

# Investigation of Oxidative Desulfurization of Light Naphtha by NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Catalyst

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**ABSTRACT:** In this research, we investigated the effects of parameters, including reaction time, reaction temperature, the mass ratio ( $m_{cat}/m_{feed}$ ), and volume ratio ( $V_{H_2O_2}/V_{feed}$ ) on sulfur removal conversion of light naphtha under oxidative desulfurization (ODS) reaction. So to achieve this goal, several active catalysts are prepared while molybdenum (Mo) was used as an active metal. Nickel (Ni) was the promoter.  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) was used as a support and modified by chelate agents such as citric acid (C<sub>6</sub>H<sub>8</sub>O<sub>7</sub>), ethylene diamine tetra acetic acid (EDTA), polyethylene glycol (PEG), Sorbitol, and urea ((NH<sub>4</sub>)<sub>2</sub>CO). These catalysts were synthesized by using the wetness impregnation in-situ method. Then they were applied to the ODS process for light naphtha. These catalysts were characterized by N<sub>2</sub>-adsorption desorption isotherms (BET, BJH), Scanning Electron Microscope (SEM), temperature-programmed desorption (NH<sub>3</sub>-TPD), and FT-IR analysis. The catalyst that synthesized in the presence of sorbitol, had the best performance. The optimization conditions for this catalyst were  $m$  (catalyst)/ $m$  (feed) = 0.013, reaction temperature of 35 °C, 50 mL of feed, 0.5 g of catalyst, 1 hour reaction time, and  $V$  (H<sub>2</sub>O<sub>2</sub>)/ $V_{Feed}$  = 0.045. It revealed the maximum performance for ODS reaction of the real feed. Under these circumstances, the sulfur of light naphtha decreased from 160 ppm to 38 ppm during the reaction.

**KEYWORDS:** Molybdenum oxide; Nickel oxide; Oxidative desulfurization catalyst; Chelating agent; Light naphtha.

## INTRODUCTION

Nowadays, the requirements exist for reducing sulfur in liquid motor fuels (10ppm) [1,2]. The sulfur content elimination is carried out by the conventional hydrodesulfurization (HDS) process in the fuel products. However, due to steric hindrance and hard reactivity of the components (sulfur compounds like benzothiophene

and its alkylated derivatives) and severe operating conditions of the HDS process which reduce the life cycle of catalysts and increase the operating cost [2]. An appropriate method for sulfur compounds reduction in oxidative desulfurization (ODS). This process uses catalysts and oxidation agents such as hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) [3-5].

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1021-9986/2021/2/417-427

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Sulfur compounds are converted into the polar compounds such as sulfoxides and/or sulfones. They can be separated from oil feed with a polar organic solvent, such as acetonitrile or alcohol. Although this reaction is carried out in the mild thermodynamic condition (less than 100 °C and atmospheric pressure), it has a very slow kinetics [6]. Recently, the researchers have applied adaptable oxidizing agents to the ODS process, such as tert-butyl hydroperoxide (t-BuOOH) [7], H<sub>2</sub>O<sub>2</sub> [8, 9], ozone [10], cumene hydroperoxide [11,12], oxygen [13,14]. However, according to literature, oxidizing hydrogen peroxide is more appropriate due to its safety, high selectivity, and high oxidation capacity. It is also environmentally-friendly and compatible with catalysts. To improve the performance of catalysts and activity of oxidant reagents, researchers investigated the application of ultrasonic waves instead of mechanical stirrer. Flores et al. [3] used ultrasound to improve the oxidative desulfurization of diesel and heavy fuel oil. Moreover, they applied ferric chloride and copper sulfate as Fenton-like catalyst. Zhao et al. [15] synthesized CdO as a photocatalyst and performed oxidative desulfurization process by using H<sub>2</sub>O<sub>2</sub> and assist oxidant (acetic acid) in an ultrasonic reactor to gain an efficient result. They followed ultrasound-assisted oxidative process. In the other study, Akbary et al. [1] investigated the influence of drying method and Mo loading on the property and performance of MoO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst in the ODS process. Many researchers have used H<sub>2</sub>O<sub>2</sub> with acid in the oxidative system. Haghighat et al. [2] that have performed oxidation of debenzothiophene in presence H<sub>2</sub>O<sub>2</sub> /formic acid (HCOOH) and sulfuric acid (H<sub>2</sub>SO<sub>4</sub>). Since separation and regeneration of homogenous catalysts were difficult, the performance of heterogeneous catalysts were considered and modified. Therefore, using of improved solid catalyst for a mild reaction is a good idea. In this way, using of transition metals as an active site in presence a promoter can be found in the literature. Luo et al. [9,16] reported the performance of molybdenum oxide on SBA-15 catalyst for ODS process. They used an ionic liquid (IL) to improve interaction between active site and support. The oxidative desulfurization of the model fuel was carried out over HPMo – IL/SBA-15 catalyst. Additionally, Mohammadi Meman et al. [5] prepared a MnO<sub>x</sub>/FMWNT nano catalyst for oxidative desulfurization of sour naphtha. Furthermore, they used palladium metal on MWNTs as a catalyst for this

purpose. The results were acceptable [17]. Azelee et al. [7] applied demethyl foramide (DMF) and tert-butyl hydroperoxide (TBHP) as a solvent and oxidant, respectively. The aim of this investigation was to eliminate the sulfur compound in the fuel oil by the ODS process. Shi et al. [13] studied deep oxidative desulfurization using (NH<sub>4</sub>)<sub>5</sub>H<sub>6</sub>PV<sub>8</sub>Mo<sub>4</sub>O<sub>40</sub> as a catalyst and molecular oxygen as an oxidant. Jin et al. [8] reported an effective oxidative desulfurization with molybdenum oxide as the active site and Ca<sup>2+</sup> as a promoter, supported on alumina. Keynejad et al. [18] reported a new data. They have studied this process in the presence of different oxidizing media. The results indicated that using acetic acid as an oxidative promoter can increase the efficiency of UODS process. Additionally, Ebrahimi et al. [19] studied the geometrical parameters of sonoreactor and optimized these parameters such as the probe, reactor diameter, and probe immersion depth. Granadeiro et al. [20] synthesized an active heterogeneous catalyst-based on polyoxomolybdate by using trimethyloctadecyl ammonium, OD, and a POM@MOF composite material of chromium (Cr). da Silva et al. [21] proposed a new application of AlMo<sub>12</sub>O<sub>4</sub> as catalyst of ODS reaction in the absence of phase transfer catalyst (PTC) in comparison with its heteropolyacid. Rezvani et al. [22] studied the oxidative desulfurization reaction of model fuel oil using (N(Bu)<sub>4</sub>)<sub>5</sub>H<sub>4</sub>PV<sub>6</sub>Mo<sub>6</sub>O<sub>40</sub> as an effective catalyst and hydrogen peroxide as an oxidant. The lipophilic cation available in the catalyst acted as a phase transfer reagent. Liao et al. [14] doped NH<sub>4</sub><sup>+</sup> on POM and prepared four kind catalysts, including ((NH<sub>4</sub>)<sub>x</sub>H<sub>4-x</sub>PMo<sub>11</sub>VO<sub>40</sub> x=1, 2, 3, 4) for the ODS reaction. Furthermore, W. Ahmad et al. [23] investigated on various transition metals impregnated on ZSM-5 as catalyst. They used H<sub>2</sub>O<sub>2</sub> and formic acid as an oxidant with air assisted. In this research, the real industrial oil fractions were used as a feed for ODS process. They understood that Fe/ZSM-5 had the most conversion for desulfurization over the real feed of between 60-80%. Also, Wang et al. [24] studied catalytic oxidative desulfurization of model feed of benzothiophene. They used iron oxide supported activated carbon as a catalyst and hydrogen peroxide as an oxidant. Sulfur removal conversion of model diesel fuel was 95.66% in the mild condition. Rafiee et al. [25] synthesized a new catalyst from PMo, encapsulated in HKUST-1 (PMo@ HKUST-1). They evaluated this catalyst in the ODS reaction over model feed, in the presence

of nitrogen compounds such as quinolone and indole and aromatic hydrocarbons. They used different extraction solvents. They provided the results that show positive effect of aromatic compound and negative effect of indole on the oxidative desulfurization reaction. Hoceva *et al.* [26] applied Ni-Mo/Al<sub>2</sub>O<sub>3</sub> catalyst to study the kinetics of hydrodeoxygenation (HDO) of the model organic compound. They investigated on oxygenated functional groups in hexane as a model compound. Additionally, Hoceva *et al.* [27] continued their studies on the removal of oxygenated materials in linear C<sub>6</sub> ketones and secondary alcohols.

The purpose of this work is to prepare an efficient catalyst for the ODS reaction. Molybdenum oxide and nickel oxide are used as an active metal and promoter, respectively. These metals were loaded on the mesoporous alumina in the presence organic additives including EDTA, PEG, sorbitol, urea and citric acid as chelate agents. Then oxidative desulfurization process is performed by using these catalysts and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an oxidant on the real naphtha. In this step, sulfur compounds are converted into the polar compounds such as sulfoxides and/or sulfones. They are separated from oil feed with a polar organic solvent, such as acetonitrile for three times. Subsequently, the catalytic reaction conditions such as reaction time, reaction temperature, mass ratio ( $m_{\text{cat}}/m_{\text{feed}}$ ), and volume ratio ( $V_{\text{H}_2\text{O}_2}/V_{\text{feed}}$ ) were investigated.

## EXPERIMENTAL SECTION

### Materials

In present work, the precursors include a  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> (surface area 215 m<sup>2</sup>/g, pore volume 0.73 cm<sup>3</sup>/g, pore diameter 13.56 nm), from an internal source. It was typically used as a catalyst support. Ammonium hepta molybdate tetra hydrate ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O, Merck, Germany, purity 100%), nickel nitrate hexa hydrate (Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, Merck, Germany, a purity of 98%), citric acid (Merck, Germany, a purity of 100%), ethylene diamine tetra acetic acid (EDTA, Merck, Germany, a purity of 99%), poly ethylene glycol (PEG, Merck, Germany, a purity of 100%), urea (Merck, Germany, a purity of 100%), sorbitol (C<sub>6</sub>H<sub>14</sub>O<sub>6</sub>, Merck, Germany, a purity of 100%), hydrogen peroxide and acetonitrile were the other chemicals used in this study. All of them were the laboratory-grade chemicals.

### Characterization techniques

The pore structure of the samples was measured by using N<sub>2</sub>- adsorption/desorption porosimetry (Belsorp mini II, BEL JAPAN, according to ASTM: ISO 15901-2-2006 and ISO 15901-3-2007) in the liquid nitrogen at the temperature of 77K. Before each measurement, all samples were degassed under vacuum and at the temperature of 250°C for 3 h. Additionally, FT-IR spectra were obtained in the wavenumber range of (400-4000) cm<sup>-1</sup> with a resolution of 1 cm<sup>-1</sup> (Unicam Matson 1000). The mixture made up of 10 mg of the catalyst sample and 200 mg of KBr. Surface morphology and particle size of the catalysts were determined by using field emission scanning electron microscopy (FE-SEM) by MIRA 3 TESCAN. The acidity of catalysts is determined by the TPD of ammonia using a TPR/TPD instrument (Micromeritics 2900). It is equipped with a Thermal Conductivity Detector (TCD). Firstly, the catalysts (0.13g) were pre-treated in the helium stream at 500°C for 1 h. After cooling to room temperature, the catalysts were saturated with ammonia to 750°C at the rate of 10°C min<sup>-1</sup>.

The total sulfur in every sample was determined by Rigaku devices (USA) with semi-conductor Silicone PIN diode detector according to ASTM D: 4294.

### Catalyst preparation

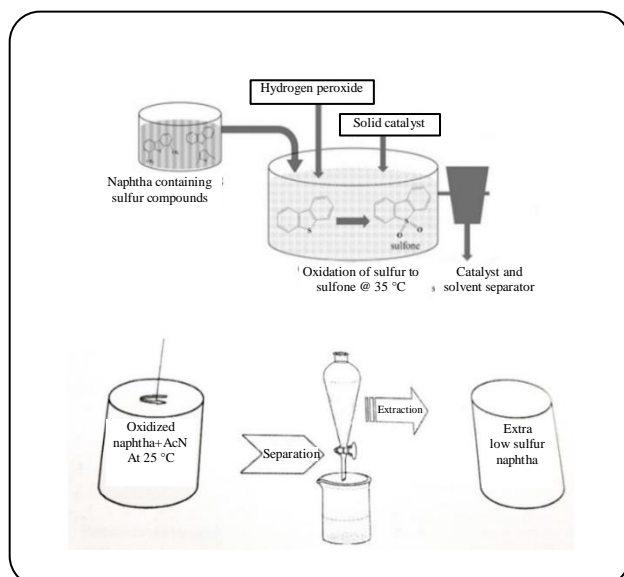
Two impregnation solutions were prepared by using 0.5 g of ammonium hepta molybdate in 10 mL of distilled water and 0.4 g of nickel nitrate, specific amount of chelate agent (according to the Table 1) in 10 mL of distilled water. The pH of the solution was adjusted on 5. Subsequently, the mixture was sprayed on 10 g of  $\gamma$ - Al<sub>2</sub>O<sub>3</sub> as a single step, at room temperature. To dry the samples, a thermal cabin was used with (155\*60\*50) cm dimension. This cabin could adjust the temperature and rotation speed. The temperature profile was from 25°C to 60°C at 45 rpm. Then the calcination of catalyst was performed by using a furnace at a rate 100 °C/h (Specify the final temperature here). The catalysts were dried in an oven at the temperature of 120°C for 2h. They were calcined in a 2-step procedure. Firstly, at the rate of 2°C min<sup>-1</sup> 300°C for 2h. Then the temperature was raised up to 520°C followed by isothermal calcination at this temperature for 5h. They are named as C-CA, C-U, C-E, C-P, C-S and C-O.

**Table 1: Specific amount of chelate agents.**

Catalyst	C-CA	C-U	C-E	C-P	C-S	C-0
amount of chelate agents	0.8 g citric acid	0.24 g urea	1.16 g EDTA	0.8 g PEG	0.728 g sorbitol	-

**Table 2: Composition of the typical feed.**

Specification	Result
Density (15.6 °C, K/gm <sup>3</sup> )	1.736
S (wt. ppm)	160
Flash point (°C)	free
IBP (°C)	75
FBP (°C)	192
Corrosion at 50 °C	a1

**Fig. 1: Schematic of the oxidative test.**

### Catalytic oxidative desulfurization

For catalytic oxidative desulfurization process, the real naphtha with a sulfur content of 160 mg/g (as a feed) was introduced in a three neck flask. This flask was equipped with a condenser, magnetic stirrer and recirculation water bath for the temperature control. This process was carried out with 50mL of feed (Table 2 shows composition of the typical feed), 0.5 g of catalyst and 2.5 g of H<sub>2</sub>O<sub>2</sub> 30% as an oxidant, at the atmospheric pressure, the temperature 35 °C for 1 hour. After this process, the mixture was cooled up to room temperature. Then the catalyst was separated from solution by using a filter paper. Subsequently, sulfur compounds that are converted into the polar compounds

such as sulfoxides and/or sulfones, are separated from oil feed by using extraction process and acetonitrile (with 1:1 volume ratio) in the separating funnel. The below phase was the mixture of the oxidative compounds and acetonitrile as a waste. The upper phase was the cleaned feed without sulfur. Fig .1 shows schematic of the oxidative test.

## RESULTS AND DISCUSSION

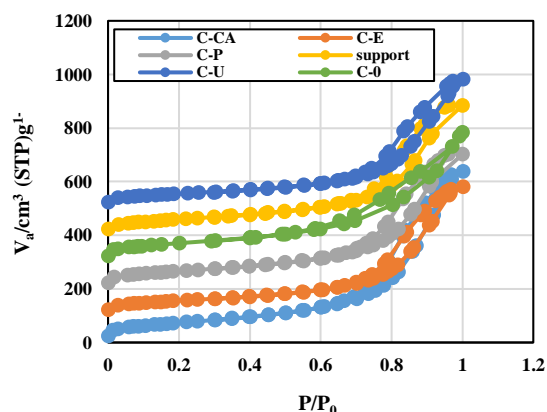
### Characterization of catalyst

#### The effect of organic additives on the textural properties of the catalyst

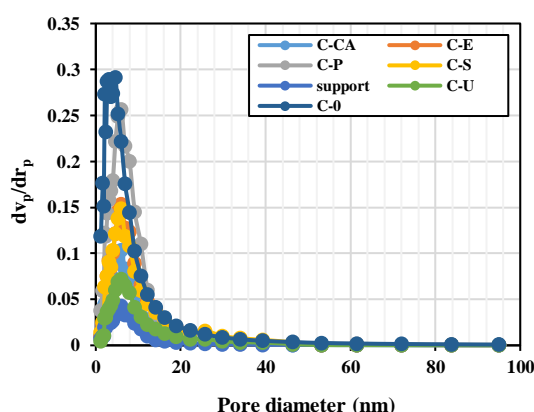
In order to recognize the effects of different chelate agents on the characterization and activity of NiO/MoO<sub>3</sub>/γ-Al<sub>2</sub>O<sub>3</sub> catalyst in the ODS system, the catalysts were prepared in the presence of organic additive compounds including EDTA, PEG, sorbitol, citric acid and urea at the same conditions. According to Fig. 2, all of the catalysts show N<sub>2</sub>-adsorption/desorption isotherms with hysteresis loop as IV type isotherm via IUPAC classification. The shape of the hysteresis loop proves that it has protected cylindrical pores, so it can be concluded that the uniform dispersion of active metals exists in the pores [28]. Fig. 3 represents typical mesoporous materials due to complex pore networks. These networks are made up of the pores with a wide pore size distribution [29]. Based on the results in the Table 3, the addition of chelate reagents with different functional groups to the impregnated solutions leads to holding active metal by coordinate bond and affects the surface. The higher the chelating functional groups, the more ligands bind to the metal. Therefore, more active sites are created on the surface and the surface area increases. Therefore, the C-CA catalyst has a higher surface than the C-U and C-P catalysts, because citric acid possesses four OH groups while urea has two NH<sub>2</sub> and PEG has two OH groups as chelating factors. Although, EDTA and sorbitol molecules have more chelating functional groups (EDTA four OH, sorbitol six OH) than PEG, citric acid and urea, the surface area of C-E and C-S catalysts is reduced. Because the bulkiness and steric hindrance of the EDTA and sorbitol molecules are high.

**Table 3: Physicochemical properties of prepared catalysts.**

catalyst	BET			BJH-ads			BJH-des		
	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Average Pore Diameter (nm)	Pore Volume (cm <sup>3</sup> /g)	Pore Radius (nm)	Surface Area (m <sup>2</sup> /g)	Pore Volume (cm <sup>3</sup> /g)	Pore Radius (nm)	Surface Area (m <sup>2</sup> /g)
$\gamma$ -Al <sub>2</sub> O <sub>3</sub>	215	0.73	13.56	0.73	6.03	238	0.81	5.27	274.78
C-0	210	0.73	13.78	0.73	6.03	225	0.78	5.27	264
C-U	196	0.73	15.00	0.73	6.03	205	0.76	5.27	250
C-CA	264	0.97	14.71	0.97	6.03	294.63	1.01	5.27	355
C-P	238	0.76	12.70	0.75	6.03	246.75	0.79	5.27	291
C-E	200	0.73	14.58	0.73	6.03	213	0.81	5.27	256
C-S	200	0.74	14.85	0.74	6.03	210	0.77	5.27	252.7



**Fig. 2: N<sub>2</sub>-adsorption/desorption isotherms of the synthesized catalysts with different Chelate agents in same conditions.**



**Fig. 3: Pore size distribution of synthesized catalysts.**

**FT-IR result**

The FTIR spectra of catalyst samples, prepared in presence different chelate agents, have been shown in Fig. 4. In these spectra, two broad bands due to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> are appeared in the range of (500–1000) cm<sup>-1</sup> (593.97, 779.11) cm<sup>-1</sup> in the spectrum of C-U catalyst, 593.97, 786.82 cm<sup>-1</sup> in the C-0 and C-P, 601.69, 825.39 cm<sup>-1</sup> in the C-CA, 601.69, 802.25 cm<sup>-1</sup> in the C-E, 632.54, 802.25 cm<sup>-1</sup> in the C-S) that prove feature of Al-O-Al stretching and bending vibrations, respectively. The other weak peak, related to H-O-H bending mode, was come out at 1635.35 cm<sup>-1</sup> in the spectra of all catalysts except C-S catalyst. It was seen at 1627.64 cm<sup>-1</sup>. Additionally, a strong peak related to stretching vibration of the hydroxyl group are appeared in the area of the wavenumber (3400-3500) cm<sup>-1</sup> (3417.27, 3440.41, 3455.84, 3440.41, 3448.13, 3432.70 cm<sup>-1</sup> in the spectra of C-U, C-0, C-P, C-E, C-CA, C-S catalysts

separately). Given that the OH functional group is important in the ODS process and effective in the catalytic activity, the FTIR spectra of catalyst samples indicate that these groups are located on the catalyst. It can be confirmed that the hydrophilic hydroxyl group exists on the catalyst surface [30,31]. In the previous sections, everything is mentioned about the FTIR spectra which were common among all catalysts. However, there are several special bands for a catalyst. As an example, a medium peak seen at 3309.28 cm<sup>-1</sup> is attributed to stretching vibration of N-H, in the C-U catalyst. Additionally, the strong bands around 2500 cm<sup>-1</sup> are shown, related to C-H stretching vibration in the other catalysts except C-0 (2869.58, 2491.60, 2553.31, 2568.74) cm<sup>-1</sup> in the spectra of C-P, C-E, C-CA, C-S catalysts, respectively). It can be found that the additive compounds exist on the catalyst surface.

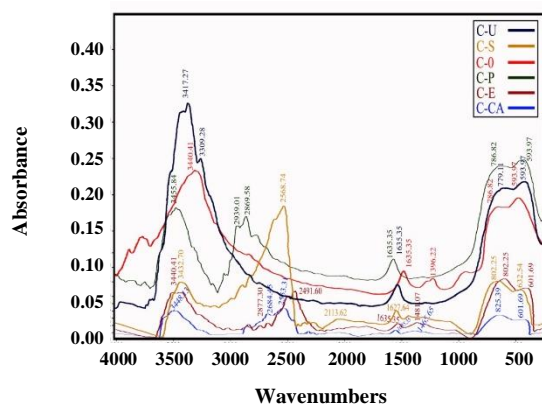


Fig. 4: The FTIR spectra of catalyst samples.

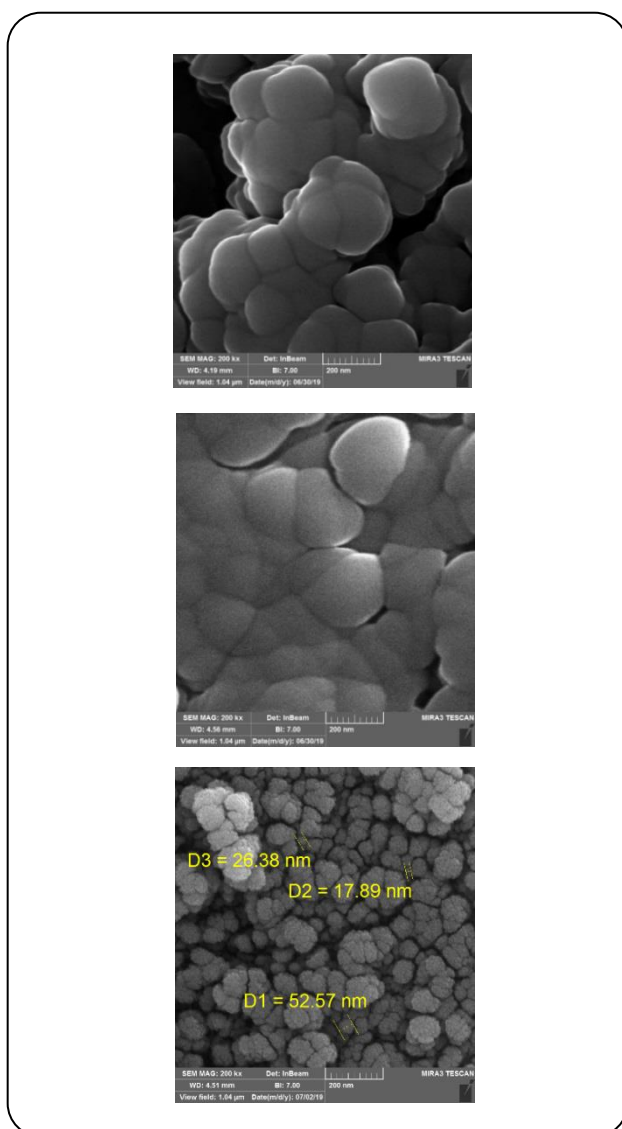


Fig. 5: SEM images of the catalysts prepared in presence/absence of chelate agent, (a) is C-O, (b) is C-U, (c) is C-S

### SEM images

The SEM images of catalysts are shown in the Fig. 5. It can be seen that the morphology of catalysts leads to spherical nanoparticles and particle size of catalysts is less than 100 nm when chelate agent (sorbitol) is used in the preparation of catalysts. Comparison of SEM images of catalysts shows that the active metals are oligomerated in the absence chelate agent (Fig. 5a) or weak chelate agent (Fig. 5b). These results are consistent with the performance test results.

### NH<sub>3</sub>-TPD

Adding chelate agent to catalyst is affected on acidity characteristics. Therefore, acidic number and strength of C-O, C-U and C-S is determined by NH<sub>3</sub>-TPD analysis. The acidic sites on catalyst surface absorb the ammonia basic molecules. Based on strength of acidic sites, the temperature of desorption of ammonia is difference. That way, the strength of acidic sites are classified to weak, medium and strong, when the desorption temperature is (<300, 300-500, >500) °C respectively [32]. As Table 4 and Fig. 6, the addition of chelating agent led to a decreasing of weak and strong acidic sites on the catalyst surface. However, comparing to C-O, C-S, amount of acidic sites in C-U are increased. Additionally, acidic strength is increased in the C-S. So, it was found that, the catalyst with lower acidic amount and higher acidic strength on the surface, exhibited the better catalytic performance.

### Catalytic oxidative desulfurization of the naphtha

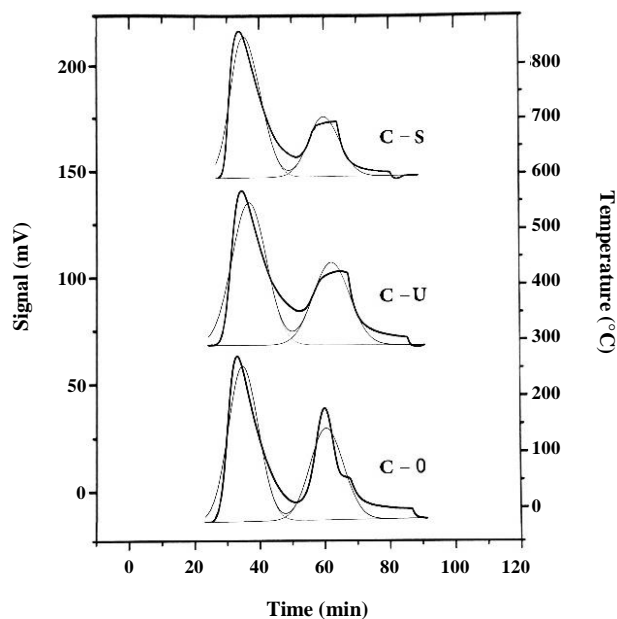
Based on the Table 5, experimental design is carried out for studying the influence of significant parameters, including time and temperature of the reaction, O/S volume ratio, and catalyst/feed mass ratio on conversion of oxidative desulfurization over prepared catalysts.

### Influence of the variation of chelate agent

Several catalysts were synthesized by using variation of chelate agents such as EDTA, PEG, Sorbitol, urea, citric acid. All of the catalysts were exposed to oxidative desulfurization reaction under the same conditions. As shown in Fig. 7, some additives have a positive effect on the performance of the catalyst and sulfur removal from the real feed. In contrast, others have a negative effect. One can see that catalyst activity is followed the order

Table 4: NH<sub>3</sub>-TPD of prepared catalysts.

catalyst	mmole NH <sub>3</sub> /g	Desorption temp. of NH <sub>3</sub> /Area	Desorption temp. of NH <sub>3</sub> /Area
C-0	1.725	216.98 / 4268	640.25 / 2832
C-U	2.027	228.39 / 3747	667.18 / 2303
C-S	1.653	209.70 / 3711	674.03 / 1672

Fig. 6: TPD profiles after NH<sub>3</sub> adsorption on prepared catalyst.

of C-S > C-CA > C-E > C-P > C-0 > C-U. This arrangement is perfectly matches with the number of the hydroxyl functional groups which belong to the molecular structure of the catalyst additives no surface area amount. It can be concluded, the role of hydroxyl groups is more significant than the surface area in the ODS process. This means that more hydroxyl groups are equal to greater efficiency in the reaction.

As shown in the following equations, there are two pathways for decomposition of H<sub>2</sub>O<sub>2</sub> and production of hydroxyl radical that depend on the temperature of the reaction. Since, the first pathway produces water. It is carried out in an unprotected manner because it reduces oxidant concentration. Due to this reason, high temperature is not suitable for the reaction. The second pathway leads to hydroxyl radicals (HO·) production, which is a potent oxidizing agent [33]. Therefore, any factor that enhances oxidizing agents will improve

the ODS process. The structure of the sorbitol contains six OH groups which produce oxidative radicals and increase oxidizing factors. While citric acid and EDTA include four hydroxyl functional groups and PEG has two hydroxyl functional groups, urea has no hydroxyl functional groups. Using hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) as an oxidizing agent in the ODS process can be a green reaction. This is due to the decomposition of H<sub>2</sub>O<sub>2</sub> produces H<sub>2</sub>O that is only considered as a byproduct [6].



#### Influence of the oxidation reaction time

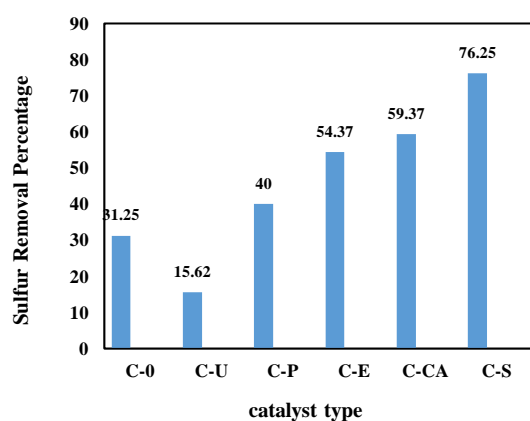
To find out the effect of reaction time on ODS efficiency and optimize this process, the oxidative desulfurization reaction was carried out over the C-S catalyst at different times ranging from (10-90) min under the same reaction conditions, m (catalyst)/m (feed) of 0.013, temperature of 35 °C, 50 mL of feed, 0.5 g of catalyst, V (H<sub>2</sub>O<sub>2</sub>)/V<sub>Feed</sub> of 0.045. Then the sulfur removal percentage was determined. The results are shown in Fig. 8. With the growth of treatment time, the desulfurization rate gradually increases up to 60 min that reaches the maximum efficiency [15]. After 60 min time, it reaches constant yield.

#### Influence of the catalyst concentration on oxidation reaction rate

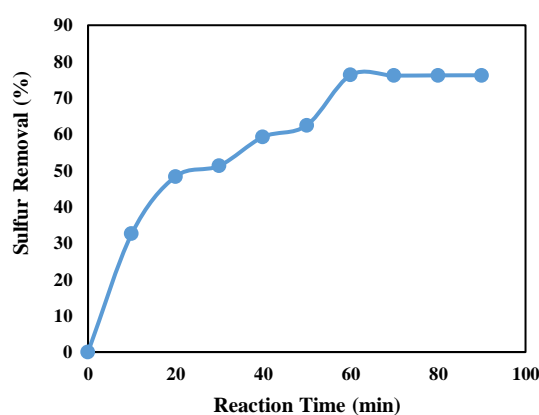
Another factor affecting the reaction is the catalyst concentration. Fig. 9 reveals how the amount of catalyst affects the ODS reaction efficiency. Increasing the catalyst concentration from 2 to 10 g/L in the feed enhances the oxidative desulfurization rate. Actually, increasing dosage of the catalyst improves the conversion effect before the concentration of 10 g/L. When mass ratio (m<sub>(catalyst)</sub>/m<sub>(feed)</sub>) reached 0.013, it is the optimum point of the sulfur removal from the light naphtha [8].

**Table 5: The effects of the additives, temperature and time reaction,  $H_2O_2$ / feed volume ratio, catalyst / feed mass ratio on the sulfur removal percentage in the feed.**

Experiment no.	Catalyst	Temp.( °C)	Time(min.)	$V(H_2O_2)/V_{Feed}$	$m(cata.)/m(feed)$	Sulfur Removal (%)
1	C-S	35	60	0.045	0.013	76.25
2	C-CA	35	60	0.045	0.013	59.37
3	C-E	35	60	0.045	0.013	54.37
4	C-P	35	60	0.045	0.013	40
5	C-U	35	60	0.045	0.013	15.62
6	C-O	35	60	0.045	0.013	31.25
7	C-S	25	60	0.045	0.013	63.42
8	C-S	45	60	0.045	0.013	62.32
9	C-S	55	60	0.045	0.013	54.67
10	C-S	35	50	0.045	0.013	62.45
11	C-S	35	40	0.045	0.013	59.24
12	C-S	35	30	0.045	0.013	51.30
13	C-S	35	20	0.045	0.013	48.32
14	C-S	35	10	0.045	0.013	32.59
15	C-S	35	60	0.018	0.013	45.62
16	C-S	35	60	0.09	0.013	59.37
17	C-S	35	60	0.045	0.0027	46.62
18	C-S	35	60	0.045	0.008	67.5
19	C-S	35	60	0.045	0.027	59.37



**Fig. 7: Sulfur removal percentage vs. catalyst types Reaction condition:  $m(catalyst)/m(feed)$  0.013, 35 °C, 1 hour,  $V(H_2O_2)/V_{Feed}$  0.045.**



**Fig. 8: The effect of reaction time on total sulfur removal in naphtha. Reaction conditions:  $m(catalyst)/m(feed)$  0.013, 35 °C,  $V(H_2O_2)/V_{Feed}$  0.045.**



#### Influence of volume ratio of $H_2O_2$ /Feed on oxidation reaction rate

To understand the optimum amount of oxidant in the sulfur removal reaction of the light naphtha, volume ratio ( $V(H_2O_2)/V_{(Feed)}$ ) is varied and the effect of this parameter on reaction efficiency is investigated. Based on the results indicated in Fig.10, when  $V(H_2O_2)/V_{(Feed)}$  reached 0.045, the sulfur removal rate of feed was at the maximum value. However, when  $V(H_2O_2)/V_{(Feed)}$  is more than 0.045, the removal rate decreases significantly. It can be explained that the application of excess  $H_2O_2$  increases the production of  $H_2O$  as a byproduct. Furthermore, the side reaction causes occupation of active sites of catalyst and increases the consumption of  $H_2O_2$ . On the other hand, a portion of the hydrophilic catalyst is transferred to the aqueous phase, so the amount of catalyst in the oil phase decreases. As a result, the desulfurization rate is reduced [28, 8].

#### Influence of oxidation reaction temperature on oxidation reaction rate

Among the other similar variables, the temperature is an important factor that affects the ODS rate. Experimental results due to the variation of temperature have been exhibited in Fig.11. According to effect of temperature on rate of the interaction between reagents and oxidability of  $H_2O_2$ , temperature plays an important role in controlling of ODS reaction rate. Based on these explanations, both high and low temperatures inhibit the reaction. In this case, the optimum temperature is  $35^\circ C$ , and higher temperatures decrease desulfurization efficiency because the high temperature causes reduction of oil collecting rate, resident time on catalyst surface and deactivation of active sites in the catalyst [15].

### CONCLUSIONS

In this study,  $MoO_3/\gamma-Al_2O_3$  catalyst promoting with transition metal Ni and different additives was synthesized. Then they were utilized in the ODS process by using  $H_2O_2$  and acetonitrile as oxidant and extraction solvent for real light naphtha, respectively. Using of organic additive sorbitol as a chelating agent in the catalyst preparation, affects catalyst properties including surface area, morphology and acidity. It resulted in the highest conversion (76.25%) in comparison with other applied additives. This can be explained based on the existence six

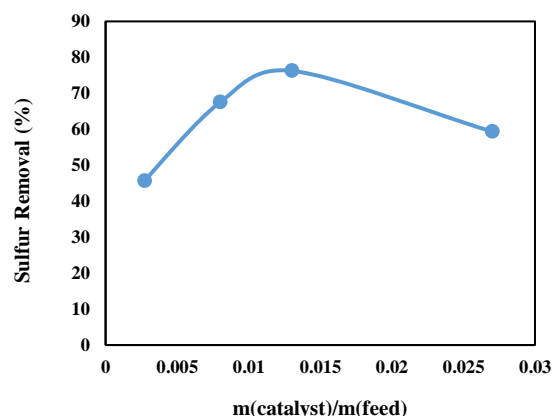


Fig. 9: The effect of  $m_{(catalyst)}/m_{(feed)}$  on total sulfur removal in naphtha. Reaction condition,  $35^\circ C$ ,  $V(H_2O_2)/V_{Feed}$  0.045, 1 hour.

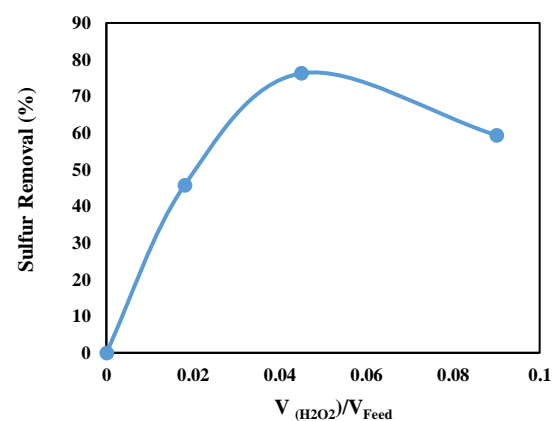


Fig. 10: The effect of  $V(H_2O_2)/V_{Feed}$  on total sulfur removal in naphtha. Reaction condition:  $m_{(catalyst)}/m_{(feed)}$  0.013,  $35^\circ C$ , 1 hour.

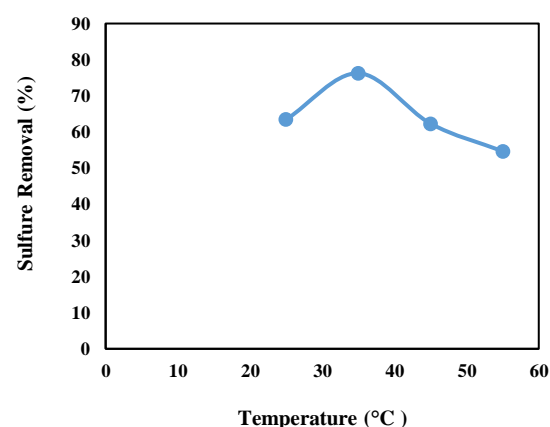


Fig. 11: The effect of temperature on the total sulfur removal in naphtha. Reaction condition:  $m_{(catalyst)}/m_{(feed)}$  0.013, 1 hour,  $V(H_2O_2)/V_{Feed}$  0.045.

hydroxyl functional groups resulting in more production of OH radicals. This is also an effective factor in the removal efficiency of the sulfur from the oil feed. Optimum operation conditions with C-S catalyst in this system include 0.5 g of the catalyst, the reaction temperature of 35°C and atmosphere pressure, the mass ratio ( $m_{\text{catalyst}}/m_{\text{feed}}$ ) of 0.013, 50 mL of feed, time of 1 hour, and the volume ratio ( $V(\text{H}_2\text{O}_2)/V_{\text{Feed}}$ ) of 0.045.

### Acknowledgment

The authors would like to thank Mrs. Zahra Shahidian and Mrs. Sara Beshkoofeh from the Iranian Institute of Research and Development in Chemical Industries (IRDCI) for their support.

Received : Jun. 16, 2019 ; Accepted : Nov. 18, 2019

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