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Preparation and characterization of Co-Mo catalyst supported on CNT coated cordierite monoliths utilized for naphta HDS process

E. Soghrati[a], M. Kazemeini[a, a*], A.M. Rashidi [b] and Kh. Jafari Jozani [b]

[a]*Chemical and Petroleum Engineering Department, Sharif University of Technology, Tehran, Iran*

[b]*Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI), Tehran, Iran*

Abstract

In the present study, an acid treatment of the cordierite monolith followed by coating of the CNT onto it by means of catalytic chemical-vapor deposition (CCVD) of methane over CoMo catalyst was performed. The resulting material utilized as the supports for the HDS catalyst onto which was deposited Co and Mo species. The as-prepared samples were characterized by the BET, XRD, FESEM and ICP-MS techniques. BET experiments showed that a significant increase in specific surface area and pore volume was observed, and a suitable pore size distribution was obtained after acid pretreatment. The FESEM images of CNT coated monolith showed that CNTs were distributed uniformly on the surface of monolith substrate, which led to a high BET surface area and relatively good adhered mesoporous layer of CNTs. Ultimately, the catalytic activity of the resulting catalysts was studied in the HDS reaction of Naphta. It was concluded that the activity of CoMo/FACNT catalyst was higher than that of a supported catalyst. Furthermore, the reaction over the this material decreased the sulfur content of Naphtha from 2670 to 53 ppm.

Keywords: Monolithic cordierite; CoMo catalyst; carbon nanotube; naphta; HDS process

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* Corresponding author. Tel.: +98 21 6616 5425; fax: +98 21 6602 2853.
E-mail address: kazemeini@sharif.edu.

1. Introduction

Hydrodesulfurization (HDS) process consisting of the catalytic removal of sulfur from refinery streams is one of the most important crude oil refining processes. An important goal of the current industrial research on the HDS processes is to prepare CoMo catalysts with improved activity and selectivity. It is well known that the properties and performance of HDS catalysts to a certain extent depend upon on the nature of their support [1]. Moreover, recently monolithic materials have attracted a good deal of attention due to its catalytic applications. Despite the advantages of monolithic cordierite such as the high void fraction, large geometric surface area, low pressure drop and thermal shock resistance, the limited use of cordierite as a catalyst support is due to the fact that cordierite monoliths have a low specific surface are (~ 1 m^2/g) and weak metal-support interactions [2]. To increase the specific surface area two different treatments have been developed including; wash coating [3, 4] and acid processing [5]. Elmer *et al.* [6] showed that after treatment in hot nitric acid, the surface area of cordierite monoliths could be increased to values as high as 414m^2/g. Also, Shigapov *et al.* [5] studied the acid leaching of cordierite with different organic (*e.g.;* formic, citric, acetic, etc) acids. Moreover, Washcoat materials, most often alumina, utilized to increase the specific surface area and to distribute the catalyst on the surface of the monolith. Recently, carbon nanotubes have attracted a great deal of interest in both fundamental and applied investigations for their extraordinary physical and chemical properties after their discovery by Iijima in 1991 [7]. Powder form CNTs have some drawbacks such as formation of fines for slurry phase operations which led to the agglomeration and difficulty of filtration; and high pressure drop for gas phase operations. New method for CNTs application has been reported to overcome such drawbacks. In particular; incorporation of CNTs onto larger porous objects for example, cordierite monoliths has been suggested. Ultimately, although the applications of CNTs and monolithic materials as catalyst support have been extensively studied, this kind of support, CNT coated cordierite monoliths, in HDS reaction has not been investigated before. Therefore, in the present work CNT coated monolith substrate synthesized and evaluated in HDS reaction of naphta.

2. Experimental

2.1. Preparation of the monolithic supports

Commercial cordierite (2Al_2O_3: 5SiO_2: 2MgO) monoliths with a density of 400 cells per square inch (cpsi) and a wall thickness of 0.2 mm was used as a ceramic substrate. Cordierite samples with a length of 20 mm and diameter of 10 mm were cut out from a commercial monolith using a diamond drill. Initially, the cut monoliths were pretreated with nitric acid solution boiling for 3h in order to increase specific surface area then washed by demineralized water and then dried at room temperature. These were referred to as the "A" monoliths. For CNT coating, initially, the cobalt and molybdenum were deposited by impregnation onto the A monolith with aqueous solutions of $Co(NO_3)_3$ and $(NH_4)_6Mo_7O_{24}·24H_2O$. After withdrawal from the solution, excess liquid inside the monolithic channels was removed with pressurized air. It was dried at 120°C for 12h, followed by calcinations in air at 500°C for 4h with a heating rate of 2°Cmin^{-1} in order to avoid any cracks. After preparation of catalysts, carbon nanotubes were grown through catalytic decomposition of methane over deposited Co-Mo on the monoliths according to the literature [8] in which however, MgO was applied as the support for the catalyst. In this case the prepared catalysts were reduced in pure hydrogen. Carbon nanotubes were grown in a quartz horizontal reactor at 900°C by passing a mixture of methane in hydrogen over the CoMo catalysts. After 1h growth of carbon nanotubes, the methane flow was turned off and the reactor was cooled down to room temperature in the presence of hydrogen. These resulting materials were referred to as the "ACNT" monoliths. Finally, the

CNT-coated monoliths were oxidized with ozone and an aqueous solution of H_2O_2 to create anchoring sites for the metal deposition. Afterwards, the monoliths were washed several times with demineralized water and then the water in the monolithic channels removed by pressurized air and finally, dried at room temperature. These were labelled as the "FACNT" monoliths.

2.2. Preparation of the monolithic catalysts

For the HDS Co-Mo catalysts, an aqueous solution including cobalt nitrate and ammonium Heptamolybdate was also prepared. The metal content of these solutions were then impregnated onto the monoliths A and FACNT. Resulting catalyst was dried at 120°C for six hours and calcinated at 500°C for 4h under N_2 atmosphere for the FACNT and in air for the A supported Co-Mo catalysts. This was done in order to make bimetallic catalysts with the content of total Co and Mo being 7, 10 and 15 wt% and controlled Co/Mo atomic ratio of 1/3 needed for the HDS process. These prepared materials were termed as CoMo/A, and CoMo/FACNT.

2.3. Characterization of the monolithic supports and catalysts

The textural surface properties of the monolithic supports were determined by physical adsorption/desorption of N_2 at -196°C with a Micromeritic ASAP 2010 analysis instrument. Before the measurements, the samples were degassed at 250°C for 2h. The specific surface area and the pore size distribution were calculated by the BET and BJH methods, respectively. The pore volume was calculated from the adsorbed volume at a relative pressure of 0.99. The X-ray diffraction (XRD) patterns of the monolithic supports and catalysts were recorded with a Philips PW1840 X-ray diffractometer using monochromatized Cu Kα radiation. The microstructures and morphologies of samples were observed by field emission scanning electron microscopy (FESEM). Also, the Co and Mo loadings of the monolithic catalysts were analyzed by inductively coupled plasma mass spectrometry (ICP-MS) using a VISTA-PRO spectrometer.

2.4. Catalytic Activity tests

The prepared catalysts were utilized in an HDS reaction in which naphtha was fed into a concurrent fixed-bed of stainless steel reactor with inner-diameter of 10mm. The electronic mass flowmeter and a pump controlled the flow of feeds. An evaporator and three heating zones each equipped with temperature controller and indicator supplied the reaction heat. The 6.5g of catalyst was loaded into the reactor and reduced by H_2 at 30bar and a space velocity of $200h^{-1}$ with $1°C\ min^{-1}$ heating rate from ambient temperature up to 180°C and maintained in this temperature for 1h. The catalysts were sulfided by a stream of 1wt% of dimethyl disulfide in ISOMAX with a liquid hourly space velocity (LHSV) of $2h^{-1}$ under hydrogen pressure of 30bar at the hydrogen to oil volumetric ratio of 175Nl/l in order to prepare CoMoS active phases. The samples were heated with a heating rate of $0.5°C\ min^{-1}$ from 180 to 260°C, then at $0.17°C\ min^{-1}$ for 260 to 310°C and finally were maintained at this temperature for 12h. After this activation step, the catalytic performances were evaluated using naphtha with total sulfur content of 2670 ppm as feed. The reaction conditions were as follows: at the temperature of 310°C, H_2/Oil= 175Nl/l, 15 bars of pressure and LHSV= $4h^{-1}$, which well approximated the industrial conditions. The reaction took place for 48h. The total sulfur amounts of products were analyzed by the X-Ray Fluorescence (XRF) technique.

3. Results and discussion

3.1. Characterization of the monolithic supports and catalysts

The physical adsorption isotherms of N_2 at -196°C for bare cordierite, pretreated monolith and the monoliths after CNT growth were shown in Figure 1. The provided isotherm corresponded to type III was observed for the bare cordierite in Figure 1(a), was characteristic of macroporous solids. However, a combination of types I and IV were found for other monolithic supports indicated the presence of micropores and mesopores. These may also be observed in Figure 2 which showed the pore size distribution (PSD) curves of the monolithic supports calculated by the Barrett-Joyner-Halenda (BJH) method. The PSD of the pretreated monolith and CNT-monolith composites were shown to be in the micropores and mesopores range (Fig. 2b). However, the pores in the cordierite substrate are larger than in the other monolithic supports (Fig. 2a). The specific surface area and porosity data of monolithic supports listed in Table 1. It may be seen that the BET surface area and pore volume significantly increased after the pretreatment with nitric acid solution which is attributed to the creation of micropores and mesopores. The leaching of Mg and Al also should be responsible for the increase of the surface area in the A monolith [5]. However, the surface area of the A monolith fell from 116.88 to 101.84m^2/g after the CNT growth. This may be ascribed to two reciprocal effects: less thermal stability of treated monolith at the CNT growth temperature (900°C) which led to the lowered surface area [5]; and presence of the CNT with high surface area. Furthermore, the increased surface area of FACNT monolith might have been due to oxidation of CNTs with ozone and an aqueous solution of H_2O_2 was an effective method to remove the active metals for the CNT growth (Co and Mo), amorphous carbon and other impurities introduced through the CVD preparation process. These impurities have a very small surface area and block the pores. This oxidation treatment not only broke carbon nanotubes by eliminating the amorphous carbon, but also introduced a more hydrophilic surface structure and a larger number of oxygen-containing functional groups such as carboxyl, hydroxyl and carbonyls [9].
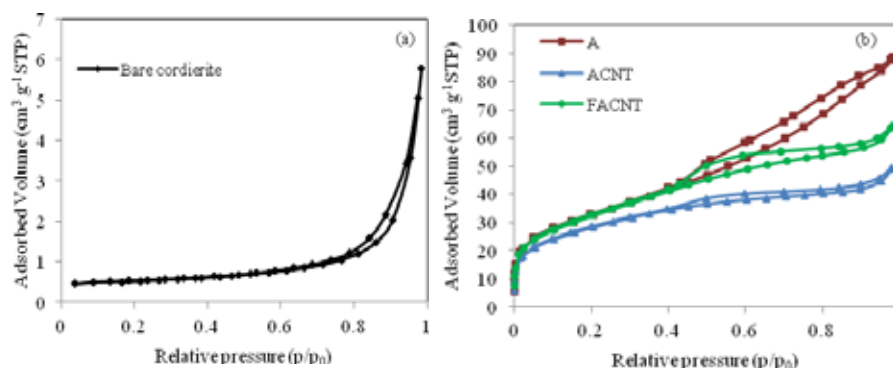

Fig. 1. N_2 adsorption-desorption isotherms of the monolithic supports (a) Bare cordierite; (b) A, CNTs coated monoliths
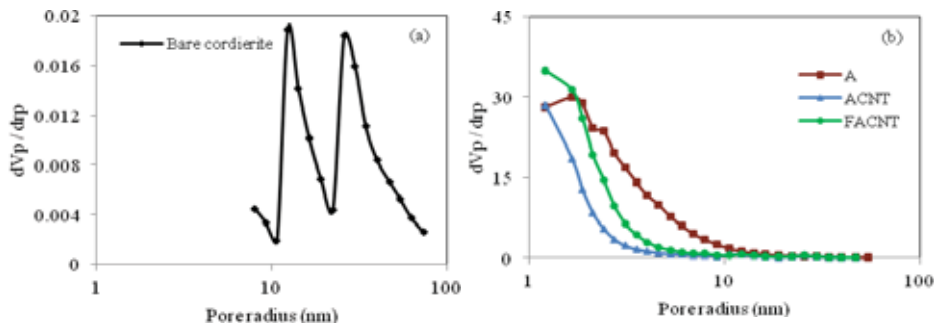
Fig. 2. BJH pore size distribution (PSD) of the monolithic supports (a) Bare cordierite; (b) A and CNTs coated monoliths

Table 1. BET surface area and porosity data of the monolithic supports

Monolithic support	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore diameter(nm)
Bare cordierite	0.16733	0.0001453	3.4733
A	116.88	0.1367	4.6768
ACNT	101.84	0.0764	3.0009
FACNT	116.32	0.0992	3.4100

Figure 3 represented the XRD patterns of monolithic supports and also prepared catalyst samples after calcinations. Form the XRD pattern of the A monolith, one may conclude that appropriate nitric acid treatment of cordierite monoliths led to destruction of the silicate structure of cordierite (see fig. 3(a)), with the removal of Mg and Al ions and generation of free silica on the surface of the cordierite, is responsible for the creation of the high surface area solids [5]. Furthermore, new diffraction peaks (2θ= 31.28°, 36.90°, 45.06°, 59.82° and 65.58°) may be clearly observed which were related to the presence of magnesium aluminate ($MgAl_2O_4$) [10]. XRD patterns of the CNT coated monoliths also presented in Figure 3(b). As shown in these patterns, CNT support had a peak at about 2θ of 26.05°, which was related to the (002) graphitic basal plane, and a peak at about 2θ of 43.0° ascribed to the diffraction of (100) plane [11]. In addition, oxidation of the CNTs in FACNT monolith removed the active metals for the CNT growth, amorphous carbon and other impurities. Therefore, no peaks related to the cobalt or molybdenum might have been detected in the XRD pattern of FACNT monolith.
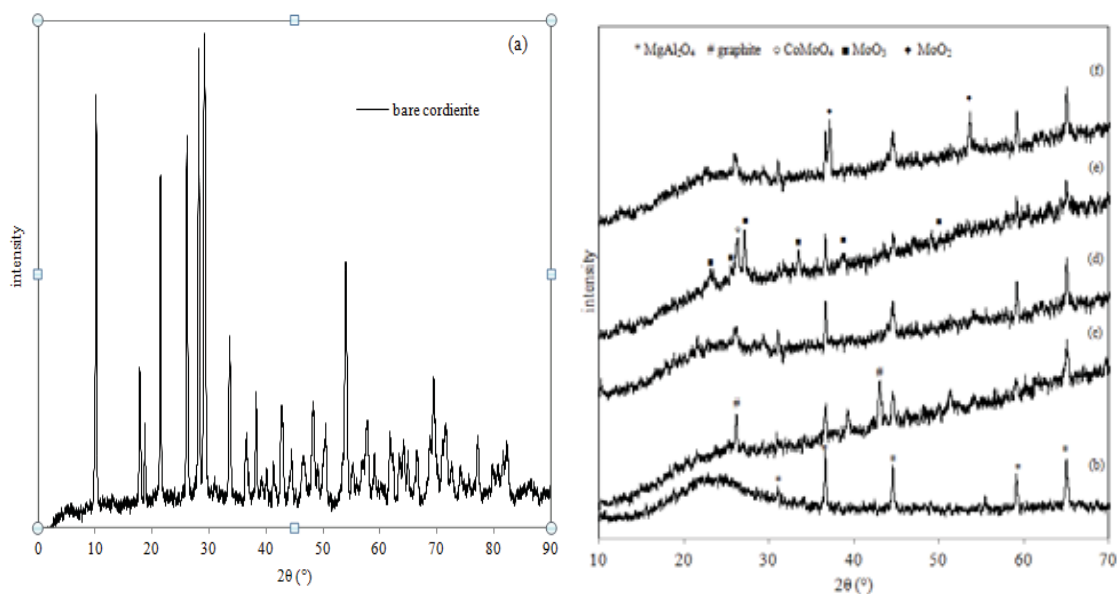
Fig. 3. XRD patterns of (a) bare cordierite; (b) A monolith; (c) ACNT monolith; (d) FACNT monolith, (e) CoMo/A catalyst and (f) CoMo/FACNT catalyst
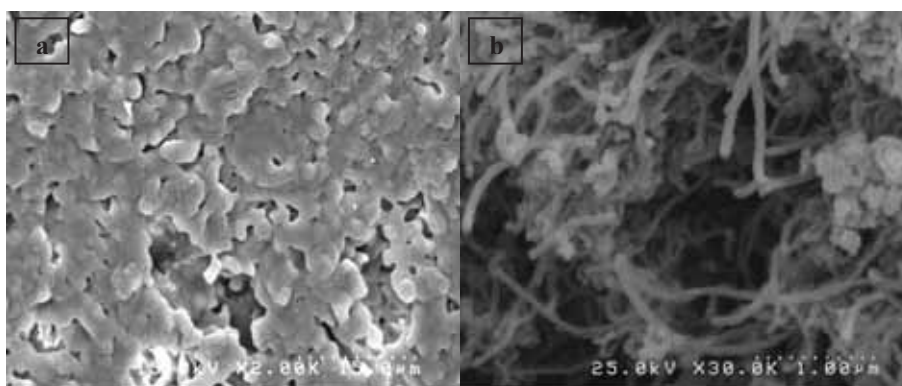

Fig. 4. SEM microphotographs of (a) bare cordierite and (b) carbon nanotubes coated monoliths

The SEM microphotographs of the surface texture of samples before and after the CNT coating were shown in Figures (4a) and (b); respectively. It might be obvious that the monolithic structures were covered with homogeneous CNTs washcoat (Fig. 4b). These revealed that the CNTs were distributed homogeneously onto the surface of the monolith substrate. Active metal particles were also observed in these images. The elemental compositions of the prepared oxide catalysts based upon the total sample mass are reported in Table 2. As shown in Table 2, the values of the total metal content were slightly below the theoretical value of 10 wt. % (Mo + Co). The Co/ Mo atomic ratio also analyzed by the ICP for the different prepared supported systems was above 0.3. This ratio for the FACNT supported system was smaller than that for the A support. This may be explained perhaps by a lower reactivity of Co precursor

with the edges of the Mo phase on the FACNT although this was not independently verified. The XRD patterns of the FACNT and A supported catalysts after calcinations were also shown in Figure 3. XRD pattern of the CoMo/A catalyst showed some $CoMoO_4$ and free Molybdenum oxide as MoO_3 as the main active species in this catalyst [11, 12]. As shown in Figure 3, FACNT support had peaks at a 2θ of 26 ^{o} and 43 ^{o}, which might have been attributed to the CNTs. In the XRD pattern of catalyst with FACNT support, new diffraction peaks at the 2θ of 36.9^o, 53.5^o and 60.5^o were clearly observed. These peaks were characteristics of the MoO_2 [11], indicating the main active phase on the surface of the CNT was the Mo species at low valence. The reason for this might have been due to the hydrophobic surface of the CNTs [11, 12] which made the metal-support interaction very weak. Therefore, the molybdenum oxides could migrate and conglomerate on the surface of the CNTs while it reduced by the carbon nanotubes during the calcinations stage [11]. On the other hand, no peaks related to the interaction of cobalt or Mo with the CNTs support could be detected in the XRD pattern of CoMo/FACNT catalyst.

Table 2. The elemental compositions of the monolithic catalysts

Monolithic catalyst	A support (wt. %)	CNT (wt. %)	Mo (wt. %)	Co (wt. %)	Co/Mo Atomic ratio
C10/A	91.32	0.0	6.85	1.83	0.43
C10/F-ACNT	80.38	10.53	7.34	1.75	0.39

3.2. Catalytic activity (HDS reaction)

The results of activity measurements and the residual sulfur content of Naphtha after hydrodesulfurizing reaction over prepared catalysts was displayed in Figures (5a) an (b); respectively. It was observed that the FACNT supported CoMo catalysts were more active than the CoMo/A material. There was no difference in surface areas for these supports; thus, it seemed that the role of morphology was as crucial as the surface area in determining the activity of catalysts. The reason for this may be due to the presence of the CNT layer which made the interaction between metal particles and support very weak. It is well known that metal content plays an important role in the catalytic activity of the HDS catalysts. In this way, to investigate the total metal content effect on activity of CoMo/FACNT catalyst; the HDS experiments were carried out over catalysts with 7, 10 and 15 wt. % (Co+Mo) loading under similar experimental conditions. Their corresponding HDS activities and residual sulfur contents were shown in Figure 5. It was concluded that the activity was increased with increasing metal content up to 10 wt. %. The S conversion increased from 97.54 to 98.08 % when the (Co+Mo) content enhanced from 7 to 10 wt. %. With metal content of 15 wt.%, the S conversion decreased to 97.79 wt.%. The better activity of 10 wt. % (Co+Mo)/FACNTs might be explained by the enhanced dispersion of the added metal particles. It might be even better explained that, when the metal content exceeded 10 wt. %, the particle size increased noticeably leading to poor performance of the catalyst. Ultimately, using CoMo/FACNT as catalyst at 310°C with LHSV of 4h^{-1} under hydrogen pressure of 15bars, more than 97% of sulfur contents of the feed were removed in the product. It is noteworthy that, the reaction over CoMo10/FACNT catalyst decreased the sulfur content of Naphtha from 2670 to 53 ppm which was a significant result in its own right.

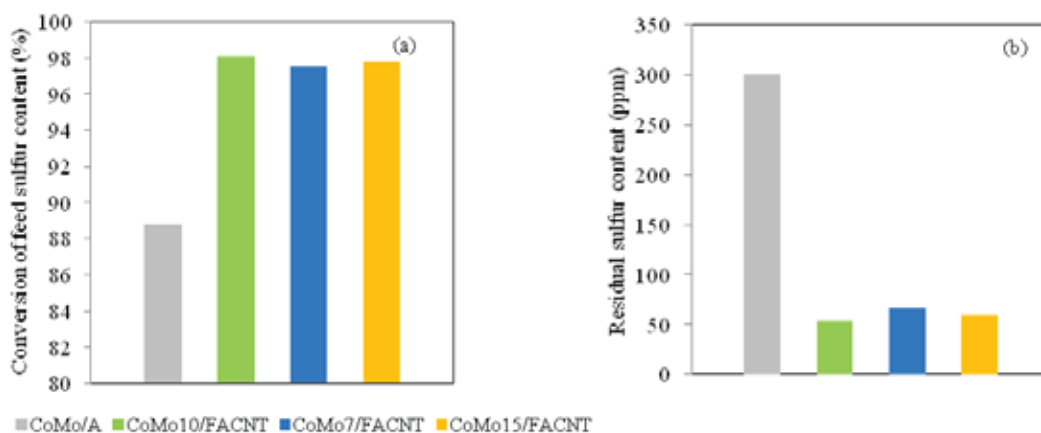■CoMo/A ■CoMo10/FACNT ■CoMo7/FACNT ■CoMo15/FACNT

Fig. 5. (a) Conversion of sulfur content of Naphtha over synthesized catalysts; (b) Residual sulfur content of Naphtha after HDS reaction

Conclusion

To prepare CNT coated monolith, an acid treatment of the cordierite monolith and the CNT growth onto it by deposition of methane over CoMo catalyst was performed successfully. The resulting material utilized as the supports for the CoMo hydrodesulfurization catalyst. BET experiments showed that BET surface area and pore volume data increased significantly, and a suitable pore size distribution was obtained after acid pretreatment. On the basis of FESEM and BET results, the CNT coated monolith showed the high BET surface area and suitable pore size distribution and uniform CNTs onto monolith substrate. In addition, the catalytic activity results revealed that more active catalyst is observed when CNT coated monoliths utilized as a support in naphta HDS process. This might have been explained by the presence of the CNT layer which made the interaction between metal particles and support very weak.

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