

Optimization of the Oxidative Desulfurization Process of Light Cycle Oil with NiMo/ γ Al₂O₃ Catalyst

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A large amount of what is produced by the fluid catalytic cracking unit in oil refineries is light cycle oil. Light cycle oil usually contains high levels of sulfur compounds, such as thiophene and dibenzothiophene. In this work, sulfur was removed by catalytic oxidative desulfurization. First, the mesoporous 5%Ni10%Mo/ γ -Al₂O₃ catalyst was prepared by the incipient wetness impregnation method. The prepared catalysts were characterized by X-ray diffraction, N₂ adsorption/desorption, inductively coupled plasma mass spectrometry, scanning electron microscopy, and NH₃ temperature-programmed desorption. The catalytic activity was measured with catalytic oxidative desulfurization, and light cycle oil was used as feed, with 13000 ppm total sulfur. To reach the optimum condition for the oxidative desulfurization process, the effects of different oxidants, catalysts, time periods, and temperatures on the oxidative desulfurization process were investigated. The optimum condition for the oxidative desulfurization process was obtained at 1 g 5%Ni10%Mo/ γ -Al₂O₃ catalyst, 1 ml H₂O₂ as an oxidant, 30 °C, and 120 min. At this optimum condition, the total sulfur in light cycle oil was reduced from 13000 to 623 ppm.

Keywords: Oxidative desulfurization catalyst, NiMo/ γ -Al₂O₃ catalyst, Light cycle oil desulfurization

INTRODUCTION

Fluid catalytic cracking units are designed to convert a mixture of refined furnace oil, produced from light cycle oil (LCO), and heavy diesel oil into lighter and more valuable products, such as liquid gas, gasoline, and light diesel fuel. The removal of sulfur from LCO is one of the main priorities of the refineries. LCO usually contains high levels of sulfur. Most of the sulfur present in LCO is found in thiophene and dibenzothiophene. It is difficult to remove sulfur compounds with thiophenic structures by catalytic hydrodesulfurization, but such compounds can be easily removed by oxidative desulfurization (ODS). In the ODS process, the thiophenic compounds are oxidized to sulfoxides and sulfones. Then, these compounds, due to

their increased polarity, can be separated from LCO using solvent extraction. Since the ODS process can be performed under mild temperature and pressure conditions, it has been used widely recently [1].

ODS takes place in two steps. Firstly, sulfur compounds change as a result of a chemical reaction between sulfur and an oxidizing agent. Then, without breaking the C-S bond, heavy sulfur compounds are oxidized to sulfoxides and sulfones by taking one and two oxygen atoms, respectively. The oxidizing agents used in this step are organic and inorganic acid peroxides, catalyzed hydroperoxides, peroxy salts, and nitrogen and ozone dioxide [2,3]. Another oxidant with low environmental pollution that can be used in the ODS process is hydrogen peroxide [4]. In the second step, the oxidized sulfur compounds are extracted from oil due to the increase in their polarity [5-7]. In this process, after sulfur compounds are converted to sulfones, they are

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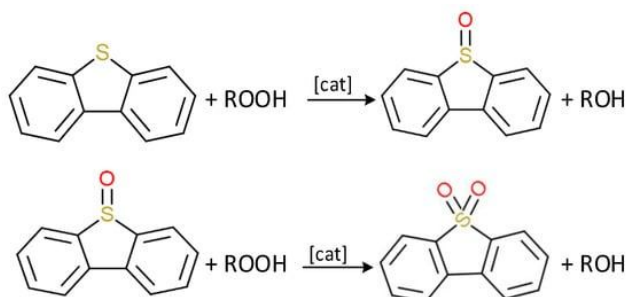


Fig. 1. The catalytic ODS process of DBT under mild conditions.

extracted using methods such as extraction, distillation, and adsorption. Oxidation of thiophene derivatives to sulfonates increases their polarity and molecular weight, which, in turn, facilitates their separation by extraction, distillation, and adsorption. Figure 1 shows the oxidation mechanism of 4,6-dimethyl dibenzothiophene (DBT) in the presence of a solid catalyst and under mild operating conditions [8].

In the ODS process, sulfones are extracted by high polarity solvents, such as methanol, acetonitrile, dimethylformamide, dimethyl sulfoxide [9]. In refineries, extraction is mainly done by solvents that can be recovered and reused in the distillation process [3]. Adsorption of sulfones on adsorbents is another method of removing sulfones [10,11]. Adsorbents such as silica-alumina and silica gel are more effective than other adsorbents such as zeolites, activated carbon, and gamma alumina ($\gamma\text{-Al}_2\text{O}_3$) in adsorbing sulfonates from oxidized diesel fuel [12].

The SulphCo and UniPure processes are two new ODS technologies commercialized to produce ultra-low sulfur oil. These two ODS processes are different in terms of oxidation mechanism, type of oxidizing agent, and method of sulfone separation [12-15].

In the SulphCo process, ultrasound is used for ODS. Ultrasonic energy increases the percentage of sulfur removal in diesel fuels. Hydrogen peroxide is used as an oxidant in the presence of tungsten phosphoric acid. If ultrasound intensity is large enough, it can lead to induced cavitation and, in the presence of hydrogen peroxide as an oxidizing agent, rapid reactions. During the same time that cavitation occurs, the bubbles grow, become unstable, and disintegrate, resulting in an increased temperature, increased

pressure, severe cutting, and mixing, which together reduces the reaction time. In addition, ultrasonic waves increase the level of molecular energy and the rate of reactions [13]. The SulphCo process is carried out under atmospheric pressure at the temperature of 80-70 °C. The first ultrasonic unit was built at Industria Piemontese Lavorazione Oli Minerali (IPLOM) oil refinery near Genoa, Italy [3].

The UniPure process is developed by UniPure and Texaco. In this process, the sulfur compounds are oxidized to sulfone using a combination of hydrogen peroxide and formic acid as the oxidizing agent. Then, the sulfone is separated, washed, and dried. In the next step, the sulfone is passed through alumina, as an adsorbent, to separate the sulfonates by adsorption and then regenerated by rinsing with methanol. The ODS process occurs at mild temperature and pressure conditions. The sulfonates obtained are sent to the refinery coking unit. The UniPure process is used at the Springs Refinery, USA [14,15]. The advantages of this process are a reasonable price, low temperature and pressure, shorter time, and no use of hydrogen gas. The UniPure process can produce feed with more than 1500 ppm sulfur, diesel, and gasoline fuel with sulfur content less than 5 ppm, which costs 50% less than the hydrogen desulfurization method [15].

Most ODS catalysts have the same chemical properties, but the differences in their production process cause them to differ in their performance, activity, and mechanical strength [16]. Due to its reasonable price, specific surface area ($170\text{-}270\text{ m}^2\text{ g}^{-1}$), and pore volume ($0.5\text{-}0.8\text{ cm}^3\text{ g}^{-1}$), Gamma alumina is the most used catalyst support [15].

Abu Bakar *et al.* (2016) studied crude oil with 1.13 wt% S [17]. They managed to decrease the desulfurization activity up to 0.74 wt% S by increasing the oxidant:sulfur (O:S) mole ratio from 1:1 to 5:1. Farshi *et al.* (2015) used the ODS method for the sulfur removal of fuel oil, and the results showed that the sulfur content decreased from 2.75 wt% S to 1.14 wt% S [18]. Ogunlaja *et al.* (2017) used the ODS of aromatic fraction of fuel oil to remove sulfur compounds oxidized with tert-butyl hydroperoxide. Nanofibers were used as adsorbents of sulfones. The sulfur content reduced from 1.8% to 0.89%. The amount of oxidant used was 10 times premier than that needed by the stoichiometry of the reaction between oxidant and sulfur (O:S ratio equal to 20), a finding confirmed by the nature of

Table 1. The Specifications of Raw Materials

No.	Chemical name	Purity	Company
1	Hydroxyethyl cellulose	Industrial grade	Iran
2	Ammonium heptamolybdate tetrahydrate	99%	Merck, Germany
3	Nickel(II) nitrate hexahydrate	98%	Applychem, Germany
4	Distilled water	Industrial grade	Iran
6	Hydrogen peroxide	Industrial grade	Iran
7	Acetonitrile	Industrial grade	Iran
8	Methanol	Industrial grade	Iran
9	Ammonia	Industrial grade	Iran

the fuel oil [19]. Krivstov *et al.* (2013) investigated of oxidation of oil feed at 35 °C. The oxidation of high sulfur fuel oil by hydrogen peroxide (H₂O₂) and formic acid, with the oxidant to acid (H₂O₂:HCOOH) molar ratio of 3:4, followed by the adsorption of oxidized products with silica gel, decreased the total sulfur from 1.19 wt% S to 0.05 wt% S within 8 h. Moreover, the composition of the fuel oil before and after adsorption was studied, and the results showed some changes in the composition of oil fuel. The comparative content of saturated HCs increased due to the removal of oxidized aromatic hydrocarbons and sulfur compounds after the ODS process and adsorption [20]. Toteva *et al.* (2009) found that the sulfones concentration reduced after 2 h of reaction time owing to their oxidation into sulfates when 0.6 wt% S of LCO was oxidized with hydrogen peroxide and acetic acid [21].

In this work, the catalytic ODS of LCO was carried out with desirable results. The mesoporous NiMo/ γ -Al₂O₃ catalysts were prepared and characterized. Moreover, the as-synthesized catalyst was characterized by X-ray diffraction (XRD), N₂ adsorption/desorption, inductively coupled plasma mass spectrometry (ICP-MS), scanning electron microscopy (SEM), and NH₃ temperature-programmed desorption (NH₃-TPD). The prepared catalysts were applied to the ODS process of LCO with 13000 ppm sulfur. The operating conditions of ODS were examined with different amounts of catalysts and oxidants and different temperatures and time periods. The optimized operating condition was chosen based on the results of the ODS process.

EXPERIMENTAL

Materials

In this research, the boehmite powder, with a surface area (SA) of > 200 m² g⁻¹, a pore volume (PV) of 0.48 cm³ g⁻¹, and an average pore diameter (APD) of 8.10 nm, 100 mesh, was used as the precursor. The specifications of other raw materials are listed in Table 1.

Characterization

The specific surface area and pore volume of catalysts were measured using N₂ adsorption/desorption porosimetry (Belsorp mini II, BEL Japan). All catalysts were degassed under vacuum at the temperature of 250 °C for 3 h before each measurement (Belprep vac-II, BEL Japan). The examination was made in liquid nitrogen at -196 °C. The N₂ adsorption/desorption isotherms were used to measure the Brunauer-Emmett-Teller (BET) specific surface area. Pore volume and pore diameter distribution were determined using the Barrett-Joyner-Halenda (BJH) method of isotherm. The total pore volume was estimated from the N₂ uptake at P/P₀ = 0.98 (ISO 15901-2-2006, ISO 15901-3-2007). The XRD patterns of the synthesized catalysts were recorded on a P analytical X'Pert Pro model, equipped with a CuK α anticathode (λ = 1.54 Å; 40 kV; 40 mA) for 2 θ between 5° and 85°. It uses a 0.1° step with an integration time of 4 s. Additionally, ICP-MS was carried out with Perkin-Elmer (Optima 7300, U.S.A.). The surface morphology of the catalysts was conducted using scanning electron microscopy (SEM) (Zeiss Sigma, VP (Germany)).

The catalysts were characterized by NH₃-TPD analysis and using a Micromeritics ChemiSorb 2750 instrument. The catalytic ODS activity test was performed by the special feed with 13000 ppm of sulfur. After this stage, the total sulfur at different conditions was determined by Rigaku devices (U.S.A.) and a semiconductor detector (*i.e.*, Silicone PIN diode detector) according to ASTM D4294.

Catalytic Oxidative Desulfurization Activity

Catalytic experiments were carried out in a 100 ml jacketed round-bottom flask, equipped with a condenser, magnetic stirrer, and recirculation water bath to control temperature and pressure. Fifty ml of LCO (13000 ppm total sulfur) was used as the oil feed. In a typical run, the prepared 5%Ni10%Mo/-Al₂O₃ catalyst and H₂O₂ were slowly suspended at a vigorous stirring speed in an oil feed. Afterward, the mixtures were left at room temperature. Then, the oil phase of samples was removed three times with the extraction agent. The total sulfur was determined by Rigaku devices. The feed specifications of the LCO used are given in Table 2.

The Preparation Extrudates 5%Ni10%Mo/-Al₂O₃ Catalyst

Boehmite powder was blended with 5% hydroxyethyl cellulose (HEC). Then, adequate water (about 5 ml) was added to it. The mixture was kneaded until a homogeneous paste was obtained. The alumina paste was passed through the extruder, dried for 2 h at room temperature, and kept in an oven at 120 °C for 24 h. Then, it was calcined up to 600 °C using a furnace, with a temperature programming rate of 100 °C h⁻¹, to catch the untreated catalyst support. In this section, the gamma alumina phase is formed from the boehmite powder. The catalyst support had the following properties: length = 2-7 mm, outer diameter = 1.50 mm, SA = 150-200 m² g⁻¹, PV < 0.73 cm³ g⁻¹, APD = 13.55 nm). 5%Ni10%Mo/Al₂O₃ catalyst was prepared by the incipient wetness impregnation method. According to the required weight percentage of 10% Mo and 5% Ni, 0.63 g of ammonium heptamolybdate and 0.81 g of nickel(II) nitrate hexahydrate were dissolved in a specific volume of distilled water. The two solutions were mixed. Then, the solutions of salts with γ -Al₂O₃ catalysts support were placed in the rotary evaporator at 50 °C for 2 h. In addition, the wet

Table 2. The Feed Specifications of the LCO

No.	Analysis	Unit	Result	Method
1	Appearance	-	Yellow liquid	Visual
2	Density at 15.6 °C	Kg m ⁻³	736.1	ASTMD1298
3	Total sulfur	ppm	13000	ASTMD4294
4	Flash point	°C	60	ASTMD93
5	Pour Point	°C	-14	ASTMD97
6	SpGr	°C	15.6	ASTMD1298
7	Distillation-FBP	°C	350	ASTMD86
8	Total nitrogen	ppm	800	ASTMD4629
9	Aromatics	wt%	64	IP 391
10	Cetane index	°C	101	ASTMD976
11	Cetane index	°C	106	ASTMD4737
12	Cetane index	°C	111	ASTMD1319
13	Olefins	wt.%	2.0	ASTMD1319

Table 3. The Results of the ODS Microreactor Test with Different Amounts of H₂O₂

H ₂ O ₂ (ml)	0	1	2	3	4
Total sulfur (ppm)	13000	3002	2589	2375	2014

γ -Al₂O₃ was placed in a thermal chamber with a thermal programming rate of 10 °C/20 min in the temperature range of 50-120 °C. The samples were dried at 120 °C for 24 h in an oven. Since the formation of molybdenum oxide requires the stabilization of molybdenum, the catalyst was calcined up to 600 °C in a furnace with a temperature programming rate of 100 °C h⁻¹.

The Effect of Oxidant Agent (H₂O₂) on ODS

Catalytic experiments were performed as described in Section 2.3. In a typical run, different amounts (0, 1, 2, 3, 4 ml) of H₂O₂ were suspended slowly at a vigorous stirring speed in an oil feed. Afterward, the mixtures were left at room temperature (30 °C). Then, the oil phase of samples was removed three times with the extraction agent. The total sulfur was determined by Rigaku devices, and the results are shown in Table 3 and Fig. 2.

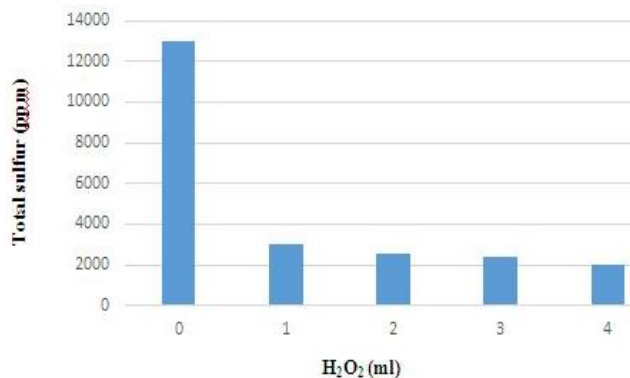


Fig. 2. Total sulfur *versus* different amounts of H₂O₂.

Table 4. The Results of the ODS Microreactor Test with Different Amounts of 5%Ni10%Mo/-Al₂O₃ Catalyst

NiMo/Al ₂ O ₃ (g)	0	0.5	1	1.5	2
Total sulfur (ppm)	3256	2689	1059	1032	1008

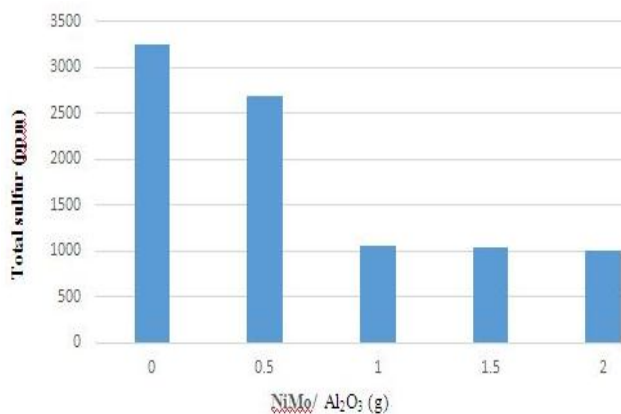


Fig. 3. Total sulfur *versus* different amounts of 5%Ni10%Mo/-Al₂O₃.

The Effect of NiMo/ γ -Al₂O₃ Catalyst Content on ODS

Catalytic experiments were performed as described in Section 2.3. In a typical run, different amounts (0, 0.5, 1, 1.5, 2 g) of the prepared 5%Ni10%Mo/-Al₂O₃ catalyst were suspended slowly at a vigorous stirring speed in an oil feed

Table 5. The Results of the ODS Microreactor Test with Different Temperatures

Temperature (°C)	30	40	50	60	70
Total sulfur (ppm)	1059	987	867	2856	4059

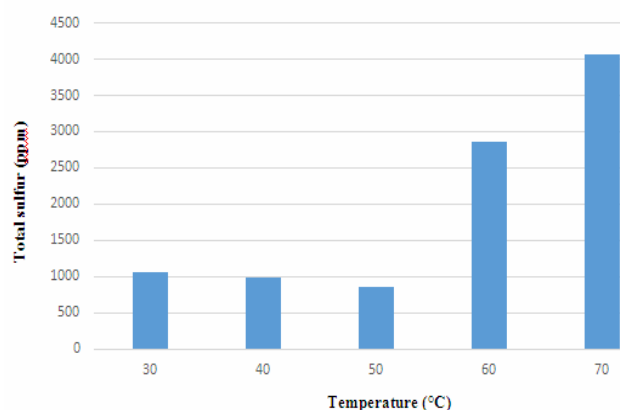


Fig. 4. Total sulfur *versus* different temperatures (°C).

with 1 ml of H₂O₂. Afterward, the mixtures were left at room temperature (30 °C). Then, the oil phase of samples was removed three times with the extraction agent. The total sulfur was determined by Rigaku devices, and the results are shown in Table 4 and Fig. 3.

The Effect of Temperature on ODS

Catalytic experiments were performed as described in Section 2.6 at different temperatures (30, 40, 50, 60, and 70 °C). The mixtures were left at room temperature. Then, the oil phase of samples was removed three times with the extraction agent. The total sulfur was determined by Rigaku devices, and the results are shown in Table 5 and Fig. 4.

The Effect of Time on ODS

Catalytic experiments were performed as described in Section 2.6 at different times (30, 60, 90, 120, and 150 min). Then, the oil phase of samples was removed three times with the extraction agent. The total sulfur was determined by Rigaku devices, and the results are shown in Table 6 and Fig. 5.

Table 6. The Results of the ODS Microreactor Test at Different Times

Time (min)	30	60	90	120	150
Total sulfur (ppm)	984	841	739	623	608

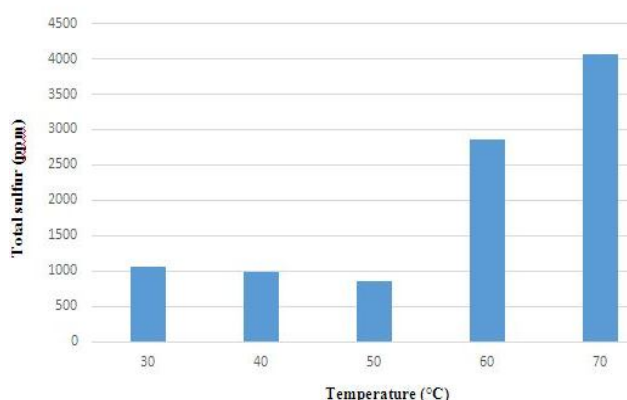


Fig. 5. Total sulfur *versus* different times (min).

RESULTS AND DISCUSSION

Catalyst Characterization

The preparation method of the catalyst can have an effect on its efficiency. The physical chemical properties and the composition of γ -Al₂O₃ and 5%Ni10%Mo/-Al₂O₃ catalyst are shown in Table 7. The N₂ adsorption/desorption results indicated that the values of SA, APD, and PV of 5%Ni10%Mo/-Al₂O₃ decreased with the impregnation of two metals on the γ -Al₂O₃ catalyst support [22]. Figure 6 catalyst had a uniform mesoporous structure. According to according to the BJH method. As can be seen in Fig. 6, the

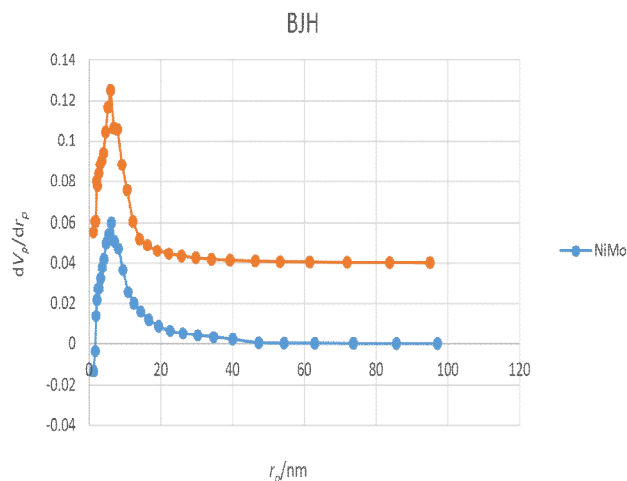


Fig. 6. The BJH plot of the γ -Al₂O₃ and NiMo/ γ -Al₂O₃ catalysts.

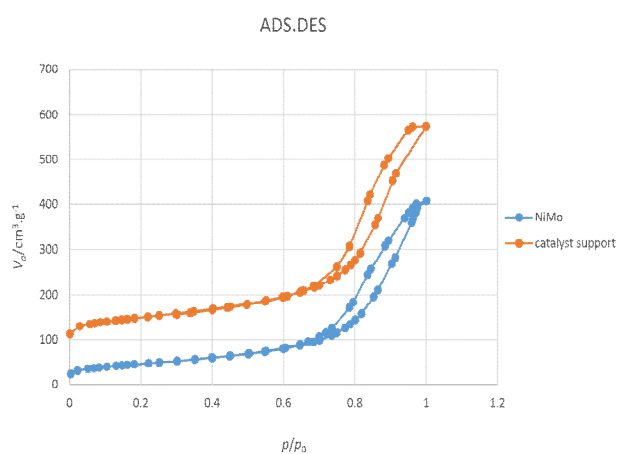


Fig. 7. Adsorption/Desorption isotherms of the γ -Al₂O₃ and 5%Ni10%Mo/-Al₂O₃ catalysts.

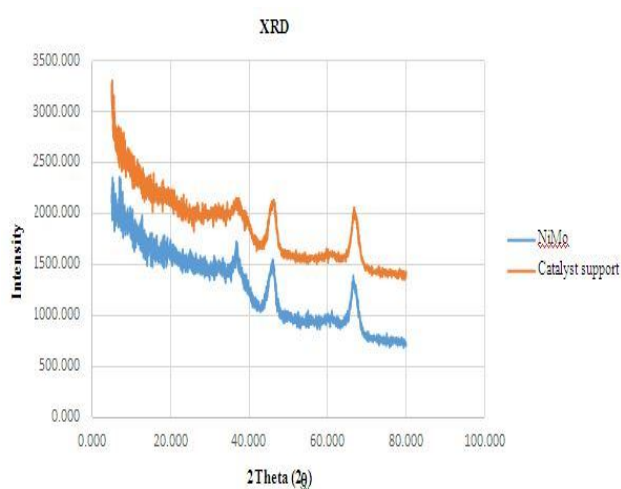
the IUPAC classification and Fig. 7, all of the prepared mesopore 5%Ni10%Mo/-Al₂O₃ catalysts exhibited type IV

Table 7. The BET and BJH Results of the γ -Al₂O₃ and 5%Ni10%Mo/-Al₂O₃ Catalysts

Catalyst	BET			BJH (Adsorption branch)		
	Average pore diameter (nm)	Surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore radius (nm)	Surface area (m ² g ⁻¹)
γ -Al ₂ O ₃	13.55	215.43	0.73	0.73	6.03	237.95
5%Ni10%Mo/-Al ₂ O ₃	14.85	166.87	0.61	0.61	6.23	146.63

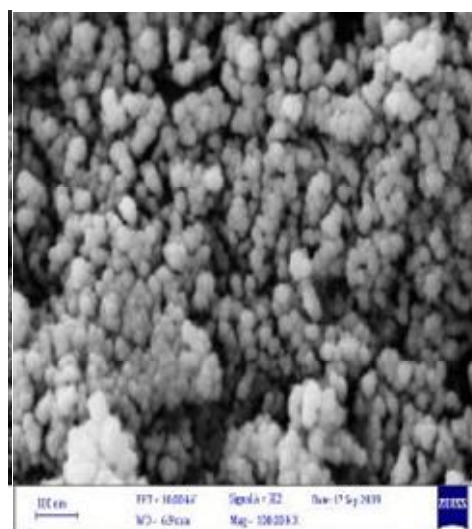
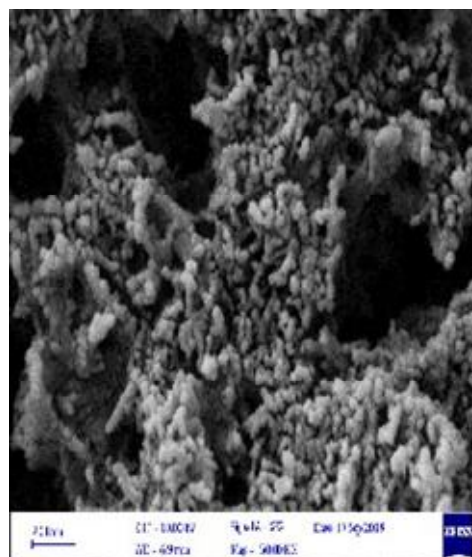
Table 8. The ICP-MS Results of the γ -Al₂O₃ and 5%Ni10%Mo/-Al₂O₃ Catalysts

Catalyst	Al wt%	Mo wt%	Co wt%
γ -Al ₂ O ₃	54.97	-	-
5%Ni10%Mo/-Al ₂ O ₃	1.16	8.31	4.02


Fig. 8. The XRD spectrum of the γ -Al₂O₃ and 5%Ni10%Mo/-Al₂O₃ catalysts.

isotherms with H₂ hysteresis loop. Due to their complex pore networks, typical mesoporous materials are made of pores with wide pore-size distribution [22]. Table 8 shows the results of ICP-MS analysis of the prepared catalysts.

Figure 8 shows the XRD spectrum of the γ -Al₂O₃ and 5%Ni10%Mo/-Al₂O₃ catalysts. For nickel oxide (NiO) at $2\theta = 32^\circ, 36^\circ, 37^\circ, 40^\circ, 45^\circ,$ and 67° [23,24], two peaks exist at $2\theta = 45^\circ$ and 67° ; these two peaks are close to the specific peaks of γ -Al₂O₃, this similarity can be attributed to the overlap of defects in NiO and γ -Al₂O₃ [25]. These data agree with the elemental analysis of the catalysts. It is further suggested that the species present in a material at concentrations lower than 5% cannot be properly detected by the XRD technique. Based on the above explanation, the very weak peaks of cobalt were observed in the cobalt oxide phases.


Fig. 9. The SEM images of Al₂O₃ (left) and the optimum sample 5%Ni10%Mo/-Al₂O₃ catalyst (right).

The SEM images (Fig. 9) indicate that no agglomeration of the two metals existed (right figure) on the prepared catalyst. Furthermore, the distribution and impregnation of the two metals were found to be effective, leading to a more homogenous impregnation. Moreover, these two metals led to the production of a catalyst with uniform particle size distribution.

Figure 10 shows the NH₃-TPD profile of the

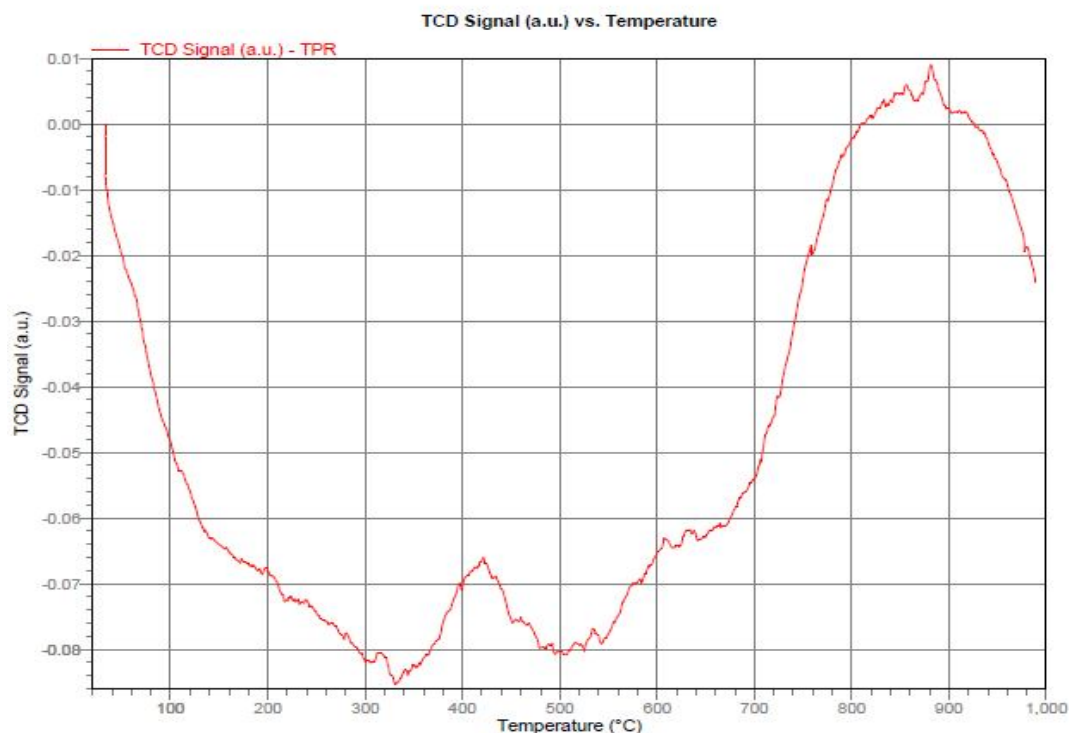


Fig. 10. The NH₃-TPD spectrum of the optimum sample (5%Ni10%Mo/-Al₂O₃).

NiMo/-Al₂O₃ catalyst. For this catalyst, the spectrum indicated two well-resolved peaks at 420 °C and 880 °C. The results showed that two types of adsorption sites were present for NH₃-TPD on the catalyst. The peak at 880 °C can be attributed to N₂ and H₂ gases produced from the decomposition of NH₃. The peak at 420 °C, which indicates the presence of strong acid sites, can be attributed to the release of adsorbed NH₃ from alumina.

The Effect of Oxidant Agent Content on ODS

H₂O₂ was also used as an oxidant in the desulfurization of LCO. The use of oxidant results in two phases: a polar aqueous phase, including the oxidant, and an oil non-polar phase. As a result, mass transfer problems can make the oxidation reaction more difficult by separating the reactants [26].

The amount of H₂O₂ used could also be one of the important parameters affecting ODS [27-29]. For environmental and economic reasons, minimizing the amount of oxidant is considered desirable in the development of the ODS process. When the H₂O₂ content

was below 1 ml, little change was observed in sulfur removal. However, when the H₂O₂ content was between 1-2 ml, a significant change was observed in sulfur removal. This high amount of oxidant could be explained not only by the initial sulfur content but also by the heavy nature of the LCO used, which requires a high amount of oxidant due to the side reactions, such as the oxidation of aromatic hydrocarbons, that may occur during this process. Therefore, due to environmental and economic considerations, the minimum content of H₂O₂ (1 ml) was selected.

The Effect of 5%Ni10%Mo/-Al₂O₃ Catalyst Content on ODS

The use of new heterogeneous catalytic systems is desirable due to their simple products, catalyst separation, and high efficiency. There are some important factors that should be taken into consideration when it comes to residues in feeds. At first, LCO has high viscosity, hence mixing conditions are very important to obtain a completely mixed system. Catalyst optimization and the heavy nature of

LCO are thought to facilitate the diffusion of large complex molecules and prevent the deposition of large molecules of LCO and metal chelates on the surface of catalysts. Therefore, attention has turned to heterogeneous catalytic systems for oxidation reactions. As mentioned above, two of the benefits of heterogeneous systems are their simple products and catalyst separation. Similar to homogeneous ODS systems, heterogeneous catalysts have also been frequently used to model LCO with high sulfur content and the ODS reaction being used as a finishing process.

In this study, the reaction was performed in the presence of H_2O_2 , as an oxidant, and 5%Ni10%Mo/- Al_2O_3 , as a heterogeneous catalyst. Concerning the ODS of LCO with high sulfur content fractions (13000 ppm), heterogeneous catalysts are mainly composed of one active phase (often based on transition metals) dispersed on a support with a large specific surface area, such as alumina [31]. Among the transition metals, molybdenum was used as the active metal and nickel was used as the promoter [30]. For environmental and economic reasons, minimizing the amount of the catalyst is considered desirable in the development of ODS. When the catalyst content was below 1 g, no considerable change was observed in the sulfur removal. However, when the catalyst content was between 1-2 g, a significant change was observed in sulfur removal. Thus, due to environmental and economic considerations, the minimum content of the catalyst (1 g) was selected.

The Effect of Temperature on ODS

In this study, the ODS reaction temperature, as a major factor in the ODS process, was investigated. Oxidation reactions are generally carried out at temperatures between 30 and 70 °C. In addition to the direct effects that higher temperatures have on improving kinetics and reaction rate, the use of higher temperatures was also investigated because of their potential effect on reducing the viscosity of highly viscous LCO fractions. If this effect of higher temperatures is supported, it is expected that higher temperatures facilitate the diffusion of sulfur molecules and thus improve oxidation conversion. In most studies, increasing the temperature from 30 °C to 50 °C enhanced sulfur reduction while temperatures above 60 °C had a reverse effect, mainly due to the degradation of oxidant used and the formation of resins and asphaltenes [21].

The obtained results (Table 5) showed that the ODS process could be carried at 50 °C but, due to the complexity and the higher viscosity of the gas-oil mixture, a higher temperature (70 °C) was needed to oxidize LCO. Therefore, 50 °C was selected as the best ODS temperature.

The Effect of Time on ODS

Reaction time is also a major factor in the ODS process because it affects the possibility of scaling up the ODS process to an industrial scale. In the ODS process, it is quite rare to find an efficient oxidant:catalyst system that allows desulfurization in a few minutes. Oxidation time varies mostly between 30 and 150 min [21].

According to the results in Table 6, the desulfurization of LCO occurred in 120 min by H_2O_2 and catalyst at 50 °C. This reaction time was mainly related to the multiple steps used for the addition of oxidant and catalyst to the LCO fraction. The results showed that increasing the reaction time up to 150 min did not significantly decrease the sulfur reduction or increase desulfurization. This explains why the best reaction time was observed at 120 min.

CONCLUSIONS

In this study, the ODS process was investigated as an alternative process to HDS to avoid or reduce the economic deficiencies associated with the operating conditions of HDS, including high temperature, high pressure, and high hydrogen consumption. To this end, we focused on the catalytic ODS process. At first, 5%Ni10%Mo/- Al_2O_3 was prepared as the catalyst. The effects of different amounts of oxidant (H_2O_2) and 5%Ni10%Mo/- Al_2O_3 catalyst and different times and temperatures on the performance of ODS were examined. The ODS process was carried out on LCO (total sulfur 13000 ppm), as a high sulfur fraction of petroleum. The results revealed that the optimal amounts of oxidant (H_2O_2) and 5%Ni10%Mo/- Al_2O_3 catalyst were $H_2O_2 > 1$ ml and 5%Ni10%Mo/- $Al_2O_3 > 1$ g, respectively. However, due to environmental and economic reasons, it is not only desirable but also necessary to minimize the amount of oxidant and catalyst in the development of ODS. Accordingly, 1 ml of oxidant (H_2O_2) and 1 g of 5%Ni10%Mo/- Al_2O_3 catalyst were selected as the optimal amounts. Then, the ODS process was examined with the

5%Ni10%Mo/-Al₂O₃ catalyst and oxidant (H₂O₂) at different temperatures and times. According to the results, 50 °C and 120 min were found to be the optimal operating condition. In this optimized ODS condition, the total sulfur was reduced from 13000 ppm to 623 ppm. Thus, it can be stated that the optimal condition is expected to occur with 1 ml H₂O₂, 1 g 5%Ni10%Mo/-Al₂O₃ catalyst, at 50 °C, and in 120 min.

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