Hydrodesulfurization of Gas Condensate containing Di-Sulfide Oil: Catalyst synthesis and evaluation

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Highlights

- Hydrodesulfurization of Gas Condensate in one step (simultaneously hydro-desulfurization of Naphtha and Gasoil cuts) was studied.
- A new solution for the Di-Sulfide Oil (DSO) production problem in oil and gas refineries (usually affected by de-mercaptanization processes) was investigated.
- $CoMo/Al_2O_3$ catalyst was successfully synthesized and applied to find the suitable operating conditions for the hydro-desulfurization of Gas Condensate feedstock containing DSO

Abstract

In this research, a catalyst based on design parameters of molybdenum percentage, Co/Mo and Urea/Co ratios by applying the Response Surface Methodology (RSM) was synthesized, characterized and optimized for the hydrodesulfurization process. The catalyst decreased sulfur content in the Gas Condensate from 2200 to 19 ppm wt. Then, various operating conditions such as temperature range of 320-340 °C, reactor pressure range of 30-40 barg, liquid hourly space

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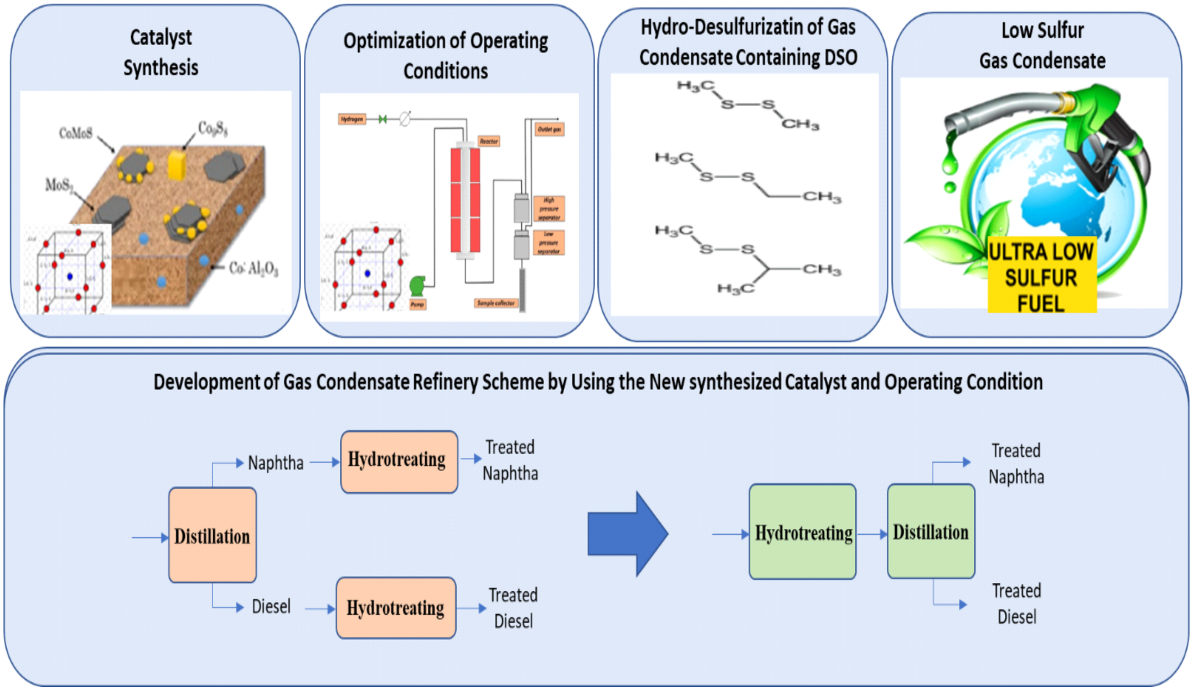
velocity (LHSV) range of 2-3 h^{-1} and H_2/Oil ratio range of 150-250 ml/ml were applied. Finally, the sulfur content in the Gas Condensate was found at 8 ppm wt. (<10 ppm wt.) at the optimum operating conditions when the synthesized catalyst with characteristics of 18% MoO_3, Co/Mo molar ratio of 0.48 and Urea/Co volume ratio of 5 was used.

Keywords: Co/Mo catalyst, DSO, Gas Condensate, Hydrodesulfurization

Graphical abstract



1. Introduction

Sulfur is as a major impure component in crude oil and its derivatives. It may form in the various sulfur types. These are responsible for a lot of environmental problems [1, 2]. The amount of sulfur in crude oil generally depends on its source. This usually varies from 0.025 to 7.89 weight percent. Burning of fossil fuels produces the sulfur oxide compounds which their emission should strictly be controlled due to the environmental regulations [3-5]. Because Leandro et al [6] scrutinized global crude oil production has increased around 12–13 million barrels from 2008 to 2017. So hence it's a great challenge to derive facile rate laws and in recent years, extensive research has been done in this regard by many researches including Guilian et al. [7]. As the sulfur content of diesel fuel in the Euro-V emission standard is limited to less than 10 ppm [8, 9].

There are various methods for desulfurization of crude oil and its derivatives [10-15]. Although Tanimu et al. generally reviewed the hydrodesulfurization (HDS) process which is the most efficient commercial technique but, the other researchers focused on the Co (Ni) Mo/Al_2O_3 as catalyst for the hydrodesulfurization process [16-19]. In fact, the hydrodesulfurization is a reaction between sulfur compounds and hydrogen. The reaction products are a saturated hydrocarbon with H_2S. This reaction is carried out in the presence of heterogeneous catalysts under extreme conditions such as high temperature and pressure. Saturated hydrocarbon molecules remain with sulfur compounds. This is main advantage of hydrogen desulfurization process compared to the other ones. Sometimes there are several active sites which promote some reactions. Topsøie et al. claimed [20] that edge and corner sites work for hydrogenation and direct removal of sulfur, respectively. Furthermore, the basic mechanism for the activation of organic sulfur compounds by HDS catalyst was the formation of a chemical bond with the metal site located on the catalyst surface. According to the literature, sulfur with organic compounds can highly be adsorbed on the sites of some promoter atoms such as cobalt and nickel compared with molybdenum. In order to investigate the mechanism of hydrogen desulfurization with Co (Ni) Mo/ɣ -Al_2O_3 catalyst, the desulfurization of thiophene as a simple model is shown in the Fig. 1. Moreover, the other models for hydrodesulfurization mechanism of benzothiophene and dibenzothiophene compounds are shown in Fig. 2. However, according to studies conducted by

Sánchez-Delgado et al. [21] disulfides react and form hydrogen sulfide and mercaptans but, mercaptans can be converted to hydrocarbons and hydrogen sulfide. Along with the increase in the consumption of natural gas resources, the production of Gas Condensate as a cost-effective hydrocarbon feedstock increased, too. Heavy hydrocarbon compounds as Gas Condensate will be extracted from the natural gas. Gas Condensate is mainly containing pentane and heavier liquid hydrocarbons (C_5^+). It is free of metals and usually contains large amounts of naphtha and gasoil cuts. According to a traditional process, after stabilizing the vapor pressure, adjusting the dew point and removing some corrosive sulfur compounds (such as mercaptans) and/or oxidizing them (Merox), the corrosive mercaptans removal and/or oxidation will conduct this valuable fuel source to the storage tanks. Each of the fractionated products will be refined after distillation process. Kidnay et al. [22] studied on a large scale undesirable by product such as disulfide oil (DSO). In order to improve the quality of Gas Condensate as a valuable hydrocarbon source, it is necessary to investigate removal of undesirable sulfur compounds from the Gas Condensate. On the other hand, simultaneous hydrodesulfurization of mercaptan and other sulfur compounds will prevent the DSO by product formation. Shabani and Royaee [23] showed that presence of DSO compounds during the hydrodesulfurization process will enable the purification of produced DSOs.

In the current research, CoMo/Al_2O_3 catalyst was synthesized, characterized and tested to apply it for the Gas Condensate feedstock under various operating conditions. For this, the synthesized catalyst in the hydrodesulfurization reactor was loaded to investigate the optimum conditions. Finally, a deep hydrodesulfurization of Gas Condensate containing DSO with the synthesized catalyst under the optimized operating conditions was carried out.

2. Materials and methods

2.1.Materials

Aluminum sulfate [Al_2O_3 $(SO_4)_3$.18 H_2O], ammonia (NH_3 25 wt. %), nitric acid (HNO_3 65 wt. %), ammonium hepta-molybdate tetrahydrate [$(NH_4)6Mo_7O_{24}\cdot4H_2O$>0.994 g/g in purity], Co(II) nitrate hexahydrate [$Co(NO_3)_2\cdot6H_2O$, analytical grade] and citric acid were supplied by Merck KGaA. Sodium aluminate (Na_2O 41%, Al_2O_3 53% and H_2O 6%) was supplied by VWR Co. All chemicals were used without further treatments.

2.2.Catalyst support preparation

γ-Al_2O_3 support was prepared by peptization of boehmite powder synthesized through precipitation method. Then, the catalyst was synthesized by the dry impregnation technique.

2.3.Catalyst characterization

The synthesized catalyst was analyzed through X-ray diffractometer (EQUINOX3000, France), HRTEM and XPS (with K-Alpha$^+$, Thermo Co.). High resolution transmission electron microscopy (HRTEM) analysis was performed by FEI 200 kV (TEC9G20, USA). The extrudates were powdered and dispersed in ethanol to take the TEM images.

Temperature programmed reduction (TPR) analysis was carried out to determine the active sites of catalyst. The TPR was obtained on a Micromeritic-2900 device. TPR profiles were exposed to gaseous mixture flow (5% hydrogen in Ar) with a flow rate of 151 ml/min to stabilize the baseline of TCD. Temperature increased with a rate of 10 °C/min from ambient temperature to 800 °C and the hydrogen consumption was reported based on the calibration curve. The pyrolysis method (multi-EA®5000 for micro-elemental analysis) was applied to measure the sulfur content of products when the reactor was filled by the synthesized catalyst.

2.4.Catalyst activation

Yamada et al. [24] employed H_2S utilized to a gaseous mixture containing 10 wt.% of H_2S and 90 wt.% of H_2 with a flow rate of 30 ml/min was used to activate the fresh catalyst under the atmospheric pressure and temperature program according to Fig. 3.

3. Synthesis of catalyst

CoMo/γ-Al_2O_3 catalyst was produced by inoculation of ammonium hepta-molybdate (dissolved in ammonia) on the dry support (with surface area of 250 m^2/g, pore volume of 0.63 cm^3/g and pore diameter of 10.5 nm). Then, the support was dried at 60 °C for 4 h. Cobalt nitrate and urea solution were then inoculated on the dry support surface. It was dried for 3 h at 60 °C followed by 10 hours in a furnace with temperature of 120 °C with a rate of 3 °C/min. Finally, the catalyst was calcined with the same rate for 4 h at 500 °C. Three factors involving MoO_3 content (12-20 wt.%), Co/Mo molar ratio (0.2-0.8), and Urea/Co ratio (0-10) was studied on the sulfur content in a fixed bed reactor filled by the activated catalyst under temperature of 320 °C, pressure of 35 barg, and H_2/Oil ratio of 200 Nml/ml, and LHSV of 3 h^{-1}. The operating conditions were extracted from the literature for naphtha and gasoil [25, 26]. According to the Box-Behnken design (BBD), fifteen runs were designed and 15 catalysts were synthesized to desulfurize Gas Condensate in a reactor. The results of experimental design and data were summarized in Table 1.

Table 1.

Table 2 shows the Gas Condensate specification.

Table 2.

As shown in Table 3, interaction between the parameters can be studied by a second-order model.

Table 3.

Although R^2 value for a good model is around 0.8 but, adj-R^2 value for the developed model is 0.98 (with$R^2 = 0.91$). A high F-value (167) and low p-value (0.0001) indicates that the model components are significant, as well.

Table 4 shows Analysis of variance (ANOVA) for the proposed second-order model (large F-values and low p-values can be observed for various parameters).

Table 4.

As shown in Table 4, quadratic model as a proposed one could predict the experimental data with a high accuracy (with large F-value and small p-value).

Results indicated the effective interactions between the parameters which can be better observed by investigating the three-dimensional diagrams of the effect of parameters on each other. Figs 2-4 reveal the effect of different parameters, Elsayed et al. [27] presented that elliptical lines in **Error! Reference source not found.** indicate a distinct interaction while the circular contours show a small effect.

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As shown in Fig. 4, the maximum catalyst activity (total sulfur content) can be observed in the Co/Mo range of 0.35-0.55 and in MoO_3 of 15-17%. It seems that an increase in Co/Mo ratio can enhance the active sites. Furthermore, the catalytic activity may be declined in the presence of CoMoS species in the molar ratios more than 0.55 .These results support the data reported in previous studies by Zhang et al [28]. Moreover, the catalyst showed a reduction in efficiency at Co/Mo ratios less than 0.35. This may be due to piling of MoS_2 layers on each other. Fig. 5 shows effect of Urea/Co and MoO_3 on the total sulfur content as a symbol of catalyst activity. Co/Mo molar ratio enhancement (with optimum value of 0.45) would improve the catalyst activity because the active sites would increase although an increase in Co-promoter amount can highly break C-S bonds. Molybdenum oxide loading increment (from 12 to 16%) would increase the catalyst activity although a decreasing in the catalyst activity was also observed. According to the obtained results by Zhang et al [29] this may be due to overlapping the layers which can limit the active sites access. Fig. 6 shows effect of Co/Mo and Urea/Co on the catalyst activity, as well. The sulfidation reaction would increase with increasing Urea/Co molar ratios. In fact, urea amount increment can substantially increase the reaction molar enthalpy which will increase the catalyst porosity and decline the interactions between the alumina support and active phase [30-33]. Van Haandel et al [34] scrutinized that this will result in the formation of type-II desirable active sites. Moreover, over-consumption of urea can lead to the accumulation of MoS_2 and lower dispersion.

Fig. 7 shows a good matching between the total sulfur content experimental data with the predicted ones by model for the Gas Condensate.

3.1.Catalyst optimization

The catalyst activity would be optimized by minimizing the sulfur content in the product (from 20 to 64 ppm). So, the molybdenum oxide percentage, Co/Mo molar ratio and Urea/Co molar ratio should respectively vary from 15.2 to 15.8, from 041 to 0.48 and from 5.1 to 5.6. The catalyst with molybdenum oxide of 15.5%, Co/Mo ratio of 0.45, and Urea/Co ratio of 5 showed the best efficiency compared with the others in this study.

3.2.TPR analysis

Fig. 8 shows TPR analysis for the various catalysts. According to this figure, urea-containing catalysts show lower temperatures in comparison with the urea-free ones. Therefore, urea consumption will lead more interaction between the active phase and support, and better dispersion of catalyst particles. The higher chart area (more hydrogen consumption) of the catalyst indicates stronger active sites and more probability of the formation of Co-Mo-S-II active sites which have higher efficiency in the desulfurization process. According to the literature, urea consumption results in the formation of type-II Co-Mo-S active phase on support [35-37]. Co/Mo ratio increment (up to the optimal value) will show no reverse effect in overlapping of layers. Therefore, an increase in Co/Mo ratio up to the optimal value will increase the active sites (promoter effect of Co can highly break the C-S bonds).

3.3.HRTEM analysis

Some microstructural properties of catalyst can be studied by HRTEM. Fig. 9 shows the HRTEM images with different magnifications along with the histogram of particle size distribution and the SAED diffraction pattern. Therefore, an image was used to measure particle size, atomic spacing, and ring diameter in the SAED diffraction pattern. The HRTEM images of $CoMoAl_2O_3$ sample at three different magnifications (a-c), the particle size distribution histogram (d), and the corresponding SAED diffraction pattern (e) are presented in Fig. 9. The clustered agglomerates of $CoMoAl_2O_3$ particles with various sizes (from 100 to 500 nm) are visible in Fig 9 (a). The agglomerates have formed due to the small size of $CoMoAl_2O_3$ particles and their tendency for the surface energy reduction through agglomeration. Since the particles size decreases and the ratio of surface to volume and surface energy increase, the aggregation minimizes the energy. Fig. 9 (b) shows the $CoMoAl_2O_3$ nanoparticles. The size distribution histogram was obtained for 100 particles using Image J processing software (open source) and depicted in Fig 9 (d). According to the histogram, 22 particles (from 100 measured particles) had sizes of 4 to 4.5 nm. The average particle size and standard deviation from these measurements were around 4.29 and 1.04 nm, respectively. These indicate the particles ultrafine size and monodispersity with a normal distribution. Furthermore, the smallest and largest particles were at 2.20 and 6.45 nm, respectively.

According to Fig 9 (e), the SAED pattern of sample shows bright rings corresponding to the crystal planes (111), (311), (400), (511), and (440) of the alumina structure with the reference code JCPDS No. 00-029-0063, which has a cubic crystal structure with an Fd3m space group. The absence of secondary phases of cobalt and molybdenum in the SAED pattern indicates an appropriate placement in the crystalline structure of alumina. This confirms high purity of the synthesized catalyst. Fig. 9 (c) shows a magnified micrograph revealing visible atomic rows of the crystal structure. As shown in Fig. 9 (e), atomic rows of crystal planes (400) and (311) can be observed at atomic row distances of 1.98 and 3.70 nm, respectively.

3.4.XPS analysis

The presence of Al 2p, Al 2s, and O 1s peaks indicates aluminum and oxygen elements in the structure of alumina. Moreover, the peaks corresponding to Co 3p, Co 3s, Mo 3p, and Mo 3d demonstrate successful doping of alumina structure by cobalt and molybdenum elements. Figs. 10 (a-d) show high-resolution spectra of Al 2p, O 1s, Co 3p, and Mo 3d. Table 5 shows the atomic percentage values of each bond.

Table 5.

According to Figs. 10 and Table 5, O 1s peak has been resolved into two peaks at 532.13 and 533.54 eV corresponding to the oxygen bonds with a metallic network structure (such as aluminum), and oxygen bond to hydrogen, respectively. Furthermore, Al 2p peak has been convoluted into two peaks at 75.31 and 76.36 eV corresponding to the aluminum-oxygen bond in the alumina structure and aluminum-hydroxide bond on the surface that presented by Batra ret al [38]. Since XPS is a surface analysis technique and about 30% of tests belong to the sample surface, the last peak would belong to hydroxide. According to the results related to convolution of Co 3p and Mo 3d peaks, the structure will be compatible with Co in both divalent (38.85%) and trivalent (50.4%), as well as Mo in hexavalent (30.98%), pentavalent (39.02%), and tetravalent (30.01%), as reported in Table 5.

4. Operating conditions of Gas Condensate

4.1. Effect of operating parameters on the catalyst activity

Temperature, pressure, H_2/Oil ratio and LHSV are the operating variables for the hydrodesulfurization process. The desulfurization efficiency and hydrogen consumption increased with temperature and pressure increment although high temperatures may produce coke and decrease the catalyst lifetime [39-42]. Furthermore, the space velocity increment can reduce conversion rate, hydrogen production and coke formation.

According to the boiling range of Gas Concentrates (as a combination of naphtha and gasoil boiling points), the operating conditions were chosen, accurately. The temperature and pressure ranges were chosen as 320-340 °C and 30-40 barg, respectively. H_2/Oil ratio and LHSV ranges were selected as 250-350 Nml/ml and 2.5-3.5 h^{-1}, respectively. Therefore, twenty seven runs were proposed under Box-Behnken Design (BBD) through Design of Experiments (DoE) software (Version 13) and illustrated in Table 6.

Table 6.

A second-order equation considering the inter-parametric interactions was proposed as a proper model by the software. As shown in Table 6, temperature and LHSV had the maximum impacts on the hydrodesulfurization. Fig. 11 indicates the effects of temperature and LHSV on the total sulfur content. As shown in this figure, desulfurization should be in maximum at higher temperatures due to the energy elevation. Since the feedstock had enough time to contact with the catalyst, lower LHSV had a positive impact on the desulfurization. Therefore, temperature and LHSV had direct and indirect relation with the sulfur content. High temperature and low LHSV can promote the cracking reaction with adverse impact on the process.

Since temperature increment was more effective parameter than pressure enhancement on sulfur content, desulfurization process was achieved at temperature and pressure ranges of 332-340 °C and 33-35 barg, respectively. According to the studies conducted by Neeraj, et al. [43] temperature had higher effect on hydrodesulfurization than H_2/Oil ratio when the other parameters were fixed as constant values. Furthermore, maximum hydrodesulfurization was observed at maximum temperature and minimum H_2/Oil ratio. Since LHSV was more effective parameter than pressure on the sulfur content, maximum hydrodesulfurization was achieved at pressure and LHSV ranges of 35-40 barg and 2.5-3 h^{-1} when the other parameters were fixed as constant values.

The pressure was more effective parameter than H_2/Oil at constant temperature and LHSV. The maximum hydrodesulfurization was found at maximum pressures and at minimum H_2/Oil ratio.

The LHSV was more effective parameter than H_2/Oil ratio. The maximum hydrodesulfurization was obtained at the LHSV range of 2.5-3, H_2/Oil range of 150-230 at constant temperature of 330 and at pressure of 35 barg.

Fig. 12 shows the experimental and predicted data which show good agreement with each other when all operating conditions were considered together.

4.2.Optimization of the operating parameters

As the software dramatically proposed the following equation, it was applied to investigate the optimum conditions. According to the software output, temperature range of 330-338, pressure range of 32-37 barg, LHSV range of 2.6-2.9, and H_2/Oil ratio range of 160-195 were found. Total sulfur content of product was at 8 ppm wt. when the optimum conditions were applied with an optimal catalyst.

$$\text{Sulfur contetnt} = 12971.75 - 75.575\,\mathrm{T} - 1.08333\,\mathrm{P} - 160.5\,\mathrm{LHSV} - 0.228333\left(\frac{\mathrm{H_2}}{\mathrm{Oil}}\right) + 0.025(\mathrm{T}\times\mathrm{P}) + 0.15\,\mathrm{T}\times\mathrm{LHSV} - 0.001\left(\mathrm{T}\times\frac{\mathrm{H_2}}{\mathrm{Oil}}\right) + 0.1\,\mathrm{P}\times\mathrm{LHSV} - 0.004\left(\mathrm{P}\times\frac{\mathrm{H_2}}{\mathrm{Oil}}\right) + 0.07\left(\mathrm{LHSV}\times\frac{\mathrm{H_2}}{\mathrm{Oil}}\right) + 0.11333\,\mathrm{T}^2 + 0.13333\mathrm{P}^2 + 18.8333\mathrm{LHSV}^2 + 0.01383\left(\frac{\mathrm{H_2}}{\mathrm{Oil}}\right)^2 \qquad (1)$$

4.3.Desulfurization of Gas Condensate containing DSO

There were two traditional techniques [Demercaptanization (DMC) process through sodium hydroxide solution consumption for the light mercaptans extraction and mercaptans oxidation (Merox) with air and catalyst for the heavier mercaptans] for desulfurization of Gas Condensate containing DSO.

Since some big oil countries such as Iran, Qatar, and Saudi Arabia produce disulfide oil and its derivatives (such as Gas Condensate), a novel efficient technique for their sweetening has been encouraged. For this, 250 ppm disulfide oil was added to the Gas Condensate to make a feedstock with 115 ppm total sulfur content which most of it was DSO.

Composition of a typical DSO is shown in Table 7:

Table 7.

The desulfurization of the Gas Condensate was carefully examined under the optimized operating conditions with the selected catalyst proposed in this research. The sulfur content was reduced to 53 ppm by increasing temperature from 330 to 345 although further increment in temperature will restrict the desulfurization due to the cracking process. Therefore, the proposed catalyst reduced the total sulfur content of product to 8 ppm wt. under the optimized operating conditions at temperature of 330 °C.

5. Conclusions

In this research, a novel efficient catalyst (instead of demercaptanization, distillation, hydrodesulfurization processes for desulfurization of naphtha and gasoil) was synthesized, characterized and applied for desulfurization of a Gas Condensate under the optimum operating conditions. The statistical results obtained from the design of experiments showed that the Mo content in the synthetic catalyst and temperature as a parameter of operating conditions had the most effect on the desulfurization of Gas Condensate. MoO_3 ratio increment had the maximum effect on the catalyst synthesis. Then, a DSO was added to the Gas Condensate and its desulfurization was investigated under the optimum conditions using the catalyst proposed in this research.

Acknowledgment

The authors thank Institute of Petroleum Industry (Tehran, Iran) for its collaboration (technical and financial supports) in this research.

Declarations

This paper is as a part of a PhD dissertation approved by Arak University and Iranian Research Institute of Petroleum Industry. The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Nomenclature

API	American Petroleum Institute
BBD	Box Behncken Design
Co	Cobalt
DSO	Disulfide oil
DMC	Demercaptanizatin of Condensate
HDS	Hydrodesulfurization
LHSV	Liquid hourly space velocity
Mo	Molybdenum
RSM	Response surface methodology
S	Sulfur
TPR	Temperature programmed reduction

Tables

Table 1. Experimental design for the synthesized catalysts

Table 2. Specification of Gas Condensate

Table 3. Various models obtained from the statistical software

Table 4. Analysis of variance

Table 5. Atomic percentage values of each bond extracted from the X-ray photoelectron spectroscopy (XPS) analysis

Table 6. Sulfur content of the product under various operating conditions

Table 7. Typical Disulfide oil composition

Run	No	MoO_3 (wt. %)	Co/Mo (molar ratio)	Urea/Co (molar ratio)	Total sulfur (ppm)
1	Cat 01	20	0.5	0	43
2	Cat 02	12	0.2	5	64
3	Cat 03	16	0.5	5	20
4	Cat 04	20	0.8	5	45
5	Cat 05	20	0.2	5	47
6	Cat 06	16	0.8	10	29
7	Cat 07	16	0.2	0	51
8	Cat 08	16	0.5	5	22
9	Cat 09	16	0.5	5	21
10	Cat 10	12	0.5	0	61
11	Cat 11	20	0.5	10	37
12	Cat 12	16	0.2	10	35
13	Cat 13	12	0.5	10	48
14	Cat 14	16	0.8	0	45
15	Cat 15	12	0.8	5	56

Table 1. Experimental design for the synthesized catalysts

Specification	Unit	Result	Method
Specific gravity @ 15.56 /15.56 °C	-	0.7451	ASTM D4052
API	-	58.4	ASTM D4052
Total sulfur content	ppm	2200	ASTM D5453
Molecular weight	g/mole	110	IP 86

Table 2. Specification of Gas Condensate

	Sum of squares	F-value	p-value prob>F	R-squared	Adj R-squared	Suggestion
Linear	142.52	2.04	0.0058	0.0956	0.0666	No adequate
2FI	185.31	13.59	0.0039	0.8702	0.2708	No adequate
Quadratic	236.54	167.11	0.000106	0.9138	0.9826	Suggested
Cubic	239.29	58.92	0.2206	0.946	0.9934	Aliased

Table 3. Various models obtained from the statistical software

Source	Sum of Squares	Degrees of freedom	Mean Square	F-value	p-value	Description
Model	2743.85	9	304.87	64.18	0.0001	Significant
A:Mo	406.13	1	406.13	85.50	0.0002	-
B:Co/Mo	60.50	1	60.50	12.74	0.0161	-
C:Urea/Co	325.13	1	325.13	68.45	0.0004	-
AB	9.00	1	9.00	1.89	0.2271	-
AC	12.25	1	12.25	2.58	0.1692	-
BC	0.0000	1	0.0000	0.0000	1.0000	-
A^2	1422.06	1	1422.06	299.38	< 0.0001	-
B^2	565.44	1	565.44	119.04	0.0001	-
C^2	162.06	1	162.06	34.12	0.0021	-
Residual	23.75	5	4.75	-	-	-
Lack of Fit	21.75	3	7.25	7.25	0.1236	not significant

Table 4. Analysis of variance

Peak	Bonds	Peak position (eV)	Peak area (CPS. eV)	%At.
O1s	O-Lattice	532.13	103288.5	67.32
	O-H	533.54	50173.7	32.68
Al 2p	Al-O	75.31	9894.0	66.76
	Al-OH	76.36	4929.1	33.24
Mo 3d	Mo^{6+} $3d_{5/2}$	233.47	2993.3	28.40
	Mo^{5+} $3d_{5/2}$	234.36	1273.6	12.08
	Mo^{4+} $3d_{5/2}$	234.81	2692.2	25.53
	Mo^{6+} $3d_{3/2}$	263.11	272.2	2.58
	Mo^{5+} $3d_{3/2}$	237.42	2843.4	26.94
	Mo^{4+} $3d_{3/2}$	239.82	473.0	4.48
Co 3p	Co^{3+} $3p_{3/2}$	764.87	6573.7	26.03
	Co^{2+} $3p_{3/2}$	766.04	5203.5	20.58
	Co^{3+} $3p_{1/2}$	783.09	6235.9	24.37
	Co^{2+} $3p_{1/2}$	789.38	4697.3	18.27
	Satellite	799.05	2781.3	10.74

Table 5. Atomic percentage values of each bond extracted from the X-ray photoelectron spectroscopy (XPS) analysis

Run	Factor 1	Factor 2	Factor 3	Factor 4	Predicted values
	Temperature (℃)	Pressure (barg)	LHSV (h^{-1})	H_2/Oil (ml/ml)	Sulfur content (ppm)
Cat 01	320	30	3	200	45
Cat 02	340	35	2.5	200	8

Cat 03	340	35	3	250	17
Cat 04	330	35	2.5	250	14
Cat 05	330	40	3.5	200	31
Cat 06	330	35	3.5	250	38
Cat 07	330	35	3.5	150	29
Cat 08	330	30	2.5	200	15
Cat 09	320	35	3	250	49
Cat 10	330	40	3	150	19
Cat 11	330	30	3.5	200	34
Cat 12	340	35	3	150	11
Cat 13	330	40	3	250	24
Cat 14	330	35	3	200	15
Cat 15	320	35	3	150	41
Cat 16	320	35	3.5	200	55
Cat 17	340	35	3.5	200	28
Cat 18	330	30	3	150	20
Cat 19	320	35	2.5	200	38
Cat 20	340	30	3	200	23
Cat 21	340	40	3	200	12
Cat 22	330	35	2.5	150	12
Cat 23	330	35	3	200	16
Cat 24	330	35	3	200	15
Cat 25	330	30	3	250	29
Cat 26	320	40	3	200	39
Cat 27	330	40	2.5	200	11

Table 6. Sulfur content of the product under various operating conditions

Parameter	Quantity (wt.%)
Sulfur content	51.2
Dimethyl disulfide	46–58
Diethyl disulfide	32
Diethyl sulfide	10–20
Dipropyl sulfide + methyl propyl disulfide + di-isopropyl + disulfide	< 2

Table 7. Typical Disulfide oil composition

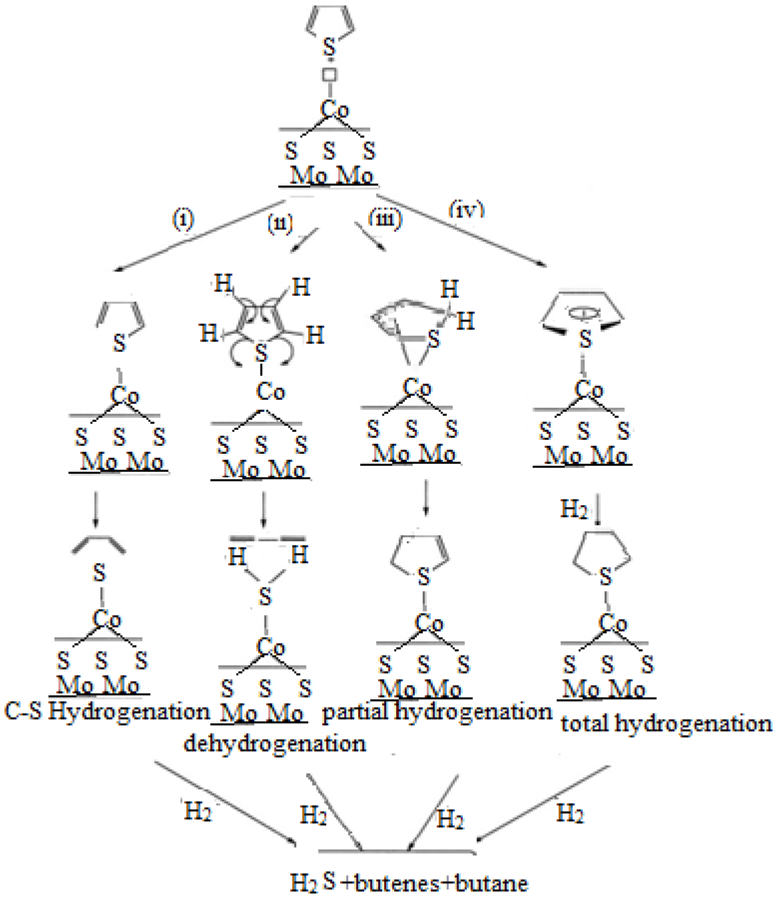


Fig. 1. Mechanism of the desulfurization of thiophene [21]

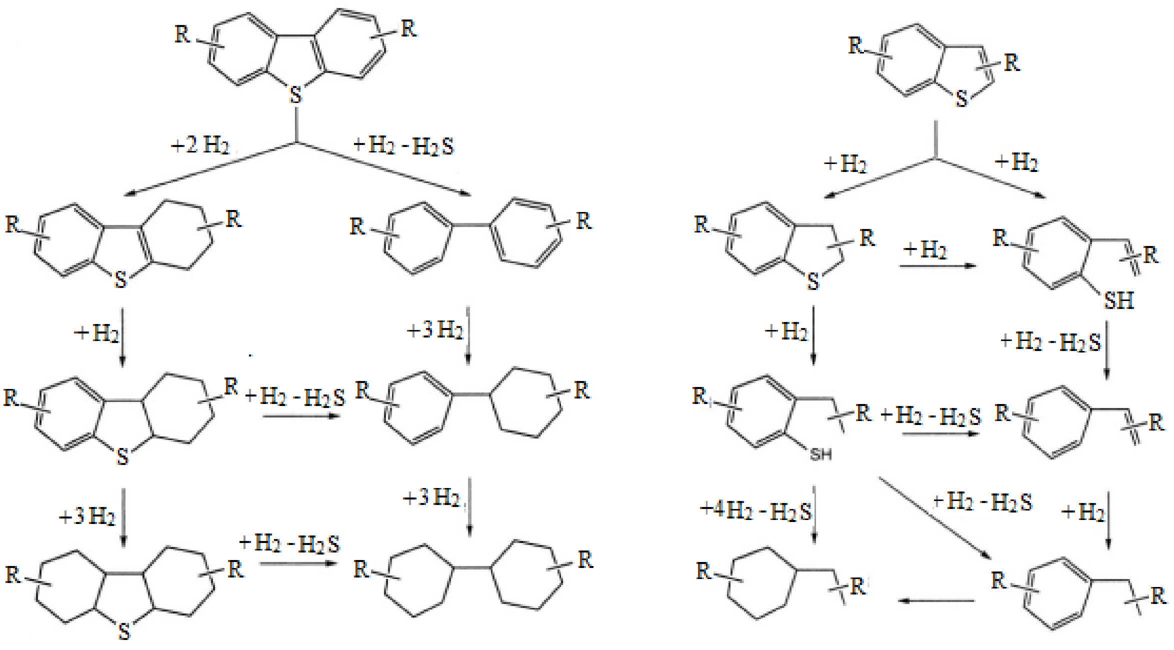


Fig. 2. Main reactions of HDS for benzothiophene (left side) and dibenzothiophene (right side) [21]

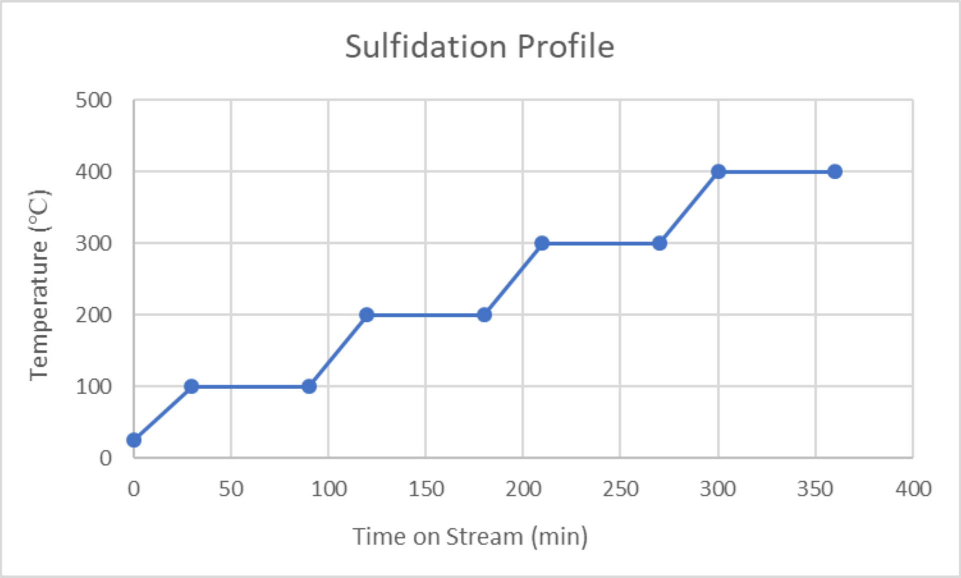


Fig. 3. Catalyst activation pattern (temperature versus time)

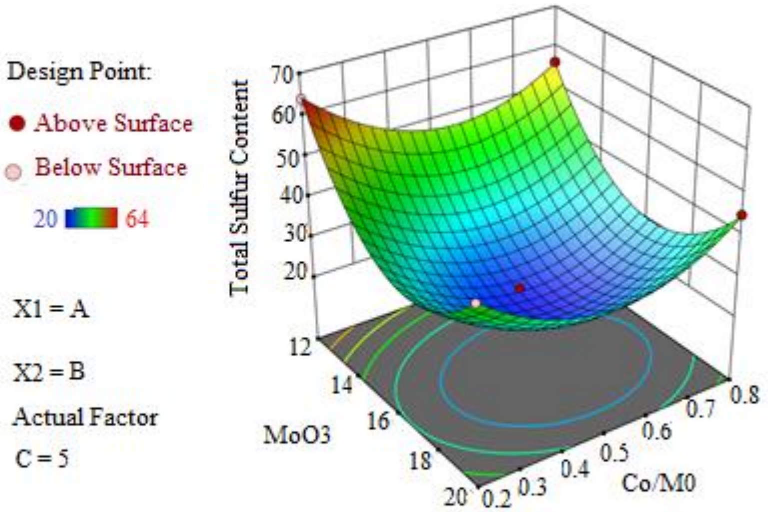


Fig. 4. Effect of Co/Mo ratio and MoO_3 on the catalyst activity

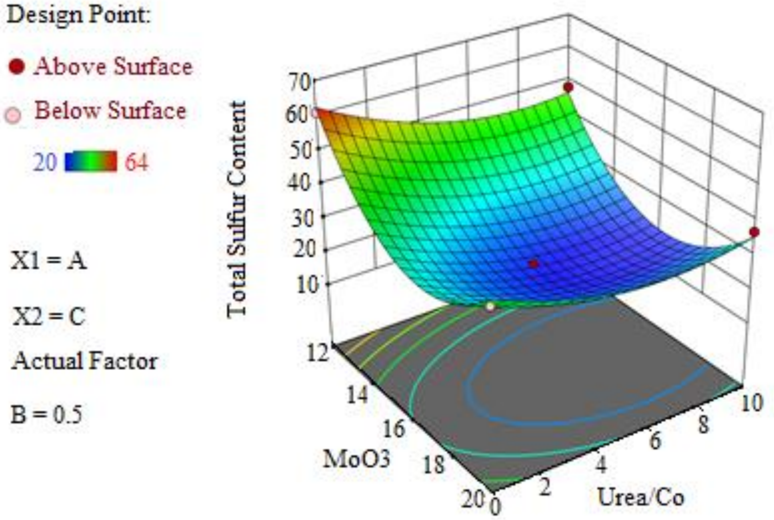


Fig. 5. Effect of Urea/Co and MoO_3 on the catalyst activity

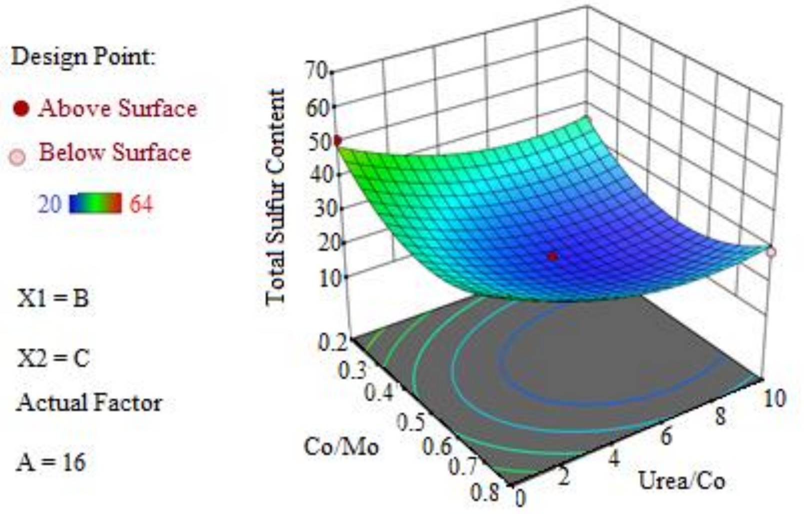


Fig. 6. Effect of Co/Mo and Urea/Co on the catalyst activity

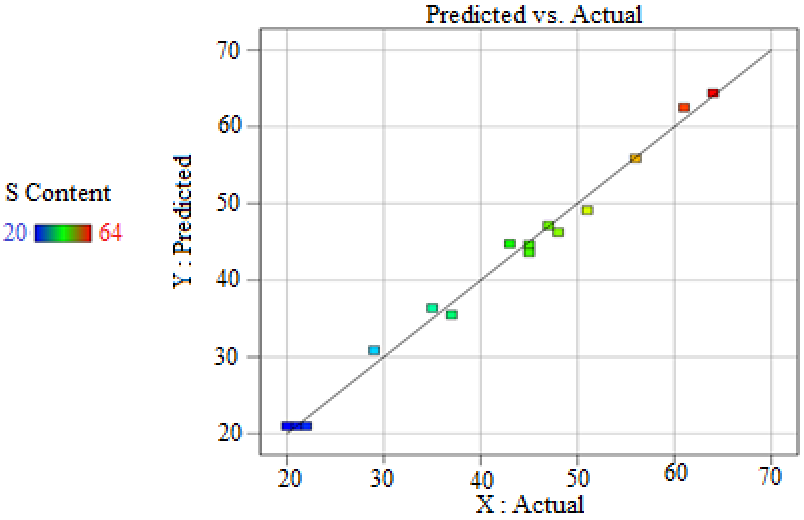


Fig. 7. Predicted total sulfur content data versus experimental ones

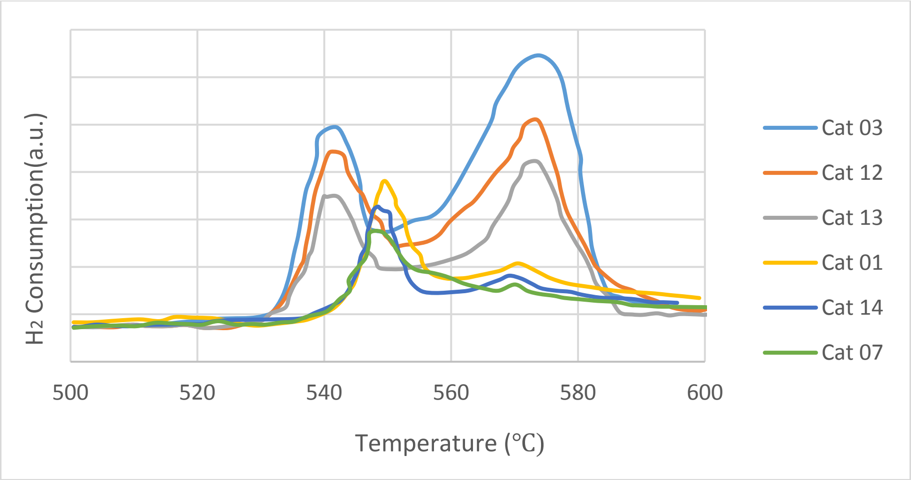
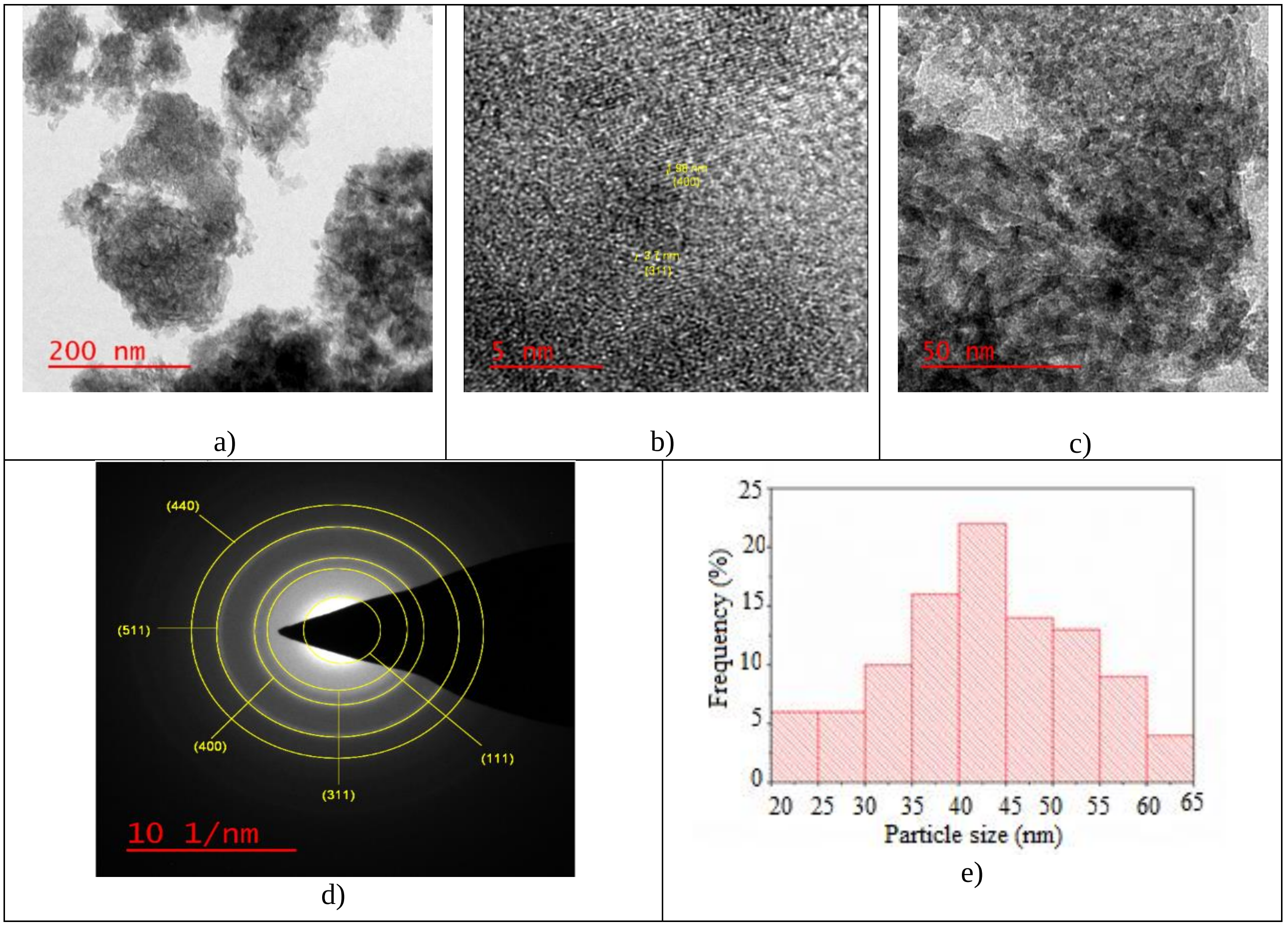


Fig. 8. TPR diagrams for various synthesized catalysts



a)

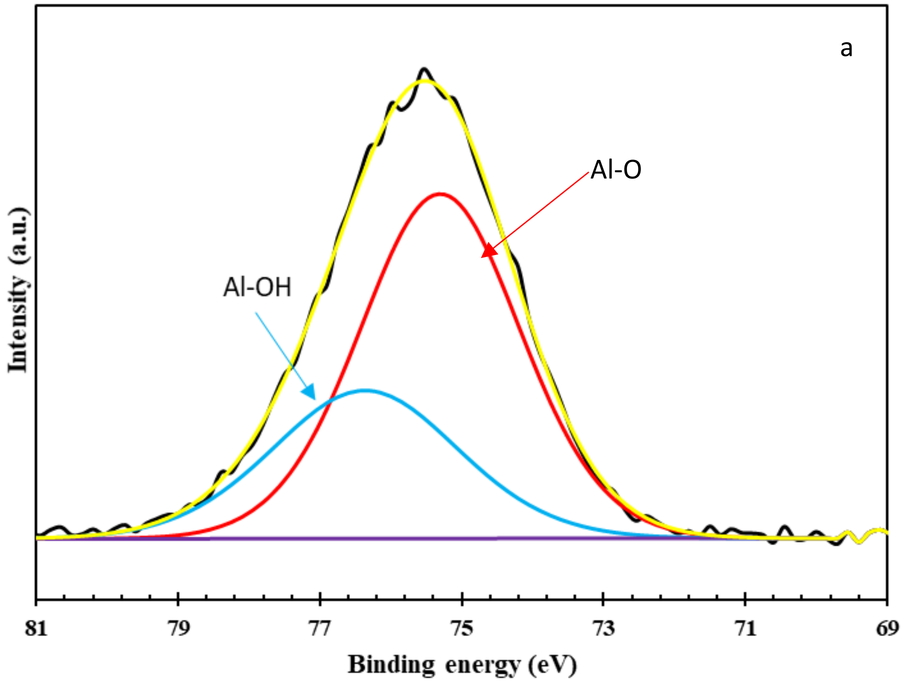
b)

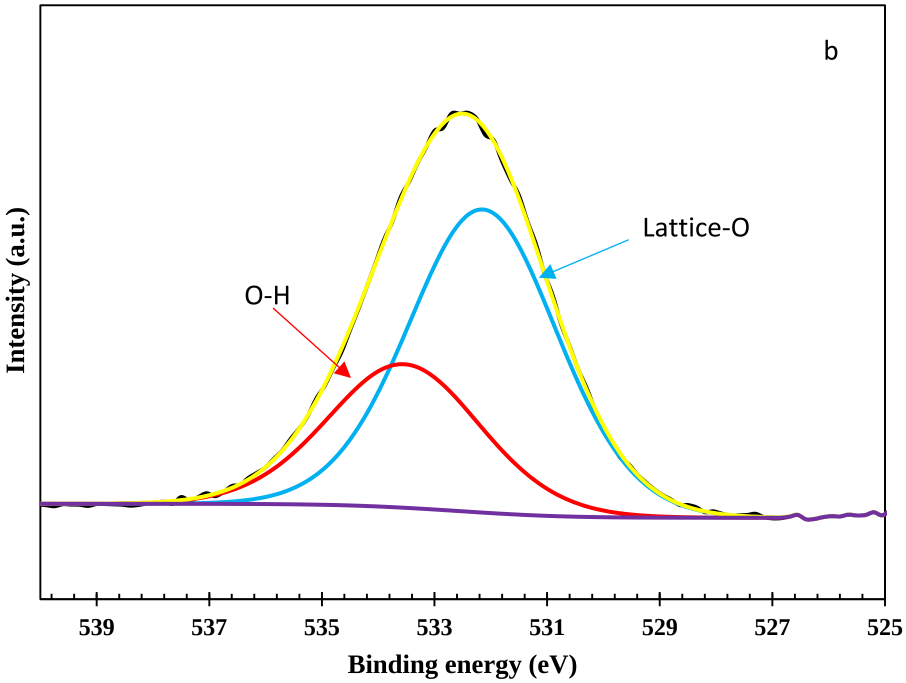
c)

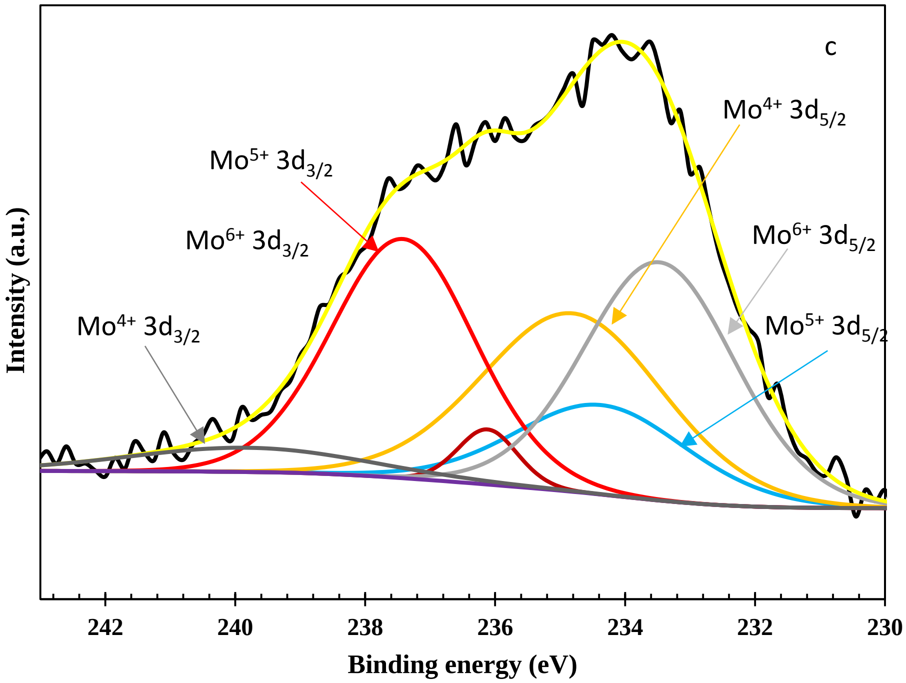
d)

e)

Fig. 9. (a-c): HRTEM images of $CoMoAl_2O_3$ catalyst with various magnifications, (d): Histogram of particles size distribution, and (e): SAED diffraction pattern of the catalyst


a
Al-O
Al-OH
Intensity (a.u.)
81
79
77
75
73
71
69
Binding energy (eV)


b
Intensity (a.u.)
Lattice-O
O-H
539
537
535
533
531
529
527
525
Binding energy (eV)


c
Intensity (a.u.)
Mo^{4+} 3d$_{5/2}$
Mo^{5+} 3d$_{3/2}$
Mo^{6+} 3d$_{5/2}$
Mo^{6+} 3d$_{3/2}$
Mo^{5+} 3d$_{5/2}$
Mo^{4+} 3d$_{3/2}$
242
240
238
236
234
232
230
Binding energy (eV)

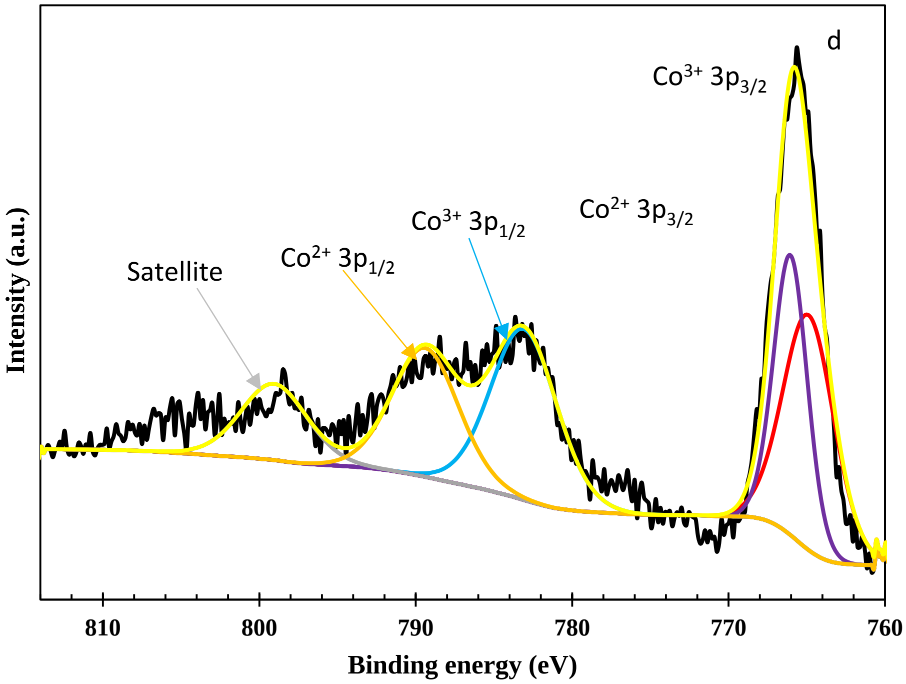


Fig. 10. XPS spectra of the catalyst with various peaks: (a) Al 2p, (b) O 1s, (c) Mo 3d and (d) Co 3p

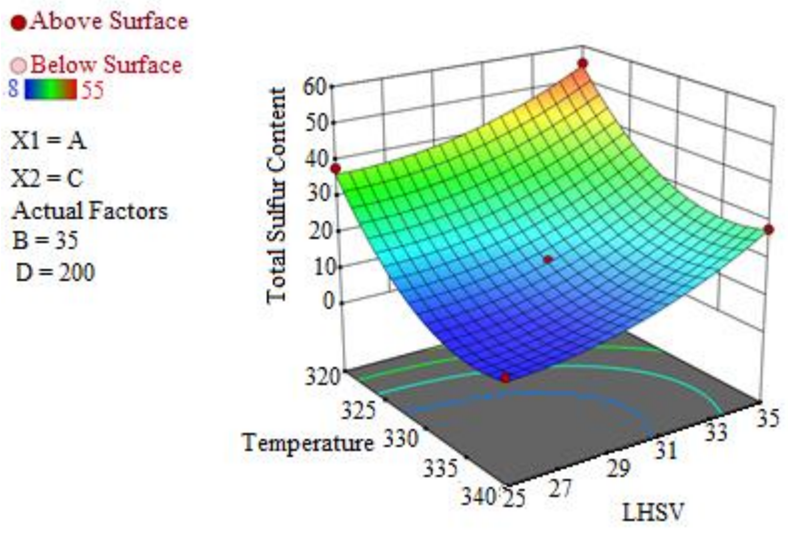


Fig. 11. Effect of temperature and LHSV on the catalyst activity

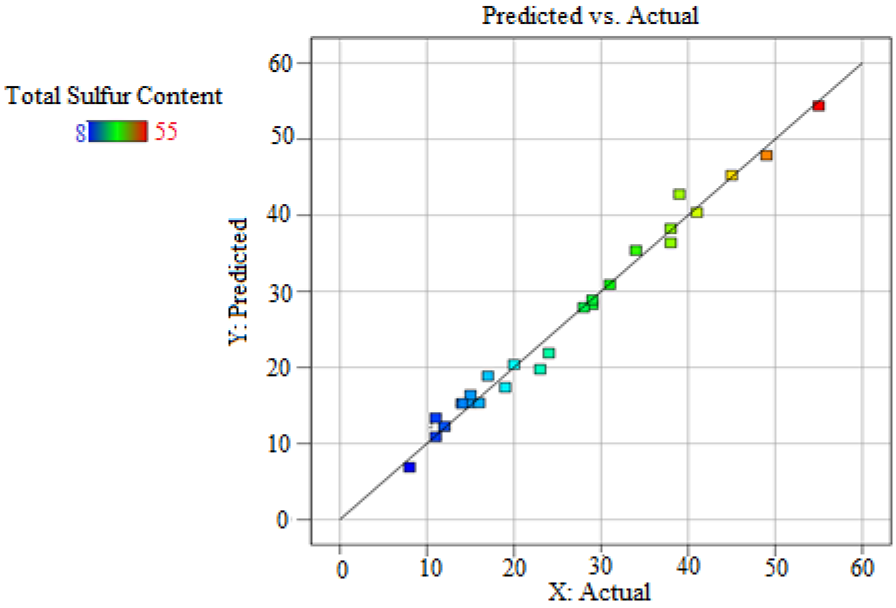


Fig. 12. Predicted total sulfur content data versus experimental ones when all parameters were considered together

Reza Davarnejad received his bachelor and master in petrochemical and chemical engineering in Iran in 2002 and 2004, respectively. University Sains Malaysia awarded PhD. degree to him in 2010 in separation processes (supercritical extraction and thermodynamics). He worked as a process engineer in Shazand Petrochemical Corporation, as a researcher assistant in University Sains Malaysia and as an invited lecturer in several universities. He has been joined the Chemical Engineering Department of Arak University as an assistant professor since 2010. He received his associate professor position from it in 2016. He was as head of chemical engineering department at Arak University from 2018 to 2020. He was as a top researcher in Markazi province in 2015 and 2019. He could publish more than 150 papers in the valid journals. He had been as a visiting professor in Chemical and Biochemical Engineering Department of Western University (London, Canada) since January 2023.

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Sayed Javid Royaee is currently works in Research Institute of Petroleum Industry (RIPI) as an associated professor from 2008 up to now. He received his bachelor and master degree in 2004 and 2006, respectively. Polytechnic University of Amir Kabir (Chemical Engineering Faculty) in Iran awarded PhD. degree to him in 2010 in advanced chemical engineering. He was research associate in many master and PhD. Thesis in Amir Kabir University and RIPI. His professional research field had been focused on technology development in Oil Refining Processes especially for Catalytic Processes including treating and conversion process Units. In this regards several technologies had been developed from laboratory and pilot scales to industrial processes. He is head of Refining Technology Development Division in Research Institute of Petroleum Industry.

Reza Seif Mohaddecy is works in Research Institute of Petroleum Industry (RIPI) as a main researchers in Catalyst field from 2003 up to now. He graduated with a BSc and MS degree in chemical engineering from Tehran University and Sharif University of Technology in 2000 and 2003 respectively. He taught chemical engineering courses such as chemical reactions engineering and reactor design, heat transfer and mass and heat balance at Arak Islamic Azad University. His executive experiences are in the field as head of RIPI’s Catalysis Technology Development Division, from 2022 till now, and head of Catalytic Reactions Engineering Department of catalysis Technology Development Division, from 2015 to 2020. Senior Lecture of Chemical Engineering Department, Arak Islamic Azad University, 1994 -2003 and Manager of the chemical engineering department, Arak Islamic Azad University, 1996- 1999. He also worked as a project manager or main project member of the RIPI on many research projects, including catalyst synthesis, kinetic determination, simulation, and catalyst formulation. He has published and presented more than 80 papers in different journalsand conferences and he has submitted three patents in Catalyst synthesis field.