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## Synthesis and Characterization of New nano catalyst Mo-Ni /TiO<sub>2</sub>- γAl<sub>2</sub>O<sub>3</sub> for Hydrodesulphurization of Iraqi Gas Oil

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### Abstract:

A new nano-sized NiMo/TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> was prepared as a Hydrodesulphurization catalyst for Iraqi gas oil with sulfur content of 8980 ppm, supplied from Al-Dura Refinery. Sol-gel method was used to prepare TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> nano catalyst support with 64% TiO<sub>2</sub>, 32% Al<sub>2</sub>O<sub>3</sub>, Ni-Mo/TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> catalyst was prepared under vacuum impregnation conditions to loading metals with percentage 3.8 wt.% and 14 wt.% for nickel and molybdenum respectively while the percentage for alumina, and titanium became 21.7, and 58.61 respectively. The synthesized TiO<sub>2</sub>- γ-Al<sub>2</sub>O<sub>3</sub> nanocomposites and Ni-Mo /TiO<sub>2</sub>- γ-Al<sub>2</sub>O<sub>3</sub> Nano catalyst were then characterized by XRD, AFM, and BET surface area, SEM, XRF, and FTIR. The performance of the synthesized catalyst for removing sulfur compounds was conducted through the pilot HDS laboratory unit, various temperatures range 275°C to 375°C, LHSV 1 h<sup>-1</sup> were studied; moreover, the effect of LHSV 1 to 4 h<sup>-1</sup> on the percentage of sulfur removal was also studied at the temperature of the best removal with constant pressure 35 bar and H<sub>2</sub>/HC ratio 200cm<sup>3</sup>/200cm<sup>3</sup>. The sulfur content results generally revealed that there was a substantial decrease at all operating conditions used, while the maximum sulfur removal was 87.75% in gas oil on Ni-Mo/TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> catalyst at temperature 375°C and LHSV 1h<sup>-1</sup>.

**Keywords:** Gas oil, Hydrodesulfurization, Hydrotreating, Nano catalyst, Titanium dioxide.

### Introduction:

Sulfur compounds are one of the most common impurities in transportation fuels such as gasoline, diesel and jet fuels<sup>1</sup>. The presence of high concentrations of sulfur compounds can lead to corrosion problems in refining equipment, and they tend to deactivate some catalysts used in crude oil processing. Emissions of SO<sub>2</sub> gases coming from petroleum fuels residual sulfur different types will cause serious risks to human health. Naturally, these gases form sulfates and acid rain by reacting with water in the atmosphere<sup>2</sup>. There are many processes applied to reduce sulfur content in refined petroleum liquid hydrocarbons (gasoline, jet fuel, kerosene, diesel fuel, and fuel oil<sup>3</sup>). HDS process is one of the most significant and effective techniques that deals with H<sub>2</sub> and reliable specific types of catalysts at elevated temperatures and pressures ranged (250-400)°C and (30-80 bar)<sup>4</sup> This process can be done using metal catalysts such as CoMo/Al<sub>2</sub>O<sub>3</sub> or Ni-Mo/Al<sub>2</sub>O<sub>3</sub> to convert a number

of organo-sulfur compounds to H<sub>2</sub>S and sulfur-free organic compounds<sup>5</sup>. Hydrotreating process using catalysts include different parameters which are identified based on the reaction. In general, any catalyst of hydrotreating usually incorporates active metals, additive, promoter, and support material<sup>6</sup>. γ-Al<sub>2</sub>O<sub>3</sub> is very important among other phases because of its structure which possesses a high surface which gains the focus for many chemical and petrochemical separation processes and catalysis<sup>7</sup>. The γ-Al<sub>2</sub>O<sub>3</sub> supported with Mo Oxide catalysts and promoted with Co or Ni is still used extensively in the process of sulfur compounds removal in refining industry. Addition of metals on the support is achieved using multiple approaches, the impregnation technique is considered to be an easier and quick procedure adopted to load active metals on the catalyst support<sup>8</sup>. Due to the increasing need to find more active HDT catalysts this led to the study of a variety of compositions that differ from standard Hydrodesulfurization

catalysts, thus, refiners have developed more efficient and selective catalysts. Other materials have also been tried as supports for hydrotreating catalysts such as various oxides like  $\text{SiO}_2$ ,  $\text{MgO}$ ,  $\text{ZrO}_2$ ,  $\text{TiO}_2$ , and mixed oxides derived from above-mentioned oxides, carbon, clays, mesoporous materials like, zeolites like Na-Y, USY<sup>9</sup>. Titanium oxide ( $\text{TiO}_2$ ) is a good new support for hydrotreating (HDT) catalysts. Titanium dioxide ( $\text{TiO}_2$ ) improves the performance of catalyst for many reactions, such as dehydrogenation<sup>10</sup>, hydrodesulphurization, water gas shift<sup>11</sup>, and thermal catalytic decomposition, but  $\text{TiO}_2$  has the disadvantages of presenting poor thermal stability, small surface area, and poor mechanical properties. There are several methods followed by a number of authors to overcome these disadvantages such as: Grafting of  $\text{TiO}_2$  with  $\gamma\text{-Al}_2\text{O}_3$ ,  $\text{SiO}_2$ , and  $\text{ZrO}_2$ .etc. to form mixed oxides of  $\text{TiO}_2$  with these oxides. Among these mixed oxides  $\text{TiO}_2\text{-Al}_2\text{O}_3$  systems received maximum attention, several authors also studied  $\text{TiO}_2\text{-ZrO}_2$  while  $\text{TiO}_2\text{-SiO}_2$  is comparatively less studied, an important requirement for improving the  $\text{TiO}_2$  catalytic activity is to increase its specific surface area, this property is increased considerably through the high surface –to-volume ratio of the nanoparticles.(Nano –object with all three external dimensions in the Nano scale or nano-scale ,size rang for approximately 1nm to 100nm) as compared to that of micro particles<sup>12</sup>.

The purpose of this research is the removal of sulfur compounds from Iraqi gas oil, which is considered to be as one of the most important oil products problems, as this work deals with preparation and characterization of a new nano catalyst to be used in hydrotreating process and studying the catalytic activity using a continuous hydrotreating pilot plant unit.

## Material and methods:

### Materials

Al-Daura Refinery Gas oil with sulfur content of (8980) part per million was used as the feedstock for catalysts evaluation in hydrodesulfurization pilot unit. The properties of gas oil specifications are listed in Table (1), which were tested in refining & gas department-PRDC / Ministry of Oil and laboratories of Al-Doura refinery.

**Table 1. Iraqi gas oil specifications.**

Characteristics	Value
Flash Point, °C	68.40
Color	Dark- yellow
Cetane Index	52
Diesel Index	60.1
Total Sulfur, (wt. %)	0.850

### Chemicals

Ti-Isopropoxide ( $\text{Ti}(\text{OC}_3\text{H}_7)_4$  96%), ISO-Propanol ( $\text{C}_3\text{H}_7\text{OH}$  99.5%), and aluminum isopropoxide ( $\text{C}_9\text{H}_{21}\text{AlO}_3$  98 %) were supplied from Sigma-Aldrich .Nickel(II) nitrate hexahydrate ( $\text{Ni}(\text{NO}_3)_2.6\text{H}_2\text{O}$  99%), and Hydrochloric acid (HCl 36%) were supplied from BDH . Ammonium hepta molybdat-tetra hydrate from Merk ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}$  99%) and deionized water.

### Gases

Nitrogen & Hydrogen with a purity of 99.9% were supplied from local “Baghdad company”

## Experimental Procedure:

### Preparation of Nano $\text{TiO}_2\text{-}\gamma\text{Al}_2\text{O}_3$

The  $\text{TiO}_2/\gamma\text{-Al}_2\text{O}_3$  was prepared through the sol-gel process that previously reported by Wenjie Zhang et al.<sup>13</sup> with modifications in starting materials, molar ratio, and calcination temperature. Titanium (IV) isopropoxide  $\text{Ti}(\text{OC}_3\text{H}_7)_4$  and aluminum isopropoxide ( $\text{C}_9\text{H}_{21}\text{AlO}_3$ ) were used as a precursor for preparing alumina-titania Nano powder. 3 gm of aluminum isopropoxide. was added to 50 ml of isopropanol with stirring for 10 min., and then 12.5 ml of titanium (IV) isopropoxide was added to aluminum isopropoxide solution with stirring at 600 rpm for 30 min to prepare solution **A**. Meanwhile, 1 ml of concentrated HCl was mixed with 30 ml of isopropanol and 10 ml of deionized water to prepare solution **B**. Solution **A** was subsequently added gradually to solution **B** under sturdy stirring within 30 min. A homogeneous solution was obtained after vigorously stirring for 4 hrs. to form sol. After 48 hrs. the sol was transformed into gel to finally obtain nanoparticles. The product was separated by centrifugations at (5000 rpm for 15 min) then it was dried at 100°C for 24 hrs. to ensure the water removal and residual organic material. The dried gel was annealed at 500°C for 3 hrs. (heating rate =3 °C/min), to acquire the desired  $\text{TiO}_2\text{-}\gamma\text{Al}_2\text{O}_3$  nanoparticles.

### Ni-Mo/ $\text{TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ Nano-Sized Catalyst Preparation

A co-wet impregnation method was adopted to prepare the Ni-Mo/ $\text{TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  nano-sized catalyst<sup>8</sup>. The produced titanium dioxide ( $\text{TiO}_2$ ) with 40 gm. was subjected to drying at 200°C for 30 min in order to reduce the moisture content, 8 gm. of (Nickel Nitrate Hexa-hydrate) and 13 gm. of (Ammonium Heptamolybdate-tetra Hydrate) were thoroughly dissolved in a sufficient volume of DI water to obtain 3.8% nickel oxide and 14 % Mo oxide on the Nano support. vacuum conditions with dropwise addition of active metals aqueous solution

on the nano support were used. The impregnation system was kept under vigorous stirring for 2-3 hrs., finally a drying process for 6 hrs. at 100°C, followed by a calcination for the nano support at 500°C for 4 hrs.

### Catalytic activity test

The experiments of catalysts activity were performed using HDS pilot unit existed in Petroleum Research & Development Center affiliated to Ministry of Oil (Iraq). The said unit is designed and manufactured by a French VINCI technologies company.

### Pilot feed part

The feed part of the laboratory pilot unit is composed of 2000 cm<sup>3</sup> glass container linked with a graduated tube, a (6 - 180) ml/hr flowrate range dosing pump of type Eldex-USA laboratories is then connected via a special valve.

### Pilot reactor part

A maximum temperature of up to 550°C and pressure above 150 bars are the designed operating conditions for reactor part of the unit, which is divided into 3 zones; top and bottom could be packed with three cm of inert material like ceramic pellets, while the central zone is filled with 40 gm of catalyst. A thermocouple of K type is installed inside the central part of reactor, 5 mm diameter stainless steel tube is used to ensure flowing of the product from bottom zone, a separation flask with 20 mm internal diameter, 28 mm external diameter, and 170 mm length is connected with the above tube. Finally, the reactor temperature is automatically controlled using 2 steel heater jackets.

### Control panel part

Operating conditions of the pilot unit are well managed through a control panel located in the upper part of the system to be used for setting up and control of the feed pump, temperature and H<sub>2</sub> gas flowrate.

### Complementary part

A stainless steel coil inserted inside a cylinder is used as the condensation part for outlet products of the reactor section, while a glass container of 50 cm<sup>3</sup> is used to collect any condensable products as it can be seen in the photographic picture of the pilot unit shown in Fig. (1).



Figure 1. Photographic Pictures of the Hydrodesulfurization pilot unit.

### Pre-sulfiding Experimental Procedure

Forty gm. of the prepared catalyst was charged into the reactor central zone (catalyst layer length 23 cm), while the upper and lower parts were filled with ceramic balls into the middle part of the reactor with a 3.5 cm of ceramic layer length. the system is cleaned from oxygen by injecting N<sub>2</sub> gas into the unit. Leaks were tested by steadily raising pressure to 65 bars at 2 hrs. then decreasing to 10 bar, with changing nitrogen by the hydrogen of 99.99% purity. Discharges were re-checked with hydrogen pressure rising to 65 bar and reducing to 5 bars for preparing the system to the sulfiding process. Pre-sulfiding is done in three stages, the first stage at 150°C for 5 hrs, the second phase took place at 250°C for 5 hrs., while the last one occurred at 300°C for 5 hrs. The sulfiding action was performed using 8980 ppm sulfur content of Iraqi gas oil with 35 bars pressure, 2 hr<sup>-1</sup> LHSV and 350 cm<sup>3</sup>/cm<sup>3</sup> H<sub>2</sub>/HC as operating conditions.

### Hydrodesulfurization experimental runs

Multiple set of hydro-desulfurization runs were conducted at a temperature range of 275, 300, 325, 350 & 375°C at 1, 2, 3, and 4 hr<sup>-1</sup> liquids hourly space velocity, while 35 bar pressure was kept constant, with a value of 200/200 cm<sup>3</sup>/cm<sup>3</sup> of catalyst hydrogen: hydrocarbon ratio. After a period of time, a steady state was reached and the desulfurized gas oil product was gathered using the unit receiver to be ready for total sulfur measurement by XRF analyzer at the refining department laboratories located in PRDC.

**Result and Discussion:**

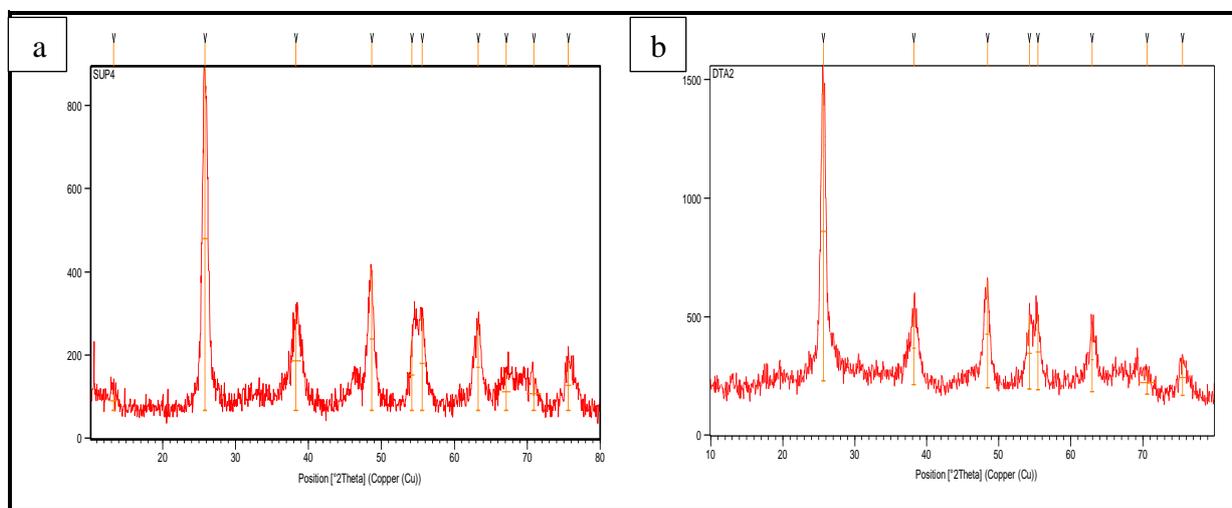
**X-Ray diffraction (XRD)**

The X-ray diffracts grams of the catalyst support (TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) and catalyst (Mo-Ni/ TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>) is presented in Fig. (2) . For catalysts mixed oxides support (TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>), it can be seen that anatase TiO<sub>2</sub> typical peaks are present at 2θ = 25°, 38°, 48°, and 55°, some poorly crystalline γ-alumina typical reflections can additionally be seen at calcined temperature of 500 °C which can be observed at the 2θ = 67°<sup>14</sup>. For catalysts observed peaks at (2θ=25°, 47.93°, 37.9°, 55°, 62°, and 70°), these peaks corresponding to TiO<sub>2</sub> with anatase structure (JCPDS 21-1272), that means the catalysis support prepared is stable during the impregnation step<sup>15</sup>.

Also, a difference of intensities for catalyst comparing with catalysis support suggests a best stability of anatase structure during the impregnation step<sup>15</sup>. These results mean that the pores did not block and were well dispersed on the support surface for the metallic phases in the catalysts<sup>16</sup>. Scherer equation is used to calculate crystallite size<sup>17</sup>.

$$D = K\lambda / (\beta \cos\theta) \dots\dots\dots 1$$

Where, n is the order of reflection, λ is the X-Rays wavelength, θ Bragg angle, while the interplanar spacing is denoted as d. The crystal size of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is 8.9 nm, where the crystal size of catalyst is 10.8 nm, as shown in Table 2.

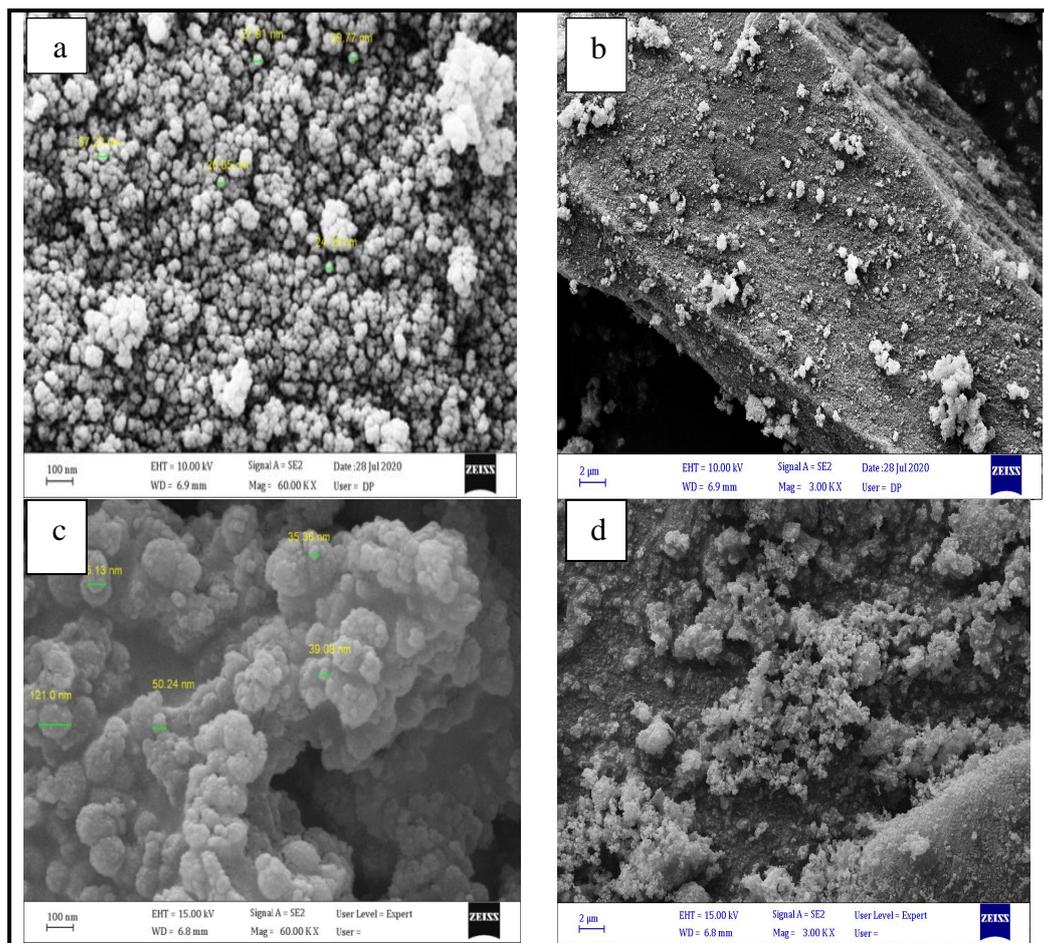


**Figure 2. The XRD for (a) TiO<sub>2</sub>- γ-Al<sub>2</sub>O<sub>3</sub> (b) Ni-Mo/TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub>**

**Scanning electron microscopic studies (SEM)**

Surface morphology is very important for the activity of the materials, and some properties are capable of providing more active centers such as rough and structured surfaces with high surface area<sup>18</sup>. The morphological transformation of (TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub>) , and (Mo-Ni /TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub>) catalysts have been studied by SEM characterization as shown in Fig. 3. The obtained SEM images indicate that the particles of synthesized (TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>), and (Mo-Ni /TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub>) samples were in the nano-sized range. Figs. 3a, b shows the surface morphologies of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> composite materials, surface is smooth with very small roughness. The irregular particles scattered on the surfaces are probably produced during grinding<sup>12</sup>, Fig. 3b. After adding Ni, and Mo, to TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, particles in catalyst seem to be covered by some species and their pores slightly decreased<sup>19,8</sup> Figs. 3c, d. It is observed that the surface of catalyst has slightly more roughness and a small-scale agglomeration was observed, compared to nano composites<sup>20</sup>. The

pores between particles for catalyst are showing a noticeable decrease comparing with composite which is consistent with BET analysis results, particle size for TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is 35.00 nm, while for catalyst are 62.16 nm ,as shown in Table 2.



**Figure 3.** The SEM for (a)  $\text{TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ , Mag 60.00KX (b)  $\text{TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ , Mag 3.00KX, (c)  $\text{Ni-Mo/TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  Mag 60.00KX, (d)  $\text{Ni-Mo/TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  Mag 3.00K

### Atomic Force Microscope (AFM)

The atomic force microscopy (AFM) technique was used to find the particle size distribution, average particle size, and the shape of the  $(\text{TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3)$ , and  $(\text{Ni-Mo/TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3)$  nano catalyst. The AFM images in two- and three-dimensions' view of  $\text{TiO}_2\text{-Al}_2\text{O}_3$ , and  $\text{Ni-Mo/TiO}_2\text{-Al}_2\text{O}_3$  nanoparticles are shown in Fig. 4. The average particle size of the prepared nano titania-alumina, and catalyst was in the nano scale, and it is larger comparison before addition Ni, and Mo, because Ni, and Mo oxides agglomerated as clusters on the surface of nano catalyst causes an increasing the particle size of prepared nano catalyst. The increasing in particle size is due to high loading of metal oxides on nano catalyst support<sup>8, 20</sup>. It is observed that the result obtained through AFM is close to what was obtained in the SEM, and XRD.

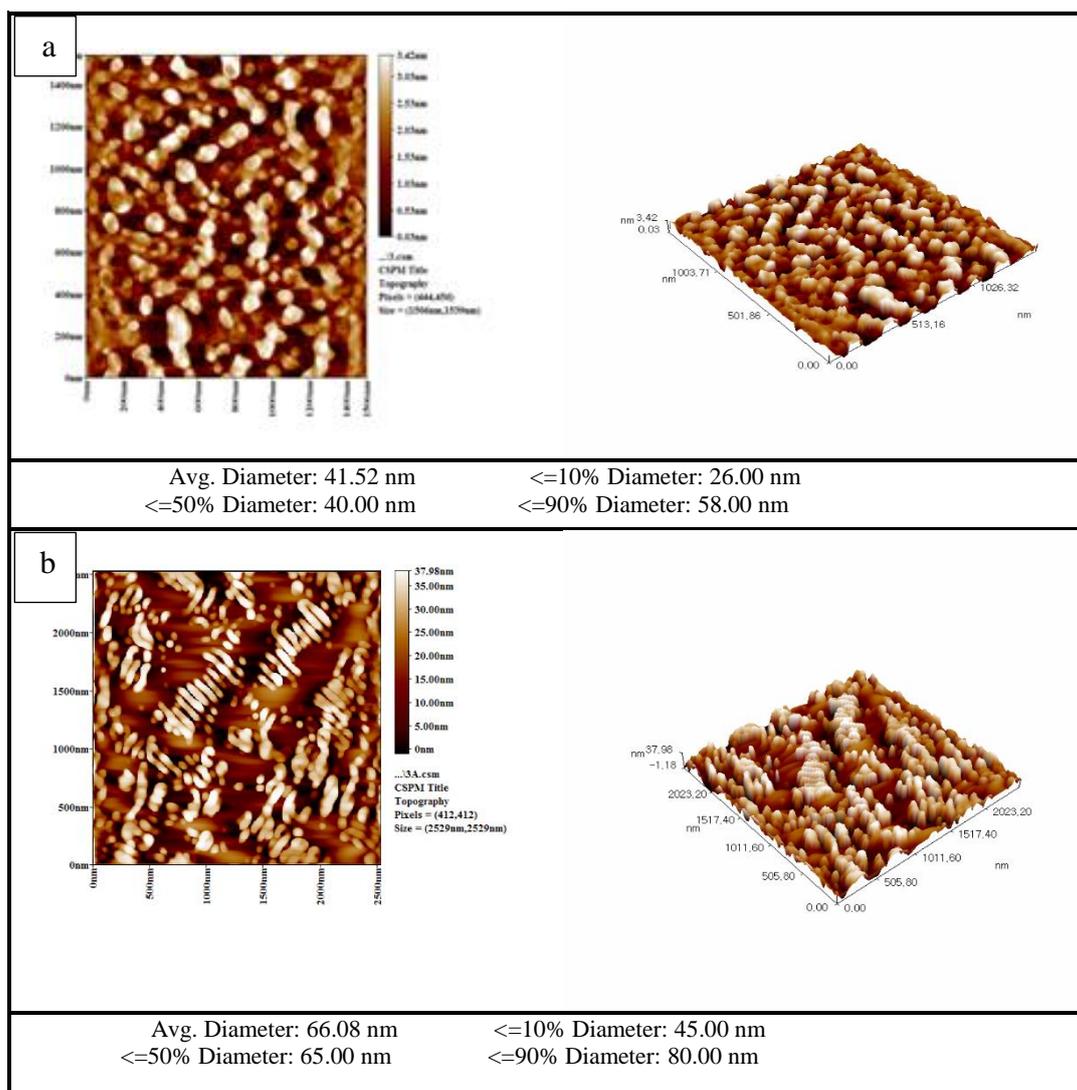


Figure 4. AFM images (3D and 2D) and distribution particles (a)for  $\text{TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  (b)  $\text{Ni-Mo/ TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ .

#### Fourier transforms infrared spectroscopy (FT-IR)

The samples were characterized by FT-IR analysis in the range between  $(4000\text{-}400)\text{ cm}^{-1}$ , where the FT-IR results is shown in Figs. 5, and 6 for  $\text{TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$ , and  $\text{Mo-Ni/TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  respectively. The FTIR spectra of the composite  $\text{TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  shows a pronounced band in sample, a broad peak at  $3434\text{ cm}^{-1}$  is referred to the stretching vibrations of O-H group from the mixed oxides for and amount of  $\text{H}_2\text{O}$  molecules in the surface were the band at  $1620\text{ cm}^{-1}$  corresponds to the bending vibration of O-H<sup>21</sup>. The low-frequency absorption band at  $476.3\text{ cm}^{-1}$  is attributed to the Ti-O-Ti vibration of the samples<sup>18</sup>. Broad band centered at  $634.54\text{ cm}^{-1}$  is detected which can be assigned to Al-O-Al and Ti-O-Ti. In addition, a small band is detected at  $582$  and  $430.1\text{ cm}^{-1}$  which can be assigned to hetero metal-oxygen bonds of Ti-O-Al<sup>21</sup>. Some weak peak appears around  $2717\text{-}$

$2935.4\text{ cm}^{-1}$  stretching C-H vibrations, which can be attributed to the organic residues, that remain in sample after low calcination temperature<sup>22</sup>.

The FTIR spectra of the catalyst  $\text{Ni-Mo/ TiO}_2\text{-}\gamma\text{-Al}_2\text{O}_3$  shows absorption band appeared in the region of  $(3400\text{-}3510)\text{ cm}^{-1}$ , for stretching vibrations of O-H group, and for bending appearing at  $1627.8\text{ cm}^{-1}$ <sup>23</sup>. It is observed a slight shift in the bands/ peaks position and change in the intensity of bands that may be due to the presence of the dopants (Mo, and Ni) in the interstitials of the lattices of the doped samples<sup>24</sup>.

Bands between  $1377\text{-}1529.4\text{ cm}^{-1}$  for catalyst nanoparticles indicate the presence of a small amount of organic material in the sample<sup>25</sup>. The spectra of lower wavenumber region of the band around  $447\text{ cm}^{-1}$  are due to the bending vibrations of M-O such as Ti-O and Ti-O-Ti frame work bonds<sup>24</sup>. A large hump around  $1091\text{ cm}^{-1}$  in catalyst Mo-

Ni/TiO<sub>2</sub>- γ -Al<sub>2</sub>O<sub>3</sub> is credited to the Ti-O-Ti vibration. This peak is shifted to higher wavenumbers comparing with support catalyst <sup>20</sup>.

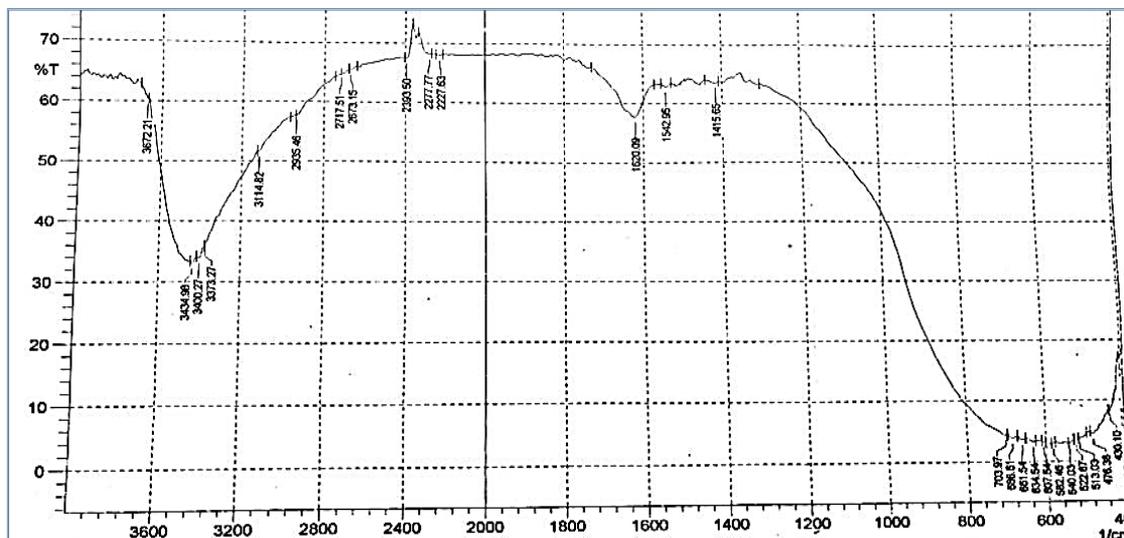


Figure 5. FT-IR for TiO<sub>2</sub>- γ -Al<sub>2</sub>O<sub>3</sub>.

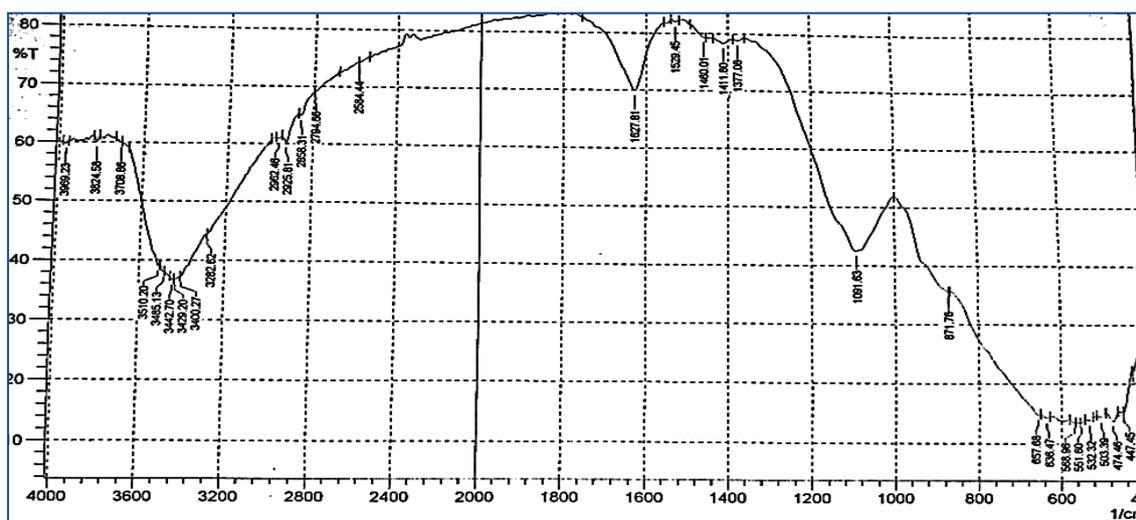


Figure 6. FT-IR for Ni-Mo/TiO<sub>2</sub>- γ -Al<sub>2</sub>O<sub>3</sub>

### X-Ray Fluorescence (XRF)

The chemical composition of the support and active metals and promoter were measured using XRF analysis, in order to enable the support active sites to be ready for contaminants adsorption in petroleum refining processes, active metals and promoters are added in specific percentages. Generally, Mo is added at percentage ranged between 10-25%. On the other hand, most of the best-known used promoters were Co and Ni that were loaded at percentage ranged between 1-6% <sup>8</sup>. XRF analysis were used to determine amounts of active metals and promoters that was added to nano TiO<sub>2</sub> and its composites by wet-co-impregnation technique. The percentage of TiO<sub>2</sub> is 63%, Al<sub>2</sub>O<sub>3</sub> 32% in catalyst support, while the percentage in

catalyst is 8.61 for TiO<sub>2</sub>, 21.7 for Al<sub>2</sub>O<sub>3</sub>, and Ni is 3.8%, while Mo is 14.0%.

### BET Surface Area & Pore Volume

The surface area and pore volume of the nano catalyst play a very important role for the activity of the nano catalyst because the high surface area leads to high active sites that cause increasing in activity. Table 2 shows the results of surface area and pore volume of the prepared samples <sup>8</sup>. TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> sample has a good surface area; this means that the addition of gamma alumina leads to an increase in the surface area of the composites, and may be due to the distribution of amorphous Al<sub>2</sub>O<sub>3</sub> into the TiO<sub>2</sub> lattice crystals <sup>13</sup>. The surface area for catalyst support and catalyst was conducted

using Brunauer, Emmett, and Teller (BET) method. The surface area of prepared support nano catalysts is 355.18 m<sup>2</sup>/gm., while pore volume is 0.416 cm<sup>3</sup>/gm. While it is tested for prepared nano catalyst Mo-Ni/TiO<sub>2</sub>- γ-Al<sub>2</sub>O<sub>3</sub> to be reduced to 341.13 m<sup>2</sup>/gm., and pore volume 0.346 cm<sup>3</sup>/gm. Table 2 shows the properties for TiO<sub>2</sub>- γ-Al<sub>2</sub>O<sub>3</sub>, and Ni-Mo/TiO<sub>2</sub>- γ-Al<sub>2</sub>O<sub>3</sub>. The reduction in surface area and pore volume of prepared nano catalysts is due

to the high loading of metal oxides on the support<sup>8</sup>, the doped sample has a lower surface area than the nano supports powder. Also, this behavior may be due to the agglomeration process. And close the pores of supports surface. This could be attributed due to the annealing temperature for the anatase stabilization, favoring the particles growth and agglomeration<sup>26</sup>.

**Table 2. Properties for TiO<sub>2</sub>- γ-Al<sub>2</sub>O<sub>3</sub>, and Ni-Mo/TiO<sub>2</sub>- γ-Al<sub>2</sub>O<sub>3</sub>.**

Sample	percentage of chemical composition%				Surface area (m <sup>2</sup> /gm)	Crystal size (nm)	Particles size (nm)	Pore Volume (cm <sup>3</sup> /gm)
	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Ni	Mo				
TiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	64	32	-	-	355.18	8.9	35.00	0.416
Mo-Ni/TiO <sub>2</sub> - Al <sub>2</sub> O <sub>3</sub>	58.61	21.7	3.8	14.0	341.13	10.8	62.16	0.346

### Catalyst Activity Testing

A hydrotreatment pilot plant located at refining department - Petroleum Research & Development Center of Iraqi Ministry of was used to test the activity of catalysts and support ability for sulfur removal.

### Effect of Temperature on Sulfur Removal

Fig. (7) shows the Percentage of sulfur removal at different temperature ranges on Ni-Mo/TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> prepared catalyst. The efficiency of sulfur removing values can be calculated by Eq. 2, (1)

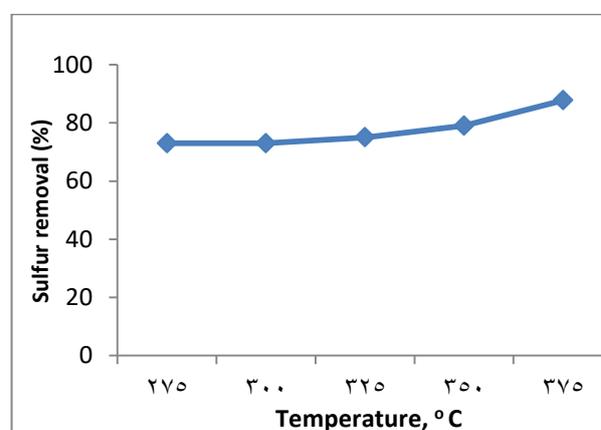
$$\text{Sulfur Removal} = [(C(S)^{\circ} - C(S))/C(S)^{\circ}] * 100 \dots\dots 2$$

Where C(S)<sup>o</sup> is denoted as the initial sulfur concentration (ppm), in this study 8980 (ppm) sulfur content, and C(S) residual sulfur concentration (ppm). Table 3 shows the effect of temperature and LHSV on percentage (%) of sulfur removal. It can be observed from the Table 3 that catalyst in general shows a better sulfur removal at 375°C, Maximum sulfur removal was 87.75 % in gas oil on Ni-Mo/TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> catalyst at temperature 375°C, LHSV 1h<sup>-1</sup>. Increasing the temperature generally leads to increasing in hydrotreating conversion. The increasing of sulfur removal at high reaction temperature may be attributed to that of the unreactive sulfur compounds which most properly belong to thiophene derivatives which become activated enough to react with hydrogen. Thus, the upper-temperature value is limited by the undesirable side

reactions such as hydrocracking reactions which are expected to occur at high temperature<sup>27</sup>.

**Table 3. Effect of Temperature and LHSV on percentage (%) of sulfur removal.**

Temperature (°C)	LHSV (hr <sup>-1</sup> )	Sulfur content (ppm)	percentage of sulfur removal (%)
275	1	2400	73.27
300	1	2370	73.60
325	1	2190	75.61
350	1	1810	79.84
375	1	1100	87.75
375	2	2280	74.61
375	3	2305	74.33
375	4	2325	74.10



**Figure 7. Percentage of sulfur removal at different temperatures.**

### Effect of LHSV on sulfur removal

The liquid hourly space velocity effect on the sulfur removal percentage was well studied using 1, 2, 3, and 4 hr<sup>-1</sup> at temperature 375°C with 35 bar pressure and 200/200 cm<sup>3</sup>/cm<sup>3</sup> H<sub>2</sub>/HC ratio. The percentage of sulfur removal is increased with decreasing LHSV at temperature 375°C. Where at 4, 3, 2, and 1h<sup>-1</sup> at 375°C the percentage of sulfur removal reached 72.69, 72.93, 73.22, and 87.75 respectively using the prepared catalyst Ni-Mo/TiO<sub>2</sub>-γ alumina, the percentage of sulfur removal shown in fig. 8.

Any decrease in LHSV could be explained as lesser quantity of gas oil is contacting the same quantity of catalyst per unit time; on the other hand, the increase in LHSV refer to a greater quantity of gas oil through the reaction per unit of time<sup>1</sup>.

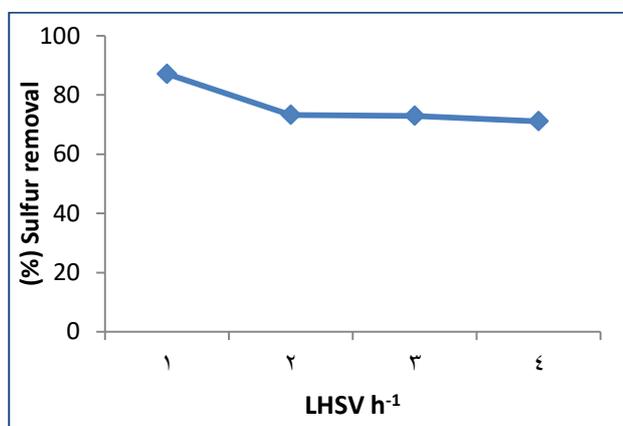


Figure 8. Percentage of sulfur removal at 375°C, and different LHSV h<sup>-1</sup>.

when comparing the removal percentage obtained in this research with other research as **Tariq**<sup>4</sup> reached to 61.5 and 59.5 % sulfur removal using NiMo/γ-alumina and CoMo/γ-alumina conventional catalyst, respectively with 350°C, 1hr<sup>-1</sup>LHSV, 40 bar pressure, and 500/500 cm<sup>3</sup>/cm<sup>3</sup> H<sub>2</sub>/Hc ratio as experimental conditions **Mohammed**<sup>8</sup> who reached 70% HDS for both types of nano catalysts using NiMo/γ-alumina and CoMo/γ-alumina nano catalysts at the same well known conditions with 200/200 cm<sup>3</sup>/cm<sup>3</sup> H<sub>2</sub>/HC ratio, we find that the catalyst has proven to be highly efficient in removing sulfur compounds from the Iraqi gas oil with a rate of 87.75%.

### Conclusion:

In present work a nano TiO<sub>2</sub>-γ Al<sub>2</sub>O<sub>3</sub> mixed oxides was successfully prepared using sol-gel method with percentage (64%-32%). The obtained crystal size and particle size for TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> were 8.9 nm, and 35.00 nm respectively. The prepared TiO<sub>2</sub>-γ Al<sub>2</sub>O<sub>3</sub> mixed oxides have a high surface

area 355.18 m<sup>2</sup>/gm. at 500°C. Active metals of Mo & Ni oxides (3.8 %Ni,14% Mo) were loaded on TiO<sub>2</sub>-γ Al<sub>2</sub>O<sub>3</sub> using impregnation technique to synthesize a new Nano catalyst Ni-Mo/ TiO<sub>2</sub>-γ Al<sub>2</sub>O<sub>3</sub>, the crystal, and particles size for prepared catalyst were 10.8 nm, and 62.16 nm respectively with a relatively high surface area (341.13) m<sup>2</sup>/gm. Investigations using Scanning electron microscopic (SEM), and Atomic force microscope (AFM) revealed that surface morphology for both TiO<sub>2</sub>-γ Al<sub>2</sub>O<sub>3</sub> mixed oxides, and catalyst Ni-Mo/ TiO<sub>2</sub>-γ Al<sub>2</sub>O<sub>3</sub> having a close AFM results to what was obtained in the SEM. In FTIR spectrum for catalyst observed a slight shift in the bands/peaks position and change in the intensity of bands cooperation with mixed oxide that may be due to the presence of the dopants (Mo, Ni) in the interstitials of the lattices of the doped samples.

Catalytic activity showed that sulfur removal from gas oil is highly dependent on the reaction temperature and LHSV h<sup>-1</sup> variation within the range of studied operation conditions which was carried out in a continuous hydrotreating pilot plant unit, at various temperatures 275°C to 375°C, LHSV 1 to 4 h<sup>-1</sup>, constant pressure 35 bar and H<sub>2</sub>/HC ratio 200 ml/200ml., Leading to Maximum sulfur removal of (87.75)% in gas oil that tested on Ni-Mo/TiO<sub>2</sub>-γ-Al<sub>2</sub>O<sub>3</sub> prepared catalyst, at temperature 375°C, LHSV 1h<sup>-1</sup>, which proves that the prepared catalyst had a remarkable HDS activity and the nano support could be a good candidate to serve in different hydrotreating processes.

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### Authors' declaration:

- Conflicts of Interest: None.
- We hereby confirm that all the Figures and Tables in the manuscript are mine ours. Besides, the Figures and images, which are not mine ours, have been given the permission for republication attached with the manuscript.
- The author has signed an animal welfare statement.
- Ethical Clearance: The project was approved by the local ethical committee in Petroleum Research & Development Center.

### Authors' contributions:

Dalya Jasim Ahmed, Basim Ibrahim Al-Abdaly, Sattar Jalil Hussein, are effectively contributed to the design and implementation of the research, laboratory work, the analysis and discussion of the results and to the writing of the manuscript.

### References:

1. Mohammed AH, Hussain HK, Naife TM. Hydrodesulfurization of Iraqi Atmospheric Gasoil by Ti-Ni-Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> Prepared Catalyst. Eng. J. 2017 Nov 1;23(11):13-24
2. Abdulnabi W A. "Synthesis of Crystalline Alumina from Waste Cans and Its Performance in Desulfurization Reaction" Ph.D. [Thesis]. Baghdad: University of Nahrain ;2018.
3. Awadh AJ. "Preparation and characterization of CuO/Al<sub>2</sub>O<sub>3</sub> nano adsorbent for adsorption of sulfur compounds from Iraqi naphtha .M.Sc. [Thesis]. Baghdad: Al-Nahrain University; 2018.
4. Naif T.M. "Activity of a Prepared Catalyst Promoted by Different Metals for the Hydrodesulfurization of Iraqi Gas Oil". Ph.D. [Thesis], Baghdad: university of Baghdad; 2017.
5. Sadare OO, Obazu F, Daramola MO. Biondesulfurization of petroleum distillates—current status, opportunities and future challenges. Environ.. 2017 Dec; 4(4):85.
6. Sushkevich VL, Popov AG, Ivanova II. Sulfur-33 Isotope Tracing of the Hydrodesulfurization Process: Insights into the Reaction Mechanism, Catalyst Characterization and Improvement. GDCh,2017 Aug 28;56(36):10872-6.
7. Ahmedzeki NS, Hussein S, Abdulnabi WA. Recycling waste cans to nano gamma alumina: Effect of the calcination temperature and pH. Int. J. Curr. Eng. Technol. 2017;7(1):82-8.
8. Mohammed SM. "Synthesis and Characterization of CoMo/ $\gamma$  Alumina and NiMo/  $\gamma$  Alumina nano Catalysts for Hydrodesulfurization of Gas Oil". Ph.D. [Thesis]. Baghdad: University of Baghdad; 2017.
9. Tiwari R, S Rana B, Kumar R, K Sinha A. TiO<sub>2</sub>-ZrO<sub>2</sub> binary oxides for effective hydrodesulfurization catalysts. Open Cata. J. 2012 Sep 7; 5(1).
10. Liang G, He L, Cheng H, Li W, Li X, Zhang C, Yu Y, Zhao F. The hydrogenation/dehydrogenation activity of supported Ni catalysts and their effect on hexitols selectivity in hydrolytic hydrogenation of cellulose. JCAT. 2014 Jan 1; 309:468-76.
11. Bagheri S, Shameli K, Abd Hamid SB. Synthesis and characterization of anatase titanium dioxide nanoparticles using egg white solution via sol-gel method. J. Chem. 2013 Jan 1;2013.
12. Koo JH. Fundamentals, properties, and applications of polymer nanocomposites. Cambridge University Press; 2016 Oct 31.
13. Zhang W, Li C, Li R. Sol-gel Preparation of TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> Composite Materials to Promote Photocatalytic Activity. NANOASI. 2015 Apr 1; 5(1):8-14.
14. Wang K, Yang B, Liu Y, Yi C. Preparation of Ni<sub>2</sub>P/TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and the catalytic performance for hydrodesulfurization of 3-methylthiophene. E& F. 2009 Sep 17;23(9):4209-14.
15. Guevara-Lara A, Bacaud R, Vrinat M. Highly active NiMo/TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> catalysts: Influence of the preparation and the activation conditions on the catalytic activity. APPL CATAL A-GEN2007 Sep 10; 328(2):99-108.
16. Ramírez J, Rayo P, Gutiérrez-Alejandre A, Ancheyta J, Rana MS. Analysis of the hydrotreatment of Maya heavy crude with NiMo catalysts supported on TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> binary oxides: Effect of the incorporation method of Ti. J.Cattod. 2005 Nov 30; 109(1-4):54-60
17. Imran SI. Synthesis and Characterization of MxOy.ConOm Nanoparticles and Study some Applications. Ph.D. [Thesis]. Baghdad: University of Baghdad; 2018.
18. Zhang W, Li R, He H. Synthesis of mesoporous TiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> binary oxides photocatalyst by sol-gel method using PEG1000 as template. IJP. 2012;2012.
19. Li M, Song J, Yue F, Pan F, Yan W, Hua Z, Li L, Yang Z, Li L, Wen G, Wu K. Complete hydrodesulfurization of dibenzothiophene via direct desulfurization pathway over mesoporous TiO<sub>2</sub>-supported NiMo catalyst incorporated with potassium. Catalysts. 2019 May; 9(5):448.
20. Manzoor M, Rafiq A, Ikram M, Nafees M, Ali S. Structural, optical, and magnetic study of Ni-doped TiO<sub>2</sub> nanoparticles synthesized by sol-gel method. Int Nano Lett. 2018 Mar; 8(1):1-8.
21. Yang C, Zhang Q, Li J, Gao R, Li Z, Huang W. Catalytic activity and crystal structure modification of Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts with different Al<sub>2</sub>O<sub>3</sub> contents. J. Energy Chem . 2016 May 1;25(3):375-80.
22. Sridevi DV, Ramesh V, Sakthivel T, Geetha K, Ratchagar V, Jagannathan K, Rajarajan K, Ramachandran K. Synthesis, Structural and Optical Properties of Co Doped TiO<sub>2</sub> Nanocrystals by Sol-Gel Method. J. Mater. Sci. Eng. 2017.9(1).
23. Pirbazari azadeh e, Monazzam P, Kisomi BF. Co/TiO<sub>2</sub> nanoparticles: preparation, characterization and its application for photocatalytic degradation of methylene blue, J.DWT.63.,283-292.2018. doi:10.5004/dwt.2017.20205.
24. Raguram T, Rajni KS. Synthesis and analysing the structural, optical, morphological, photocatalytic and magnetic properties of TiO<sub>2</sub> and doped (Ni and Cu) TiO<sub>2</sub> nanoparticles by sol-gel technique. Appl. Phys. A. 2019 May 1;125(5):288
25. Guan B, Yu J, Guo S, Yu S, Han S. Porous nickel doped titanium dioxide nanoparticles with improved visible light photocatalytic activity. Nanoscale Adv.,2020;2(3):1352-7.
26. Cao, G. and Wang Y. Nanostructures and Nanomaterials: Synthesis, Properties, and Applications: . New York: World Scientific Series in Nanoscience and Nanotechnology, 2011.
27. Steiner P, Blekkan EA. Catalytic hydrodesulfurization of a light gas oil over a NiMo catalyst: kinetics of selected sulfur components. J.FPT 2002 Aug 20;79(1):1-2.

## تخليق وتشخيص العامل المساعد النانوي الجديد Mo-Ni /TiO<sub>2</sub>- γAl<sub>2</sub>O<sub>3</sub> لازالة المركبات الكبريتية من زيت الغاز العراقي

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### الخلاصة:

تشتمل دراسة هذا البحث عملية ازالة المركبات الكبريتية من مقطع زيت الغاز العراقي المأخوذ من مصفى الدورة الذي يحتوي على 8980 جزء من المليون محتوى كبريتي بواسطة طريقة المعاملة بالهيدروجين وباستخدام العامل المساعد النانوي Ni-Mo/TiO<sub>2</sub>- Al<sub>2</sub>O<sub>3</sub> γ-alumina ، تم تحضير ال TiO<sub>2</sub>-γalumina باستخدام طريقة الهلام-جيل . وبنسبة 64%للـTiO<sub>2</sub> و 32% للـ Al<sub>2</sub>O<sub>3</sub>. وتم استخدام عملية التثريب الفراغي لتحميل المعادن على المتراكب الذي تم تحضيره وبنسبة تحميل كانت للـ Ni 3.8 % والـ Mo 14% . تم تشخيص النماذج النانوية المحضرة باستخدام فحوصات حيود الاشعة السينية(XRD)، الاشعة تحت الحمراء(FT-IR) ، (امتصاص وامتزاز النتروجين)(BET) ، مجهر القوة الذرية(AFM) ، والمجهر الالكتروني الماسح(SEM). تم دراسة كفاءة العامل المساعد المحضر لاستخلاص الكبريت بواسطة المعاملة بالهيدروجين بدرجة حرارة (300,325,350، 375) مئوية وبسرعة فراغية 1 ساعة<sup>1</sup> وبضغط 35 بار وبنسبة هيدروجين الى هيدروكربون تصل الى 200/200 سم<sup>3</sup>/سم<sup>3</sup> . وكانت اعلى نسبة ازالة عند الدرجة الحرارية 375 مئوي حيث وصلت نسبة الازالة الى 87.75 % عند الظروف اعلاه، كذلك تم دراسة كفاءة هذا العامل المساعد مع تغيير السرعة الفراغية 1- 4 LHSV عند الدرجة الحرارية التي كانت عندها اعلى ازالة للكبريت . اظهرت النتائج كفاءة العامل المساعد المحضر في تقليل نسبة المركبات الكبريتية في الظروف التشغيلية المستخدمة .

**الكلمات المفتاحية:** زيت الغاز ، ازالة المركبات الكبريتية بالهدرجة ، المعاملة بالهيدروجين، العامل المساعد النانوي ،ثاني اوكسيد التيتانيوم(TiO<sub>2</sub>).