Arab J Sci Eng (2017) 42:1381–1387
DOI 10.1007/s13369-016-2249-5

RESEARCH ARTICLE - CHEMICAL ENGINEERING

# Synthesis of Nanocatalyst for Hydrodesulfurization of Gasoil Using Laboratory Hydrothermal Rig

**Mohammed I. Mohammed**[1] · **Adnan A. Abdul Razak**[1] · **Mohammed A. Shehab**[1]

Received: 9 February 2016 / Accepted: 8 June 2016 / Published online: 28 June 2016

**Abstract** This study presents a simple fabrication procedure for obtaining a nanocatalyst by homogeneously implanting CoMo within the structure of multiwall carbon nanotubes. The nanocatalyst efficiency was determined by applying the catalyst in a laboratory hydrothermal testing rig to remove sulfur from gasoil using various methods. The conventional catalyst (CoMo/$Al_2O_3$) was also used as a reference. Scanning electron microscope (SEM), high- resolution transmission electron microscope (HRTEM), an X-ray diffractometer (XRD), and Brunauer, Emmett, and Teller (BET) method were used to study the morphology and the structure of prepared samples, and the X-ray fluorescence technique (XRF) was used to determine the sulfur content in gasoil. After preparation, the nanocatalyst composite structure observed the formation of network structure between metal catalysts and CNTs, and almost all CoMo particles were homogeneously decorated within the bulk of CNTs. Experiments using nanocatalysts reveal better results than the conventional catalyst (CoMo/$Al_2O_3$) in removal of sulfur from gasoil. As a result, an improvement of about 10 % (73.5 % max. HDS) in hydrodesulfurization (HDS) over conventional catalyst was obtained with a 10 h contact time, 280 °C reactor temperature, 10 bar system pressure, and 2 $h^{-1}$ space velocity of gasoil, which may be an optimum condition for removal of sulfur from gasoil within the conditions and design parameters of our experimental system.

**Keywords** Gasoil · Hydrodesulfurization (HDS) · MWCNTs · Nanocatalyst

---

✉ Mohammed I. Mohammed
mohab1964@yahoo.com

[1] Department of Chemical Engineering, University of Technology, 52 AlSinaa Street, Baghdad, Iraq

## 1 Introduction

The concentration of sulfur in crude oil is typically between 0.05 and 5.0 % (by weight), although values as high as 13.95 % have been reported [1].Upon combustion, sulfur in fuels can contribute to air pollution in the form of particulate material and acidic gases, such as sulfur dioxide. To reduce sulfur- related air pollution, the level of sulfur in fuels is regulated and sulfur must be removed from fuels during the refining process. Hydrodesulfurization (HDS) is a catalytic chemical process that typically uses a heterogeneous cobalt- or nickel-doped molybdenum sulfide catalyst supported on alumina [2]. HDS is widely used to remove sulfur compounds from refined petroleum products such as gasoline, jet fuel, kerosene, diesel fuel, and fuel oils.

The purpose of removing sulfur is to decrease atmospheric pollution caused by the emission of sulfur dioxide as a result to fuel combustion [3].

The conventional hydrodesulfurization (HDS) process is usually conducted over sulfidized CoMo/$Al_2O_3$ and NiMo/$Al_2O_3$ catalysts [4]. 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 $H_2S$), the nature and concentration of the sulfur compounds present in the feed stream, and the reactor and process design [5]. Alumina is the most widely used support among hydrodesulfurization catalysts [6]. A notable feature of alumina supports is their ability to provide high dispersion of the active metal components. However, numerous chemical interactions exist between alumina and transition metal oxides. Some of the formed species are very stable and resist completely sulfidizing; therefore, the catalytic activity of such catalysts is low [7]. Coke formation during the hydrodesulfurization process of petroleum fractions is another disadvantage of alumina-supported catalysts; it causes deactivation and decreases the lifetime of catalysts [8]. Carbon nanomaterials have received attention as a support in heterogeneous catalysts [4] due to its unique properties: the possibility to control surface chemistry and porosity, its resistance to basic and acid media, and the easy recovery of metals by support burning. Multiwall carbon nanotubes (MWCNTs) have been studied extensively as a novel support material [9,10].

Our aim is to provide hydrodesulfurization nanocatalysts to overcome the problems of conventional art catalysts. The catalyst, according to our research, may have an increased surface area and therefore better activity. The more common catalyst, according to our research, provide improved dispersion of the active metals over the support material, while chemical interactions between the support material and active metal are minimized. We also analyze catalysts that function under relatively mild operating conditions as compared to alumina-supported conventional catalysts.

## 2 Experiment

### 2.1 Preparation of the Nanocatalyst

MWCNTs were prepared by chemical vapor deposition (CVD), purified, and functionalized according to our previously published work [11]. Functionalized MWCNTs were used in preparation of the nanocatalyst as a carrier for CoMo metal. A solution including 5.00 g of a cobalt nitrate, 6.00 g of ammonium heptamolybdate, and 100 ml of double-distilled water was prepared. The metal content of the solution was then impregnated on 35 g of multiwall carbon nanotubes of a 20–100 mesh size. The catalyst was then dried at 120 °C for 6 h and transferred to a temperature- programmed tubular electric furnace in which the material was calcinated under argon atmosphere at 450 °C for 2 h. After heat treatment, the resulting catalyst powder mixed with solution consisted of 2 % novolac in 50 ml of ethanol, which was then extruded as pellets ($1.5-20\,\text{mm}\times 3.5-5.0$ mm) and dried at 160 °C to forma hard, porous structure of catalyst composite. Commercial catalyst type $\text{CoMo}/\gamma-\text{Al}_2\text{O}_3$ (supplied by Midland Petroleum refinery, Iraq) has been used as reference. The activity HDS % of nanocatalysts were evaluated using a laboratory-scale reactor to measure hydrodesulfurization (HDS) activity, and their performance will be compared with commercially available catalysts. Images of both catalysts are shown in Fig. 1.

### 2.2 Hydrodesulfurization Process

The laboratory scale of reactor rig for HDS experiments shown schematically in Fig. 2.

Hydrodesulfurization was performed using the CoMo/CNT nanocatalysts. An alumina-supported catalyst (CoMo/alumina) was also used for comparison. Gasoil (Supplied by Midland Petroleum refinery, Iraq) was used as feed for catalyst evaluation. The sulfur content of the feed was 1300 ppm (by mass). The hydrodesulfurization process was performed on a stainless steel, fixed bed reactor (250 mm length, 12 mm in diameter) using 1.6 g of catalyst in each run placed inside stainless steel holder.

A K-type thermocouple was kept in touch with the holder to ensure a reliable reading of temperatures at the catalyst position. All of the catalysts were evaluated under similar operating conditions. A solution containing 1 % of dimethyl disulfide was used to sulfidize the catalysts by

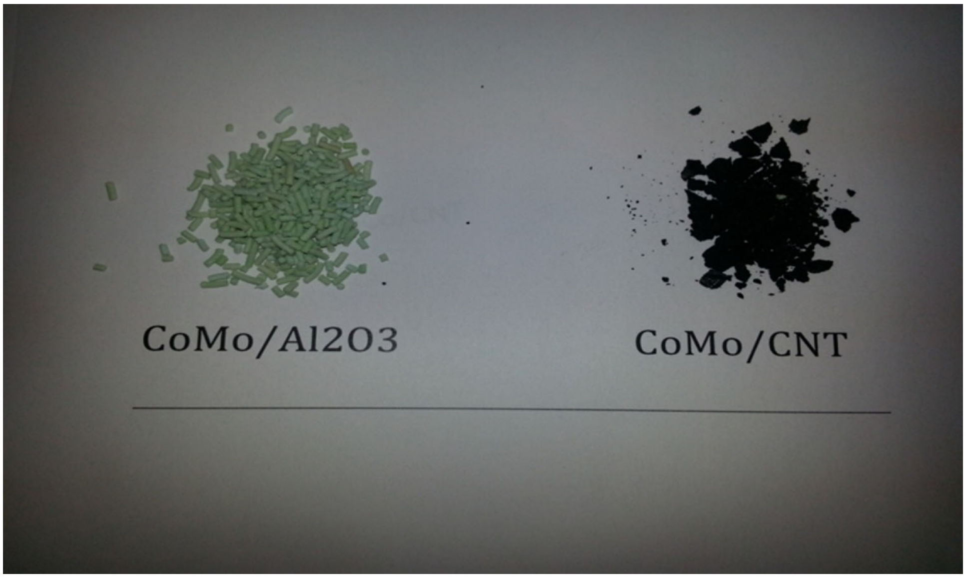

**Fig. 1** Image of commercial($\text{COMO}/\text{Al}_2\text{O}_3$) catalyst and present work CoMo/CNT nanocatalyst

**Fig. 2** Schematic diagram in Experimental HDS rig

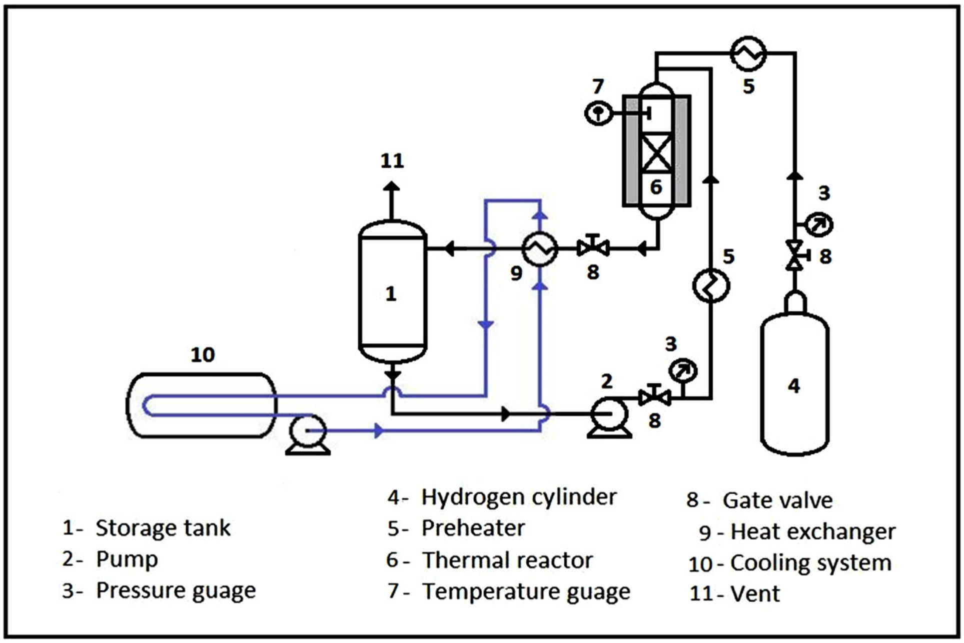

**Table 1** Summary of HDS Experiments

| Experiment | Temp. (°C) | Time (h) | Space Velocity ($h^{-1}$) | Pressure (bar) |
|---|---|---|---|---|
| Effect of temperature (240–280) | Variable (240–280) | 10 h | 6 | 10 |
| Effect of time (2–10) | 280 | Variable (2–10) | 6 | 10 |
| Effect of space velocity (2–6) | 280 | 10 | Variable (2–6) | 10 |
| Effect of pressure (5–10) bar | 280 °C | 10 | 6$h^{-1}$ | Variable (5–10) bar |

injecting sulfidizing feed. The sulfidizing step was carried out with hydrogen/feed ratio of 40lN/l and pressure of 10 bar at 300 °C. After this step, the reaction product (collected in a condenser) was discharged, and the hydrodesulfurization started, with gasoil as the feed, under variable conditions, such as temperature, pressure, time, and space velocity on HDS. A summary of all experiments is listed in Table 1.

A hydrogen/feed ratio of 40lN/l was kept constant for all of experiment runs. Each reaction was performed continuously for 24 hours, and a final sample after this time was used for total sulfur analysis. Samples were collected at each run and analyzed by a PHONIX11XRF Analyzer. An average of three readings was taken to reduce the error. The hydrodesulfurization activity of the catalysts was calculated using the following equation:

$$\text{HDS}\ \% = \left(\text{ST}_{\text{feed}} - \text{ST}_{\text{product}}\right)/\text{ST}_{\text{feed}}, \qquad (1)$$

where HDS% is hydrodesulfurization activity, $\text{ST}_{\text{feed}}$ is the total sulfur content of the feed, and $\text{ST}_{\text{product}}$ is the total sulfur content of the product.

### 2.3 Characterization

In this study, a scanning electron microscope (SEM) (typeS-4160, HITACHI Company, Japan), a high-resolution transmission electron microscope (HRTEM) (type CM30 Philips, Netherlands), the X-ray patterns were recorded with a PAN analytical, Netherland powder diffractometer, and Brunauer, Emmett, and Teller (BET) method (QSurf1600, USA) were used to determine the surface morphology, crystalline structure, and surface area of the prepared materials. PHONIX11XRF was employed to determine the concentration of sulfur in gasoil.

## 3 Results and Discussion

### 3.1 Characterization of the Nanocatalyst

This new process produces a network structure of CoMo/MWCNT, where Mo and Co are homogeneously introduced within the CNTs' structure; at the same time, the interfacial bonds between the CNTs and CoMo nanoparticles are stable.

SEM micrographs of functionalized MWCNTs are presented in Fig. 3a. Well-defined multiwall carbon nanotubes with an average diameter of 10–25 nm were obtained.

After preparation, the structure of nanocatalyst observed the formation of network structure between metals catalysts and CNTs and almost all CoMo particles were homogeneously decorated within the bulk of the CNTs (as shown in SEM image of Fig. 3b and HRTEM result (Fig. 3c). The size of the catalysts particles ranged from 5–10 nm, while the diameter of the carbon nanotubes increased by a factor of three due to the implantation of metal particles within the tube structure as can be gathered from the results of Fig. 3b and 3c.

XRD pattern for laboratory prepared MoCo/CNTs nanocatalyst is shown in Fig. 4. It indicates that a polycrystalline structure formed during the heat treatment of the catalyst by 2 h at 550 °C. Diffraction peaks at 26.48° are due to CNTs. Peaks at 31°, 45°, and 48.7° are assigned to molybdenum, while peaks at 35.6°, 43°, and 63° are assigned to cobalt. No peaks related to impurities are detected which confirm the uniformity as well as the high purity of the MoCo/CNTs catalyst structure. The uniformity as well as the high purity of the catalyst structure of MoCo/CNTs may lead to obtained a high performance catalytic.

However, the mechanism of preparation is now clear and will help control the quality of nanocatalyst fabrication for future work. These results are in good agreement with the results obtained by Paymanetal [12].

BET method was applied to determine the specific surface area, the pore volume, and average pore diameter of the CNTs, CoMo/CNTs, and CoMo/$Al_2O_3$,and the results are listed in Table 2.

As can be gathered from the result in Table 2, a reduction of 14 % in surface area of CNTs has been observed after loaded with CoMo particles, due to the interaction between these particles and part of CNTs surface. Comparing with conventional catalyst, the surface area is approximately the same, while the average pore diameter slightly increased. The total pore volume of nanocatalyst was also increased by a factor of two, and it might be the main reason for the increase in HDS efficiency of nanocatalysts.

## 3.2 Results of HDS

In order to determine the activity of novel CNT-supported catalysts relative to conventional catalysts, both conventional and nanocatalysts were analyzed under similar experimental conditions the laboratory desulfurization rig. In each case, 1.4 g of catalyst was placed inside the hydrothermal catalytic

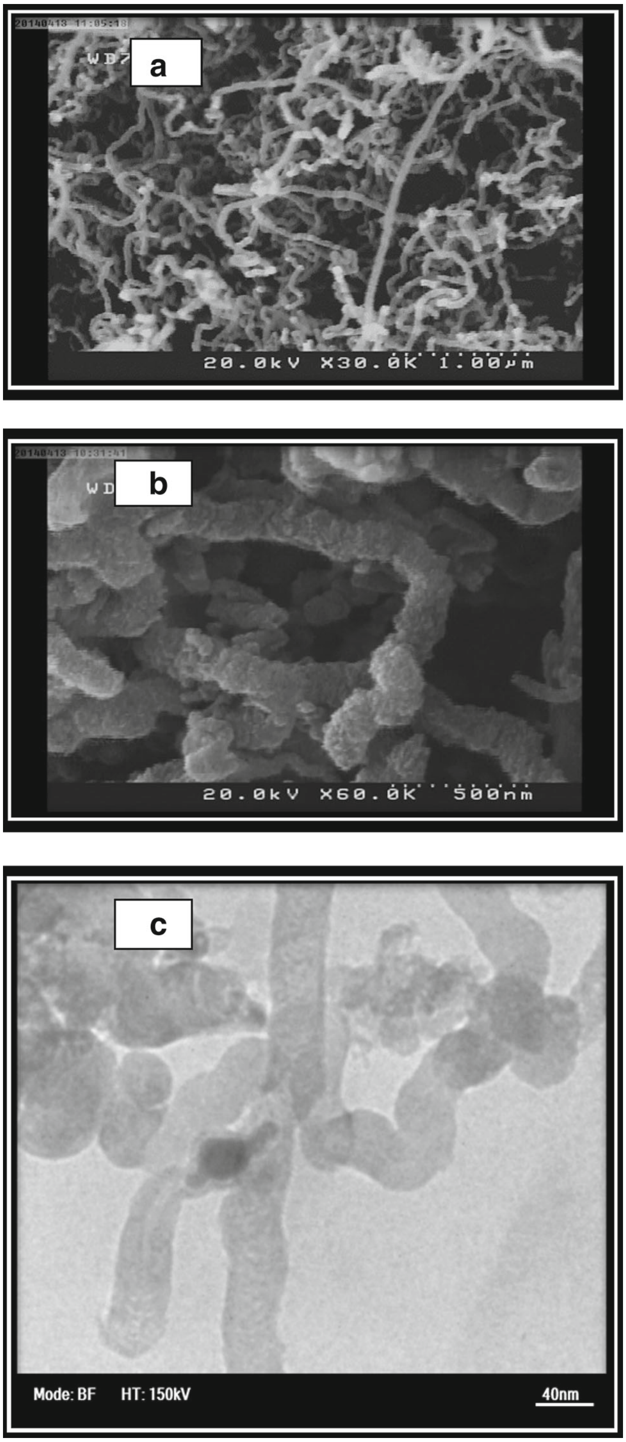

**Fig. 3** **a** SEM image of CNTs prepared by CVD method, **b** SEM image of CNTs after decorated with CoMo metal particles, **c** HRTEM of CNTs, shows the dispersion of CoMo particles inside the CNTs. The diameter of the tubes increased in (**b**) and (**c**) due to CoMo particles insertion within the structure of CNTs

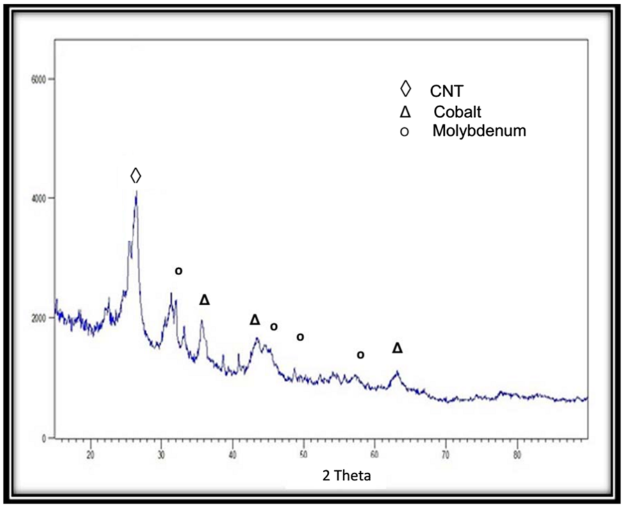

**Fig. 4** XRD spectra of CoMO/MWCNT nanocatalyst

**Table 2** Physical properties of MWCNT, MWCNT support Co-Mo and $Al_2O_3$ support Co-Mo catalysts

| No. | Sample | Surface area ($m^2/g$) | Total pore volume diameter ($Volcm^3/g$) | Average pore volume diameter (nm) |
|---|---|---|---|---|
| 1. | MWCNTs | 141.6 | 0.45 | 8.4 |
| 2. | CoMo/CNTs | 128.3 | 0.41 | 7.9 |
| 3. | CoMo/$Al_2O_3$ | 122.8 | 0.23 | 6.3 |

reactor for desulfurization, and the effect of parameters such as temperature, pressure, time, and space velocity on HDS is studied.

### 3.2.1 *Effect of Time on Desulfurization Efficiency (HDS %)*

Figure 5 shows the effect of time on HDS for conventional and CNT catalysts. The results show that the HDS % for both catalysts increased with increasing time. The desulfurization efficiency of the nanocatalyst was increased by about 10 % over the conventional catalyst. Also the sulfur content decreased with increased time, as more sulfur component converted to $H_2S$ during the HDS process [13].

### 3.2.2 *Effect of Temperature on Desulfurization Efficiency (HDS %)*

The effect of temperature is shown in Fig. 6. The results obtained indicate that a significant enhancement in HDS efficiency was obtained when the temperature increased. The HDS % of the nanocatalyst increased about 10 % over the conventional catalyst. In this case, increasing the temperature gives the same effect as time. This can be explained as an increase in reaction temperature, which can increase the rate of catalytic reaction by opening the active site of the catalyst, raising the rate of diffusion, and increasing the rate of reaction [14].

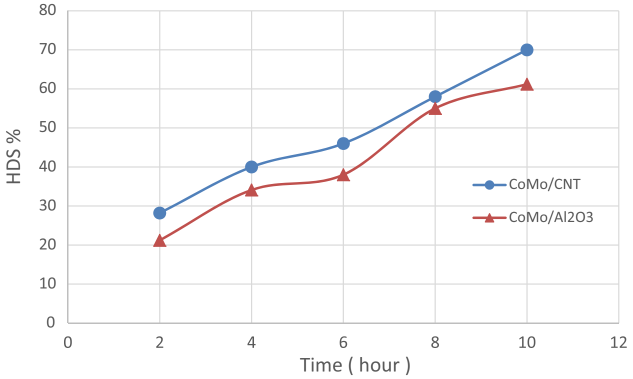

**Fig. 5** Desulfurization efficiency versus time of gasoil at temperature 280 °C, pressure 10 bar, and space velocity 6 $h^{-1}$

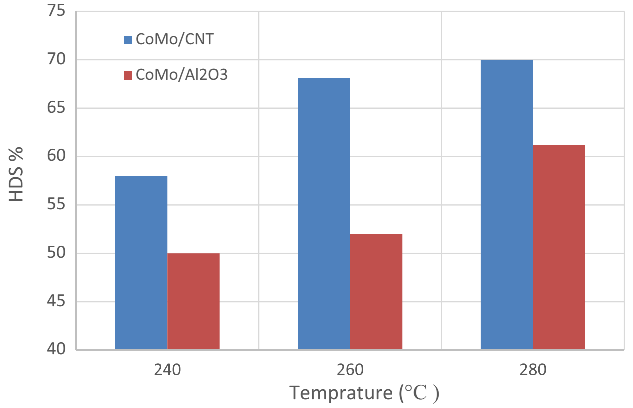

**Fig. 6** Desulfurization efficiency versus temperature of gasoil at time 10 h, pressure 10 bar, and space velocity 6 $h^{-1}$

### 3.2.3 *Effect of Space Velocity on Desulfurization Efficiency (HDS %)*

Figure 7 shows the effect of space velocity on HDS %. The results show that desulfurization efficiency increases from 70 to 73.5 % and from 61.2 to 63 % for CNT and conventional catalysts, respectively, by decreasing the space velocity from 6 to 2 $h^{-1}$, respectively.

It can be concluded that space velocity is the inverse of residence time. Increasing residence time led to increasing HDS %, and the reduction in space velocity caused channeling, which led to poor gasoil distribution and underutilization of the catalyst. High space velocity does not only reduce the feed stock–catalyst contact time, but it also increases the reactor pressure drop and may present some hydraulic challenges [15].

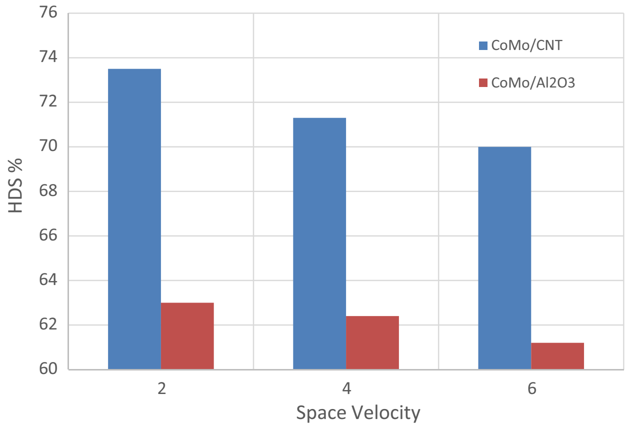

**Fig. 7** Desulfurization efficiency versus space velocity of gasoil at time 10 h, temperature 280 °C, and pressure 10 bar

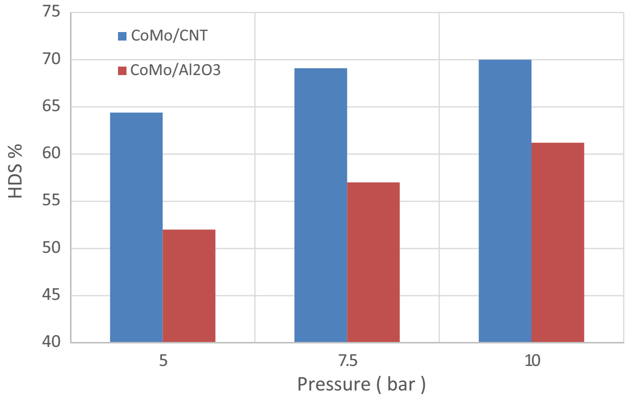

**Fig. 8** Desulfurization efficiency versus pressure of gasoil at time 10 h, temperature 280 °C, and space velocity 6 $h^{-1}$

### 3.2.4 *Effect of Pressure on Desulfurization Efficiency (HDS %)*

The effect of pressure on desulfurization efficiency is illustrated in Fig. 8.

The results obtained indicate an increase in the desulfurization efficiency with an increase in pressure from 5 to 10 bar. A higher conversion of (70 %) in HDS % was obtained at 10 bar, which may be an optimum condition for removal of sulfur from gasoil within the optimized conditions and design of our experiment rig. We expected the nanocatalyst would give a higher result when the pressure increased over 10 bar. Comparison between HDS% of the CoMo/CNT and COMo/$Al_2O_3$ catalysts is shown in Fig. 9. It was concluded that the nanocatalyst was more active than the conventional catalyst and the best efficiency was obtained at10 bar system pressure, 10 h contact time, 280 °C reactor temperature, and 2$h^{-1}$ space velocity.

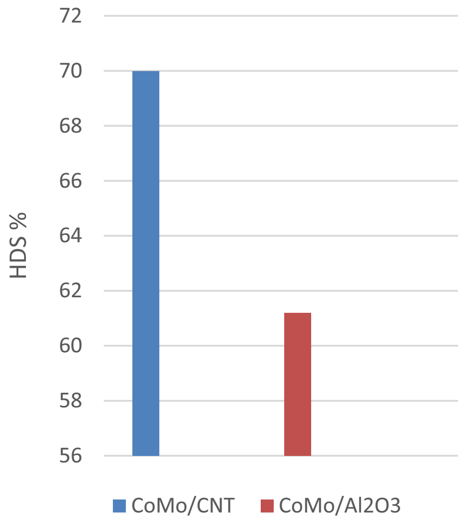

**Fig. 9** Comparison between HDS % of the CoMo/CNT and COMo/$Al_2O_3$ catalysts

## 4 Conclusion

On the basis of the experimental work described in the text of this work, the main conclusion can be summarized as follows:

1. CoMo/CNTs nanocatalyst was successfully prepared and tested in hydrothermal reactor.
2. SEM image showed well dispersed of CoMo within the structure of MWCNTs. The dispersion of Co and Mo metals was also confirmed by XRD pattern in which the main characteristic peaks of nanocatalyst have been identified.
3. The effect of parameters such as temperature, pressure, time, and space velocity on HDS was studied for both conventional and nanocatalyst using hydrothermal reactor, and the highest hydrodesulfurization activity obtained is 73.5 % for nanocatalyst (CoMo/CNTs) at temperature 280 °C, pressure 10 bar, time 10 hours, and space velocity 2 $h^{-1}$ compared with 63 % for CoMo/$Al_2O_3$ catalyst.
4. It can be concluded the HDS would be improved in the case where the total pressure of the system is increased up to 10 bar without make change in reaction time, or increasing the time of reaction while keeping the pressure constant.

**Acknowledgments** We would like to express our thanks to the Department of Chemical Engineering, University of Technology/Baghdad, Iraq, for their financial support.

## References

1. International council on clean transportation. US report, October 24 (2011)
2. Topsøe, H.; Clausen, B.S.; Massoth, F.E.: Hydrotreating Catalysis Science and Technology. Springer, Berlin (1996)
3. Sanchez-Delgado, R.A.: Organometallic Modeling of the Hydrodesulfurization and Hydrodenitrogenation Reactions. Kluwer Academic Publishers, Dordrecht (2002)
4. Eswaramoorthi, I.; Sundaramurthy, V.; Das, N.; Dalai, A.K.; Adjaye, J.: Application of multi-walled carbon nanotubes as efficient support to NiMo hydrotreating catalyst. Appl. Catal. A Gen. **339**, 187–195 (2008)
5. Babich, I.V; Moulijn, J.A: Science and technology of novel processes for deep desulfurization of oil refinery streams: a review. Fuel **82**(6), 607–631 (2003)
6. Li, X.; Han, D.; Xu, Y.; Liu, X.; Yan, Z.: Bimodal mesoporous $\gamma$-$Al_2O_3$: a promising support for CoMo-based catalyst in hydrodesulfurization of 4,6-DMDBT. Mater. Lett. **65**, 1765–1767 (2011)
7. US patent 20100167915 A1 Hydrodesulphurization Nanocatalyst, Its Use and a Process for Its Production
8. Ternan, M.; Furimsky, E.; Parsons, B.I.: Coke formation on hydrodesulphurization catalysts. Fuel Process. Technol. **2**(1), 45–55 (1979)
9. Zhang, H.B. Zhang; Lin, G.D.; Chen, P.; Yuan, Y.Z.; Tsai, K.R.: Preparation, characterization and catalytic hydroformylation properties of carbon nanotubes- supported Rh-phosphine catalyst. Appl. Catal. A Gen. **187**, 213–224 (1999)
10. Steen, P.: Comparison of preparation methods for carbon nanotubes supported iron FT catalysts. Catal. Today **71**, 327–334 (2002)
11. Mohammed, M. I.; Abdul Razak, Adnan A.; Dhiyaa A.: Hussein Al-Timimi Modified Multiwalled Carbon Nanotubes for Treatment of Some Organic Dyes in Wastewater Advances in Materials Science and Engineering, volume 2014, Article ID 201052 (2014)
12. Khorami, Payman; Kalbasi, Mansour: Hydrodesulphurisation activity of CoMo catalyst supported on multi wall carbon nanotube sulphur species study. J. Exp. Nanosci. **6**(4), 349–361 (2011)
13. Xiang, H.; Wang, T.: Kinetic study of hydrodesulfurization of coker gas oil in a slurry reactor. Front Chem. Sci. Eng. **7**(2), 139–144 (2013)
14. Jarullah, A.T.: Kinetic modelling simulation and optimal operation of trickle bed reactor for hydrotreating of crude oil. Ph.D. thesis, University of Bradford, UK (2011)
15. Mapiour, M.: Kinetics and Effects of H2 Partial Pressure on Hydrotreating of Heavy Gas Oil, M.Sc. thesis, University of Saskatchewan, Saskatoon (2009)