellulose (HEC) as a binder. At the same time, the powder was blended with adequate distilled water (about 5 ml). The mixture was kneaded until it get a homogeneous paste. Next, the paste was passed through the extruder and dried for 2 h at room temperature. Then, the

Table 2. Specifications of the Light Oil Naphtha

No.	Analysis	Unit	Result	Method
1	Appearance	-	Yellow liquid	Visual
2	Density at 15.6 ºC	kg m^{-3}	736.1	ASTMD1298
3	Total sulfur	ppm	250	ASTMD4294
4	Flash point	ºC	Free	ASTMD93
5	Corrosion at 50 ºC	-	1a	ASTMD130
6	Distillation-IBP	ºC	75	ASTMD86
7	Distillation-5%	ºC	90	ASTMD86
8	Distillation-10%	ºC	95	ASTMD86
9	Distillation-20%	ºC	101	ASTMD86
10	Distillation-30%	ºC	106	ASTMD86
11	Distillation-40%	ºC	111	ASTMD86
12	Distillation-50%	ºC	115	ASTMD86
13	Distillation-60%	ºC	119	ASTMD86
14	Distillation-70%	ºC	125	ASTMD86
15	Distillation-80%	ºC	134	ASTMD86
16	Distillation-90%	ºC	146	ASTMD86
17	Distillation-95%	ºC	162	ASTMD86
18	Distillation-FBP	ºC	192	ASTMD86
19	Distillation-residue	Vol.%	1	ASTMD86
20	Distillation-loss	Vol.%	0	ASTMD86
21	Distillation at 380 ºC	Vol.%	-	ASTMD86

extruded was dried in an oven at 120 ºC for 24 h. Eventually, it was calcined up to 600 ºC in the furnace with temperature programing rate of 100 ºC h^{-1} to reach the extruded γ-Al$_2$O$_3$ catalyst support. Properly, the extruded γ-Al$_2$O$_3$ catalyst support had the following specifications (length = 2-7 mm, SSA = 155-205 m^2 g^{-1}, TPV < 0.75 cm^3 g^{-1}, APD = 13.58 nm). FeMo/γ-Al$_2$O$_3$ extruded catalyst was prepared by incipient wetness impregnation technique. In order to obtain FeMo/γ-Al$_2$O$_3$ extruded catalysts with 10%Mo and 5%Fe, 0.63g of ammonium hepta molybdate and 1.64 g iron(III) chloride hexahydrate were dissolved in a specific volume of distilled water. Afterwards, two solutions were mixed with 0.35 g phosphoric acid until to reach the solution with pH = 7. The extruded γ-Al$_2$O$_3$ catalyst support was placed in the rotary evaporator at 50 °C for 2 h with the solution of the mixed of the salts. Then, the wet extruded γ-Al$_2$O$_3$ catalyst support was impregnated in a thermal cabinet with a thermal programming rate of 10 ºC/20 min in the temperature range of (40-120) °C. The samples were dried in an oven at 120 °C for 24 h. In order to sit molybdenum and iron on extruded γ-Al$_2$O$_3$ catalyst support a, it must appear molybdenum oxide and iron oxide on the γ-Al$_2$O$_3$ catalyst support So, the extruded catalyst was calcined up to 600 ºC in the furnace with a temperature programing rate of 100 ºC h^{-1}.

The Effect of Oxidant Agent (H$_2$O$_2$) Quantity on the ODS Activity Test

ODS activity tests were done as in section 2.3. In a typical test, H$_2$O$_2$ with different quantities (0, 1, 2, 3, 4 ml) were blended with the light oil naphtha under the intense stirring speed. Next, the mixtures were maintained at 30 º C. Finally, the oil phase of the samples was decanted with extracted solvent three times. The total sulfur was measured by the Rigaku apparatus. Table 3 and Fig. 1 show the results

Table 3. The Results of the ODS Activity Test with Different Quantities of H$_2$O$_2$

H$_2$O$_2$ (ml)	0	1	2	3	4
Total sulfur (ppm)	250	115	105	98	82
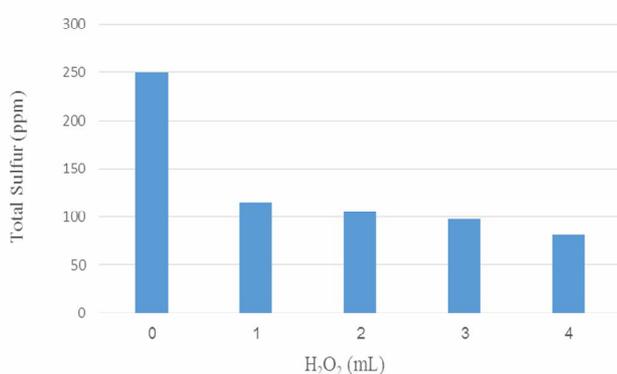
Fig. 1. Total sulfur verse different quantities of H$_2$O$_2$.

of the ODS activity test with different amounts of H$_2$O$_2$.

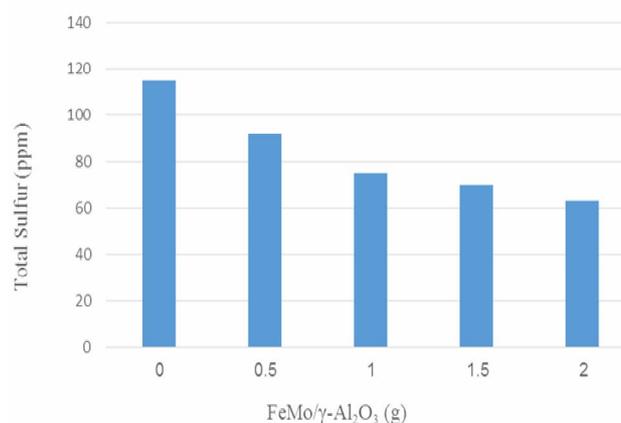## The Effect of the FeMo/γ-Al$_2$O$_3$ Extruded Catalyst Quantity on the ODS Activity Test

ODS activity tests were accomplished as the same as section 2.3. In a typical test, the FeMo/γ-Al$_2$O$_3$ extruded catalysts with different quantities (0, 0.5, 1, 1.5, 2 g) were slowly mixed with light oil naphtha and 1 ml H$_2$O$_2$ under the intense stirring speed. Next, the mixtures were maintained at 30 ºC. Finally, the oil phase of the samples was decanted with extracted solvent three times. The total sulfur was recorded by the Rigaku apparatus. Table 4 and Fig. 2 show the results of the ODS activity test with different amounts of FeMo/γ-Al$_2$O$_3$ extruded catalyst.
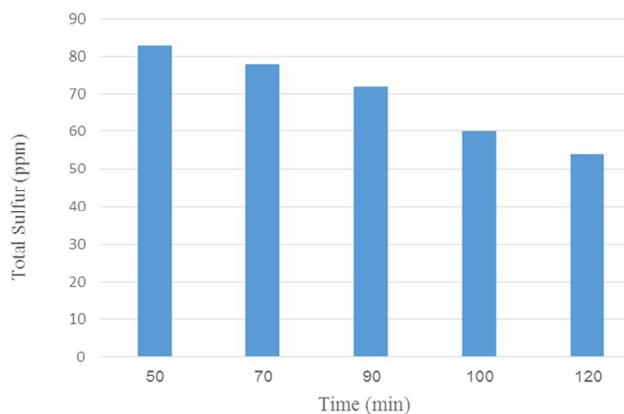
The Time Effect on ODS Activity Test

ODS activity tests were accomplished as the same as section 2.6 at different time (50, 70, 90, 100, and 120 min) at 30 ºC. Then the oil phase of samples was decanted with extracted solvent three times. The total sulfur was recorded by the Rigaku apparatus. Table 5 and Fig. 3 show the results of the ODS activity test at different times.

Table 4. The Results of the ODS Activity Test with Different Quantities of FeMo/γ-Al$_2$O$_3$ Extruded Catalyst

FeMo/γ-Al$_2$O$_3$ (g)	0	0.5	1	1.5	2
Total sulfur (ppm)	115	92	75	70	63

Fig. 2. Total sulfur verse different quantities of the FeMo/γ-Al$_2$O$_3$ extruded catalyst.

Fig. 3. Total sulfur verse different times (min).

Table 5. The Results of the ODS Activity Test with Different Times

Time (min)	50	70	90	100	120
Total sulfur (ppm)	83	78	72	60	54

The Temperature Effect on ODS Activity Test

ODS activity tests were accomplished as the same as the previous section at different temperatures (30, 40, 50, 60, and 70 ºC). The mixtures were blended for 100 min. Then, the oil phase of samples was decanted with extracted solvent three times. The total sulfur was recorded by the Rigaku apparatus. Table 6 and Fig. 4 show the results of the ODS activity test with different temperatures.

RESULTS AND DISCUSSION

Catalyst Characterization

Catalyst synthesized procedure can also play an important role in evaluating the efficiency of the catalyst. Table 7 shows the physical chemistry properties of γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalyst. The BET results show that the amounts of SSA, APD, and TPV of FeMo/γ-Al$_2$O$_3$ extruded catalyst decreased with the impregnation of two metals on the γ-Al$_2$O$_3$ [29]. The pore size distribution of the γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalysts that were analyzed by the BJH method were shown in Fig. 5. The figure shows that the γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalysts have the same mesoporous structure. According to Fig. 6 and IUPAC classification, γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalyst showed type IV isotherms with H$_2$ hysteresis loop. Most mesoporous materials owing to complex pore networks are made up of pores with wide pore size distribution [29].
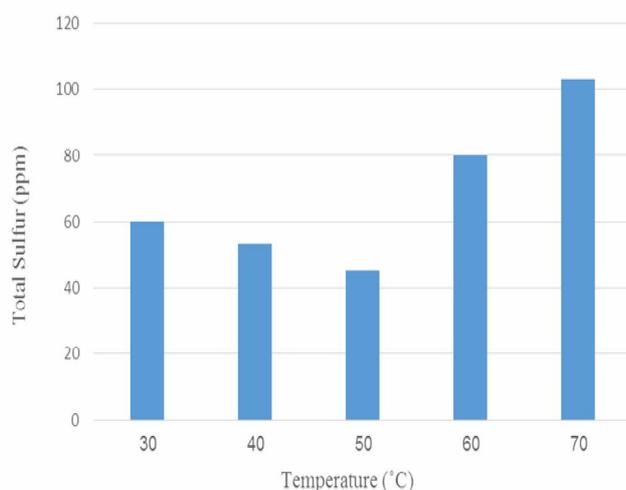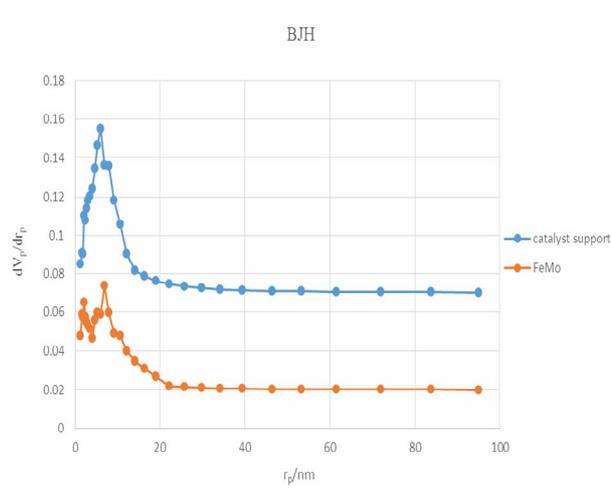

Fig. 5. BJH plot of the γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalyst.
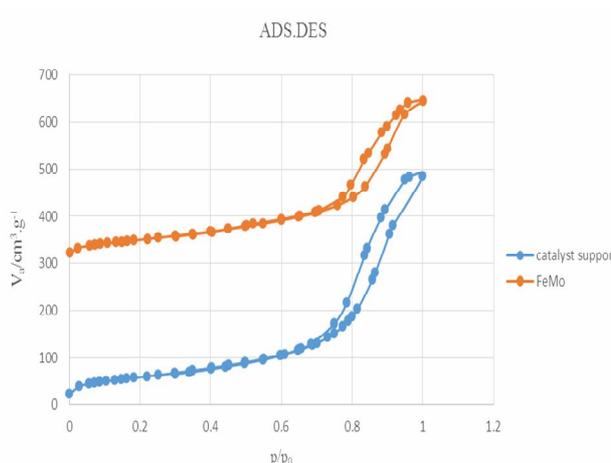

Fig. 6. Adsorption/Desorption isotherms of the γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalyst.

Table 6. The Results of the ODS Activity Test with Different Temperatures

Temperature (º C)	30	40	50	60	70
Total sulfur (ppm)	60	53	45	87	103

Fig. 4. Total sulfur verse different temperatures (ºC).

Table 8 shows the results of the ICP-MS analysis of the γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalyst [30]. The presence of phosphorus is often applied as a secondary

Table 7. The BET, BJH Results of the γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ Extruded Catalyst

| Catalyst	BET			BJH (Adsorption branch)		
	APD (nm)	SSA (m^2 g^{-1})	TPV (cm^3 g^{-1})	TPV (cm^3 g^{-1})	PR (nm)	SSA (m^2 g^{-1})
γ-Al$_2$O$_3$	13.58	215.43	0.75	0.75	6.03	237.97
FeMo/γ-Al$_2$O$_3$	11.49	162.48	0.52	0.52	6.91	173.60

promoter. To improve the efficiency of the catalyst for the ODS activity test by having a useful influence, the addition of phosphoric acid during the catalyst synthesis is required. The increased influence of phosphorus on the activity of a FeMo/γ-Al$_2$O$_3$ extruded catalyst is rarely described as a function of an improvement of dispersion of the precursor on the γ-Al$_2$O$_3$. Because of the large solubility of the metal salts on the γ-Al$_2$O$_3$ in the phosphoric acid-containing impregnation solution, the deposition of large crystalline aggregates on the γ-Al$_2$O$_3$ surface is minimized [30].

XRD technique was used to gain insight into the crystallites of catalyst, chemical component, and presence of Fe and Mo on γ-Al$_2$O$_3$. XRD wide-angle analyses were accomplished at 2θ (10°- 90°) and the scans are shown in Fig. 7. Two obvious diffraction peaks that appeared at 2θ (45° and 67º) for γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalyst are appointed to γ-Al$_2$O$_3$. It is concluded that the impregnation of iron and molybdenum did not affect the γ-Al$_2$O$_3$ crystalline phase of γ-Al$_2$O$_3$ [31]. The results of XRD analysis can be approved that almost two metals appeared at their previously reported peaks, iron oxide (Fe$_2$O$_3$) at 2θ = 24°, 33°, 35°,37, 45°, and 67° [31]. Two peaks exist at 2θ = 45° and 67° for Fe$_2$O$_3$. They are near specific peaks of γ-Al$_2$O$_3$ and they can be assigned to the overlap of Fe$_2$O$_3$ and γ-Al$_2$O$_3$ [33]. Furthermore, Fe$_2$O$_3$ (having a relative peak) was confirmed in XRD scan that indicates the presence of crystalline iron oxide, though in small amount. It is further believed that the species exists in a material present at concentrations lower than 5wt%, so they cannot be properly detected by the XRD technique. According to the above explanations, very weak peaks of iron were observed for all the oxide phases.

Figure 8 shows the SEM images and shows that no agglomeration of iron and molybdenum exists (right figure) on the FeMo/γ-Al$_2$O$_3$ extruded catalyst. It was found that

Table 8. The ICP-MS Results of the γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ Extruded Catalyst

Catalyst	Al wt.%	Mo wt.%	Fewt.%	Pwt.%
γ-Al$_2$O$_3$	54.97	-	-	-
FeMo/γ-Al$_2$O$_3$	54.68	8.34	3.02	1.17
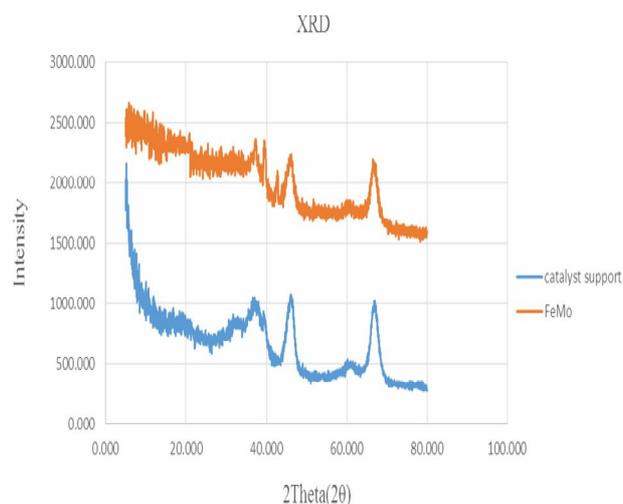
Fig. 7. XRD analysis spectrum of the γ-Al$_2$O$_3$ and FeMo/γ-Al$_2$O$_3$ extruded catalyst.

impregnation and distribution of iron and molybdenum happened excellent on the γ-Al$_2$O$_3$. Thus, a more homogenous impregnation occured. Moreover, these two metals (iron and molybdenum) lead to the synthesis of FeMo/γ-Al$_2$O$_3$ extruded catalyst with identical particle size distribution.
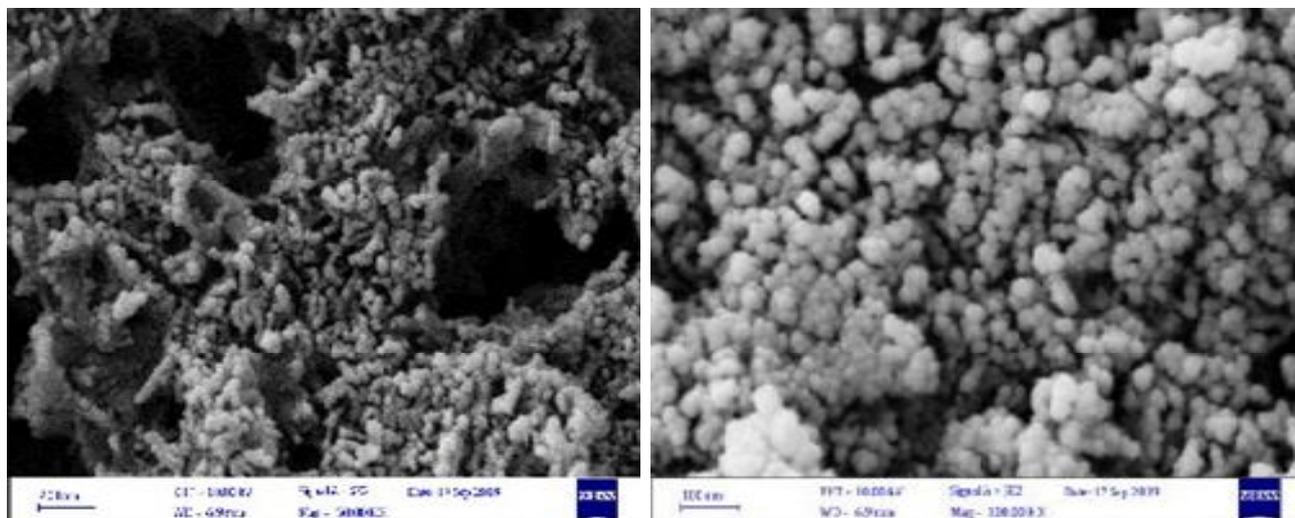
Fig. 8. SEM Images of the γ- Al_2O_3 (left) and FeMo/γ-Al_2O_3 extruded catalyst (right).

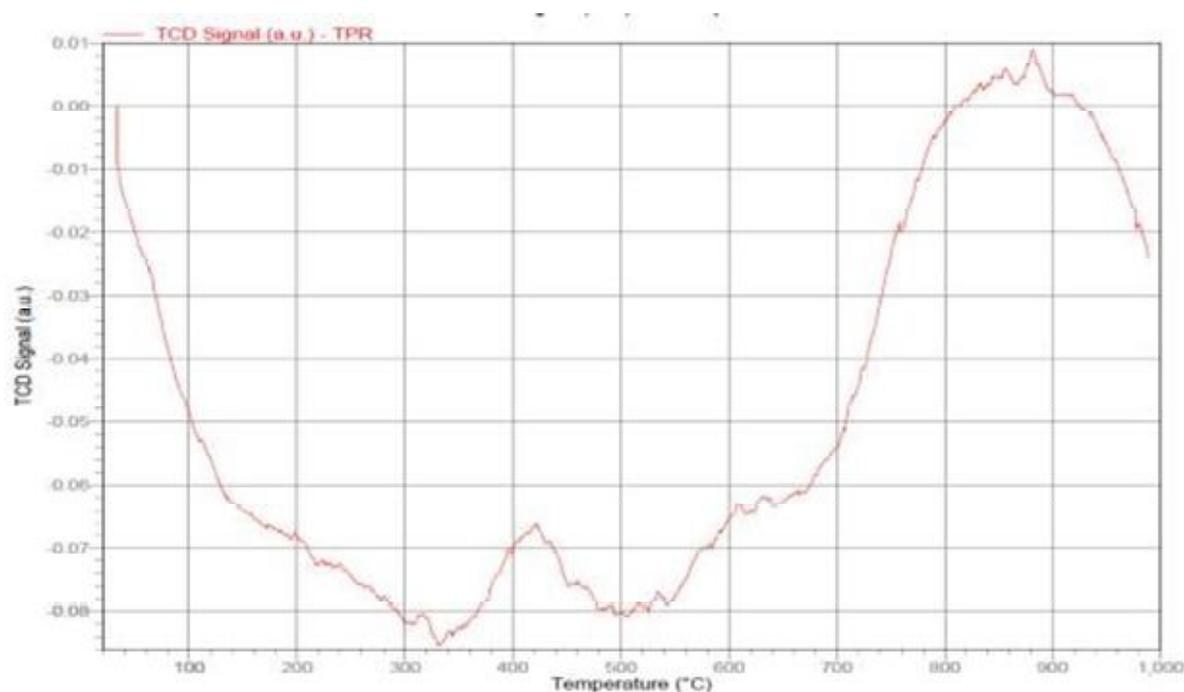**Fig. 9.** NH_3-TPD analysis spectrum of the FeMo/γ-Al_2O_3 extruded catalyst.

Figure 9 shows the NH_3-TPD pattern of the FeMo/γ-Al_2O_3 extruded catalyst. For FeMo/γ-Al_2O_3 extruded catalyst, the spectrum showed two well determined peaks at 420 °C and 880 °C. The results of this part showed that two kinds of adsorption sites for NH_3-TPD were present on the FeMo/γ-Al_2O_3 extruded catalyst. The peak at the temperature of 880 °C is owing to the release of N_2 and H_2 from the decomposition of NH_3. The peak at the temperature of 420 °C is owing to the release of the adsorbed NH_3 from γ-Al_2O_3 and shows strong acidic sites.

The Effect of the Oxidant Agent Quantity on ODS Activity Test

Hydrogen peroxide (H$_2$O$_2$) as an oxidant was used for the ODS activity test of light oil naphtha. By using H$_2$O$_2$, two phases as an aqueous polar phase including an oil nonpolar phase and the oxidant were cleared. As a result, mass transfer challenges can happen to make the ODS more hard by the separation of the reactants [34]. The quantity of H$_2$O$_2$ consumed could also be one of the important parameters that influence the ODS activity test [35-37]. For economic and environmental challenges, reducing the quantity of H$_2$O$_2$ is a purpose in the improvement of the ODS activity test. When the H$_2$O$_2$ quantity was under 1 ml, small significant sulfur removal occurred. When the H$_2$O$_2$ quantity was between 1-2 ml, sulfur removal is significantly increased. This high quantity of H$_2$O$_2$ could be explained, not only by the initial sulfur content, but also by the nature of the light oil naphtha used requiring high H$_2$O$_2$ quantity because of side reactions that can happen, such as oxidation of aromatic hydrocarbons. Thus, according to the economic and environmental aspects, 1 ml H$_2$O$_2$ was selected as the best and optimum quantity of the oxidant.

The Effect of the FeMo/γ-Al$_2$O$_3$ Extruded Catalyst Quantity on the ODS Activity Test

The improvement conditions are favorable using developed heterogeneous catalytic systems because of the catalyst's excellent performance and separation. The main important factors must be taken into regard when it gains to low sulfur of light oil naphtha. Firstly, light oil naphtha has medium viscosity, accordingly, the conditions of mixing are very important to affirm a through the mixed system. The ODS activity test was done in the presence of FeMo/γ-Al$_2$O$_3$ extruded catalyst and H$_2$O$_2$. This paper concentrated on the ODS activity test of light oil naphtha with 250 ppm sulfur content, catalysts mostly have one impressive phase such as transition metals which are impregnated on extruded γ-Al$_2$O$_3$ with a large specific surface area [38]. Among transition metals, the molybdenum [39] was applied as an active metal and iron was used as a promoter. Because of economic and environmental challenges, reducing the quantity of FeMo/γ-Al$_2$O$_3$ catalyst is a target for the improvement of ODS activity. When the quantity of FeMo/γ-Al$_2$O$_3$ extruded catalyst was below 1 g, it was seen no remarkable sulfur removal. Indeed, when the quantity of FeMo/γ-Al$_2$O$_3$ extruded catalyst was between 1-2 g, it was seen considerable sulfur removal. So, regarding the economic and environmental aspects, 1 g was the best quantity of FeMo/γ-Al$_2$O$_3$ extruded catalyst.

The Reaction Time Effect on the ODS Activity Test

The reaction time is one of the main and important factors of the ODS activity test. The reaction time was investigated between 50 and 120 min in six ODS activity tests [24]. Table 5 shows the results of the ODS activity tests. According to Table 5, it has specified the best desulfurization of light oil naphtha in 100 min by using 1 ml H$_2$O$_2$ and 1 g catalyst. This reaction time was often related to the multiple steps used for the addition of catalyst and oxidant with light oil naphtha. According to the results, sulfur removal has not remarkably reduced by increasing the reaction time to 100 min. So, 100 min was selected as the best ODS reaction time.

The Reaction Temperature Effect on ODS Activity Test

The reaction temperature is the other main factor in the ODS activity test that was investigated in this research. The reaction temperature of the ODS activity test is usually between 30 and 70 °C. Because of the low viscosity of the light oil naphtha, the high reaction temperature was not investigated. According to the ODS activity test results, sulfur removal was increased by increasing the reaction temperature from 30 °C to 50 °C. But by increasing the reaction temperature to more than 50 °C, had an inverse on sulfur removal [24].

Table 5 showed the obtained results of the catalytic ODS activity tests were done at different temperatures of light oil naphtha, taking into consideration the complexity and the higher viscosity of the gas oil mixture. Therefore, 50 °C was chosen as the optimum catalytic ODS temperature.

CONCLUSIONS

The HDS process is done at high pressure, high temperature, and consumes large amounts of hydrogen. Because of that, the HDS process is an expensive and not economical method. Therefore, in this research, the ODS

process is introduced as an alternative to the HDS process and is investigated the ODS operating conditions. Firstly, 5%Fe10%Mo/γ-Al$_2$O$_3$ extruded catalyst was synthesized as an ODS catalyst. The effect of the different quantities of H$_2$O$_2$ and FeMo/γ-Al$_2$O$_3$ extruded catalyst, time, and temperature on the ODS process were tested with light oil naphtha as feed (total sulfur 250 ppm). The results of these ODS activity tests showed that the best quantity of H$_2$O$_2$ and FeMo/γ-Al$_2$O$_3$ extruded catalyst were 1 ml and 1 g, respectively. According to the results of the ODS activity test, 100 min and 50 ℃ were chosen as the best ODS operating conditions. With the best ODS condition, the total sulfur reached 45 ppm from 250 ppm. As the result of impregnated Mo and Fe on the γ-Al$_2$O$_3$ catalyst support, the performance of the ODS catalyst was increased and caused to improve the ODS activity.

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