Synthesis and Characterization of Co-Mo/γ-Alumina Catalyst from local Kaolin clay for Hydrodesulfurization of Iraqi Naphtha

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Abstract:

This work deals with the hydrodesulfurization of three types of naphtha feedstocks; mixed naphtha (WN), heavy naphtha (HN) & light naphtha (LN) with a sulfur content of 1642.1, 1334.9 & 709 ppm respectively, obtained from Missan refinery using prepared Co-Mo/γ-Al₂O₃ catalyst. The Iraqi white kaolin was used as a starting material for the preparation of γ-Al₂O₃ support, transferring kaolin to meta-kaolin was studied through calcination at different temperatures and durations, kaolin structure was investigated using X-Ray diffraction techniques.

High purity 94.83%. Crystalline γ-Al₂O₃ with a surface area of 129.91 m²/gm, pore volume 0.9002 cm³/g was synthesized by extraction of Iraqi kaolin with H₂SO₄ at different acid to clay weight ratios, acid concentrations & leaching time. Ethanol was used as precipitating agent; the resultant gel was dried and calcined at 70°C, 10 hrs & 900°C, 2 hrs respectively.

The effects of different parameters on the average crystallinity and extraction % of synthesized γ-Al₂O₃ were studied like; acid: clay ratio, sulfuric acid concentration, leaching time, leaching temperature & kaolin conversion to metakaolin. Characterization of prepared γ-Al₂O₃ & Co-Mo catalyst were achieved by X-ray diffraction, FTIR-spectra, texture properties & BET surface area, BJH N₂ adsorption porosity, AFM, SEM, crush strength & XRF tests.
Co-Mo/γ-Al₂O₃ catalyst with final loading 5.702 wt% and 21.45 wt% of Co and Mo oxides respectively was prepared by impregnation methods.

The activity of prepared Co-Mo/γ-Al₂O₃ catalyst after moulding to be tested for hydrodesulfurization (HDS) of naphtha feedstock W.N, H.N & L.N was performed using a pilot hydrotreating unit at petroleum research & development centre, at different operating conditions. Effects of temperature, LHSV, pressure, time & pore size distribution were studied, the best percentage of sulfur removal is increased with decreasing LHSV to 2 hr⁻¹ as a general trend to be 89.71, 99.72, 99.20 % at 310°C for the whole naphtha, heavy naphtha and light naphtha feedstocks respectively, at 34 bar pressure and 200/200 cm³/cm³ H₂/HC ratio.

**Keywords:** Hydrodesulfurization, impregnation, Co-Mo/γ-Al₂O₃, kaolin, naphtha, hydrotreating.

**Summary:**

The catalyst was prepared using impregnation methods with final loading of 5.702 wt% Co and 21.45 wt% Mo. The catalyst was evaluated for hydrodesulfurization (HDS) of naphtha feedstock W.N, H.N & L.N using a pilot hydrotreating unit at petroleum research & development centre. The best percentage of sulfur removal was observed at 310°C, 34 bar pressure, and 200/200 cm³/cm³ H₂/HC ratio.

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1. Introduction

In refinery, high sulfur levels lead to deactivate the catalysts that promote desired chemical reactions in certain refining processes and releases emissions of sulfur compounds to air [1, 2]. The main objective of environmental legislation is to reduce sulfur dioxide, nitrogen oxides, aromatics, and vapor and soot particulate emissions from both refineries and its products after combustion. [3].

Hydrotreating catalysts are used exclusively for enhancing the conversion rate of heavy feedstock and for improving the purity of final products. It also plays an important key in pre-treating streams for some chemical processes such as catalytic reforming, fluid catalytic cracking (FCC) and hydrocracking. Sulfided Co and Ni promoted Mo on gamma-alumina catalysts are active for hydrodesulphurization [4, 5].

Conventional systems include CoMo and NiMo mixed sulfide catalysts supported on gamma–alumina, CoMo specifically being used when a large Hydrodesulphurization (HDS) duty is demanded, NiMo for hydrodenitrogenation (HDN) operations [6, 7]. $\gamma$-Al$_2$O$_3$ is widely used as a support in heterogeneous catalysis because it is thermally stable and allows the dispersion of active phases due to its high surface area [8].

Alumina is used as a catalyst and catalyst support material in many industries and different processes such as hydrotreating processes, the low cost of kaolin has been identified as a
potential raw material for the production of zeolite and in addition for the production of alumina (γ-Al₂O₃) [9, 10].

Gamma alumina can be formed from several methods such as sol-gel, hydrothermal processing, and controlled precipitation. While the others are produced from inorganic aluminum salts, alkoxides, metallic powders, waste alumina and kaolin [11].

The traditional synthesis of promoted MoS₂/Al₂O₃ catalyst is by simultaneous or successive impregnation of molybdenum and promoter salts onto alumina, followed by calcination (producing oxides), and sulfidation prior to use [12, 13].

The active component is normally molybdenum sulfide, although tungsten containing catalysts are also used (though seldom, and that generally for special applications such as lube oil processing). For molybdenum catalysts both cobalt (CoMo) and nickel (NiMo) are used as promoters. The promoter has the effect of substantially increasing the activity of the active metal sulfide.

Preparation of molybdenum -based supported catalyst with higher concentration of active metals on the exterior surface and high dispersion still represents a synthetic challenge in advanced catalysis [14]. Many researchers studied working with HDS catalyst of relatively high metals oxides loading and gain the sulfide active phase at low pre-sulfiding temperature to avoid sintering of the catalyst associated at elevated temperatures [15].

The performance, in terms of desulfurization level, activity, and selectivity, depends on the properties of the specific catalyst used concentration of the active species, support properties, synthesis route, the reaction conditions sulfidizing protocol, temperature, and partial pressure of hydrogen and H₂S, the nature and concentration of the sulfur compounds present in the feed stream, and the reactor and process design [16].

This work includes Preparation of γ-Al₂O₃ support from Iraqi kaolin, Characterization of the prepared γ-Al₂O₃ using the well-known techniques and Preparation of HDS catalyst by loading active metallic oxides on γ-Al₂O₃, Formation and characterization of the prepared catalyst, then a Study for its activity in HDS process of Iraqi whole naphtha, heavy naphtha and light naphtha using a continuous pilot HDS unit with different operation conditions.
2. Experimental work

2.1 Materials & Feed Stock

Iraqi mixed naphtha, heavy naphtha and light naphtha produced by Missan Refinery was used as the feedstock for hydrodesulphurization evaluation, Table (1) shows the properties of the produced Iraqi naphtha.

| Characteristics       | Light naphtha | Heavy naphtha | Mixed naphtha |
|-----------------------|---------------|---------------|---------------|
| Sulfur content, ppm   | 709           | 1334.9        | 1642.4        |
| Sp. Gravity @ 15.6 °C | 0.7161        | 0.7703        | 0.7168        |
| Doctor test           | Post          | Post          | Post          |
| API gravity@ 15.6 °C  | 66.1          | 52.2          | 65.9          |
| Octane No.(Research)  | 54.4          | <40           | 52            |
| D.V.P.E@37.8 °C (bar) | 0.598         | 0.041         | 0.569         |

2.2 Chemicals used:

Cobalt nitrate 97% Co (NO$_3$)$_2$, 6H$_2$O, Ammonium molybdate 99% (NH$_4$)$_6$MO$_4$O$_{24}$.4H$_2$O,
Sulfuric acid 98% H$_2$SO$_4$,
Ethanol 99% C$_2$H$_5$OH, white kaolin Al$_2$Si$_2$O$_5$ (OH)$_4$,
Poly vinyl alcohol 99% (CH$_2$CHOH)$_n$.

2.3 Preparation of Gamma-Alumina Procedure

Gamma alumina was prepared by certain steps depending on the previous work of authors in [10] who used 800°C, 2 hrs for kaolin calcination, and 900 °C, 2 hrs for calcination of precipitated alumina gel, extracted by H$_2$SO$_4$ and using ethanol with some modifications, while other kaolin calcinations, different acid ratios, were suggested by our team to study best temperature to transfer of kaolin to metakaolin

1. The Iraqi white kaolin was used as a starting material; the kaolin was ground and sieved to obtain fine particles below 45 μm in size, because large particle size would decrease the alumina extraction efficiency.
2. The powdered kaolin was transferred to metakaolin by calcination in an electric furnace at either 550°C for 4 hrs, 720 for 45 min, 750 for 30 min, 800°C for 2 or 3 hrs, and 900°C for 2 or 6 hrs, also temperature 1000°C for 24 hrs was studied.

3. Kaolin powder was added to a 2.0 N H₂SO₄ solution and the solid-liquid ratio was at 1:20 by weight. While the same procedure was used with 1.0 N & 4.0N H₂SO₄ for the samples of kaolin that were calcined at 550°C & 900°C respectively. A solid-liquid ratio of 1:10 was also studied for some samples for comparison.

4. A mixture of kaolin powder (12.5 gm) and acid (250 ml) was moved to a 500-ml round flask. The reaction flask fitted with a reflux condenser and the mixture was mixed with magnetic stirrer with temperature control to be leached for either 18 hrs or 3 hrs, the temperature of mixture was set at 70 -90°C.

5. The mixture of kaolin and acid was cooled to room temperature and filtered to remove each residue, which is containing silica.

6. The precipitate was filtered using a Buchner set under vacuum, then it was washed with sufficient amount of ethanol and distilled water.

7. The resulted gel was air dried overnight then oven dried at 70°C for 10 hrs and finally calcined at 900°C for 2 hrs in an electric furnace to get gamma alumina powder.

2.4 Preparation of Co-Mo/γ-Al₂O₃ Catalyst

The Co-Mo/γ-Al₂O₃ was prepared using dry impregnation technique for loading the cobalt oxide to ensure obtaining the desired loading percentage while incipient wetness impregnation technique was used for loading molybdenum oxide, the active metals loading was carried out as in the following steps:

1. Prior to active metals loading, γ-Al₂O₃ support was pre-heated at temperature of 250°C for 30 min to 1 hr. using an electrical oven to ensure eliminating moisture and undesired impurities from the support internal pores, and preconditioning for impregnation stage by using the impregnation apparatus which is consisting of a two-neck round flask 500 ml
connected to a separating funnel on the top to control the flow of the active metal solution on the catalyst support, the round flask is connected to a vacuum pump on the side to ensure an efficient impregnation.

2. 10 grams of the prepared gamma alumina powder was moved to a round flask under vacuum for 15-30 min, and then 3.6 gm of cobalt nitrate hexa-hydrate salt was dissolved in sufficient amount of deionized water (8-10 ml).

3. The aqueous solution of cobalt nitrate hexa-hydrate was added to the support dropwise under vacuum with stirring by a magnetic stirrer in a dry impregnation technique, where the support still in powder form and observed to be colored with a faint pink color with continuous stirring for 2-3 hrs under vacuum.

4. The impregnated support was then dried at 120°C for 1 hr to prepare it for the next impregnation, then it was moved to the round flask and subjected to the vacuum and re-impregnated again which is known as sequential impregnation with additional amount of cobalt nitrate hexa-hydrate 3.6 gm as in the previous.

5. A (5 - 5.5) gm of ammonium heptatamolybdate-tetra hydrate was gradually dissolved in a sufficient amount of deionized water (22-25 ml) at 50°C for 2-3 hrs to ensure complete dissolving of the salt, the solution of ammonium heptamolybdate was added to the gamma alumina by using incipient wetness impregnation technique, with continuous stirring for 2-3 hrs under vacuum, the slurry was aged overnight, then it was oven-dried at 110°C 10 hrs, and calcined at 550°C for 2hrs.

2.5 Formation of CoMo Catalyst

Mini Screw Extruder type Caleva / UK, located in the Petroleum Research and Development Center – Catalyst Section, was used for the formation of the catalyst powder. PVA solution of 5% concentration was used as a binder, dissolved with deionized water using heater magnetic stirrer, with continuous heating up to 50 °C and stirring for about 2 hrs, the catalyst powder was mixed with a sufficient amount of PVA, added just enough to be a paste. The obtained paste was pushed inside the Mini Screw Extruder to get the extrudate shape of the CoMo catalyst. The formed catalyst average size was 2 mm diameter and 10 mm in length, the catalyst was then oven-dried at 110°C for 10 hrs and calcined at 550 °C for 2 hrs.
2.6 Catalyst Testing using HDS Pilot Plant Unit
Catalytic activity is carried out in a continuous hydrotreating pilot plant unit designed by (VINCI technologies) located in refining section / Petroleum Research and Development Center. The unit consists of four sections. These are feed section, reactor section, control section, and cooling, condensation, and collecting section.

50 gm of the prepared CoMo catalyst with catalyst layer length 23 cm loaded into the fixed bed reactor of the pilot unit. The upper and lower sections were packed with ceramic balls had a layer length 3 cm. The unit was cleaned with nitrogen to remove oxygen from the system, nitrogen was tested for moisture content 340 ppm which was decreased to 270 ppm by heating up to 150- 200°C for 90 min. at 10 bar pressure and flow rate of 300 Nl/min. until final moisture content reached to 11 ppm after five runs, with total 7.5 hrs at the same conditions.

2.7 Hydrodesulfurization Experiments Procedure
The hydrotreating of naphtha was carried out at temperatures range 280, 290, 300 & 310 °C, LHSV range 1, 2 & 4 h⁻¹, hydrogen pressure were 18 & 34 bars and hydrogen to hydrocarbon ratio 200 ml/ml. these conditions were applied on three types of Iraqi naphtha feedstocks supplied from Missan refinery in order to test the prepared CoMo catalyst efficiency to reduce the relatively high levels of sulfur content in the feed to minimum levels as it is usually obtained with the commercial Hydrodesulfurization catalysts. For each run, the final product was collected after the stabilization time (1.5 h) to reach a steady state from analysis of sulfur content.

3. Results & Discussions
3.1 Thermal treatment of Kaolin clay
The thermal treatment of kaolin samples at different temperatures, were investigated through XRD analysis for different heating times. It can be concluded that kaolin clay was transferred to the meta-kaolin amorphous phase at all studied conditions where all kaolinite peaks were diminished. However, the existence of silica affected the crystallinity to approximately 50% for all samples. As shown in Figure (1) which represents Average Crystallinity of thermally treated Iraqi kaolin clay at different heating temperature and time for conversion to Meta-
Kaolin based on tested Iraqi raw kaolin XRD values, these findings agree with most investigations of Iraqi kaolin which was published earlier by [17, 18].

![Figure 1](image)

**Fig. (1) Average Crystallinity of thermally treated Iraqi kaolin clay at different heating temperature and time for conversion to Meta-Kaolin based on tested Iraqi raw kaolin XRD values**

3.2 Characterization of the prepared $\gamma$-$\text{Al}_2\text{O}_3$ & Co-Mo/$\gamma$-$\text{Al}_2\text{O}_3$ Catalyst

3.2.1 $\gamma$-$\text{Al}_2\text{O}_3$ XRD pattern analysis

XRD analysis was done to the prepared gamma alumina samples at different preparation conditions of leaching acid concentration, temperature and extraction time, the XRD patterns confirmed the identity of $\gamma$-alumina. From comparing standard XRD peaks ($2\theta=37.6, 2\theta=45.788, 2\theta=66.761$) with the other obtained from the present study for A2 sample as an example ($2\theta=37.13, 2\theta=45.82, 2\theta=66.54$), it's clearly unmask that the prepared material is $\text{Al}_2\text{O}_3$ of gamma type which was prepared from locally available kaolin clay the characteristic peaks of $\gamma$-alumina of x-ray diffraction were shown in Figures (2) to (7) represented relatively high crystalline gamma alumina at different conditions; the highest crystallinity obtained was 93.06% for samples A2 & A3 and 86.53% for A8 which is only 6.53% decreased as compared to A2 & A3.

From this part, it can be concluded that kaolin clay is strong candidate for gamma alumina resources.
Fig. (2) XRD pattern for A1 Gamma alumina produced by 2N H2SO4 & 6 hr 900 °C Calcination for kaolin, 18hrs leaching @70 °C

Fig. (3) XRD pattern for A3 Gamma alumina produced by 2N H2SO4 & 2.5hr, 800 °C Calcination for kaolin, 18hrs leaching @70 oC

Fig. (4) XRD pattern for A8 alumina produced by 1N H2SO4 kaolin 3hrs leaching@70 °C, with 550oC 4hrs Calcination for kaolin, clay: acid ratio 1:10
Fig. (5) XRD pattern for A12 gamma alumina mixed of best conditions

Fig. (6) XRD pattern for A2 Gamma alumina produced by 2N H$_2$SO$_4$ & 2 hr, 900 °C Calcination for kaolin, 18hrs leaching @70 °C

Fig. (7) XRD pattern for A11 Gamma alumina produced by 2N H$_2$SO$_4$ & 2 hr, 550°C 4 hrs Calcination for kaolin, 3 hrs leaching @70 °C
3.2.2 Purity of produced $\gamma$-$\text{Al}_2\text{O}_3$

The main composition of the prepared alumina is given in Table (2) which revealed on a high purity material (94.83% $\text{Al}_2\text{O}_3$, 0.914% $\text{Fe}_2\text{O}_3$, 0.55% $\text{SiO}_2$), the balance of other components were as traces while another sample of produced $\gamma$-$\text{Al}_2\text{O}_3$ (A8) in different conditions (1.0 N $\text{H}_2\text{SO}_4$) was also tested with XRF to show a very close value of purity (94.54% $\text{Al}_2\text{O}_3$, 0.423% $\text{Fe}_2\text{O}_3$, 0.518% $\text{SiO}_2$) the balance of other components were also as traces, it was observed that the $\text{Fe}_2\text{O}_3$% was decreased with 53.71% and a slight decrease in silica for this sample, this decrease in $\text{Fe}_2\text{O}_3$ might be due to the metals dissolution in the low acid concentration which it is might be preferred for $\text{Fe}_2\text{O}_3$ to be done. From that we can conclude that using 1.0 N $\text{H}_2\text{SO}_4$ in extraction of alumina is considered to be more economical and result in a high purity gamma alumina.

Table (2) Comparisons of gamma alumina compositions at different preparation methods

| Method of alumina production | $\text{Wt}.ua\%$ | $\text{Al}_2\text{O}_3$ | $\text{Fe}_2\text{O}_3$ | $\text{SiO}_2$ | $\text{TiO}_2$ | $\text{Zn}$ |
|-----------------------------|------------------|------------------|------------------|-----------------|-------------|-------------|
| This study ($\text{H}_2\text{SO}_4$ – method, 2.0 N) | 94.83 | 0.914 | 0.55 | 0.0112 | 0.01123 |
| This study ($\text{H}_2\text{SO}_4$ – method, 1.0 N) | 94.54 | 0.423 | 0.518 | 0.0019 | 0.0128 |
| $^1$Produced commercially | 94 – 99.5 | 0.005 – 0.03 | 0.005 – 0.01 | 0.005 | 0.03 – 0.01 |

$^1$[16, 17]

3.2.3 Texture Properties: Surface Area and porosity measurements

Surface area and pore volume play a very important role for the activity of the catalyst support, because high surface area leads to high active sites causes increasing in activity. Table (3) shows the results of surface area and pore volume of both final prepared $\gamma$-$\text{Al}_2\text{O}_3$ & CoMo/ $\gamma$-$\text{Al}_2\text{O}_3$ catalyst. $\text{N}_2$ sorption measurements of the synthesized gamma alumina and CoMo/ $\gamma$-$\text{Al}_2\text{O}_3$ prepared catalyst have been studied, the $\text{N}_2$ adsorption/desorption isotherm obtained was assigned to type IV shape according to IUPAC classification [19] & [20]. The hysteresis loop in Figures (8 & 9) proved the presence of meso-pores in both the prepared alumina and catalyst structures and some macro pores.
Table (3) Texture Properties of the Prepared $\gamma$-Al$_2$O$_3$ & CoMo/\gamma-Al$_2$O$_3$ catalyst

| Catalyst type | BET S.A m$^2$/gm | Meso pore S.A m$^3$/gm | Micro pore S.A m$^3$/gm | Total pore volume cm$^3$/gm | Meso pore volume cm$^3$/gm | Micro pore volume cm$^3$/gm |
|---------------|-------------------|------------------------|-------------------------|----------------------------|-----------------------------|-----------------------------|
| $\gamma$-Al$_2$O$_3$ | 129.91            | 110.38                 | 19.53                   | 0.9048                     | 0.8949                      | 0.009856                    |
| CoMo/\gamma-Al$_2$O$_3$ | 64.31             | 52.99                  | 11.32                   | 0.314                      | 0.3083                      | 0.00568                     |

Fig. (8) N$_2$ adsorption/desorption isotherm & hysteresis loop for final product of $\gamma$-Al$_2$O$_3$

Fig. (9) N$_2$ adsorption/desorption isotherm & hysteresis loop for of CoMo/\gamma-Al$_2$O$_3$

3.2.4 Atomic Force Microscope (AFM) Report
The range of the diameters was between 110 - 260 nm, most volume percentage of particles was 19.86 % at size distribution of 120 nm, and 16.31% at size of 110 nm and the volume percentage of particles was 0.71% at size 210 nm, while the average particle size is 136.93 nm, which is close to the Nano scale, where particles of sizes in the range of 1 to 100 nm are classified as Nano materials [21], this could be attributed to the use of ethanol alcohol as surfactant and precipitating agent. The bar charts of particle size distribution of prepared sample are shown in Figure (10), while the surface shape can be seen in Figure (11) which is for the morphology of prepared gamma alumina that was studied to show the images of AFM on two-dimensional surface profile at calcination temperature 900°C, which represents the two-dimension surface morphology of the prepared sample with irregular hexagonal structure.

**Fig. (10) Bar chart of particle size distribution of prepared gamma alumina at best conditions**

**Fig. (11) Two-dimensional surface of gamma alumina**
3.2.5 Scanning Electron Microscopy (SEM)
The morphology of the synthesized gamma-alumina is tested by scanning electron microscopy type AIS2300C Angstrom Advanced, where it showed platelet structure of $\gamma$-alumina of irregular hexagonal shape particles associated with gamma-alumina at 900°C calcination temperature.

SEM images of the prepared $\gamma$-alumina sample of best conditions are shown in Fig. 12 (a-c) at different magnification degrees, revealing an evidence of transfer from the amorphous phase to the crystalline phase. The synthesized $\gamma$-alumina showed relatively high crystallinity, which is also consistent with XRD profile. SEM images showed that $\gamma$-alumina is consisting of clusters of irregular shape.

![SEM images](image)

- a. SEM at a magnification of 250 x
- b. SEM at a magnification of 340 x
- c. SEM at a magnification of 190 x
- d. SEM at a magnification of 200 x

**Fig. (12) SEM image of prepared gamma alumina**

3.2.6 Fourier Transform Infrared Spectroscopy (FTIR)
FTIR spectra tests were done by FTIR-600 Biotech Spectrometer for some of the prepared gamma alumina samples and prepared CoMo\$\gamma$-alumina catalyst with wave range between (400-4000) cm$^{-1}$, the sample pressed to disk shape after added 1% $\gamma$-alumina to 99% KBr, FTIR spectum are shown in Figure (13) which shows large bands in the region between 400-
1000 cm$^{-1}$ represent the stretching vibration of Al-O-Al bands. The broad bands between 500-750 cm$^{-1}$ refer to gamma alumina as mentioned by [22, 23]. Mesoporous alumina synthesized can be distinguished by two bands in the region of 4000 cm$^{-1}$ – 1500 cm$^{-1}$.

The broad band around 3450 – 3500 cm$^{-1}$ may be attributed to the adsorbed water molecules, the broad band shown for the adsorbed water is a characteristic of porous materials which are usually found in zeolites and mesoporous materials [24].

![FTIR spectrum](image)

**Fig. (13) FTIR spectrum for prepared gamma alumina at best conditions**

### 4. Characterization of Hydro Desulfurization Catalyst

Different evaluation tests were conducted to show the specifications of both of the gamma alumina and the catalysts, such as true & bulk density, crush strength, loss on ignition, active metals loading percentages & purity, all these properties proved that the prepared materials were meeting the requirements and very close to commercial specifications as shown below in Table (4).
Table (4) general specifications of prepared γ-alumina & CoMo/γ-Al₂O₃ catalyst

| Catalyst Name       | Test name           | True density gm/cm³ | Loose bulk density gm/cm³ | Compact bulk density gm/cm³ | Grain Crushing strength N/mm | Carbon wt% after HDS | Loss on ignition @ 650 1 hr wt% | Active metal wt% | Purity wt% | Shape & Color          |
|---------------------|---------------------|---------------------|---------------------------|-----------------------------|-----------------------------|----------------------|---------------------------------|-----------------|------------|------------------------|
| Prepared CoMo Catalyst |                    | 3.493               | 0.589                     | 0.756                       | 7.1                         | 2.5                  | 2.8                             | 21.45           | 5.702      | Bluish Extrudate 2x10mm |
| Prepared Gamma alumina |                    | 3.186               | 0.1370                    | 0.1806                      | --                          | --                   | 3.68                            | 94.83           |            | Fine white powder 136.93nm |

4.1 CoMo Catalyst HDS Activity test

The activity of Co-Mo/γ-alumina catalyst was tested for HDS process of three types of feedstocks; mixed naphtha, light naphtha and heavy naphtha which were supplied from Missan Refinery with 1642.1, 709 and 1334.9 ppm respectively of sulfur content. The prepared catalyst was loaded in the reactor and was examined for sulfur removal at continuous runs covering different temperatures and liquid hourly space velocities. The effect of LHSV on HDS activities of Co-Mo catalyst at five different temperatures was studied. Other parameters including reaction pressure and H2/HC ratio were kept constant at 34 bars and 200 ml/ml, respectively for the three types of feed stocks, except for whole naphtha was further studied at low pressure 18 bar and LHSV 2 h⁻¹. All studied parameters are shown in the below graphs;

![Fig. (14) Effect of Temperature on Sulfur Removal for Whole Naphtha at different temperature and constant pressure 34 bar](image)
Fig. (15) Effect of Temperature on Sulfur Removal for Heavy naphtha @ Different Temp. and LHSV & Constant Pressure 34 bar

Fig. (16) Effect of Temperature on Sulfur Removal for Light Naphtha at different temperature & LHSV and constant pressure 34 bar

Fig. (17) Effect of LHSV on Sulfur Removal for whole Naphtha
Fig. (18) Effect of LHSV on Sulfur Removal for Heavy

Fig. (19) Effect of LHSV on Sulfur Removal for Light Naphtha

Fig. (20) Effect of Pressure on Sulfur Removal for Whole Naphtha
It can be concluded from the above figures the effect of different factors of naphtha HDS activity test that were studied like; effect of temperature as shown in Figures (14-16), LHSV, pressure and time, the best percentage of sulfur removal is increased with decreasing LHSV to 2 hr\(^{-1}\) as a general trend to be 89.71, 99.72, 99.20 % at 310\(^{\circ}\)C for whole naphtha, as shown in Figures (18-20), heavy naphtha and light naphtha feed stocks respectively, at 34 bar pressure and 200/200 cm\(^3\)/cm\(^3\) H2/HC ratio.

LHSV of the through a catalytic packed bed reactor is the reciprocal of time therefore it reflects the residence time of the reaction [25]. So, as the LHSV increases the residence time of the reactants in the reactor is decreased or in other words the feed flow rate is high so that there is not enough time for the reaction. By this, the value of LHSV of 4 hr\(^{-1}\) causes lower sulfur removal efficiency than that at LHSV of 2 hr\(^{-1}\) for all types of feed and at different temperatures.

Also, it can be seen that the value of sulfur removal at LHSV of 2 hr\(^{-1}\) is higher than that at LHSV of 1 hr\(^{-1}\) which can be explained by that the feed flow rate at 1 hr\(^{-1}\) is could not cover all the catalyst area or channeling may be occurred due to a bad distribution of the feed at this low flow rate at LHSV. The decrease in LHSV means that lesser quantity of feed contacting the same quantity of catalyst per time, while increasing in LHSV provides for a greater quantity of naphtha through the reaction per unit of time, these observations agree well with the results of Steiner and Blekkan [26].

5. Conclusions
Nominate the following issues were concluded that Iraqi raw kaolin is a promising source for production of crystalline gamma alumina an average particles size was of 136.93 nm, all the prepared gamma alumina samples at different conditions were of relatively high crystallinity. It was clear that most coordinates of the peaks of prepared samples matched the three strong standard peaks of standard gamma alumina quite well. Results showed that best feasible conditions for \(\gamma\)-alumina synthesis from Iraqi kaolin considered being ;( kaolin calcination 550 \(^{\circ}\)C 4 hrs. 3hrs leaching @ 70 \(^{\circ}\)C, 2N H\(_2\)SO\(_4\), clay: acid ratio 1:20).

The final specifications of produced \(\gamma\)-alumina and collected from different batches of best conditions were; surface area 129.91 m\(^2\)/gm, pore volume 0.9002 cm\(^3\)/g, pore size 27.71nm, 17.33 pore diameter, average crystallinity 87.53%, high purity 94.83% and extraction of 44.45%. The best percentage which gave good crushing strength value of formulated gamma
alumina was 5% aqueous solution of PVA binder. Catalyst evaluation showed that prepared Co-Mo/γ-alumina catalyst was relatively active due to active metals high loading used 5.702 and 21.45 % of Co and Mo oxides respectively, while the overall behavior of HDS process of naphtha feedstock W.N, H.N & L.N showed increasing of sulfur removal with increasing temperature from 280 to 310 °C and decreasing LHSV from 4 hr⁻¹ to 2 hr⁻¹ using prepared Co-Mo/γ-alumina catalyst.

The highest percentage of naphtha feed stocks sulfur removal that was achieved; 99.72% for HN, 99.20 % for LN & 89.71% for WN respectively, at 310°C, 34 bar pressure and 200/200 cm³/cm³ H₂/HC ratio achieving total sulfur content of 3.7,5.7&169 ppm in the effluent HN, LN and WN respectively. It can be expected for this catalyst to serve efficiently for heavier oil distillates like kerosene, light gasoil and heavy gasoil, with good ability of sulfur compounds removals, due to its relatively wide range of pore size distribution in addition to the high purity of the product and the relevant percentages of Co-Mo loading which can be promising for future work.
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