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Preparation and Catalytic Activity of Co-Mo/γ-Al₂O₃ Catalyst for Hydro-desulfurization Reaction

Fouad K. Mahdi[a], Mushtaq T. Albdiry[b*], Abbas A. Diwan[c]

[a] Department of Chemical Engineering, College of Engineering, University of Al-Qadisiyah, Iraq

[b] Department of Materials Engineering, College of Engineering, University of Al-Qadisiyah, Iraq

[c] Nanotechnology and Advanced Materials Research center, College of Engineering, University of Al-Kufa, Iraq

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ABSTRACT

In this study, a bimetallic CoMo spicy supported on γ-Al₂O₃ heterogeneous catalyst was successfully prepared by an incipient wetness impregnation for Hydrodesulphurization (HDS) reaction of An-Najaf oil refinery heavy naphtha. The structural characteristics of the prepared 5Co-15Mo/γ-Al₂O₃ catalyst were evaluated by Scanning Electron Microscopy (SEM) and X-Ray Powder Diffraction (XRD) spectroscopies. The surface area, pore volume and pore size were determined by a Brunauer–Emmett–Teller (BET) method. The catalytic activity in the removal of sulphur compound from a heavy naphtha through the HDS at four different reaction temperatures (523, 548, 573, 598 °K) and four different liquid hourly space velocities (3, 4, 5, and 6 hr⁻¹) under a constant ratio of 150 mL H₂/1 mL naphtha and a hydrogen gas pressure of 1.5 MPa, has revealed that the prepared catalyst was efficient to remove 82 % of sulphur at 598 °K temperature and 3 hr⁻¹ time. The enhanced selectivity of the CoMo/γ-Al₂O₃ catalyst through a hydro-treating reaction ascribes to the bimetallic-support interaction and the dispersion of MoS₂ particles that leaded to a large edge-to-corner ratio of CoMoS slabs.

1. Introduction

The increasing demand for the energy consumption has led to an increase in levels of sulphur compounds emitted from the oil refineries and this in turn has led to large challenges on the environment Hamid [1]. Hence, the environmental laws and restrictions have imposed on the oil refiners to produce high quality fuels with as low as sulphur contents Yang et al. [2]. The oil refining is a very complex process where the crude oil passes through different chemical processes including a hydrotreating and hydrocracking, thermal cracking, catalytic reforming, Fluid Catalytic Cracking (FCC), and Hydrodesulphurization (HDS) Meyers [3]. The

hydrodesulphurization process has shown its efficiency to remove different sulphur compounds such as hydrogen sulfide (H₂S), thiols (R-SH) and polysulphides (-SX²⁻) with the aid of catalyst at an appropriate pressure and temperature Saeeded et al. [4]. The HDS process is a chemical reaction using a stream of hydrogen gas to react with sulphur compounds associated with the petroleum product such as natural gas, light and heavy naphtha, diesel fuel and fuel oil James et al. [5]. The HDS process is classified on of the hydrogenolysis mechanism with a C-X chemical bond, where C is carbon atom and X is a sulphur nitrogen (N) or

oxygen (O) atom, using ethanethiol (C_2H_5SH) to form the C-H and the H-X chemical bonds as per the reaction shown in **Eq. 1** Nigam et al. [6]

$$C_2H_5SH + H_2 \rightarrow C_2H_6 + H_2S \quad \dots (1)$$
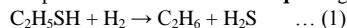
One of the most applicable catalysts in the HDS reaction is Cobalt (Co) or Nickel (Ni) decorated active Molybdenum (Mo) metal supported on a mesoporous Alumina carrier Hensen et al. [7]. Alumina support is used to carry CoMo or NiMo spicy for its high surface area, high mechanical and thermal resistance and good chemical stability Robinson et al. [8]**.** The Co or Ni metal is working as promotor for the active Mo metal. The active Mo metal plays a role in the HDS reaction for the connection between the Hydrogen gas (H_2) and the oil products through the framework of MoS_2 and $CoMoS_2$ active sites on the catalyst Montalvan-Sorrosa et al. [9]**.** The activity and selectivity of heterogeneous catalyst used in the HDS reaction is influenced by different parameters including the synthesis method, type of active metal and its loading percentage, type of promotor or support materials, calcination temperature, sulfidation of metal active, etc. Song [10]**.** The efficiency of the HDS reaction is also influnced by the hydrotreating operation conditions such as the reaction's temperature, Liquid Hourly Space Velocity (LHSV), pressure, H_2/oil ratio. These conditions considerably contribute in the determination of the required specifications of the oil product and the quality of feedstock Thomas et al. [11].

Several studies have been performed to investigate the activity of the binary CoMo heterogeneous catalysts in the Hydrodesulphurization (HDS) process. For instance, Chen et al. [12] determined the selectivity of CoMo catalyst of the sulfide in the HDS reaction of 4,6-dimethyldibenzothiophene (4, 6-DMDBT). It was shown that the formation of CoMoS and MoS_2 active connection sites resulted in a higher removal of the sulfide compounds. The use of the unsupported NiMo catalyst showed a better removal of sulphide from a Dibenzothiophene (DBT) through the HDS process as presented by Liu et al. [13]. However, understanding the activity of such catalyst in the HDS reaction and obtaining a clean Iraqi naphtha by changing the main operation conditions of the HDS is still under consideration of research. This study aims to determine the catalytic activity of a binary CoMo supported on Alumina carrier through the HDS reaction of An-Najaf naphtha at four different reaction temperatures and four different LHSVs under constant pressure. It also aims to determine the chemical kinetic and the activation energy of the HDS reaction of the naphtha with the use of the prepared catalyst.

2. Experimental part

2.1. Catalyst preparation

The bimetallic CoMo spicy supported on a gamma alumina (γ-Al2O3) was prepared by an incipient wetness impregnation method as described in Fig. 1. To prepare a 60 g of Co5Mo15/γ-Al2O3 catalyst having of 5 wt. % Cobalt (Co) and 15 wt. % Molybdenum (Mo), a 14.8 g of cobaltous nitrate hexahydrate, Co(NO3)2.6H2O (CNH, Aldrich, 99 % purity and MW = 290.93) dissolved in DI (1 g: 1 mL), and a molybdenum precursor salt of 17.73 g ammonium molybdate tetra-hydrate (NH4)6Mo7O24·4H2O (AMH, Aldrich, 98 % purity and MW = 1235.72) dissolved in deionised water, DI (1g : 10 mL ratio) were used. The aqueous solution of both dissolved precursors was drop by drop impregnated on the γ-Al2O3 (Aldrich, MW = 101.96) carrier nanoparticles. Thereafter, the wet nanoparticles were dried at 120 °C for 2 h, and the resultant impregnated material was calcined at 500 °C for 4 h.

2.2. Catalyst Formation

After calcination, the resultant Co_5Mo_{15}/γ-Al_2O_3 catalyst powder as shown in **Fig. 2**, was mixed with 1, 3, 5, and 7 wt. % of Polyvinyl Alcohol (PVA) as a binder followed by extrusion using a mini-screw extruder, model (Caleva/UK) to obtain the catalysts' bullets with dimensions of 20 mm length and 2 mm diameter. The resultant material was heated at 50 °C for 10 h.
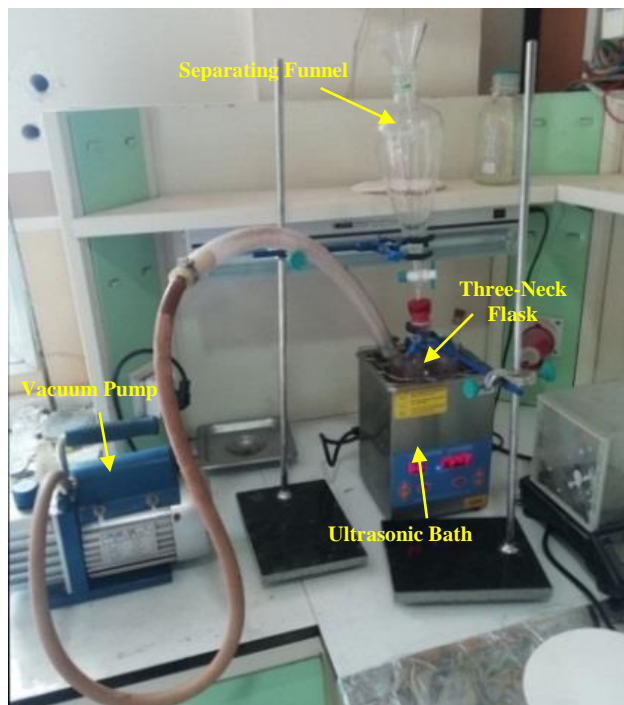

Figure 1- The preparation method setup used in the study.

Figure 2- The prepared CoMo/Al_2O_3 catalyst powder after calcination.

2.3. Characteristics of the catalyst

The synthesized bimetallic CoMo catalyst was examined in their oxide state. The surface area, total pore volume, porosity and bulk density were measured by using Brunauer–Emmett–Teller (BET). The crystalline structure of the active metals was investigated by using X-Ray powder

Diffraction (XRD) with a scan ranging of $2\theta = 10 - 80°$ at a step of 0.05°. The surface morphology and structure characteristics of the prepared binary CoMo/Al$_2$O$_3$ catalyst were conducted by using a FESEM, ZEISS-SEM model. The catalytic activity of the catalyst was evaluated through the HDS reaction of An-Najaf oil refinery (Iraq) heavy naphtha having specifications given in **Table 1**.

Table 1. Properties of a heavy Iraqi naphtha from An-Najaf oil refinery

Specifications	Value
API gravity at 15.6 °C	**72.3**
Specific gravity at 15.6 °C	**0.696**
Sulphur (ppm)	**755**
Octane number	**51.1**
Average Molecular weight	**120**
Distillation: I.P.B. °C	**30**
Distillation: E.P.B °C	**167**
Color	**Colorless**

To determine the activity of the prepared catalyst through the hydrodesulphurization reaction, a pilot plant with a fixed bed catalytic reactor designed by VINCI technologies was utilized as a hydrotreating unit. The unit was designed to allow a continuous hydrogen flow up to 180 mL/h on a catalyst volume of 70 cm^3, a temperature up to 550 °C and pressure of 150 bar. The HDS reaction was performed with the use of layers from the prepared CoMo/Al$_2$O$_3$ catalyst (50 g) inside the stainless steel catalytic reactor while a H$_2$ gas passes over the naphtha feedstock at a high pressure. The sulphur amount was measured after 16 different HDS operations including four different temperatures i.e., 250, 275, 300, 325 °C (523, 548, 573, 598 °K) and four different liquid hourly space velocities (LHSVs) i.e., 3, 4, 5, and 6 hr^{-1} under constant ratio of 150 mL H$_2$/1 mL heavy naphtha and a hydrogen gas pressure of 1.5 MPa. The percentage of sulphur removed through the HDS reaction is determined using **Eq. 2**.

$$S\ (\%) = \frac{S_F - S_P}{S_F} \quad … (2)$$

where S$_F$ and S$_P$ are the sulphur amounts in the feed and the final oil product, receptivity.
The X-ray fluorescence (XRF) analyser was used to measure the sulphur concentration in the feed and the final product.

2.4. Kinetics of the HDS reaction

The chemical kinetic and the activation energy of the HDS reaction of heavy naphtha with presence of the prepared catalyst were determined using the Arrhenius equation as shown in **Eq. 3**.

$$k = k_o e^{\frac{-E_a}{RT}} \quad … (3)$$

where k is the reaction constant (sec^{-1}), k$_o$ is a pre-exponential factor (or Arrhenius constant), E$_a$ is the activation energy (kJ.mol^{-1}), T is the absolute reaction temperature (°K) and R is the gas constant (8.314 J.mol^{-1}. K^{-1}).
The enthalpy and the entropy for the naphtha oil product was calculated by applying **Eq. (4).**

$$\frac{K}{T} = \frac{KmKb}{h} exp^{\Delta S/R}\ exp^{-\Delta H/RT} \quad … (4)$$

Plotting ln (K/T) versus 1/T gives a straight line with slopes equal to $\left(\frac{-\Delta H}{R}\right)$ and intercept equal to $[\left(\frac{\Delta S}{R}\right)+\ln\frac{Km\,Kb}{h}]$

The slope was correlated from the obtained experimental results of the relationship between the chemical reaction and the temperature at 325 °C (598 °K) applying a second-order reaction as per **Eq. 5**:

$$-r_A = (k\frac{1}{s.\ kg\,cat.\ mol})(C_A)^2 \quad … (5)$$

where k is the slope of the straight line reaction (obtained from **Table 3** and **Fig. 7**), C$_A$ is the concentration of the reactant A (mol.).

3. Results and discussion

3.1. Physicochemical Properties of the Prepared Catalyst

The physicochemical properties of the prepared binary CoMo/Al$_2$O$_3$ catalyst i.e., its surface area, porosity, pore volume, bulk density, and the mean pore diameter were measured by the BET method. **Table 2** lists these physical properties where the surface area is 52.339 m^2/g which is adequate to efficiently perform the catalysis of the HDS reaction. **Table 2** also shows the elemental practical analysis of the prepared CoMo/γ-Al$_2$O$_3$ catalyst where the percentage of the Mo active metal is 18.9 % that is fairly capable to handle the HDS reaction of the heavy naphtha. These findings are in conformance with previous published studies [14], [15].

Table 2. Physical properties and the elemental practical analysis of the prepared binary CoMo/γ-Al$_2$O$_3$ catalyst.

Catalyst Property	Value	Catalyst content	Weight (%)
Surface Area (m2/g)	52.339	Al2O3	76.697
Total pore volume (p/p0=0.990), cm3/g	0.1637	Mo	18.929
Mean pore diameter, (nm)	12.51		
Porosity	0.358	Co	4.3739
Bulk density, (g/cm3)	1.237		

3.2. XRD analysis

The X-Ray Diffraction (XRD) analysis of the prepared CoMo)/γ-Al$_2$O$_3$ catalyst was performed to conduct the crystalline phases of its oxide site. **Fig. 3** shows the XRD pattern of the binary prepared catalyst powder. From the figure, several major peaks at 2θ values of 23° and 27° can be observed indicating the formation of (201) and (211) planes for the α-MoO$_2$ phase formed from Mo^{4+} ion and α-MoO$_3$ phase formed from Mo^{6+} ion, respectively. The other intensity peaks at 33°, 38° and 48° are attributed for the deposition of Mo and Co oxides on the catalyst surface such as CoMoO$_4$ phase and β-CoMoO$_4$ and CoO Deraz [19]. The highest peak at 67° or exactly 66.8° represents the (440) plane for the γ-Al$_2$O$_3$ substrate. In addition, there are several weak intensity peaks indicating that the prepared catalyst has a nanosize particles.

Furthermore, by analyzing the XRD spectrum of the prepared catalyst, the crystalline structure was shown as a hexagonal structure, and the relative crystallinity percentage of the final powder was measured

following **Eq. 6** Alrubaye [16]. The Relative Crystallinity (%) of the binary CoMo/γ-Al$_2$O$_3$ catalyst was measured to be 89.56 %, which means that the preparation method is perfect to obtain a high degree of atoms arrangement of the prepared catalyst, and resulted in a higher characteristics of the catalyst.

$$\text{Relative Crystallinity \%} = \frac{\text{sum of peak intensites for samples}}{\text{sum of peak intensites for reference}} * 100 \quad \ldots (6)$$

Also, by using the XRD spectrum, measurement of the particle size for the prepared catalyst powder was performed by applying the Scherer equation, **Eq. 7** Rafael et al. [17]. By which, the average nanoparticle size for the prepared CoMo/γ-Al$_2$O$_3$ catalyst is 12.32 nm.

$$\text{Scherer's equation, } D_p = \frac{0.94\lambda}{\beta Cos\theta} \quad \ldots (7)$$

where DP is the average nanocrystalline or the mean particle size, λ is the X-ray wavelength, β is the width of line in a half the second maximum peak, and θ is the Bragg angle.
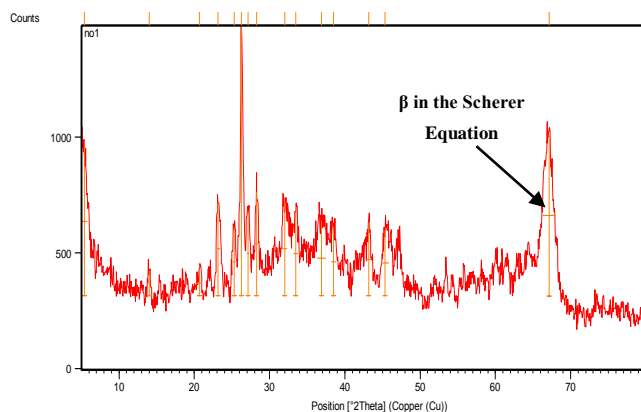

Figure 3- The XRD spectrum for Prepared CoMo/γ-Al2O3 catalyst

3.3. FE-SEM analysis

The SEM images (**Fig. 4**) illustrate the surface morphology of the prepared bimetallic CoMo/γ-Al$_2$O$_3$ catalyst. It can be clearly shown that a good dispersion of the active metal Mo nanoparticles and the promotor metal Co nanoparticles on the mesoporous alumina carrier. This is also confirmed by the penetration and transferring of molecules between these nanoparticles with the mesoporous structure of alumina substrate Mohammed [18]. In addition, there are some irregular particles and small cavities which could attribute to the gas formation which resulted in a segregation or cavity in the material. The smaller size of the catalyst powders and thereby a smaller pore diameter which in turn resulted in a larger surface area that requires to effectively complete the HDS chemical reaction Deraz [19]**.**

3.4. Effect of the reaction temperature

The catalytic activity of the prepared bimetallic Co$_5$Mo$_{15}$/Al$_2$O$_3$ catalyst in the removal of sulphur compounds through the HDS reaction was conducted in four different reaction temperatures (523, 548, 573, 598 °K) and four different LHSVs (3, 4, 5, and 6 hr^{-1}) under constant hydrogen volumetric ratio and pressure. **Fig. 5** shows the relationship between the

sulphur removed percentage (the efficiency of the HDS reaction) and the reaction temperatures for four different LHSVs. It can obviously observe that the percentage of sulphur removed from the naphtha feedstock has increased with increasing of the reaction temperatures from 523 to 598 °K at the same LHSV value. For example, the sulphur removed (%) increased from 59 % at 523 °K to 82 % at 598 °K with the use of CoMo/γ-Al$_2$O$_3$ at LHSV = 3 hr^{-1}. The efficiency of the HDS reaction enhances with the increase of the reaction temperature since the higher temperature leads to enhance the internal molecular motion and reduce the free energy (kinetic energy) that required to compete the reaction Abid et al. [14].
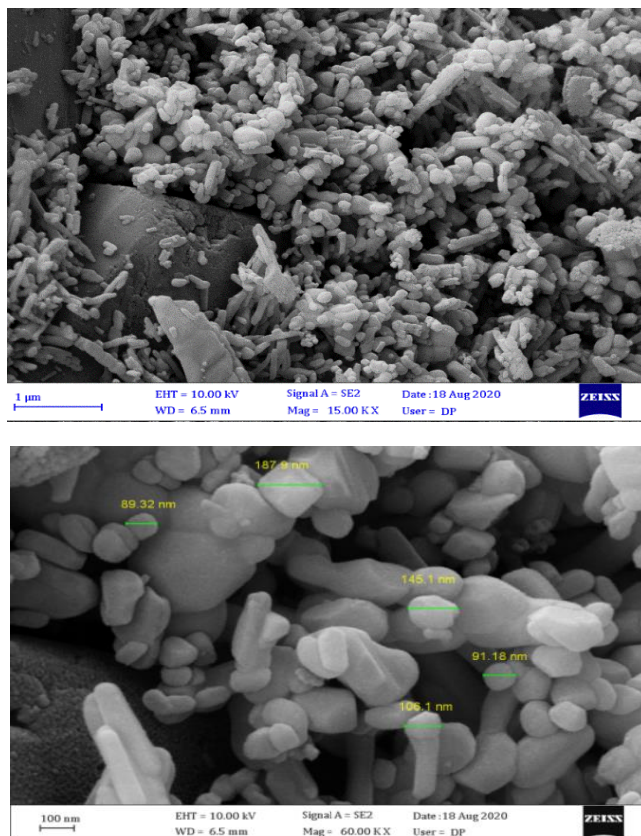

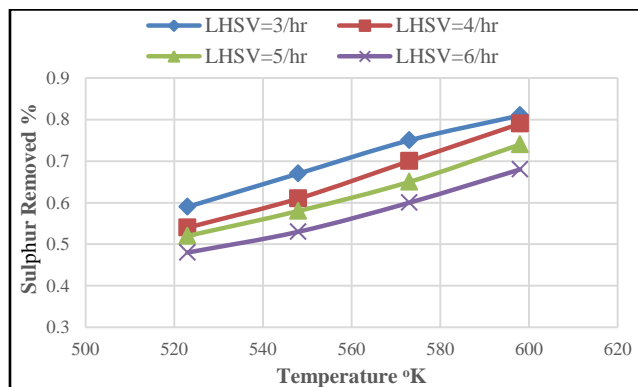**Figure 4- The SEM images of the prepared CoMo/γ-Al$_2$O$_3$ catalyst.**

Figure 5- Effect of reaction temperature on the removal of Sulphur through the HDS at different LHSVs.

3.5. Effect of the LHSV

Fig. 6 shows the percentage of the sulphur removed from the naphtha product through the HDS reaction at different LHSVs and different reaction temperatures. From the figure, it can be seen that the sulphur percentage removed has decreased with the increasing of LHSV values at the same temperature. This behaviour is attributed to the increase in the LHSV values and hence increasing the flow rate of naphtha, leading to a decrease in the period time of contacting between the hydrogen gas and the oil naphtha inside the batch reactor with the presence of the catalyst [15].
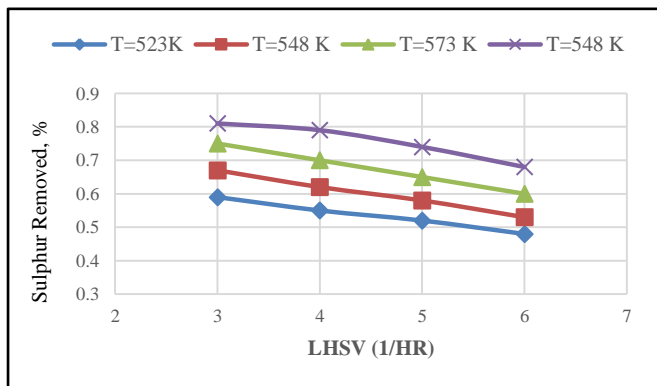

Figure 6- Effect of changing the LHSVs on the removal of sulphur through the HDS at different reaction temperatures.

Changing of the reaction temperature and the LHSV values plays a role in the efficient completion of the sulfidation process of the oxide state of the catalyst that results in the formation of MoS_2 active site. The new sulphide site acts as a bridge between the sulphur compounds and the hydrogen gas. The initial temperature to start the HDS chemical reaction must not exceed the range of 260 – 315 ℃ to avoid coke formation which represents the first stage of the pre-sulfiding where the MoO_3 catalyst oxide states react with H_2S. By increasing the reaction temperature, a second stage and the formation of oxy-sulphides starts Alrubaye [16]. In this study, the MoO_3 and CoO oxide sites of the prepared catalyst were pre-sulphured in H_2S/H_2 at temperature between 300-400 ℃. Increasing the feed's velocity of the petroleum liquid on the surface of the catalyst results in reducing the contact time required to convert the oxide site into the sulphide site as well as reducing the adsorption process of sulphur and in turn leads to disintegrate it again. This would result in returning some parts of sulphur particles with the feeder and that is lowering the sulphur removed percentage [19], [20].

3.6. Kinetics of the HDS Process

In this study, the rate models were developed based on the conditions that is (1) the HDS process follow the integral analysis model, (2) the sulphur remove reactions are irreversible and a stable density system, and (3) the influence of hydrocracking of C=C on the HDS process is not essential since the reaction temperature was less than 400 ℃ and higher pressure. The integral analysis to calculate the rate of the HDS reaction of a heavy naphtha was used based on an ideal plug flow model.

Kinetics of the HDS reaction to remove the sulphur from the naphtha were determined based on the second order reaction where the relationship between $1/C_A$ versus $W.C_{Ao}/F_{Ao}$ was plotted as shown in **Fig. 7**, and getting the straight line, the slope that is representing the $(K^{`})$
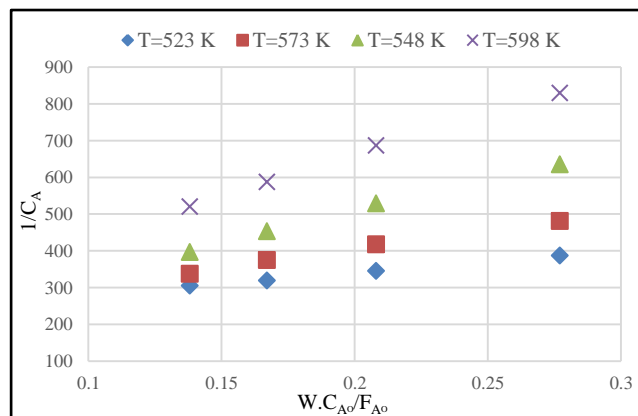

Figure 7- The second order HDS reaction rate of the naphtha at different temperatures based on integral analysis

The activation energy (E_a) as well as the enthalpy (ΔH) and the entropy (ΔS) energy of the HDS reaction for a heavy naphtha with presence of the bimetallic $CoMo/\gamma$-Al_2O_3 catalyst were calculated by using **Eqs. 3 and 4** at different reaction temperatures (523-598 ℃K).

The results revealed that the activation energy was (46.199 KJ/mol.), the entropy energy was (-111.85 J/mol.), and the enthalpy energy was (41.56 KJ/mol.). This means that the use of the prepared CoMo supported on alumina catalyst has increased the rate of reaction and modified the transition state through the reduction of the activation energy with changing the energies of the naphtha feedstock or changing the equilibrium. A similar finding was revealed by Alwan [21]. The activation energy of the CoMo/graphene catalyst was calculated based on the integral analysis. The catalyst increases the reaction rate owing to the binding energy occurred when the substrate binds to the active site of a catalyst.

The HDS reaction rate constants for the $CoMo/\gamma$-Al_2O_3 catalyst were calculated by using **Eq. 5**, based on the slopes obtained from the experimental results of these straight lines at different temperatures. The results of the rate constants are shown in **Table 3**.

Table 3. The rate constants (k) for the HDS reaction of the naphtha at different temperatures.

Temperature (° K)	k` (l /s. Kg cat. mol)
523	0.166
548	0.283
573	0.474
598	0.618

4. Conclusions

In this study, the bimetallic $CoMo/Al_2O_3$ heterogeneous catalyst was successfully prepared by a wet impregnation method for the Hydrodesulphurization (HDS) reaction of a heavy An-Najaf naphtha. The catalytic activity of the prepared catalyst was determined at different reaction temperatures and different liquid flow rates in a pilot HDS plant.

The results revealed that the efficiency of the HDS reaction has enhanced to 82 % sulphur percentage removed with the use of the catalyst at 598 °K and 3 hr^{-1}. Increasing of the reaction's temperature has shown its effective on the enhancement of the HDS efficiency of the naphtha feedstock. Increasing of the LHSVs values has obviously revealed a reduction in the HDS efficiency due to lowering of the time of contacting between the oil product and the hydrogen gas with presence of the catalyst. The surface morphology showed that the prepared active metals are uniformed dispersed on the alumina carrier substrate.

Acknowledgment

REFERENCES

[1] W. Hamid, "Studying of the performance of hydro rating process for mixture of gas oil and lighter fraction," *Univ. Technol.*, vol. M.Sc. Thesis, 2017.

[2] A.J. Hernandez-Maladonado. and R.T. Yang, "Desulfurization of transportation fuels by adsorption," *Cata Rev*, 2004.

[3] Meyers R., "Handbook of petroleum refining processes," *Mc Graw-Hill*, 1997.

[4] Saeeded et al, "Advents of Nano catalysts in hydro treating process benefits and Development," *Am. J. Oil Chem. Technol.*, 2004.

[5] James et al, "Petroleum Refining Technology and Economic," *Marcel Dekker Inc N. Y.*, 2004.

[6] A. Kundu and D. P. Nigam, "Recent Developments on Hydro Processing Reactors," *Rev Chem Eng*, 2003.

[7] E.J.M Hensen *et al.*, "The Relation between Morphology and Hydrotreating Activity for Supported MoS2 Particles," *J. Catal.*, vol. 199, no. 2, 2001.

[8] Paul R. Robinson and Geoffrey E. Dolbear, "Handbook of Petroleum Technology, Hydro treating and Hydrocracking: Fundamentals," *Springer*, 2007.

[9] D. Montalvan-Sorrosa et al, "Nanotechnology applied to the bi desulfurization of fossil fuels and spent caustic streams process," *Pet Eng*, 2016.

[10] C. Song, "An overview of new approaches to deep desulfurization for ultra-clean gasoline, diesel fuel and jet fuel," *Catalysis Today*, vol. 86, 2003.

[11] John Meurig Thomas and W. John Thomas, "Principles and Practice of Heterogeneous Catalysis," *Wiley*, 2015.

[12] Chen W., Long X., Li M., Nie H., and Li D., "Influence of active phase structure of CoMo/Al2O3 catalyst on the selectivity of hydrodesulfurization and hydrodearomatization," *Catalysis Today*, 2016.

[13] Huan Liu, Quanzhen Liu, Jianzhong Zhang, Changlong Yin, Chenguang Liu, and Wangfu Sun, "PVP-assisted synthesis of unsupported NiMo catalysts with enhanced hydrodesulfurization activity," *Fuel Processing Technology*, vol. 160, pp. 93–101, 2017.

[14] Mohammad F. Abid et al., "Synthesis and Characterization of Unsupported Catalyst for Gas Oil Desulfurization," *AL-Qadisiyah Journal for Engineering Sciences*, vol. 11, no. 3, 2018.

[15] Abid M Fadhil et al., "Experimental Study on Catalyst Deactivation by Nitrogen Compounds in a Hydro-processing Reactor," *Arabian Journal for Science and Engineering*, 2017.

[16] Alrubaye, R., "Generation and Characterization of Catalytic Films of Zeolite Y and ZSM-5 on Fe Cr Alloy Metal," *University of Manchester*, 2013.

[17] Nidia Rafael and T.A. Zepeda, "Trimetallic RuxMoNi Catalysts Supported on SBA-15 for the Hydrodesulphurization of Dibenzothiophene," *International Journal of Chemical Reactor Engineering*, 2018.

[18] Mohammed Sabah Mohammed, "Synthesis and Characterization of CoMo/ γ –Alumina and NiMo/γ–alumina Nano Catalysts for Hydrodesulphurization of Gas Oil"," *Ph.D Thesis, University of Baghdad*, 2016.

[19] Nasrallah M Deraz, "Importance of catalyst preparation," *Journal of industrial and environmental chemistry*, 2018.

[20] Fereshtech et al, "Alumina nanotube/Nanorod supported desulfurization Nano catalyst, method of preparation and application," *Research Institute of Petroleum industry*, 2012.

[21] Hameed Hussein Alwan, "Synthesis of Graphene as Support for the Catalysts in the Hydrodesulphurization of Heavy Naphtha," *PhD Thesis, University of Baghdad*, 2018.