BULETINUL Universităţii Petrol – Gaze din Ploieşti	Vol. LX No. 4B/2008	95 -98	Seria Tehnică

Synthesis and Characterization of Mesoporous Mn-MCM-41 Molecular Sieves

Ana Maria Dogariu, Diana Luciana Cursaru, Dragoş Ciuparu

* Universitatea Petrol-Gaze din Ploieşti, Bd. Bucureşti 39, Ploieşti
e-mail: amdogaru@upg-ploiesti.ro

Abstract

This paper presents our investigation on the synthesis and characterization of Mn-MCM-41. Three catalysts with different total metal loading were prepared. The synthesized mesoporous materials were characterized using several techniques, such as: nitrogen physiosorption, UV-VIS spectroscopy, transmission electron microscopy and temperature programmed reduction (TPR). The aim of our investigations was to study the influence of the structure of the catalytic centers (Mn ions) on their oxygen release capacity.
Keywords: *mesoporous materials, manganese, MCM-41, TEM, TPR,UV-VIS*

Introduction

Since the discovery of the MCM-41 materials in the early 1990 s by Mobil Scientists[1-6] several studies concerning the preparation conditions, synthesis mechanism, characterization and use of these materials as catalysts and catalyst supports in various reactions, were reported [7]. In this paper, the structural and oxygen release properties of the MCM-41 with total metal loading of 1 wt %, 2 wt % and 3 wt% have been compared. For the characterization of oxide species we applied the TPR technique, UV-Vis Spectroscopy and nitrogen physisorption. UV-Vis spectroscopy is used in the study of interactions between metal and oxygen and support in a large number of catalytic systems [8-11].

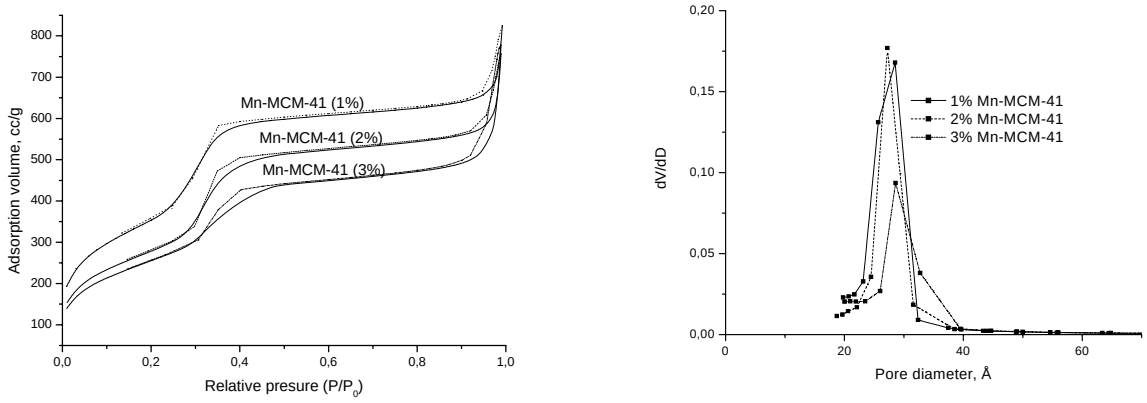
Experimental study

The first step, was the preparation process of catalysts, which is exemplified here for the sample C16-Mn-MCM-41 (2wt%). The surfactant solution was prepared using cethylmethylammonium bromide (CTMA Br) and deionized water to make a 20.0 wt % solution. The Amberjet 4400 OH anion exchange resin was added into the solution to exchange Br ions with OH ions. This process was performed under strong stirring. The resulting solution was filtered and ready for use. The silica source Cab-O-Sil was added to the tertramethylammonium silicate aqueous solution and the mixture was stirred with deionized water to improve mixing. The manganese aqueous solution (2 wt % $MnSO_4$ H_2O) was added and the solution was stirred for another 60 min. Two drops of antifoaming agent was added, followed by addition of the surfactant

solution. The pH was adjusted to 10.5 by adding acetic acid and the mixture was stirred for another 30 min. After mixing the synthesis solution was poured in a polypropylene recipient and placed in an autoclave for 6 days. After the solution was cooled to the room temperature, it was filtered and the resulting solid washed with deionized water and dried at the 348 K. The solid was heated at a constant rate from room temperature to 813 K under He, held for 1 h under the same condition and 5 h under air to remove the residual surfactant incorporated in the solid.

Results

Our next step was, the characterization of the three catalysts of Mn-MCM-41 (1wt%, 2wt%, 3wt% total metal loading). To determine how the incorporation of manganese affects the structure of MCM-41, the Mn-MCM-41 prepared was characterized by nitrogen physisorption. Nitrogen adsorption – desorption isotherms were measured at 77.253 K with an ASAP analyzer. Adsorption – desorption isotherms characterize the structure of the resulting material. Figure 1 shows the nitrogen adsorption - desorption isotherms. The higher the slope, the pore are more uniform. This can be further translated into pore size distributions obtained using the BJH method. From figure 1 we can tell the sample with 1wt% and 2wt% Mn loading have rather good structure. All three samples show the MCM-41 structure, however, the increase of the manganese content seems to lead to the loss of the pore structure. This can be easily confirmed by the evolution of BET surface aria of the pore volume with the manganese content data presented in Table 1.



a b

Fig. 1. Nitrogen physisorption results for Mn-MCM 41 with 1 wt%, 2 wt% and 3 wt% total metal loading**:** a. Adsorption/Desorption isotherms; b. Pore size distribution

Table 1. Characteristics of Mn-MCM-41

Catalysts	BET surface area (m^2/g)	Pore volume (cm^3/g)
Mn-MCM-41 (1wt%)	1286.4664	1.050
Mn-MCM-41 (2wt%)	1013.6431	0.937
Mn-MCM-41 (3wt%)	932.5987	0.877

Temperature programmed reduction (TPR) is a powerful technique for studying the reduction behaviour of supported oxide catalysts quantitatively. In this study TPR was carried out to investigate the reduction behaviour of the manganese species in Mn-MCM-41. The stability and the reducibility of the Mn-MCM-41 samples prepared were investigated by temperature

programmed reduction using a CHEMBET (QuantaChrome) instrument. For a quantitative comparison, data from the three catalysts were normalized to the metal loading of each sample in Figure 2. The aria below each sample represents the oxygen release capacity of each samples. As expected, the total oxygen release capacity increases as the concentration in the sample increases, thus a better performance is expected in oxidation reactions for samples with higher Mn content.

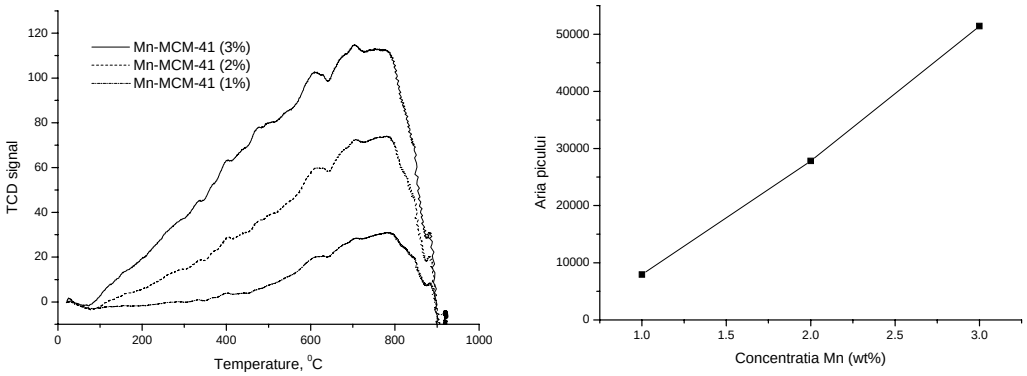


Fig. 2. Temperature Programmed Reduction profile for Mn-MCM 41 sample (1 wt%, 2 wt% and 3wt%)

Anchoring of the complex on MCM-41 surface was also followed by diffuse reflectance UV-VIS spectroscopy. The spectra were recorded between 190-1000 nm on a SPECORD 250-222 P 108 and the results are presented in figure 3.

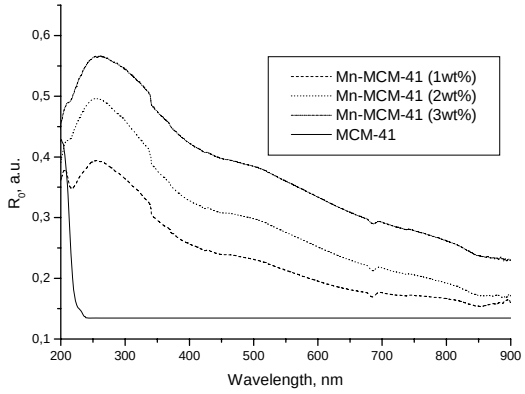
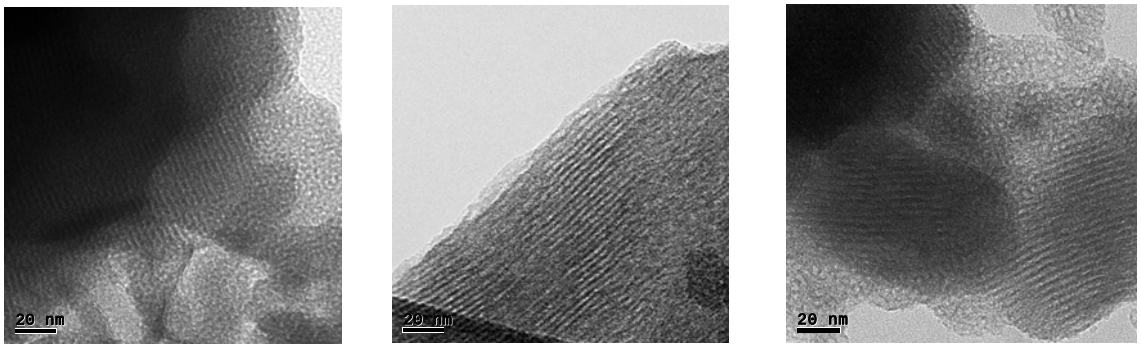


Fig. 3. Diffuse reflectance UV-VIS spectra for Mn-MCM 41 sample (1 wt%, 2 wt% and 3wt%)

The spectra of MCM-41show no obvious absorption in the region of 200-900 nm. The UV-VIS spectra of the prepared catalysts show a main absorption band centered near 250 nm and a wide band about 500 nm which covers almost all the visible range of the spectrum. According to the literature, absorption near 250 nm is associated with $O^{2-} \rightarrow Mn^{2+}$ charge transfer transition [12,13].

The most powerful tool to image nanoscale materials remains transmission electron microscopy with atomic scale resolution. In our work we used the TEM images to evaluate the pore structure of MCM-41. Images collected for our samples are presented in figure 4, and shows long range order of the synthesized materials for all samples, samples with 1wt% and 2wt% Mn loading showing slightly better structure than the one with 3wt%.



a **b** **c**

Fig.4. TEM images of the Mn-MCM-41 catalyst with: a -1 wt%, b - 2 wt% and c - 3 wt% total metal loading

Conclusions

Mesoporous materials were successfully prepared with Mn isomorphously substituted for Si ions in the silica matrix of MCM-41 materials. The synthesized Mn-MCM 41 materials showed good structure and narrow pore size distribution. Mn-MCM-41 samples show good oxygen release capacity suggesting potential for applications in oxidation reactions.

Acknowledgements

This work was partially founded by the Romanian Authority for Scientific Research under grant number 51-006-PNCDI 2/2007.

References

1. Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmith, K.D., Chu, C.T.W., Olson, D.H., Sheppard, E.W., McCulle, S.B., Higgins, J.B., Schlender, J.L., *J. Am. Chem. Soc.* 114, **1992**, 10834.
2. Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C., US Patent 5, 102, 643, 1992.
3. Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C., US Patent 5, 098, 684, 1992.
4. Beck, J.S., Chu, C.T.W., Johnson, I.D., Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C., US Patent 5, 108, 725, 1992.
5. Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C., Beck, J.S., Nature 1992, 359, 710.
6. Beck, J.C., US Patent 5, 057, 296, 1991.
7. Selvaraj, M., Sinha, P.K., Lee, K., Ahn, I., Pandurangan, A., Lee, T.G., *Microporous and Mesoporous Materials* 78 2005, 139.
8. Lim, S.; Haller,G. L. *Journal of Physical Chemistry* B 2002 , 106,8437.
9. Lim,S.; Ciuparu,D.; Pak,C.; Dobek,F. ; Chen, Y. ; Harding,D. ; Pfefferle,L.; Haller,G. *Journal of Physical Chemistry* B 2003, 107, 11048.

Sinteza şi caracterizarea sitelor moleculare mezoporoase de tipul Mn-MCM-41

Rezumat

În această lucrare sunt prezentate rezultatele experimentale în ceea ce priveşte sinteza şi caracterizarea Mn-MCM-41. Au fost preparate trei şarje de catalizatori cu diferite concentrații de metal înglobare respectiv 1wt%, 2wt% şi 3wt%. Materialele mezoporoase au fost caracterizate prin: reducere programată de temperatură, adsorbție fizică, spectroscopie UV-VIS si TEM.