Hydrodesulfurization of FCC Gasoline over Ni-Mo Catalyst supported on MCM-41

CHOL RYONG JANG[1], VASILE MATEI[2*], VIOREL VOICU[2], ANCA BORCEA[2], DRAGOS CIUPARU[2]
[1] Hamhung University of Chemical Industry, Str. Jongsong, Hamhung, D. P. R. of Korea
[2] Petroleum-Gas University of Ploieşti, 39 Bucureşti Blv., 100680, Ploieşti, Romania

The applicability of MCM-41 as support for Ni-Mo hydrotreating catalysts of fluid catalytic cracking (FCC) gasoline was tested in a fixed bed reactor under operating parameters similar with the industrial ones. The pure MCM-41 synthesized using a C_{16} surfactant following the classical mesoporous silica preparation steps, has high specific surface area and uniform pore diameter. X ray diffraction (XRD) patterns of the MCM-41 supported catalysts show good dispersion of the catalytically active components, NiO and MoO_3. This good dispersion suggests that MCM-41 can be used for the preparation of supported catalysts with high surface area and high dispersion. Ni-Mo/MCM-41 catalysts showed good activities for HDS and hydrogenation reactions. Increasing the NiO content of the catalyst, higher conversions of thiophene and 1-octene were observed at the same temperature. For hydrofining of FCC gasoline, the HDS activity of the Ni-Mo/MCM-41 catalyst at 350°C, 2.5 MPa, LHSV of 6 h-1 and H2 flow rate of 1 L/min is significantly higher than that of the commercial Ni-Mo/γ-Al_2O_3 catalyst under the same operating conditions. The MCM-41 supported catalyst led to some loss in the octane number of the processed gasoline at temperatures higher than 350°C.

Keywords: MCM-41, Ni-Mo/MCM-41 catalyst, XRD, FTIR, hydrotreating, FCC gasoline, HDS

Hydrodesulfurization (HDS) is one of most important petroleum refining processes, sulfur being removed from gasoline and gas oil by hydrogenation, resulting H_2S and hydrocarbons. This hydrodesulfurization process has been successfully carried out over Co-Mo and Ni-Mo sulfides catalysts, supported on γ-alumina [1]. It is very well known that γ-alumina is the most largely used material as support, not only in petroleum refining processes, but also in organic synthesis [2]. Due to its good mechanical and textural properties, γ-alumina has remarkable features such as the capability to provide high dispersion of active metal components [3]. In spite of its proven qualities, a deficiency of γ-alumina support is the incomplete sulfurization due to strong interactions between support and metals.

Recently, the development of petroleum refining is directed toward production of clean gasoline having sulfur content of less than 10 ppm. Developing clean fuels with low sulfur level is the main requirement in order to obtain high performance hydrotreating catalysts [4]. Changing the support of hydrotreating catalysts may be one of the successful approaches for preparation of better catalysts with enhanced performance in hydrotreating of gasoline and even gas oil. Many studies were reported on zeolites [5-7], TiO_2 [8, 9], SiO_2 [10], ZrO_2 [11], mixed oxides [12-14], mesoporous materials [15-18] and carbon nanotubes [19, 20] used as support of catalysts for HDS and these catalysts have better activities.

Since 1992 when MCM-41 was produced at Mobil Oil Company [21] and, six years later, SBA-15 was produced at the University of California [22], these mesoporous molecular sieves have applications in catalysis, biosensors [23], drug delivery and imaging [24]. Mesoporous materials such MCM-41 and SBA-15 are intensively investigated as catalytic supports and numerous studies are focused on their application to hydrotreating process. Shi et al. [15] used MCM-41 to support Co(Ni)-Mo(W) species in order to prepare catalysts with high hydroisomerization and relatively low hydrogenation activity. In this study, the authors used thiophene and 1-hexene as feedstock, as key components for FCC naphtha, finding that Co-Mo/MCM-41 showed the highest selectivity to the hydroisomerization of 1-hexene and relatively low hydrogenation activity. On the other hand, Rodríguez-Castellón et al. [25] studied high performance HDS catalysts, using MCM-41 doped with zirconium to increase the support acidity. A dibenzothiophene HDS reaction model has been used to estimate the performance of the catalysts prepared for HDS. All the catalysts supported on the MCM-41 showed very good performance in the investigated conditions, with conversions up to 92 %.

In this paper, we report the preparation and characterization of MCM-41 aiming to use it as support for HDS catalysts for fluid catalytic cracking (FCC) gasoline hydrotreatment. MCM-41 supported Ni-Mo catalysts have been prepared, characterized by X-ray diffraction and FTIR spectroscopy techniques and tested. Their catalytic performance was compared to that of a conventional, alumina supported Ni-Mo catalyst.

Experimental part

The preparation of the MCM-41 used as support for No-Mo catalyst was carried out in two steps: preparation of a surfactant C_{16} and preparation of the mesoporous silica, using a method modified by Ciuparu et al. [26]. For the preparation of the surfactant C_{16}, cetyl-trimethyl-ammonium bromide (CTAB), as template, and ion exchange resin Amberjet 4400 are used and tetramethylammonium silicate (TMAS) as silica source, fumed silica Cab-O-Sil M5, antifoam A and nitric acid are used for the synthesis of the silica.

Ni-Mo catalysts were introduced by incipient wetness impregnation of the synthesized MCM-41 sieve. Aqueous solutions of $Ni(CH_3COO)_2 \cdot 4H_2O$ and $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ were used for the catalysts Ni-Mo/MCM-41. The MCM-41

---

* email: vmateiph@yahoo.com

was impregnated first with the required amount of aqueous solution of $(NH_4)6Mo_7O_{24}\cdot 4H_2O$ and dried at 120°C for 14 h; the dried material was calcined at 450° for 6 h and at 500 °C for 2 h in air. Then, the Mo/MCM-41 was impregnated with the required amount of $Ni(CH_3COO)_2\cdot 4H_2O$, also dried at 120° and calcined at 450° for 6 h and at 500 °C for 2 h in air. In the case of Mo/MCM-41, MoO_3 content was of 12 wt.% and, in the case of Ni-Mo/MCM-41 catalyst, the promoted NiO content was varied at 3, 6 and 9 wt.%, respectively. These catalysts are further referred to as Ni-Mo-0.25/MCM-41, Ni-Mo-0.50/MCM-41 and Ni-Mo-0.75/MCM-41, respectively, where 0.25, 0.50 and 0.75 are the Ni/Mo atomic ratio.

Nitrogen adsorption/desorption isotherm of the MCM-41 were measured at -196°C with a static volumetric instrument Quantachrome Autosorb Automated Gas Sorption System using liquid nitrogen. Prior to the measurement, the sample was outgassed at 100°C for 30 min and at 200°C for 2 h to a residual pressure below 133.32 . 10^{-10} MPa.

X-ray diffraction (XRD) patterns were collected at ambient atmosphere by a Bruker D8 Advance diffractometer with Cu K_a radiation (λ_{Cu} =0.1541 nm, 40 kV, 40 mA). The XRD patterns of the MCM-41 and the MCM-41 supported Ni-Mo catalysts were recorded at 2θ range of 1 - 6 ° and 1 - 60 ° with a step of 0.1 °.

The FT-IR spectra were collected on a Varian 3100 Excalibur Series spectrometer equipped with Michelson interferometer with dynamic and automatic alignment, using a ceramic light source (min 40 mW) at a 0.25 cm^{-1} resolution. Spectra were scanned in mid-IR region in the wavenumber range from 400 to 4000 cm^{-1} by reflection on Attenuated Total Reflection (ATR) mode using a diamond crystal.

The catalytic performance of the prepared Ni-Mo catalysts has been tested on thiophene HDS and 1-octene hydrogenation reactions. For measuring the catalytic performance of the No-Mo catalysts, a fixed-bed flow microreactor with an inner diameter of 3 mm and 200 mm length, connected to gas chromatograph, was used in case of the thiophene HDS and one with an inner diameter of 10 mm and 300 mm length was used in case of the 1-octene hydrogenation. For the thiophene HDS, 0.20 g of the catalysts were loaded in the microreactor and a mixture of i-octane (80 wt.%) and 1-octene (20 wt.%) was taken as feedstock. Prior to each HDS activity test, the sulfidation catalysts was made by injecting a mixture of i-octane and thiophene at a pressure and temperature of 0.35 MPa and 250°C, respectively, for 2 h. Following sulfidation of the catalyst, the HDS reaction has been carried out from 200 to 450°C, at a system pressure 0.35 MPa and at a H_2 flow of 85 cm^3, introducing 5 μL of the feedstock into the reaction system, for each HDS activity tests. On the other hand, for the hydrogenation, the catalyst bed of approximately 30 mm length was packed between two quartz wool layers in the center of the reactor. The reaction temperature was continuously measured with a thermocouple placed inside the reactor in the catalytic bed. For each activity tests, about 2 g of the Ni-Mo/MCM-41 catalysts were used and a mixture of i-octane (88 wt.%) and 1-octene (12 wt.%) was taken as feedstock. The catalytic hydrogenation activity was tested from 200 to 350°C, at 0.3 MPa pressure and at liquid hourly space velocity (LHSV) of 8 h^{-1}. The hydrogenation reaction products were quantitatively analyzed using a Varian 450-GC. The thiophene and 1-octene conversions were respectively calculated from the analysis results.

To reconfirm the catalytic performance of the MCM-41 supported Ni-Mo catalyst, tested with model compounds by using the microreactor, an extended hydrotreating reaction system was employed. The reaction system used in subsequence experiments simulates the industrial hydrotreating process. It consist of liquid and H_2 gas feeding section, a high pressure rector with the inner diameter of 24 mm and 400 mm length, respectively, the temperature of the catalyst bed in which can be precisely controlled by a heater with temperature controller, and a gas-liquid separator. Reaction zone volume was 20 cm^3. For MCM-41 supported catalyst testing in the extended reaction system, the Ni-Mo-0.75/MCM-41 was chosen and a commercial Ni-Mo catalyst supported on γ-alumina (0.1 - 1% NiO, 3 - 7% MoO_3, 92 - 96% Al_2O_3) was used for a comparative study under the same experimental conditions.

For hidrotreating studies, the FCC gasoline is used as a feedstock. Table 1 gives the important characteristics of the FCC gasoline used. To observe the influence of experimental conditions on the quality of reaction products, the reaction temperature was varied from 320 to 410°C and pressure of the reaction system was maintained at 0.5, 1.5 and 2.5 MPa, respectively. The H_2 constant flow rate was 1 L/min and LHSV varied at 4, 6, 8 and 10 h^{-1}, respectively. Each hydrotreating experiment was carried out at constant conditions. The quality of the FCC gasoline before and after the hydrotreating experiment was quantified by the sulfur content and the octane number. The sulfur content was measured using a Phillips MiniPal PW 4025 X ray fluorescence spectrometer, which was operated at 6.00 kV and 0.400 mA, following the SR ISO 8754 method. The octane number of the feedstock and hydrotreated FCC gasoline was determined on an IROX 2000 instrument.

Table 1

IMPORTANT CHARACTERISTICS OF THE FCC GASOLINE USED AS THE FEEDSTOCK.

Characteristic	FCC gasoline
Sulfur (wt.%)	0.1094
Density (g/cm^3)	0.823
Simulated distillation (°C)	45 - 250
Octane number:	
MON	81.6
RON	91.8
API	86.7

Results and discussions

Characterization of pure MCM-41 and Ni-Mo/MCM-41 catalysts

Figure 1 shows nitrogen adsorption/desorption isotherm of the MCM-41. The isotherm exhibits the typical shape of

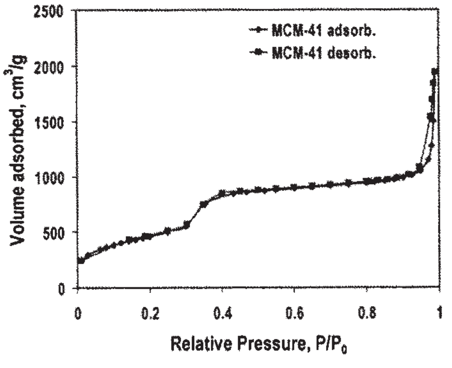

Fig. 1. N_2 adsorption/desorption isotherm of the MCM-41

type IV isotherm associated with MCM-41 mesoporous materials with finely ordered hexagonal structure.

The specific surface area of the MCM-41 calculated using the BET equation was 1690.81 m^2/g and its pore diameter calculated by the BJH method was 2.7 nm.

The XRD patterns of the MCM-41 supported catalysts in comparison with the low-angle ones of the pure mesoporous silica MCM-41 are shown in figure 2. The low-angle XRD pattern of the MCM-41 exhibits an intense peak corresponding to the (100) plane reflection at 2θ angle of 2.4° and two weak peaks at 4.0 and 4.4°, which are attributed to the diffraction of the (110) and the (200) planes, respectively. These peaks show the good long range ordered hexagonal structure of the prepared material. From the low-angle XRD patterns of the Ni-Mo catalysts, the disappearance of the characteristic peaks of the pure MCM-41 is observed, indicating the loss of its long range order after loading the catalytic active components. This suggests that the surface area, pore volume and pore size decrease after loading of the active components [15]. On the other hand, the XRD patterns of the catalysts in the range of 10 - 60^0 do not show any peaks corresponding to the catalytic active components, NiO and MoO_3, indicating that the added active components are finely dispersed in the support, and thus particle sizes of the active phases are below the detection limit of the XRD instrument used. The good dispersion of the active phases in the support indicates that the MCM-41 supported Ni-Mo catalysts have significantly high surface area. Also, this good dispersion suggests that MCM-41 can be used as the support material for the preparation of supported catalysts with high surface area and high dispersions. Even if the MCM-41 has lost its long range order due to the loading of the catalytic active components, it maintains its other initial properties such as high surface area and ordered mesoporous structure.

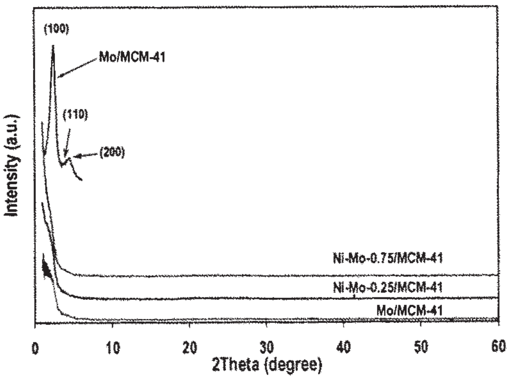

Fig. 2. XRD patterns of the MCM supported Ni-Mo catalysts and pure MCM-41

Figure 3 shows FTIR spectra of the Ni-Mo/MCM-41 as well as the pure MCM-41, recorded in the wavenumber range 400 – 2000 cm^{-1}. In the FTIR spectra of the MCM-41, there are four principal characteristic peaks for MCM-41 at 438, 812, 966 and 1055 cm^{-1}. Clearly visible peaks at 812 and 1055 cm^{-1} are assigned to the symmetric and asymmetric stretching vibrations, respectively, of the framework Si-O-Si [26]. A weak peak at 966 cm^{-1} reflects the stretching vibration of surface Si-O- groups and a intense peak at 438 cm^{-1} indicates the bending vibration of Si-O- groups [27]. In addition, there is a narrow peak at 3744 cm^{-1}, attributed to the symmetric stretching vibration of terminal isolate silanol (Si-OH) group (the results of peaks have not been shown in fig. 3). The FTIR spectra of the MCM-41 confirm that pure mesoporous silica with ordered hexagonal structure was obtained in the synthesis of the MCM-41. On the other hand, in the FTIR spectra of the MCM-41 supported catalysts, the peaks characteristic to the MCM-41 are clearly visible in wavenumber range observed. It is well known that the spectra between 900 and 1000 cm^{-1} give in details useful informations on the interactions between MoO_3 and MCM-41. In the spectra between 900 and 1000 cm^{-1} of the Mo/MCM-41, two weak peaks deviated from the peak relative to the MCM-41 are observed. The peak shifted to 955 cm^{-1} and new peak appeared at 926 cm^{-1} indicate existence of weak interaction between MoO_3 and MCM-41 and appearance of these peaks can be explained as a generation of Si–O–Mo linkage in the catalyst [28]. Moreover, visible peak at 1060 cm^{-1} correspond to the asymmetric Si-O-Si stretching vibration blueshifted of the Mo/MCM-41 catalyst, compared to the MCM-41. This blueshift of the asymmetric Si-O-Si stretching vibration should be due to the increase of the average length of Si-O in walls of the MCM-41, caused by the substitution of the Si ion of small size (radius 40 pm) by the Mo ion of large size (41 pm) [29]. Additionally, in case of the Ni-Mo-0.25/MCM-41 catalyst, the appearance of new peaks is attributed to the generation of Si-O-Ni bond at 974 and 940 cm^{-1} and blueshifted peaks corresponded to Si-O-Mo bond was observed in the spectra between 900 and 1000 cm^{-1}. Also, a new peak appeared at 1070 cm^{-1}. These blueshift appearance of the new peaks could be a proof of the presence of catalytic active components, NiO and MoO_3, finely dispersed in the support.

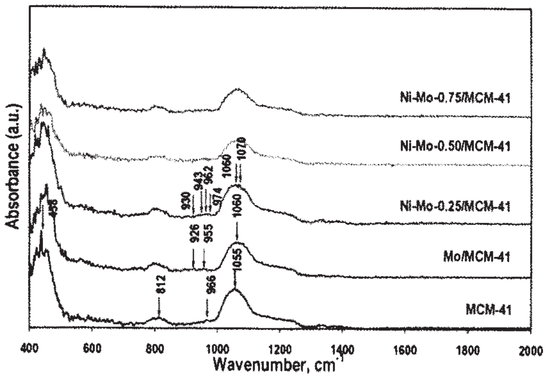

Fig. 3. FTIR spectra of the MCM supported Ni-Mo catalysts and pure MCM-41

HDS and hydrogenation activities of Ni-Mo/MCM-41 catalysts

The Ni-Mo catalysts supported on the MCM-41 were tested for the HDS of thiophene in the mixture prepared as model compound. Figure 4 shows thiophene conversion from 200 to 450°C over the catalysts. All the investigated catalysts have good activities for the HDS reaction of tiophene at reaction temperatures observed. The thiophene conversion increases with the increase of the reaction temperature, and moreover the catalyst with higher NiO content shows higher conversion of thiophene at the observed temperature. From figure 4 we can observe that the Ni-Mo-0.75/MCM-41 shows thiophene conversion up to100 % at 310°C, but the Ni-Mo-0.50/MCM-41 and Ni-Mo-0.25/MCM-41 show thiophene conversion up to 100 % at 410 and 450!, respectively. This fact suggests the increase of the dispersion of MoO_3 particles in the support with the increase of the NiO content. Ni-Mo-0.75/MCM-41 has best dispersion of the catalytic active components in the investigated catalysts. This is in good agreement with the XRD results above-mentioned.

In figure 5 it can be clearly observed that 1-octene conversion also increases with the increase of the reaction temperature for the Ni-Mo catalysts investigated and the

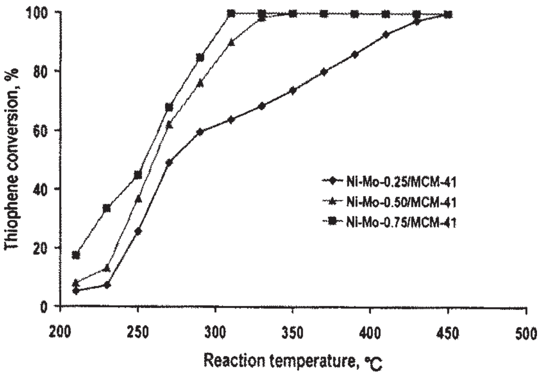

Fig. 4. Thiophene conversion over MCM-41 supported Ni-Mo catalysts with the reaction temperature

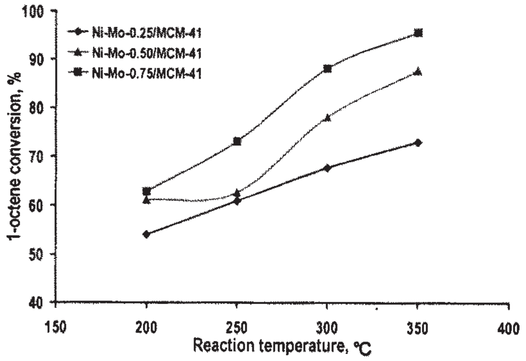

Fig. 5. 1-octene conversion over MCM-41 supported Ni-Mo catalysts with the reaction temperature

catalyst with higher NiO content shows better activity (up to 95%) for 1-octene hydrogenation at reaction temperatures, suggesting the good dispersion of the catalytic active components in the support.

Influence of reaction conditions on sulfur conversion in the extended system

Figure 6 shows the sulfur conversion depending on variation of LHSV at a temperature of 350°C, a system pressure of 2.5 MPa and a H_2 flow rate of 1 L/min. The HDS reaction of the FCC gasoline was carried out in the presence of the Ni-Mo-0.75/MCM-41 catalyst. The increase of the sulfur conversion until a maximum value, which is obtained at LHSV of 6 h^{-1}, is observed from figure 6, suggesting that in these conditions the HDS reaction is carried out in kinetic zone of the surface of the catalyst. Beyond this LHSV, the sulfur conversion is decreasing with the increase of LHSV. A possible explanation could be that a certain amount of the sulfur is not able to react with hydrogen because of a too short contact time at higher LHSV values.

The sulfur conversion as a function of the reaction pressure in the presence of the Ni-Mo-0.75/MCM-41 catalyst is given in figure 7. The HDS reaction was carried out at following conditions: a temperature of 350°C a LHSV of 6 h^{-1} and a H_2 flow rate of 1L/min. From figure 7 it is clearly observed that the sulfur conversion is not modified with the increase of the reaction pressure, suggesting that it has no significant influence on the HDS reaction of the FCC gasoline in the investigated pressure range.

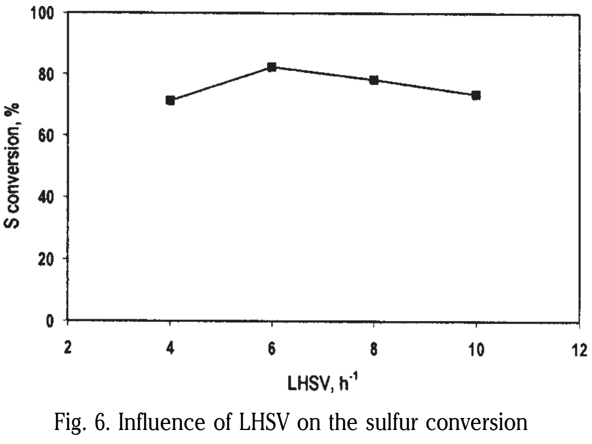

Fig. 6. Influence of LHSV on the sulfur conversion

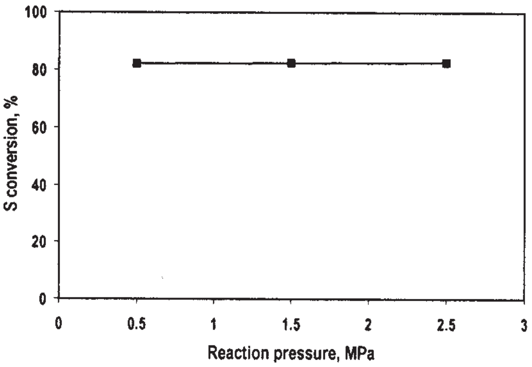

Fig. 7. Influence of reaction pressure on the sulfur conversion

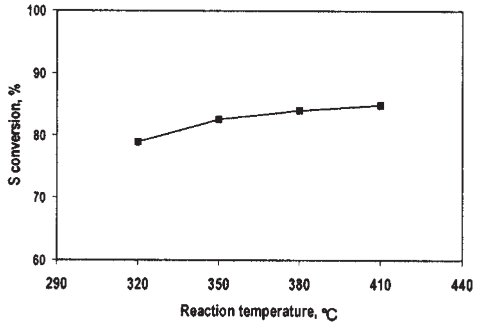

Fig. 8. Influence of reaction temperature on the sulfur conversion.

Figure 8 shows the influence of the reaction temperature on the sulfur conversion in presence of the Ni-Mo-0.75/MCM-41 catalyst. The HDS reaction was carried out at a reaction pressure of 2.5 MPa, a LHSV of 6 h^{-1} and a H_2 flow rate of 1 L/min. The sulfur conversion increases with the increase of the reaction temperature from 78.9 % at 320^0 to 84.9% at 410^0. These results are in good agreement with those obtained in the microreactor above-mentioned.

Comparative study of Ni-Mo/MCM-41 with commercial Ni-Mo/γ -Al_2O_3 catalyst

For practical applicability of the MCM-41 supported Ni-Mo catalyst, the comparative study was carried out with γ-alumina supported commercial Ni-Mo catalyst under the same experimental conditions. The experimental conditions were: constant system pressure of 2.5 MPa, LHSV of 6 h^{-1} and H_2 flow rate of 1 L/min and variable reaction temperature from 350 to 410°C. For each experiment, the catalyst volume in the reactor was 20 cm^3. The results obtained for both HDS catalysts are presented in figure 9 (catalyst activity) and figure 10 (octane number).

The sulfur conversion shows that the MCM-41 supported catalyst has higher activity than γ-Al_2O_3 supported at all the reaction temperatures tested (fig. 9). It is interesting to observe that at lower temperature (350°C) the HDS activity of the Ni-Mo/MCM-41 catalyst (sulfur conversion of 82.6 %) is significantly higher than that of the Ni-Mo/ γ-Al_2O_3 (sulfur conversion of 76.3 %), but at higher temperatures than 350°C, differences in the HDS activities between both catalysts decrease gradually. A possible explanation could be that the HDS activities reached in maximum at higher temperatures.

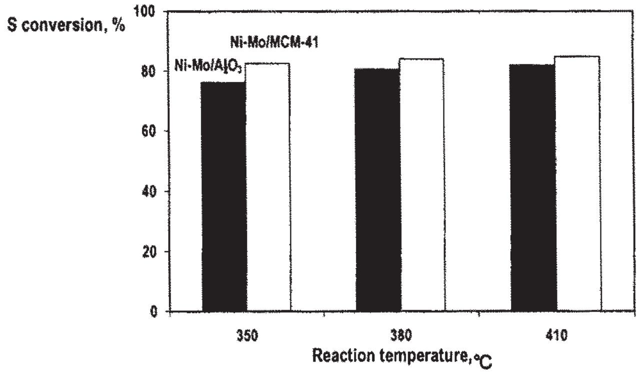

Fig. 9. HDS activities of MCM-41 and γ-Al_2O_3 supported catalysts

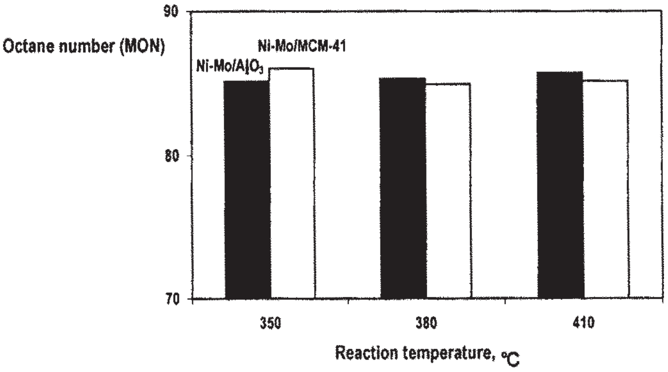

Fig. 10. Octane number (MON) of hydrotreated FCC gasoline over MCM-41 and γ-Al_2O_3 supported catalysts

From figure 10 it is observed that the octane number (MON) of the FCC gasoline hydrotreated at 350°C over the Ni-Mo/MCM-41 catalyst is higher than that of one hydrotreated at the same temperature over the Ni-Mo/γ-Al_2O_3 catalyst. However, the MCM-41 supported catalyst has octane number losses at higher temperatures than 350°C.

Conclusions

Synthesis of pure MCM-41 was carried out with C_{16} surfactant and mesoporous silica. Finely ordered hexagonal structure of pure MCM-41 was demonstrated by nitrogen adsorption/desorption isotherm, XRD and FTIR spectroscopy. Using BET equation and BJH method, specific surface area and pore diameter of the pure MCM-41 were calculated respectively: 1690.81 m^2/g and 2.7 nm. The XRD analysis of MCM-supported Ni-Mo catalysts shows that they have catalytic active components finely dispersed in the support due to its high specific surface area. The catalytic performance tests were carried out using model compounds in the microreactor over Ni-Mo/MCM-41 catalysts and they showed that these catalysts have high HDS and hydrogenation activities at all the temperatures observed. The Ni-Mo/MCM-41 catalyst with higher NiO content shows higher conversions of thiophene and 1-octene at the observed temperature. From comparative study it is clearly observed that catalytic performance of MCM-41 supported catalyst is better than that of commercial γ-alumina supported one, suggesting that MCM-41 with high specific surface area and uniform pore diameter could be a viable support for industrial hydrotreating catalyst.

Acknowledgements: This research has been supported by the doctoral program of Romanian Ministry of National Education (No. 37526/CMJ/22.11.2007, No. 38194/CMJ/12.05.2011).

References

1. SHIMADA, H., SATO, T., YOSHIMURA, Y., HIRAISHI, J., NISHIJIMA, A., J. Catal., 110, 198, p. 275.
2. V.GEORGESCU, D.BOMBOŞ, R.SCURTU, I.SPASOVA, D.MEHANDJIEV, L.DUMITRACHE, Rev. Chim. (Bucharest), **59**, no. 2, 2008, p. 243
3. TOPSOE, H., CLAUSEN, B.S., Appl. Catal., 25, nr. 1-2, 1986, p. 273.
4. SONG, C., Catal. Today, 86, 2003, p. 211.
5. COLLINS, N.A., HARANDI, M.N., MCGRAW, R.D., U.S. Patent 5401391, 1995.
6. DE LASA, H., HERNANDEZ, R., TONETTO, G., Industrial & Engineering Chemistry Research, 45, 2006, p. 1291.
7. CHICA, A., STROHMAIER, K., IGLESIA, E., Langmuir, 20, 2004, p. 10982.
8. CAERO, L.C., ROMERO, A.R., RAMIREZ, J., Catal. Today, 78, nr. 1-4, 2003, p. 513.
9. MAITY, S.K., RANA, M.S., BEJ, S.K., ANCHEYTA-JUAREZ, J., MURALI DHAR, G., PRASADA RAO, T.S.R., Appl. Catal. A: Gen., 205, 2001, p. 215.
10. MURALI DHAR, G., MASSOTH, F.E., SHABTAI, J., J. Catal., 85, 1984, p. 44.
11. MAITY, S.K., RANA, M.S., SRINIVAS, B.N., BEJ, S.K., MURALI DHAR, G., PRASADA RAO, T.S.R., J. Mol. Catal. A: Chem., 153, nr. 1-2, 2000, p. 121.
12. RANA, M.S., MAITY, S.K., ANCHEYTA, J., MURALI DHAR, G., PRASADA RAO, T.S.R., Appl. Catal. A: Gen., 268, nr. 1-2, 2004, p. 89.
13. MURALI DHAR, G., SRINIVAS, B.N., RANA, M.S., KUMAR, M., MAITY, S.K., Catal. Today, 86, 2003, p. 45.
14. RANA, M.S., CAPITAINE, E.M.R., LEYVA, C., ANCHEYTA, J., Fuel, 86, nr. 9, 2007, p. 1254.
15. SHI, G., FANG, D., SHEN, J., Microporous and Mesoporous Materials, 120, nr. 3, 2009, p. 339.
16. KHODAKOV, A.Y., ZHOLOBENKO, V.L., BECHARA, R., DURAND, D., Microporous and Mesoporous Materials, 79, nr. 1-3, 2005, p. 29.
17. RAMÍREZ, J., CONTRERAS, R., CASTILLO, P., KLIMOVA, T., ZÁRATE, R., LUNA, R., Appl. Catal. A: Gen., 197, nr. 1, 2000, p. 69.
18. MURALI DHAR, G., KUMARAN, G.M., KUMAR, M., RAWAT, K.S., SHARMA, L.D., RAJU, B.D., RAMA RAO, K.S., Catal. Today, 99, 2005, p. 309.
19. DONG, K.M., MA, X.M., ZHANG, H.B., LIN, G.D., J. Nat. Gas Chem., 15, nr. 1, 2006, p. 28.
20. SHANG, H.Y., LIU, C.G., XU, Y.Q., QIU, J.S., WEI, F., Fuel Processing Technology, 88, nr. 2, 2007, p. 117.
21. BECK, J.S., VARTULI, J.C., ROTH, W.J., LEONOWICZ, M.E., KRESGE, C.T., SCHMITT, K.D., CHU, C.T-W., OLSON, D. H., SHEPPARD, E.W., MCCULLEN, S.B., HIGGINS, J.B., SCHLENKERT, J.L., American Chemical Society, 114, nr. 27, 1992, p. 10834.
22. ZHAO, D.Y., FENG, J.G., HUO, Q.S., MELOSH, N., FREDRICKSON, G.H., CHMELKA, B.F., STUCKY, G.D., Science, 279, nr. 5350, 1998, p. 548.
23. TREWYN, B.G., SUPRATIM, G., SLOWING, I.I., LIN, V.S.Y., Chemical communications, 31, 2007, p. 3236.
24. TREWYN, B.G., NIEWEG, J.A., ZHAO, Y.N., LIN, V.S.Y., Chemical Engineering Journal, 137, 2007, p. 23.
25. CIUPARU, D., CHEN, Y., LIM, S.Y., YANG, Y.H., HALLER, G.L., PFEFFERLE, L., Journal of Physical Chemistry B, 108, 2004, p. 15565.
26. SELVARAJ, M., SINHAB, P.K., LEE, K., AHN, I., PANDURANGAN, A., LEE, T.G., Microporous and Mesoporous Materials, 78, 2005, p. 139.
27. AHMAD, A., RASID, H. M., FADZIL, A.H., RASHID, S. H., KASSIM, K., 2nd International Conference on Chemistry and Chemical Engineering, IPCBEE, vol.14, 2011, IACSIT Press, Singapore.
28. LI, Z., GAO, L., ZHENG, S., Materials Letters, 57, 2003, p. 4605.
29. SELVARAJ, M., LEE, T.G., Microporous and Mesoporous Materials, 85, 2005, p. 39.

Manuscript received: 14.03.2014