Hydrotreating of Egyptian Heavy Vacuum Gas Oil over Co-Mo/Carbon Nanotube Catalyst

W. Ahmed [#], Hoda S. Ahmed, H.S. El-Sheshtawy, Nadia A. Mohamed[*] and Asmaa I. Zahran

Egyptian Petroleum Research Institute, Naser City and [*]Chem. Dept., Faculty of Education & Science, Ain-Shams University for Girls, Cairo, Egypt.

THE HYDROTREATING catalyst development is an essential factor to produce clean fuels. The catalytic performance of CoMoS/CNT on Hydrotreating of the Egyptian heavy vacuum gas oil was investigated. Firstly the CNT was functionalized with concentrated HNO_3. The Mo and Co wt% were loaded on CNT by impregnation methods. The catalyst was characterized by X-ray diffraction, Raman Spectroscopy, TEM, and BET. The hydrotreating experiments were conducted on autoclave reactor at various operating conditions of Temperature (325-375) ^oC, pressure (20- 60) bar, time (2-6) h and cat/oil ratio of 1:75, 33 and 10. The result indicated that the CoMoS/CNT was an efficient for the hydrotreating process. Also, the hydride-sulfurization (HDS) enhanced with increasing catalyst/oil ratio. Moreover, Results revealed that the optimum condition (temperature 350 ^oC, Pressure 40 bar, catalyst/oil ratio of 1:75 for 2 hr, was chosen. Additionally, even at low catalyst ratio of 1:75 an acceptable HDS% of 77.1 was achieved.

Keywords: Hydrotreatment, Heavy vacuum gas oil (HVGO), Carbon nanotubes and CoMo/CNT.

Due to economical and pollution control aspects, up 2010 the world legislations limited the sulfur content in fuels to <15 ppm[1-4]. In order to meet this challenge, Nemours efforts to develop the hydrotreatment process, responsible for S and N removal, were potentially developed. Commercially, the MoS promoted by Co or Ni and supported on γ-Al_2O_3 are the most active catalysts for hydrotreating process[5-6]. The Co-Mo based catalyst is highly selective for HDS whereas Ni-Mo based catalyst is more selective for hydrodenitrogenation (HDN) and hydrogenation. consequently, Ni-Mo based catalysts consumes higher hydrogen than Co-Mo based catalysts for the same extent of HDS with identical feed[7]. Despite the good thermal and textural properties and the high metal dispersion ability of γ-Al_2O_3[8], it forms a strong metal-support interaction[9].This interaction prohibits the complete metals sulfidation which decline the required active sites[10].

[#]Corresponding author e- mail:
Waelepri2@yahoo.com, Fax: + (202)22747433, Tel: + (202)22747847-2015

Nevertheless, this drawback motivates the researchers to propose another supports to CoMo catalysts for various gas oils and model compounds [9,11-14].

Carbon nanotube (CNT) provide not only the γ-Al$_2$O$_3$ advantages of high thermal, mechanical strength and high surface area but also other unique properties such as excellent electron transporting capability[15]. The CNT have interesting features make it a potential catalyst support for many reactions [16,17].It has a high surface area with controlled pore volume and pore size which reduce the carbon deposition and provide enough surface for metal dispersion [18].Unlike alumina, the CNT hydrophobic surface limited the metal support interaction which facilitates the metal sulfidation process. Additionally, the acid treatment of CNT creates OH$^-$ or COO$^-$ functional groups that enhance the Co and Mo dispersion [19-20].

Dong *et al.* [21] reported a significant increase in active MoO$_2$ species molar percentage in Co-Mo/CNT and so enhanced HDS activity. Shang *et al.* [22] reported a much higher selectivity of Co–Mo/CNTs catalyst than Al$_2$O$_3$-based catalyst. The author attributed the observation to the formation of MoO$_2$ species rather than MoO$_3$ formed over alumina support. Furthermore, it is also concluded that the highest catalytic performance can be achieved over the catalyst with 0.7 Co/Mo atomic ratios.

Despite number of reports on Co-Mo/CNT for HDS were explored, there are no reports on the hydrotreating of Egyptian heavy vacuum gas oil (HVGO). Also there are rare researches in Co-Mo/CNT catalyst to feed ratio effect on the hydrotreating.

Therefore this study, concerns the Co-Mo/CNT catalytic performance toward the Egyptian HVGO hydrotreatment. In addition, the hydrotreating experimental conditions were optimized.

Experimental

Feedstock

Heavy vacuum gas oil (HVGO) kindly supplied by Suez Oil Petroleum Company (SOPC), has been used as the feedstock in the present investigation. The main characteristics of the feedstock are indicated in Table 1.

Catalyst preparation

Synthesis and purification of carbon nanotube

Carbon nanotube was kindly supplied by Awadallah research group (at Egyptian Petroleum Research Institute). They were prepared the CNT by CVD method according to Awadallah *et al.*[23] The CNT were purified and functionalized by adding a conc. HNO$_3$ and then stirred for 4 hr. Then it was filtered and washed by doubly distilled water several time, followed by drying at 120 °C over night.

TABLE 1. Properties of heavy vacuum gas oil feedstock.

Experiment	Method	Result
Density @ 15.56 °C, g/ml	ASTM D-1298	0.8867
Specific gravity	ASTM D-1298	0.8876
API gravity @ 60 °F	ASTM D-1298	27.9
Total sulfur content, wt %	ASTM D-4294	1.66
Aniline point	ASTM D-611-82	74
Diesel Index	ASTM D 611	46.09
Refractive Index @ 20	ASTM-1218	1.4860
Kinematic viscosity, cSt, @ 40° C		5.11
Pour point, °C	ASTM D-97	+9
Flash point, °C	ASTM D-92	87
Color		2
Carbon, wt%	-	86.66
Hydrogen, wt%	-	11.69
Oxygen, wt%	-	0.325
Component analysis	-	
Total saturates,wt.%	-	63.875
Total aromatics, wt.%	-	34
Resin	-	2.125

Co-Mo loading

In this study ammonium heptamolybdate tetrahydrate and cobalt acetate were used as the precursor for molybdenum and cobalt, respectively. The catalyst with 12 wt% MoO_3 loading and Co/Mo atomic ratio of 0.7 were prepared by a pore volume impregnation method. The impregnation was carried out in two stages to avoid the precipitation of catalyst metal from the saturated solution. Firstly, the Mo loading, was carried out by dissolving the required weight of ammonium heptamolybdate tetrahydrate in a predetermined volume of doubly distilled water with a few drops of H_2O_2 to give a transparent solution. The solution was added to the needed CNT amount and stirred for 30 min. After impregnation; the formed moist paste was preliminary dried in an oven at 120 °C over night. The dried samples were calcined in a muffle furnace with a heating rate of 10°C min^{-1} up to 400 °C for 4 h. Afterwards, the Co precursor introduced by pore volume impregnation, followed by drying at 120 °C over night. Finally the bimetallic catalysts were calcined at 400 in a muffle furnace for 4 hr.

Catalyst Characterization

X-ray diffraction

The X-ray diffraction for the prepared catalyst analysis was performed using X'Pert PRO PANalytical apparatus. The patterns were conducted using Cu Kα radiation (λ= 0.1541 nm). The 2 θ ranges from 10◦ to 70◦ at a scanning rate of 0.05 s^{-1} were used to record the patterns.

Transmission Electron Microscopy

The morphological properties for the CNT and Co-Mo/CNT catalysts were conducted using a JEOL 2010F TEM apparatus. The images were taken at an accelerating voltage of 200 kV. To prepare the samples, it diluted with 5 ml ethanol to make a suspension. The mixture was sonicated for 20 min then a drop of solution was placed on a carbon coated Cu grid. Ethanol was then slowly evaporated from the Cu grid under a glass cover.

Raman Spectroscopy

Raman spectra of the as-grown carbon nanotube and Co-Mo/CNT samples were recorded by SENTERRA Dispersive Raman Microscope (Bruker). The apparatus was equipped with a diode Nd: YAG laser and wave length of 532 nm. The experiments were carried out at room temperature in range of 10 to 2000 cm^{-1}.

Surface area measurement

The phesico-chemical properties of the prepared catalyst were determined by N_2 adsorption-desorption method at -196 ^{o}C. The BET surface area was measured by using Autosorb 1, Quanta chrome instrument. Prior to the measurement, the catalyst was degassed at 200◦C for 4 hr to remove the adsorbed gases and moisture. Surface area was calculated using the adsorption data up to a relative pressure of 0.1 by BET method.

Catalytic activity test

Prior to the activity tests (*i.e.* hydrotreating), the catalyst is presulfied *in-situ* (in the autoclave) at the following conditions: 15 bar, initial hydrogen pressure, 350 °C reaction temperature and 5 hr reaction period. A mixture of light gas oil contains 8% (of the catalyst weight) dimethyldisulfide (DMDS) was used as sulfiding agent.

The hydrotreating run experiments were carried out in a static phase using batch reactor (parr.model 7575). After sulfiding experiment, the temperature of the autoclave is lowered to room temperature, then the sulfided catalyst is transferred out and kept in a vacuum environment, so that contact with air is avoided, till used. The hydrotreating run experiments were carried out in a static phase using batch reactor. The reactor is housed in a furnace; there is programmed control system for controlling temperature and speed of the stirrer. Pressure and flow of gases are controlled manually. Amount of 150 g feed and 2g of the investigated sulfided catalyst are loaded inside the reactor. After tightly closing the reactor, reactant and catalyst was purged in N_2 in order to check the pressure leakage. The hydrotreatment operation conditions of temperature (325-375), initial pressure (20-60 bar), time (2-6 hr) and catalyst to feed ratio of 1: 75, 33 and 10 were investigated.

After the required temperature, pressure over a constant catalyst/oil ratio has reached; the experiment was conducted for the desired time. Afterwards, the

autoclave was maintained to cool to room temperature overnight and the total pressure decreased. The liquid products were collected out of the autoclave and then the catalyst was filtered and washed by solvent (naphtha). The filtered catalyst was heated in an electric oven at 110 °C for 2hr. Liquid product is purged out the reactor under sufficient N_2-pressure, and collected for analysis using the recommended standard methods (*i.e.* ASTM or IP methods).

Result and Discussion

X-ray diffraction

Figure 1 demonstrated the XRD patterns of the acid treated CNT and supported catalyst after calcinations. Figure 1.a. indicated that the functionalized CNT support had peaks at about 2θ of 26.05° and 43.08° which ascribed to the (002) graphitic basal plane and the diffraction of (100) plane, respectively[22,24,25]. This observation indicated the low graphitization degree of CNT used in this study. Neither peaks for Mg nor Ni were assigned in the pure CNT diffractogram. This result revealed that the appropriate nitric acid treatment of CNT led to removal of all Ni and Mg ions. Additionally, the results might generally have been responsible for catalysts high surface area [26]. The XRD patterns of Co-Mo loaded CNT and S-Mo/CNT was illustrated in Fig. 1b and 1c, respectively. The main CNT peaks intensities were decreased by metals loading. Tan *et al.*[27] reported that this decrease in CNT patterns may attributed to a change in ordered structure because of metals loading.

Mo loaded CNT sample (Fig. 1 b) showed the diffraction peaks at 2θ of 26.18°, 36.98°, 53.58° and 60.58° which characteristics for MoO_2[22,28]. Furthermore, very low intensity peaks for MoO_3 crystalline phase were measured. The presence of MoO_3 weak peaks might be attributed to slightly incomplete acidification of some CNT surface and hence lower functional groups [9]. These results concluded that the majority of Mo species present under reaction conditions on the surface of the CNT were those at low valence values. This may explained by the CNTs surface hydrophobicty which weakening the metal-support interaction[29]. The lower metal-support interaction allows the MoO_3 to migrate and conglomerate on the CNTs surface. Meanwhile, the Mo species reduced into the lower valence state during the calcination. Previous studies were also reported the same observation[22,25,30].

It is rather well known for HDS catalyst that, Mo oxide form must be sulfided to the active MoS_2 at which the Mo becomes the Mo^{4+}. Literature stated that the MoO_3 supported alumina catalyst was easily sulfided to the active MoS_2 rather than MoO_2/Al_2O_3. Meanwhile, the ease of either CNT-supported MoO_3 or MoO_2 sulfidation of is still a dark area.

Figure 1.c. showed the XRD patterns of Co–Mo/CNT after sulfiding. The figure demonstrated that neither Co_3O_4 nor its sulfide phases were detected.

Weak broad peaks at 14.4° and 32.71° which attributed to Mo_3S_4 crystallite formation were assigned. Moreover, a small peak at 29.0° was observed. This peak may be due to the low valence $Co-MoS_{3.13}$ or $Co-MoS_{2.17}$ species formation [22]. Also, the peaks for molybdenum oxide species intensity were lowered. This might be explained by the replacement of the Co atoms on the MoO_3 crystals and limiting their growth. Furthermore, no peaks related to the CNT, Co and Mo interactions were recorded. It maybe concluded that the cobalt loading and the sulfiding process emphasizes the active phase's dispersion on the CNT.
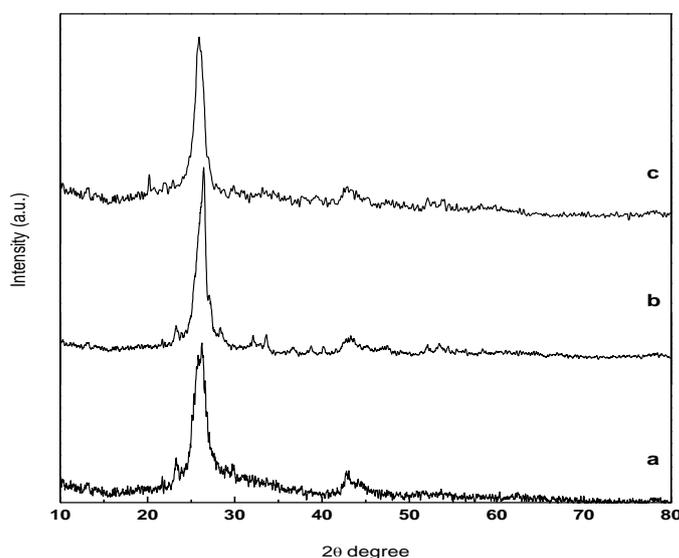
Fig. 1. XRD pattern of different samples (a) CNT, (b) CoMoO /CNT; (c) CoMoS /CNT.

Transmission Electron Microscopy (TEM)

The micrograph of the pure CNT and S-CoMo/CNT catalyst were shown in Fig. 2. The TEM image (Fig. 2.a.) showed the CNT morphological characteristics with uniform diameter. The TEM images revealed that the nanotubes had the average outer diameters of around 20 nm. The nanotubes had wall thickness of about 10 nm. The TEM images of the S-Co-Mo/CNT catalyst were shown in Fig. 2 b. The images demonstrated good metals dispersed over CNT support. This observation confirmed the data obtained from XRD. Additionally, no noticeable agglomeration of active phase was demonstrated. Furthermore, no Co metals inside the CNTs were detected. These results maybe explained via CNT inner diameter and its functional groups. Comparing Fig. 2a and 2b, it's clear that the CNT functional groups provide anchoring sites that prevent the cobalt particles immigration into the tubes and the particles sintering by calcination. Moreover, the narrow inner CNT channels diameter (9–10 nm)

hinders the small cobalt crystallites growth inside the tube [31]. It is reported that the TEM images of the CNT supported catalyst showed the smaller cobalt crystallites are lying inside the CNT channels and the larger ones are on the outside [32-34]. The EDX analysis (image entire in Fig. 2b) confirms the Co and Mo loadings with good intense peaks for both.
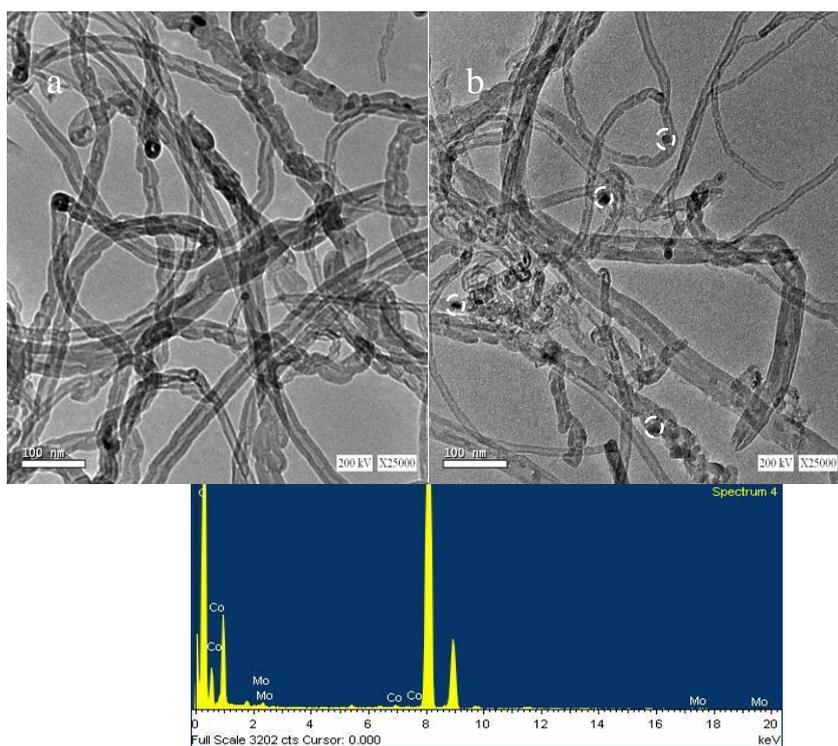
Fig. 2. TEM images of (a) CNT (b) CoMoS/CNT and EDX of CoMoO/CNT.

Textural characteristics of CoMo/MWCNT

The physical adsorption-desorption isotherms of N_2 at -196 °C for pure CNT and CoMoS/CNT catalysts were shown in Figure 3I. The isotherm corresponding to type IV was obtained for the pure CNT indicating the presence of mesopores. Figure 3 II showed the pore size distribution (PSD) calculated by the BJH method. The pretreated CNT and CoMoS/CNT PSD had the average of about 12 and 18 nm, respectively. The specific surface area and pore volume data of CNT and CoMoS/CNT were listed in Table 2. It maybe concluded that, the BET surface area and pore volume were increased significantly after the nitric acid pretreatment. After metal impregnation, a consistent decrease in the S_{BET} and average pore diameter were observed. The decline of the surface area and pore size may due to the blocking of some microspores and surface smoothing by the

metal deposition on the support. Thus, metal loading has a great effect in decreasing textural characteristics of catalyst.

TABLE 2. Physical properties of supports and CoMoX/support catalysts.

Sample	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)
CNT	120.9	0.25	38.02
CoMoO/CNT	101.1	0.18	35.28
CoMoS/CNT	73.58	0.12	32.57
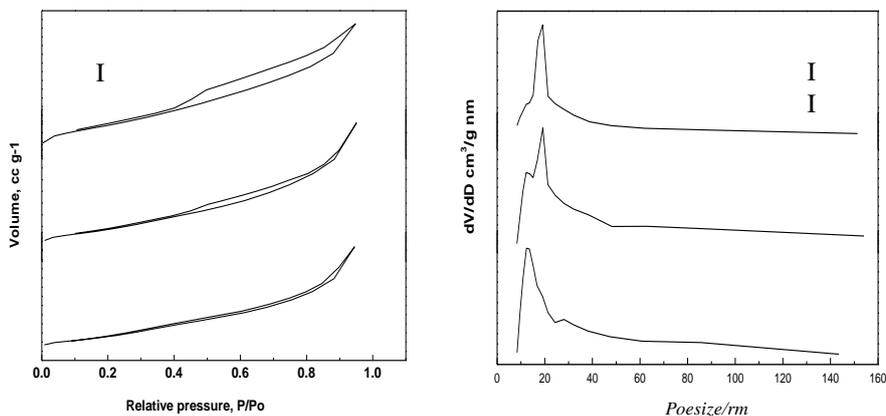
Fig. 3. N_2 adsorption/desorption isotherm (I) and particle size distribution (II) exhibited for pure (a) CNT, (b) CoMoO/CNT and (c) CoMoS/CNT catalysts.

Raman spectroscopy

Figure 4 presents the Raman spectra for the supplied CNT, $CoMoO_4$/CNT and sulfided catalyst. The pure CNT spectrum (Fig. 4 a) was displayed two prime intense peaks at about 1343 and 1575 cm^{-1}. The peak at1343 cm^{-1}, which known as the D-band, was attributed to the disordered carbon [35]. The second peak, referred as G band, can interpret to the highly graphitized CNT. It is known that the D to G band relative intensity indicating the quality and purity of the produced CNTs. the lower intensity ratio of ID/IG proved the higher crystallinty and purity of the CNTs [36]. The spectra of the pure CNT acquire the low ID/IG ratio of 0.22 which reflect the very high CNTs crystallinty. Clearly, these results are in a good agreement with the XRD and TEM results (Fig. 1, 2).

Raman spectra of the CoMoO4/CNT (Fig. 4 b.) showed only the peaks of the pure CNT. This result may be attributed to the good dispersion of the loaded metal oxides onto the carbon nanotubes. The Raman spectrum of the sulfided CoMo/CNT catalyst was showed in Fig. 4 c. The catalyst exhibited a band at 335 cm^{-1} and a large sharp peak at 940 cm^{-1} that can be assigned to the symmetric Mo=O stretching of tetrahedral MoO4 $^{2-}$ [22]. This result proved the higher dispersion of Mo during through preparation method. Moreover, our results indicted none of these known peaks for polymeric molybdates, bulk CoMoO$_4$ or bulk Co or Mo were recorded. The literature stated that the bands at about 320 and 920 cm^{-1} are assigned for the monomeric Mo species while bands at about 220, 360, and 960 cm^{-1} ascribed to the well-dispersed octamolybdates [37]. Additionally, the bands at ca. 820, 945, and 952 cm^{-1} are attributed to the bulk CoMoO$_4$. While, the characteristic bands of bulk Co and Mo oxides were normally assigned at 696 cm^{-1} and 820 cm^{-1}, respectively[22,38].
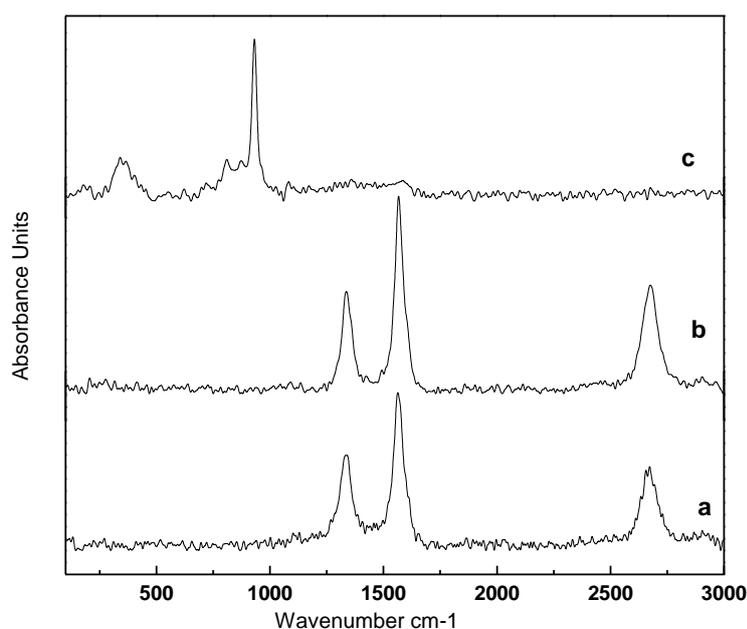
Fig. 4. Laser Raman spectra of (a) CNT, (b) CoMoO /CNT (c) CoMoS/CNT.

Catalytic activity

Effect of reaction temperature

Table 3 represented the effect of reaction temperature on the product quality. It was shown that yield of heavy vacuum gas oil (HVGO) was clearly affected by the reaction temperature (*i.e.*) decreased as the activity of the sulfided CoO MoO$_3$ / carbon nanotube catalyst was increased due to the increasing in reaction severity. As a result the hydrodesulfrization (HDS) activity of the catalyst was

increased continuously from (61.4 to 79.26 %) at 325 °C and 375 °C, respectively at constant pressure (40 bar), constant time (2hr). The effects of temperature on aniline point, diesel index (DI) are given in Table 3. These properties give an indication on the hydrogenation activity of the CoMoS/CNT catalyst. As the reaction temperature increased the aromatic content was decreased from (25 to 17.6 %) at 325 °C and 375 °C, respectively. At the same time, the total saturates content, increased from 75 to 82.4% as the reaction temperature was increased from 325 to 375 °C, This is due to the hydrogenation of aromatics which is an exothermic reaction and was favored at low reaction temperature[39].

TABLE 3. Effect of reaction temperature on Hydrotreating of HVGO by CoMoS/CNT at P= 40bar T=2h C/ F=1:75.

Characteristics	Temperature, °C			
	Feed	325	350	375
Total liquid yield, wt %	150	83.66	78	54
Total sulfur content, wt %	1.66	0.64	0.38	0.34
Sulfur reduction (HDS), %	-	61.4	77.1	79.26
Aniline point @°F	165.2	170.24	170.6	171.32
DI	46.09	57.37	59.65	60.56
Density @15.56°C, g/ml	0.8867	0.8557	0.8492	0.8486
Specific gravity	0.8876	0.8565	0.8500	0.8494
API gravity @ 60 °F	27.9	33.70	34.97	35.35
RI @ 20	1.4860	1.4775	1.4730	1.4695
Kinematic viscosity, cSt, @ 40° C	5.11	4.38	3.27	2.72
Pour point, °C	+9	3	3	0
Flash point, °C	87	76	58	54
Color	8	1	1	1
Component analysis				
Total saturates, wt.%	63.88	75	78.5	82.4
Total aromatics, wt.%	34	25	21.5	17.6
Resin	2.12	-	-	-
Hydrodearomatization (HDA), wt%	-	26.47	36.76	48.23

Effect of hydrogen pressure

Results pricked on Table 4 show the following facts. As the total hydrogen pressure is increased from 20 to 60 bar, the effect on yield and quality characteristics of heavy vacuum gas oil were observed, (*i.e.*) HDS increased from (60.24 to 79.5 %), DI and aniline point increased from (56.59 to 61.18 %) and (169.7 to172.4 %) respectively, while total aromatics content decreased from 24 % at 20 bar to 16.8 % at 60 bar, which can be attributed to the increase of hydrogenation activity of the catalyst with increasing total hydrogen pressure besides the increase of saturation activity and reduction of coke formation [39,40].

TABLE 4. Effect of reaction pressure on Hydrotreating of HVGO by CoMoS/CNT at T=: 350 ⁰C   T=2h   C/ F=: 1:75.

Characteristics	Pressure, bar			
	Feed	20	40	60
Total liquid yield, wt %	150	85.33	78	72
Total sulfur content, wt %	1.66	0.66	0.38	0.34
Sulfur reduction (HDS), %	-	60.24	77.1	79.5
Aniline point @°F	165.2	169.7	170.6	172.4
DI	46.09	56.59	59.65	61.18
Density @15.56°C, g/ml	0.8867	0.8562	0.8492	0.8486
Specific gravity	0.8876	0.8570	0.8500	0.8494
API gravity @ 60 °F	27.9	33.35	34.97	35.49
RI @ 20	1.4860	1.4775	1.4730	1.4680
Kinematic viscosity, cSt, @ 40° C	5.11	4.74	3.27	2.48
Pour point, °C	+9	6	3	3
Flash point, °C	87	80	58	44
Color	8	1.5	1	1
Component analysis				
Total saturates, wt.%	63.88	76	78.5	83.2
Total aromatics, wt.%	34	24	21.5	16.8
Resin	2.12	-	-	-
Hydrodearomatization (HDA), wt%	-	29.41	36.76	50.58

Effect of time

Table 5 represented the effect of time on the product quality of HVGO. Increasing the time from 2 to 4 hr, the hydrogenation function of the catalyst was increased due to the increase in the contact time between the reacting HVGO molecules and the acid hydrogenation sites of the catalyst.

As a result the HDS activity of the catalyst increased from (77.1 to 83.1%) and the improvement of, color, total aromatics content, aniline points and diesel index were observed. This means that improvement in the quality of heavy vacuum gas oil by increasing time from 2 to 6 hr.

TABLE 5. Effect of reaction time on Hydrotreating of HVGO by CoMoS/CNT at P= 40 bar, T= 350 ºC, C/ F ratio = 1:75.

Characteristics	Time, h			
	Feed	2	4	6
Total liquid yield, wt %	150	78	75.33	69.2
Total sulfur content, wt %	1.66	0.38	0.36	0.28
Sulfur reduction (HDS), %	-	77.1	78.3	83.1
Aniline point @°F	165.2	170.6	170.96	172.04
DI	46.09	59.65	60.1	60.66
Density @15.56°C, g/ml	0.8867	0.8492	0.8489	0.8482
Specific gravity	0.8876	0.8500	0.8497	0.8490
API gravity @ 60 °F	27.9	34.97	35.16	35.26
RI @ 20	1.4860	1.4730	1.4695	1.4675
Kinematic viscosity, cSt, @ 40º C	5.11	3.27	2.97	2.43
Pour point, °C	+9	3	3	3
Flash point, °C	87	58	55	45
Color	8	1	1	1
Component analysis				
Total saturates, wt.%	63.88	78.5	82	84
Total aromatics, wt.%	34	21.5	18	16
Resin	2.12	-	-	-
Hydrodearomatization (HDA), wt%	-	36.76	47.05	52.94

Effect of catalyst/oil ratio

The amount of catalyst was also very important for hydrotreating process. Figure 5 Showed the effect of weight of catalyst on the HDS of heavy gas oil, when the amount of catalyst was 2g the HDS reached (77.1%) due to the absence of enough active sites for the reaction due to the least amount of catalyst. With farther increase the weight of catalyst to (4.54) and (15) g the HDS increased to (82.7) and (94.8), respectively, due to the increased in the amount of catalyst and hence the increase in the number of acid sites available.
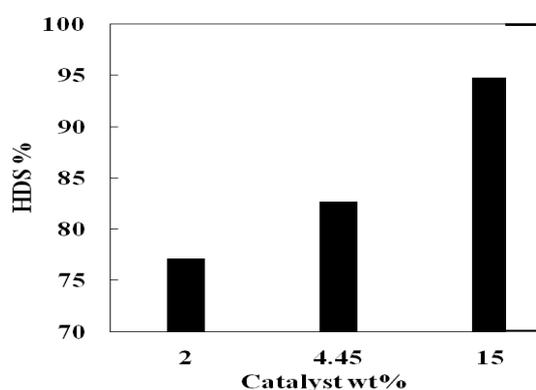
Fig. 5. Effect of catalyst/oil ratio (catalyst, wt) of CoMoS/CNT on HVGO at pressure: 40bar, temperature: 350ºC, time: 2hr.

Conclusion

The CoMoS/CNT hydrotreating catalyst was prepared by impregnation method. The TEM analysis of purified CNTs proved their morphological and structural features. Additionally, TEM indicated a good dispersion of Mo species and uniform Co particles deposition over the CNTs surface. The CNTs crystallinty and graphitic nature was determined by XRD and Raman Spectroscopy.

The catalyst, with 12 wt% Mo loading and 0.7 Co/Mo atomic ratios supported on CNT, exhibited an excellent catalytic performance towards hydrotreating process under the experimental conditions. Consequently, the desired promoted Co–Mo–S phase formation upon sulfidation process was confirmed. Also, from the high catalytic activity, it can be claimed that almost 90% of the sulfur compounds adsorb on CoMoS/CNT are in an endon manner. The high catalytic performance of CoMoS/CNT can be achieved at low operating condition of 350 °C, 40 bar and catalyst/ratio of 1:10 for 2 hr. A fairly high HDS% of 77.1 % can be achieved over a low catalyst to oil ratio of 1:75.

Reference

1. **Topsoe, H. and Clausen, B.S.,** Importance of Co-Mo-S type structures in hydrodesulfurization. *Cat. Rev. - Sci. Eng.* **26**, 395-420 (1984).

2. **Prins, R., De Beer, V.H.J. and Somorjai G.A.,** Structure and function of the catalyst and the promoter in Co-Mo hydrodesulfurization catalysts. *Cat. Rev. - Sci. Eng.,* **31**, 1-41 (1989).

3. **Medici, L. and Prins, R.,** The influence of chelating ligands on the sulfidation of Ni and Mo in NiMo/SiO$_2$ hydrotreating catalysts. *J. Catal.* **163**, 38-49 (1996).

4. **Shimizu, T., Hiroshima, K., Honma, T., Mochizuki, T. and Yamada, M.,** Highly active hydrotreatment catalysts prepared with chelating agents. *Catal. Today*, **45**, 271-6 (1998).

5. **Van Looij, F., Van der Laan, P., Stork, W.H.J., DiCamillo, D.J., and Swain, J.,** Key parameters in deep hydrodesulfurization of diesel fuel. *Appl. Catal., A: General,* **170**, 1-12 (1998).

6. **Shimada, H., Sato, T., Yoshimura, Y., Hiraishi, J. and Nishijima, A.,** Support effect on the catalytic activity and properties of sulfided molybdenum catalysts. *J. Catal.* **110**, 275-84 (1988).

7. **Vishwakarma, S.K.,** Sonochemical and impregnated Co-W/γ-Al$_2$O$_3$ catalysts: Performances and kinetic studies on hydrotreatment of light gas oil. University of Saskatchewan Saskatoon (2007).

8. **Topsoe, H. and Clausen, B.S.,** Active sites and support effects in hydrodesulfurization catalysts. *Appl. Catal.* **25,** 273-93 (1986).

9. **Eswaramoorthi, I., Sundaramurthy, V., Das, N., Dalai, A.K. and Adjaye, J.,** Application of multi-walled carbon nanotubes as efficient support to NiMo hydrotreating catalyst. *Appl. Catal., A: General,* **339,** 187-95 (2008).

10. **Sigurdson, S., Sundaramurthy, V., Dalai, A.K. and Adjaye, J.,** Effect of anodic alumina pore diameter variation on template-initiated synthesis of carbon nanotube catalyst supports. *J. Mol. Catal. A: Chem.* **306,** 23-32 (2009).

11. **Dhar, G.M., Srinivas, B.N., Rana, M.S., Kumar, M. and Maity, S.K.,** Mixed oxide supported hydrodesulfurization catalysts-a review. *Catal.Today,* **86,** 45-60 (2003).

12. **Wang, A., Wang, Y., Kabe, T., Chen, Y., Ishihara, A. and Qian, W.** Hydrodesulfurization of dibenzothiophene over siliceous MCM-41-supported catalysts: I. sulfided Co-Mo catalysts. *J. Catal.* **199,** 19-29 (2001).

13. **Maity, S.K., Rana, M.S., Bej, S.K., Ancheyta-Juarez, J., Dhar, G.M. and Rao, T.S.R.P.** Studies on physico-chemical characterization and catalysis on high surface area titania supported molybdenum hydrotreating catalysts. *Appl. Catal., A: General,* **205,** 215-25 (2001).

14. **Vradman, L., Landau, M.V., Herskowitz, M., Ezersky, V., Talianker, M. and Nikitenko, S. *et al.*,** High loading of short WS 2 slabs inside SBA-15: promotion with nickel and performance in hydrodesulfurization and hydrogenation. *J. Catal.* **213**, 163-75 (2003).

15. **Pour, A.N., Rashidi, A.M., Jozani, K.J., Mohajeri, A. and Khorami, P.,** Support effects on the chemical property and catalytic activity of Co-Mo HDS catalyst in sulfur recovery *J. Nat.Gas Chem.* **19**, 91-5 (2010).

16. **Serp, P., Corrias, M. and Kalck, P.,** Carbon nanotubes and nanofibers in catalysis. *Appl. Catal., A: General,* **253,** 337-58 (2003).

17. **van Steen, E. and Prinsloo, F.F.,** Comparison of preparation methods for carbon nanotubes supported iron Fischer-Tropsch catalysts. *Catal. Today*, **71,** 327-34 (2002).

18. **Auer, E., Freund, A., Pietsch, J. and Tacke, T.,** Carbons as supports for industrial precious metal catalysts. *Appl. Catal., A: General,* **173,** 259-71 (1998).

19. **Shang, H.Y., Liu, C.G., Xu, Y.Q., Zhao, H.J. and Song, H.H.,** Effect of the surface modification of multi-walled carbon nanotubes (MWCNTs) on hydrodesulfurization activity of Co-Mo/MWCNTs catalysts. *Carbon Mater*, **19,** 131-6 (2004).

20. **Kyotani, T., Nakazaki, S., Xu, W.H. and Tomita, A.,** Chemical modification of the inner walls of carbon nanotubes by HNO_3 oxidation. *Carbon*, **39,** 782-5 (2001).

21. **Dong, K., Zhang, S., Wang, D. and Yao, X.,** Hydrogen bonds in imidazolium ionic liquids. *J. Phys .Chem. A,* **110,** 9775-82 (2006).

22. **Shang, H., Liu, C., Xu, Y., Qiu, J. and Wei, F.,** States of carbon nanotube supported Mo-based HDS catalysts. *Fuel Process Technol*. **88,** 117-23 (2007).

23. **Awadallah, A.E., Aboul-Enein, A.A., El-Desouki, D.S. and Aboul-Gheit, A.K.,** Catalytic thermal decomposition of methane to CO x-free hydrogen and carbon nanotubes over MgO supported bimetallic group VIII catalysts. *Appl. Surf. Sci.* **296,** 100-7 (2014).

24. **Sundaramurthy, V., Dalai, A.K. and Adjaye., J.,** Effect of EDTA on hydrotreating activity of CoMo/γ-Al_2O_3 catalyst. *Catal. Lett*. **102,** 299-306 (2005).

25. **Hogg, J.C., Chu, F., Utokaparch, S., Woods, R., Elliott, W.M. and Buzatu, L. *et al.*,** The nature of small-airway obstruction in chronic obstructive pulmonary disease. *Engl. J. Med.* **350,** 2645-53 (2004).

26. **Shigapov, A.N., Graham, G.W., McCabe, R.W., Peck, M.P. and Plummer, H.K.,** The preparation of high-surface-area cordierite monolith by acid treatment. *Appl. Catal., A: General,* **182**, 137-46 (1999).

27. **Tan, Z.l., Xiao, H.N., Zhang, R.D., Zhang, Z.S. and Kaliaguine, S.,** Potential to use mesoporous carbon as catalyst support for hydrodesulfurization. *New Carbon Mater,* **24,** 333-43 (2009).

28. **Zhang, Y., Zhang, H.B., Lin, G.D., Chen, P., Yuan, Y.Z. and Tsai, K.R.,** Preparation, characterization and catalytic hydroformylation properties of carbon nanotubes-supported Rh-phosphine catalyst. *Appl. Catal., A: General*, **87,** 213-24 (1999).

29. **Dujardin, E., Ebbesen, T.W., Hiura, H. and Tanigaki, K.,** Capillarity and wetting of carbon nanotubes. *Science,* **265,** 1850-2 (1994).

30. **Dandekar, A., Baker, R.T.K. and Vannice, M.A.,** Characterization of activated carbon, graphitized carbon fibers and synthetic diamond powder using TPD and DRIFTS. *Carbon,* **36,** 1821-31 (1998).

31. **Karimi, A., Nasernejad, B. and Rashidi, A.M.,** Synthesis and characterization of multiwall carbon nanotubes/alumina nanohybrid-supported cobalt catalyst in Fischer-Tropsch synthesis. *J. Energy Chem.* **22,** 582-90 (2013).

32. **Trépanier, M., Tavasoli, A., Dalai, A.K. and Abatzoglou, N.,** Fischer-Tropsch synthesis over carbon nanotubes supported cobalt catalysts in a fixed bed reactor: Influence of acid treatment. *Fuel Process.Technol.* **90,** 367-74 (2009).

33. **Karimi, A., Nasernejad, B., Rashidi, A.M., Tavasoli, A. and Pourkhalil, M.,** Functional group effect on carbon nanotube (CNT)-supported cobalt catalysts in Fischer-Tropsch synthesis activity, selectivity and stability. *Fuel,* **117,** 1045-51 (2014).

34. **Abbaslou, R.M.M., Tavassolim, A., Soltanm, J., and Dalai, A. K.,** Iron catalysts supported on carbon nanotubes for Fischer-Tropsch synthesis: Effect of catalytic site position. *Appl. Catal., A: General*, **367,** 47-52 (2009).

35. **Dresselhaus, M.S., Dresselhaus, G., Jorio, A., Souza Filho, A.G. and Saito, R.,** Raman spectroscopy on isolated single wall carbon nanotubes. *Carbon,* **40,** 2043-61 (2002).

36. **Li, Q., Yan, H., Zhang, J. and Liu, Z.,** Effect of hydrocarbons precursors on the formation of carbon nanotubes in chemical vapor deposition. *Carbon,* **42,** 829-35 (2004).

37. **Kohler, S.D., Ekerdt, J.G., Kim, D.S. and Wachs, I.E.,** Relationship between structure and point of zero surface charge for molybdenum and tungsten oxides supported on alumina. *Catal. Lett.* **16,** 231-9 (1992).

38. **Jeziorowski, H., Knozinger, H., Grange, P.and Gajardo, P.,** Raman spectra of cobalt molybdenum oxide supported on silica. *J. Phys. Chem.* **84,** 1825-9 (1980).

39. **Gary, J.H., Handwerk, G.E. and Kaiser, M.J.,** *Petroleum Refining: Technology and Economics*: CRC press, (2007).

40. **Bartholomew, C.H.,** Catalyst Deactivation in Hydrotreating of Residua: A Review: Marcel Dekker: New York, (1994).

المعالجة المائية لزيوت الشفط المصرية الثقيلة في وجود حافز كوبالت ــ موليبدنيوم في أنبوبة من النانوكربون

وائل أحمد ، هدى أحمد ، هدى الشيشتاوي ، نادية محمد* و أسماء زهران

معهد بحوث البترول و*قسم الكيمياء ــ كلية التربية والعلوم (بنات)- جامعة عين شمس ــ القاهرة - مصر.

قدم هذا البحث طريقة جديدة لتنقية السوائل مثل الزيوت البترولية المصرية الثقيلة والتى تستخدم فى أجهزة الشفط باستخدام أبوبة مصنوعة من النانوكربون حيث تعالج أولا بحمض النتريك المركز ثم تملؤ بحافز مكون من فلزي الكوبالت والموليبدنيوم حيث تتم معالجة الزيوت بالماء فى مفاعل أوتوكلاف وتم تحديد أنسب الظروف لاتمام هذه المعالجة وهي درجة حرارة 350 مئوية تحت ضغط 40 بار لمدة ساعتين وبحيث تكون نسبة الحافز الى الزيت المعالج هي 1 : 75.