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RESEARCH PAPER

Egyptian heavy vacuum gas oil hydrotreating over Co-Mo/CNT and Co-Mo/γ-Al_2O_3 catalysts

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Abstract: The catalytic activity of CoMoS/CNT towards the Egyptian heavy vacuum gas oil hydrotreating was studied. The delivered CNT was functionalized with 6 mol/L HNO_3. The CNT were loaded with 12% MoO_3 (by weight) and 0.7 Co/Mo atomic ratio with impregnation methods. The γ-Al_2O_3 catalyst was also prepared by impregnation method to compare both catalysts activities. The analysis tools such XRD, Raman spectroscopy, TEM, and BET were used to characterize the catalysts. The autoclave reactor was used to operate the hydrotreating experiments. The hydrotreating reactions were tested at various operating conditions of temperature 325–375°C, pressure 2–6 MPa, time 2–6 h, and catalyst/oil ratio (by weight) of 1:75, 1:33 and 1:10. The results revealed that the CoMoS/CNT was highly efficient for the hydrotreating more than the CoMoS/γ-Al_2O_3. Also, the hydrodesulfurization (HDS) increased with increasing catalyst/oil ratio. Additionally, results showed that the optimum condition was temperature 350°C, pressure 4 MPa, catalyst/oil ratio of 1:75 for 2 h. Furthermore, even at low CoMoS/CNT catalyst/oil ratio of 1:75, an acceptable HDS of 77.1% was achieved.

Keywords: hydrotreatment; hydrodesulfurization; carbon nanotube; heavy vacuum gas oil (HVGO)

Because of economical and pollution control aspects, up the year 2010, the international low limit of the sulfur content in fuels is to $<1.5\times10^{-5}$[1−4]. For such propos, enormous effects have been done to develop the hydrotreatment process, responsible for S and N removal. Commonly, the MoS promoted by Co or Ni active phases supported on γ-Al_2O_3 is the most active hydrotreating catalyst[5,6]. The Co-Mo based catalyst is highly selective for HDS while Ni-Mo based catalyst is known as selective for hydrodenitrogenation (HDN). So that, Ni-Mo catalysts has the drawback of consuming higher hydrogen than Co-Mo based catalysts for HDS process with identical feed[7].

Although the γ-Al_2O_3 support has good thermal, textural properties and high metal dispersion ability[8], it strongly interacts with the active metal[9]. This interaction hinder the complete metals sulfidation which decreases the required active sites[10]. Nevertheless, this drawback motivates the researchers to suggest another supports to Co-Mo catalysts for hydrotreating[9,11−14].

Among many supports carbon nanotube (CNT) is an attractive alternative support. It possesses the advantages of high thermal, mechanical strength and high surface area as γ-Al_2O_3, and also other unique properties such as excellent electron transporting capability[15]. So, it is used as 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 limits 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 that an appreciable active MoO_2 species were formation in Co-Mo/CNT catalyst and HDS activity was enhanced. Shang et al[22] reported a considerable higher selectivity of Co-Mo/CNTs catalyst than Al_2O_3-based catalyst. This observation was attributed 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 ratio.

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

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in Co-Mo/CNT catalyst to feed ratio effect on the hydrotreating.

Considering the above argument, this study investigated the Co-Mo/CNT catalytic activity toward the Egyptian HVGO hydrotreatment. In addition, the hydrotreating experimental conditions were optimized. For more convenient the catalytic performance was compared to the conventional Co-Mo/γ-Al_2O_3 catalyst.

1 Experimental

1.1 Feedstock

Heavy vacuum gas oil (HVGO) feedstock in this study was purchased from Suez Oil Petroleum Company (SOPC). The main characteristics of the feedstock are indicated in Table 1.

1.2 Catalyst preparation

1.2.1 Synthesis and purification of carbon nanotube

Carbon nanotube were prepared by CVD method and kindly supplied by Awadallah research group (at Egyptian petroleum research institute)[23]. The CNT were purified and functionalized with 6 mol/L HNO_3 and then stirred for 4 h. Then it was filtered and washed by doubly distilled water several times, followed by drying at 120°C overnight.

1.2.2 Co-Mo loading

Ammonium heptamolybdate tetrahydrate and cobalt acetate precursors were used for molybdenum and cobalt preparation respectively. The pore volume impregnation method was used to prepare the catalyst with 12% MoO_3 loading and Co/Mo atomic ratio of 0.7. The impregnation was carried out in two stages to avoid the precipitation of catalyst metal from the saturated solution. Firstly, the Mo species was loaded by dissolving the required weight of ammonium heptamolybdate tetrahydrate in an estimated doubly distilled water volume with a few H_2O_2 droplets 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 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°C in a muffle furnace for 4 h.

For alumina supported catalyst, the same procedures were used to deposit the Mo and Co over the alumina at the same drying and calcination conditions.

Table 1 Properties of heavy vacuum gas oil feedstock

Experiment	Method	Result
Total sulfur content w/%	ASTM D-4294	1.66
Aniline point/°F	ASTM D-611-82	74
Diesel index/%	ASTM D 611	46.09
Total aromatics w/%	–	34

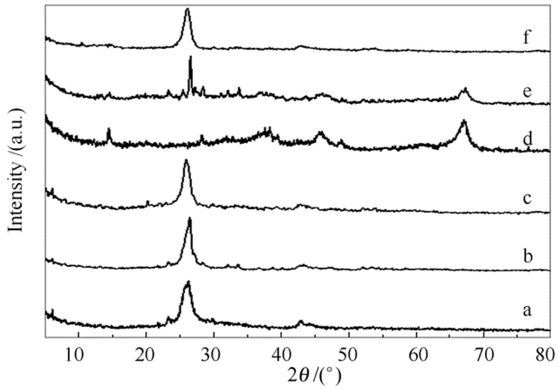

Fig. 1 XRD patterns of different samples

a: CNT; b: CoMoO/CNT; c: CoMoS/CNT; d: γ-Al_2O_3; e: CoMoO/γ-Al_2O_3; f: CoMoS/γ-Al_2O_3

1.3 Catalyst characterization

1.3.1 X-ray diffraction

The catalysts formed phases were determined by the X-ray diffraction analysis using X'Pert PRO PANalytical apparatus. The patterns were recorded using Cu $K\alpha$ radiation (λ= 0.15418 nm). The 2θ ranges from 10° to 70° at a scanning rate of 0.05 s^{-1} were used to record the patterns.

1.3.2 Transmission electron microscopy

The CNT and Co-Mo/CNT catalysts morphology were determined using a JEOL 2010F TEM apparatus. An accelerating voltage of 200 kV was used to obtain the images. Before measurements, the samples suspensions were prepared with 5 mL ethanol. The mixture was sonicated for 20 min then a solution droplet was placed on the Cu grid. The ethanol was then slowly evaporated in open air from the Cu grid under a glass cover.

1.3.3 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}.