

Effect of CoMo/HSO₃-functionalized MCM-41 over Heavy Oil

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Abstract. The potential of Co-Mo metals supported on functionalized MCM-41 as catalyst to hydrodesulfurization of heavy oil has been explored in this work. The MCM-41 functionalized sample was synthesized according to methods previously reported in the literature. Co and Mo metals were incorporated into the support by simultaneous impregnation. The catalyst was characterized by specific surface area and X-Ray Diffraction. The pore channel of MCM-41 was confirmed by transmission electronic microscopy and infra red spectroscopy. Catalytic activity tests were carried out using heavy oil from Gulf of Mexico. The API gravity was increased from 12.5 to 20.2, the kinematics viscosity was decreased from 18,700 to 110 cSt at 298 K, the contents of asphaltene and sulfur were also reduced.

Keywords: Functionalized MCM-41, Heavy Oil, HDS.

Resumen. En el presente trabajo se explora el potencial del catalizador Co-Mo/MCM-41 funcionalizado en la reacción de hidroconversión de aceite crudo pesado. El material MCM-41 fue sintetizado conforme a métodos reportados en literatura. El Co y Mo se incorporaron al soporte empleando la técnica de impregnación simultánea. Así mismo, el catalizador sintetizado fue caracterizado determinando su área específica, difracción de rayos X; se confirmó su distribución de canales de poros por medio de microscopía electrónica de transmisión. También se estudiaron las propiedades ácidas por espectroscopía de infra-rojo así como también de la adsorción de piridina. Para medir la actividad catalítica, se empleó aceite crudo pesado del Golfo de México. La gravedad API se incrementó de 12.5 a 20.2, la viscosidad cinemática se redujo de 18700 a 110 cSt determinada a 298 K, el contenido de asfaltenos y azufre también se reducen notablemente.

Palabras clave: MCM-41 funcionalizado, aceite pesado, HDS.

Introduction

The world reserves of light oil are fast diminishing, at the same time the world demands for oil is increasing. Therefore, heavy oil is being considered as a future option for fuel production. In addition to containing different complex hydrocarbons with large amounts of sulfur, nitrogen and metals, the heavy oil is difficult to produce and presents the following problems: [1] low mobility through the reservoir due to the high viscosity which affects the index of productivity of the wells, [2] difficulty in transportation, and [3] low capacity of processing in the refineries. For these reasons, it is fundamental upgrade the heavy oil in both directions aboveground and underground. As for aboveground, several process options have been studied and applied at industrial level to improve the bottom barrel conversion. The main processes are as follows: thermal processing [1-3] (delayed coking, fluid coking, flexicoking, visbreaking), hydroprocessing [4-7] (fixed-bed, ebullating bed, slurry phase), and extractive Processes [8-10] (FW solvent deasphalting, Demex). However, all these processes are focused on converting the atmospheric and vacuum oil residues (1000+ °F) to more valuable products such as gasoline, middle distillates and FCC feed stock. The hydroconversion of heavy oil aboveground has been applied at semi-industrial level because it needs special design of fractionation towers. The hydroprocessing of large volumes of heavy oil requires high cost equipment and consumes large hydrogen amounts.

During the hydroprocessing the presence of high contaminants content, heavy metals and Conradson Carbon in

heavy oil will cause poisoning and a rapid deactivation of the catalysts. This is another problem of the heavy oils. The asphaltenes and asphaltene molecules associated with sulfur, nitrogen and metals are the most difficult to process. Therefore, to remove sulfur from the heavy oil it is necessary to carry out the cracking of asphaltene molecule. It has been reported that an increase in the content of asphaltene brings high deposition of carbon, and the asphaltene fractions may provide different concentration of carbon deposition on the catalyst [11-12]. In addition the asphaltene polar fraction have high tendency to adsorb on the surface of the catalyst [13].

Thermal hydrocracking produces a significant increase of API gravity with a high coke undesirable formation which affects the product yields, meanwhile the catalytic hydrocracking produces a similar increase of the API gravity, with a better product quality because of the higher sulfur removal and low content of coke. The right balance between the metallic function and acid function in the catalysts will provide better product quality. An increase of the metallic load and the acidity on the catalyst usually produced an increased API gravity even at low reaction temperature [14].

MCM-41 as support of catalyst possesses excellent properties, such as high surface area, uniform distribution of pore size, large pore size, a large number of Si-OH but has a low intrinsic acidity that limit their potential application in the fields of catalysis [15-19]. The introduction of strong acids functional groups like alkyl or aril sulfonic acid on the Si-MCM-41 produces higher numbers of improved acid centers and enhances the behavior in reactions catalyzed by the acid

function. Such reactions are the hydroprocessing of heavy oil molecules asphaltenes and asphaltenes associated with sulfur, nitrogen and metals. The acidity incorporated on the surface of the catalyst may also convert molecules of heavy molecular weight into light hydrocarbons [15, 20].

The upgrading of heavy crude oil is a current challenge for petroleum refining industry. Therefore, catalyst companies are looking for best catalysts with high stability supports.

MCM-41 has been proposed as a good material to meet that purpose. Early results show good activity levels of this material. In order to improve these results, in this paper a sample of MCM-41 was treated with HSO_3 to achieve higher levels of active metal dispersion. The functionalized sample has been tested in hydrocracking of heavy oil.

In the present work the effect of incorporating Brønsted acid sites of HSO_3 with CoMo/MCM-41 catalyst was studied to determine its effect on the hydroconversion reactions. Furthermore, the relationship of surface properties of the catalyst, their structure and the acid interaction are discussed, including the activity test of the catalyst with the heavy oil.

Results and discussion

X-ray diffraction

Fig. 1 presents the powder X-ray diffractograms of MCM-41 functionalized and non-functionalized. The samples show the typical XRD pattern of the MCM-41 with a well defined (1 0 0) reflection peak, as described by Beck [21-23]. The main peak of this sample becomes less intense and wider, indicating more degree of disorder. There is also a displacement of the main peak towards a larger diffraction angle, indicating a reduction of the cell parameter. The secondary peaks on MCM-41 functionalized material could not be well-resolved, relating to a less regular structure. The main diffraction peak of this sample was displaced from a diffraction angle of 2.5-3.5.

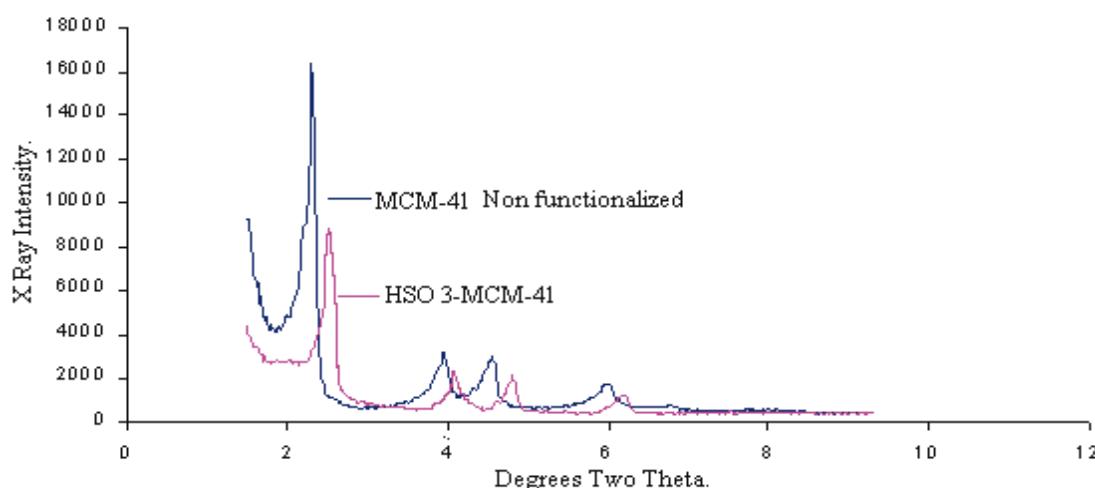


Figure 1. X-ray diffraction patterns of MCM-41 functionalized and non-functionalized.

BET analysis

Fig. 2 shows the nitrogen adsorption-desorption isotherms at 77 K of the MCM-41 materials, before and after of the functionalization treatment. The isotherms have a sharp inflection at a relative pressure about 0.36 which is characteristic of capillary condensation within uniform mesopores.

This capillary condensation in the nitrogen adsorption curve was observed between 0.3 and 0.4 p/p_0 at 392 MPa pressure. These results show the isotherms Type IV nitrogen adsorption-desorption, which indicate the presence of mesopores, while the hysteresis loop observed type is typical of cylindrical channels [22, 23].

Table 1 shows the nitrogen sorption data of the functionalized samples compared with non-functionalized pure siliceous samples. The MCM-41 lattice parameter, calculated with $a_0 = 2d100/\sqrt{3}$, was of 40.9 Å and after of the treatment of functionalization it became 41.7 Å [24, 25]. The functionalized sample has similar values of pore diameter, interplanar distance, and lattice parameter and thickness wall. However, the specific area and the pore volume is about one half of the non-functionalized sample. This result indicates that the crys-

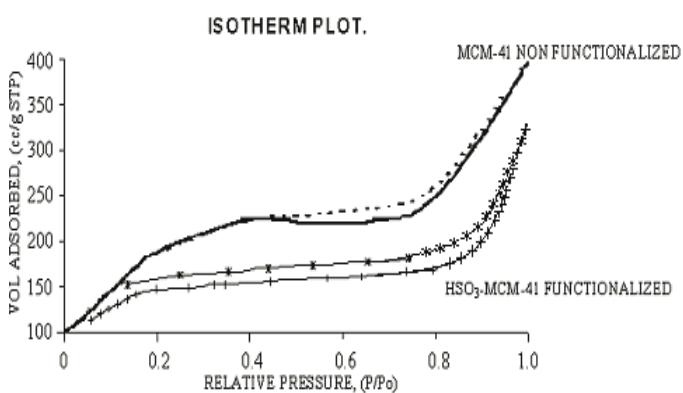


Figure 2. Adsorption-desorption nitrogen isotherms on MCM-41 functionalized and non-functionalized.

Table 1. Textural properties of HSO₃-MCM-41 functionalized and non-functionalized.

| Samples | S _{BET} (m ² /g) | APD (Å) | PV cm ³ /g | d ₁₀₀ [Å] | a ₀ (Å) | Wall thickness (Å) |
|---|--------------------------------------|---------|-----------------------|----------------------|--------------------|--------------------|
| MCM-41 Non-functionalized | 996 | 25.7 | 0.71 | 35.5 | 40.9 | 15.2 |
| HSO ₃ -MCM-41 functionalized | 530 | 22.4 | 0.3 | 36.1 | 41.7 | 19.3 |

tal structure of MCM remains after the catalyst preparation. The diminution of surface area and pore volume can be the results of filling pore with active metals. The total amount of active metals on catalysts is about 17 wt% and also affects in less degree the thickness wall.

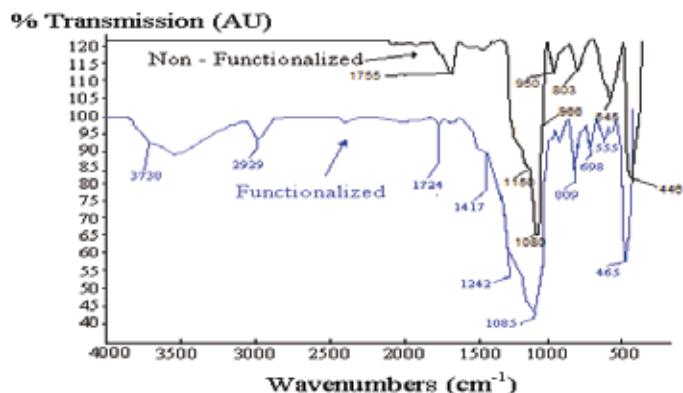
FT-IR

Figure 3 shows the infrared spectra of the samples functionalized and non-functionalized. The non-functionalized sample presents a symmetric stretching band at 803 cm⁻¹ and two asymmetric stretching bands at 1080, 966 cm⁻¹ for the tetrahedral TO₄ structure units of silanol groups. The peak at 446 cm⁻¹ results from the T-O bending vibration of the silanol groups. The broad peak from 950 cm⁻¹ to 1150 cm⁻¹ indicates the characteristic asymmetric of the O-Si-O stretching of polysiloxanes on particles of mesoporous silica (Si-MCM-41) [26, 27].

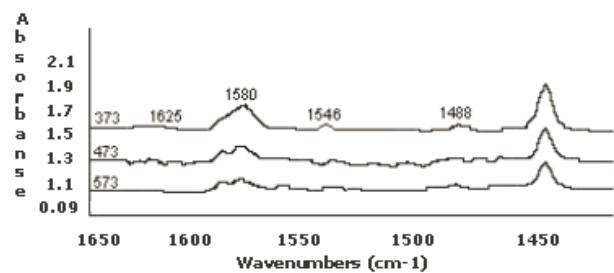
Both samples (functionalized and non-functionalized) were analyzed as wafers supported on 2 wt % KBr as background to see the whole structural bands of the spectrum. The spectrum shows mainly the characteristic bands of materials based on silica oxides with some extra bands that suggest framework like modified zeolites or mixtures of other materials. It is notable the presence of other bands at 2929, 1724 and 1417 cm⁻¹ which can be associated to organic materials obtained from the decomposition of cetyl trimethylammonium bromide, of aqueous solution of cetyl trimethylammonium chloride used during the synthesis of MCM-41 [28-30].

The FT-IR spectra of the adsorption of pyridine are shown in the Figure 4. The non-functionalized sample shows acid sites Bronsted (1546 cm⁻¹) and Lewis (1445 cm⁻¹) in spectrum (a). According with the framework of MCM-41 it is expected that the absorption of pyridine on the Lewis sites

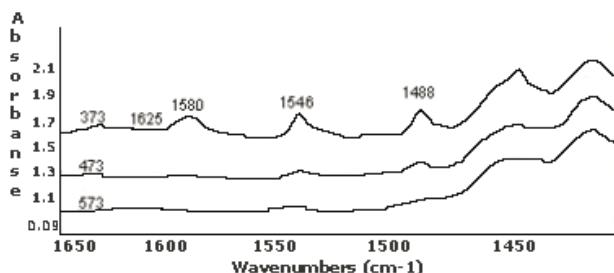
corresponds to silicon atom which has associated a positive electronic charge. This band is intense at low temperature at 1445 cm⁻¹ and decreases quickly at higher temperature, meaning that this signal is partially due to the physisorption of the pyridine on support. At high temperature the signal at 1445 cm⁻¹ remains corresponding to pyridine adsorbed on silicon atom. The relative population of Bronsted acid sites with respect to Lewis acid sites is lower, although, it is well known that its strength is higher. Figure 4b shows the spectra of the MCM-41 mesoporous functionalized material. The presence of Bronsted acid sites is the result of sulfuric acid addition. Protons will be directed to free electrons of oxygen atoms. The sulfate ions will be associated to silicon atoms. The addition of Mo and Co salts to functionalized supports will favor the dispersion of active metals (cations). Finally, during the calcinations process, all the volatile material will be eliminated and active metals will be converted in oxide compounds with very high dispersed combined with the oxygen atoms of the support. The impregnation of active metals in this way is expected to increase the activity, selectivity and stability of catalysts [29, 30].

**Figure 3.** FT-IR of MCM-41 functionalized and non-functionalized.

(a)



(b)

**Figure 4.** FT-IR of pyridine adsorption at different temperatures of non-functionalized support (a) and functionalized support (b).

Transmission electronic microscopy

Figures 5 (a), (b), (c), and (d) show the micro-graphs from transmission electron microscopy (TEM) of the MCM-41 obtained at different resolution. The TEM analysis confirms the well-ordered lattice of the hexagonal channels in MCM-41 mesoporous functionalized and non-functionalized samples. The TEM images of the sample MCM-41 show a clear hexagonal arrangement of pores with uniform size. The well-aligned channels running parallel to organosilica rods are also observed in Fig. 5a and b. Despite the large pore size, this high degree of order is maintained over extensive regions of observation. These observations confirm that the pore structure consists of a hexagonal array of uniform 1D channel for the 2D-hexagonal sample. The pattern of functionalized samples (TEM images) showed in Figure 5c and 5d suggest strong evidence that the mesoporous structure of the supports is retained compared with like structures, which has been

reported in the literature [31-33]. They show channels with porous lattice very ordered complemented by the XRD and N_2 adsorption data.

Catalytic evaluation

The catalysts CoMo/MCM-41 non-functionalized and CoMo/HSO₃-MCM-41 functionalized were evaluated under the same operating conditions using heavy oil. Table 2 shows the products distribution obtained in the hydroconversion process of heavy oil. The results obtained for non-functionalized sample allowed increasing the API gravity from 12.5 to 20.2, a reduction of kinematics viscosity from 18,700 to 110 cSt, and a reduction of the sulfur content from 5.13 to 1.8 wt%. The oil composition Saturates, Aromatics, Resins and Asphaltenes (SARA) changed because of the hydrocracking process on Resins and Asphaltenes. These compounds were changed from 14.3 to 15.1 and from 10 to 7.2 wt%, respectively. On the other

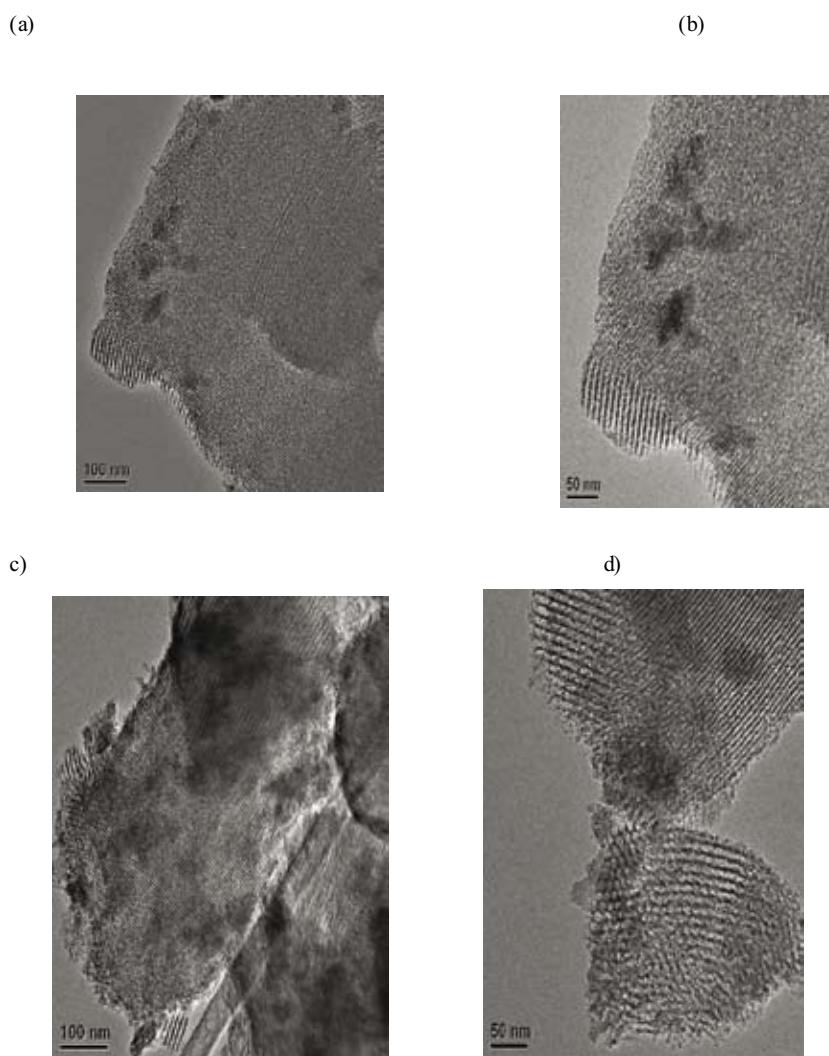


Figure 5. TEM micrographs of MCM-41 of non-functionalized (a, b) and functionalized (c, d) samples.

hand, the concentration of Saturates and Aromatics were transformed from 46.6 to 40.5 and 29.1 to 37.2 wt% respectively.

The hydroconversion of heavy oil with functionalized catalysts (CoMo/HSO₃MCM-41) showed a higher catalytic activity than the non-functionalized catalyst at 613 K. The API gravity was increased from 12.5 to 24.5; the kinematics viscosity was reduced from 18,100 to 71 cSt at 298 K, the sulfur removal was 72.7 wt%. Finally the chemistry of distribution of hydrocarbon was as follows: Compared to the heavy oil, the asphaltene content decreased from 10 to 5 wt%, the content of resins (polar) was also reduced from 14.3 to 12.5 wt%, and the paraffin and aromatics contents were changed from 46.6 and 29.1 to 43.0 and 39.5 wt% respectively.

The behavior of the catalysts can be explained by its high specific area (996 m²·g⁻¹), average pore diameter of the support (25.7 Å) and high dispersion of the catalytic active species of Mo and Co sulfides which are incorporated on the support [34, 35].

An empirical calculation on hydrodesulfurization reaction activity can be done using the sulfur reduction on feed and specific area of each catalyst. For these calculations, we consider a reduction from 51300 ppm of sulfur in feed to 18000 ppm for non-functionalized sample and 14000 ppm for functionalized sample. The total reduction in ppm of sulfur during the 8 hours that the experimentation took place and considering the specific area of each catalyst we can calculate the normalized data of sulfur reduction. 0.0695 ppmS/(min·m²g⁻¹) was removed with non-functionalized sample, meanwhile 0.1465 ppmS/(min·m²g⁻¹) was removed with functionalized catalysts. More than 2 times of sulfur is removed with functionalized sample.

The higher catalytic activity can be explained by the increasing of the metal dispersion as a consequence of presence of Bronsted acid sites during the impregnation process as well as the larger dimensions of the channels in the mesoporous materials. The larger molecules that were formed during the transition into light products require large reaction cavities

that are provided by the large mesoporous cavity from the catalyst.

Conclusions

The introduction of HSO₃ groups on the MCM-41 structure improved the catalytic activity compared with the Si-MCM-41 catalyst. The increased acidity and the large catalytic cavities are responsible for the increase API gravity and the lesser viscosity, providing in this way a good alternative to upgrading of the heavy oil.

Experimental

Synthesis

Pure siliceous MCM-41 were synthesized hydrothermally with the following molar composition: SiO₂:0.28 xTMAOH:0.12 xCTABr:2 H₂O where x represents the number of molecules of cations, such as tetramethylammonium (TMA⁺), and cetyltrimethylammonium bromide (CTMABr) which were added as hydroxides. In a typical synthesis, an aqueous solution of tetramethylammonium silicate obtained from the reaction between silica (Aerosil 200, Degussa) and tetramethylammonium hydroxide solution (25% TMAOH, 10% SiO₂), was added to an aqueous solution containing 9.80 wt % of CTMABr. Then, amorphous silica was added under continuous stirring. The homogeneous gel was sealed in Teflon-lined stainless steel autoclaves and heated at 423 K under static conditions. The time of crystallization was 48 h. The resulting solid products were recovered by filtration and then doubly washed with deionized water and they were dried at room temperature for 24 h. Finally, the material was calcined at 813 K for 6 h. The formulation was modified according to a procedure previously reported [35-37].

Table 2. Comparative results between MCM-41 functionalized and non-functionalized catalysts in the hydroconversion of heavy oil.

| | Feed Heavy Oil | MCM-41 Non-functionalized | HSO ₃ -MCM-41 functionalized |
|----------------------|----------------|---------------------------|---|
| API gravity | 12.5 | 20.2 | 24.5 |
| Viscosity, cSt | | | |
| 298.0 K | 18700 | 110 | 71.0 |
| 310.8 K | 7500 | 59.9 | 42.3 |
| 327.4 K | 1950 | 28.3 | 20.7 |
| Total Sulfur, wt % | 5.13 | 1.8 | 1.4 |
| Total Nitrogen, wt % | 0.78 | 0.55 | 0.40 |
| SARA, wt % | | | |
| Saturates | 46.6 | 40.5 | 43.0 |
| Aromatics | 29.1 | 37.2 | 39.5 |
| Resins | 14.3 | 15.1 | 12.5 |
| Asphaltenes | 10.0 | 7.2 | 5.0 |

The prepared sample was functionalized by keeping it in toluene, adding 3-Mercaptopropyltrimethoxysilane (TMPTS) and stirring for 4 h. The organic phase was separated and dried at room temperature for 12 h. After this procedure the dried sample was added to a solution of methanol and hydrogen peroxide and stirred for 2 h at room temperature. After this procedure, the solid was added to a 0.1M sulphuric acid solution for 4 h. Finally, the solid was washed many times with distilled water and dried at 373 K during 2 h [38-41].

Preparation of Catalyst

The support was simultaneously impregnated by the pore volume method, with an aqueous solution containing the proper amounts of ammonium heptamolybdate $[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}]$, Aldrich 99%, cobalt nitrate $[\text{Co}(\text{NO}_3)_2]$, Aldrich 98% and phosphoric acid $[\text{H}_3\text{PO}_4]$, Baker 86 %] to obtain catalysts with nominal composition of 13.5 wt. % Mo, 3.5 wt% Co (Co/(Co+Mo) atomic ratio of 0.35) and 2 wt % P. The impregnated catalysts were dried at room temperature overnight, then dried at 393 K for 12 h, and finally calcined at 732 K for 5 h.

Characterization

The specific surface area of the sample was determined by the Brunnauer-Emmett-Teller (BET) method, using a Micromeritics ASAP 2000 sorptmeter. The X-ray diffraction (XRD) spectra were recorded employing a Siemens D-5000 instrument fitted with a monochromator for Cu K α radiation operating at 40 kV, 40 mA. In order to characterize acidic properties of catalytic materials, a spectrophotometer Nicolet 7000 FT-IR with a quartz cell was used. The infrared spectrometry analysis was performed obtained with a JEOL 100CX TEM. Recorded spectra were obtained on MCM-41 functionalized and non-functionalized in dried form.

Activity Tests

The tests for catalytic activity were carried out in a batch reactor (Parr, 500 mL) at 673 K of reaction temperature, 8.5 MPa total pressure, and 1000 rpm stirring rate. In a typical test, 150 g of heavy oil was mixed with 7.5 g of catalyst (100 mesh = 0.15 mm) MoCo/HSO₃MCM-41, and both were loaded into the reactor. Prior to reaction, the catalyst was dried under N₂ flow of 100 mL/min at 423 K during 0.5 h. Then the catalyst was sulfided in-situ at atmospheric pressure with a gaseous flow of H₂S/H₂ (10/90 vol/vol) bubbled in a stirred mixture of straight run naphta and catalyst. The gaseous flow rate was 60 mL/min for 4 h at 673 K. Straight run naphta was used to avoid active metals reduction and favor the contact of catalyst particles with H₂S. After the sulfidation, the naphta was decanted from reactor and catalyst was purged with N₂ and kept overnight under a N₂ flow of 5 mL/min.

The activated catalyst was mixed with heavy oil feed, the reactor was tested for leaks. Before the experimental runs, H₂ pressure was increased to the desired value, and the reac-

tor was heated up to the reaction temperature. The reaction initiated once all the pressure, temperature and stirring rate conditions were stabilized. Product samples were recovered every hour during the 8 h test, the composition analyses were performed on-line with a Perkin Elmer gas chromatograph equipped with a 50 m HP Ultra 2 capillary column and a Flame Ionization Detector (FID). The physical and chemical properties of the heavy oil were characterized according to the ASTM methods.

Abbreviations:

- MCM-41 Mobil Composition of Matter
- HDS Hydrodesulfurization
- API American Petroleum Institute
- FW: Foster Wheeler
- XRD: X-ray diffraction
- FT-IR: Fourier transform infra red spectroscopy
- TEM: Transmission electronic microscopy
- SBET: Specific area
- APD: Average Pore Diameter
- PV: Pore volume
- d₁₀₀: Interplanar distance
- a₀: Lattice parameter

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