

SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF X (wt.%) MoO₃/MCM-41 CATALYSTS FOR ETHYLBENZENE DEHYDROGENATION

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HOA HUU THU¹, NGUYEN DINH DUY², DOAN THI HONG MINH³, NGUYEN THANH BINH¹

¹*Faculty of Chemistry, VNUH*

²*Faculty of Petroleum Chemistry, University of Mine and Geology*

³*Institute for Conservation of Monument*

ABSTRACT

Two catalysts series of x (wt.%) MoO₃ (x=3; 6; 9) oxides dispersed onto the surface of MCM-41 support by different methods: solution impregnation and solid-state thermal spreading were prepared and characterized by XRD, N₂ adsorption-desorption, SEM, TEM. MoO₃ loading influences on catalysts morphology. The catalytic activity and selectivity of these catalysts in vaporous phase dehydrogenation of ethylbenzene to styrene were studied. The results showed a high activity and selectivity of catalyst having MoO₃ loading of 3 wt. % obtained by precursor solution impregnation method.

I - INTRODUCTION

Hexagonal mesoporous material MCM-41 is being used as a catalyst support even it does not have such a widespread range of applications as alumina support [1]. Up to now, there are a lot of works which have exploited the support properties of MCM-41 as its replacement for classical supports [2 - 4]. The majority of studies of MCM-41 as supports were focused on the immobilization of homogenous catalysts on the surface of MCM-41 [1]. Besides, some metal oxides loaded on MCM-41 material have been used as base catalysts, specially, the transition metal oxides deposited on and in the pores of MCM-41. Their catalytic behaviours range from oxidation to acid-base catalysis. These transition metal oxides need to be highly dispersed under nanometer size in order to exhibit a good catalytic activity. To achieve this, the following conditions must be fulfilled [1]:

The entire catalytic phase must be located inside the pore system of MCM-41 and there must be minimal blocking of the host's pore system by the catalytic phase dispersions at high loading.

It is observed that MoO₃ shows a highly catalytical activity in ethylbenzene dehydrogenation reaction to styrene-an important monomer in petrochemistry. MoO₃ dispersion on the surface of MCM-41 may obtain the better performance of the catalyst in reaction in question. Up to now there are not to much information about the interaction between the catalytic phase MoO₃ and the support MCM-41; but, Li et al. [5] showed that the critical dispersion capacity of MoO₃ on the surface of MCM-41 was 26 wt.%. The ordered porous structure of MCM-41 will be destroyed when the loading of MoO₃ exceeded this critical dispersion value [1].

In this report, two series of x wt.% MoO₃/MCM-41 (x=3; 6; 9%) catalysts were

synthesized following two methods: solution impregnation and solid-state thermal spreading, and the ethylbenzene dehydrogenation was chosen as a model reaction to test their catalytic activity and selectivity in styrene.

II - EXPERIMENTAL

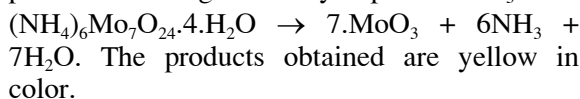
1. Catalyst preparation

a) Support preparation

The mesoporous silica support MCM-41 was prepared according to the published method [6] using $C_{16}H_{33}N(CH_3)_3Br$ (CTAB) as the template, $Si(OC_2H_5)_4$ (TEOS) from Aldrich (purity $\geq 98\%$) as the silicic source, and the pH of synthesis solution from 9 to 11. The samples obtained were calcined at $550^\circ C$ in a flow of air for 5h in the post-synthesis treatment to eliminate the template.

b) MoO_3 wet impregnation onto MCM-41

The solution with 0.01 M ammonium molybdate, $(NH_4)_6Mo_7O_{24}$ precalculated was added to MCM-41 as-treated. The mixture was stirred at room temperature for 4h then let the sample over night. The solid obtained was dried at $110^\circ C$ in an oven for 4h and then calcined at $550^\circ C$ for 6h. The reaction following takes place for forming the catalytic phase MoO_3 :



c) Solid \square state thermal spreading process

The dried template-free MCM-41 and a desired amount of molybdenum trioxide were carefully mixed at room temperature and then calcined in air at $550^\circ C$ for 6h.

2. Catalyst characterization

The obtained solids were characterized by XRD (HUT—PCM Bruker D8 diffractometer, Germany), N_2 adsorption—desorption (Micromeritics ASAP 2010, USA), SEM (JEO_JSM_5410LV, Japan), TEM (JEOL-JEM 1010, Japan).

3. Catalytic reaction

The ethylbenzene dehydrogenation reaction

to styrene was performed in a catalyst fixed bed reactor with vapor phase flow of ethylbenzene; the reaction temperature was maintained constant, a space velocity of $1.86 h^{-1}$. The products of reaction were analysed by GC-HP 6890 with detector MS. HP5689, USA.

III - RESULTS AND DISCUSSION

MCM-41, a member of the M41S family, has been widely investigated, because of the relative ease of synthesis, the simple structure and controllable pore size. There are several factors that affect the physical structure of MCM-41 such as the mol ratio of each component in the synthesis solution, autoclaving time and temperature, pH, silica source. In present work, the mol ratio of components $TEOS/CTAB/H_2O = 0.0226/0.0066/3.7222$ in the synthesis solution was maintained constant, pH modified from 9 to 11. The solids obtained were analysed by small angle X-ray diffraction method. The results of XRD pattern analysis have showed the sample obtained at pH 11 and reflux of synthesis solution exhibits at the peaks about 4° corresponding to reflections of regular hexagonal pores (Fig. 1a) while the sample obtained at pH 11 and maintained in autoclave at $125^\circ C$ for 12h gave 4 peaks corresponding to reflections of MCM-41 published (Fig. 1b) with a lattice parameter $a_0 = 49.1 \text{ \AA}$.

Figure 2(a) presents SEM micrograph of this MCM-41. It is easily observed that the material obtained having the relative same particles size, approximately $1 \mu m$. Its transmission electron micrograph (Fig. 3) shows the ordered structure with hexagonal arrangement of channels.

The results of the N_2 adsorption-desorption measurements following BET method of the sample (2a) showed:

BET surface area: $809.58 \text{ m}^2/\text{g}$

Pore volume: $0.67 \text{ cm}^3/\text{g}$

Pore size: 33.03 \AA .

All results presented above have affirmed the formation of MCM-41 mesoporous material on which the different contents of MoO_3 were supported in obtaining x(wt.%) $MoO_3/MCM-41$

($x = 3; 6; 9$) catalysts in two manners: $\text{Mo}_7\text{O}_{24}^{6-}$ precursor solution impregnation and MoO_3 solid-state thermal spreading at 550°C for 6h. All these catalysts have been calcined in air before performing ethylbenzene

dehydrogenation reaction to styrene. The reaction was done at temperature of 500°C , space velocity of 1.86 h^{-1} . The results of obtained products analysis were represented in the table 1.

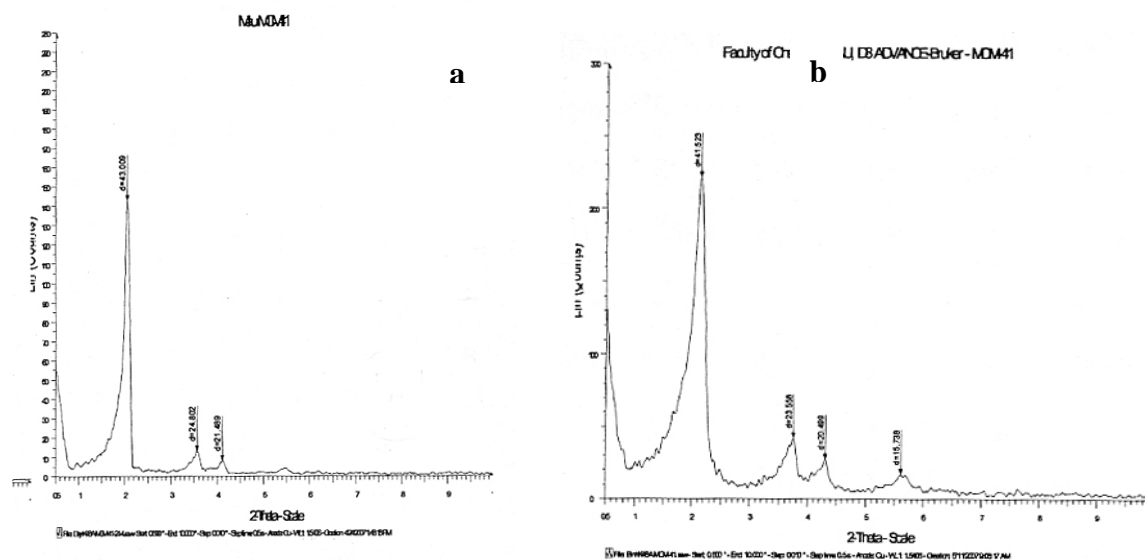


Figure 1: Small angle XRD patterns of MCM-41 sample obtained at pH 11 and reflux of synthesis solution for 24h (a) and the sample obtained at pH 11 in autoclave at 125°C for 12 h

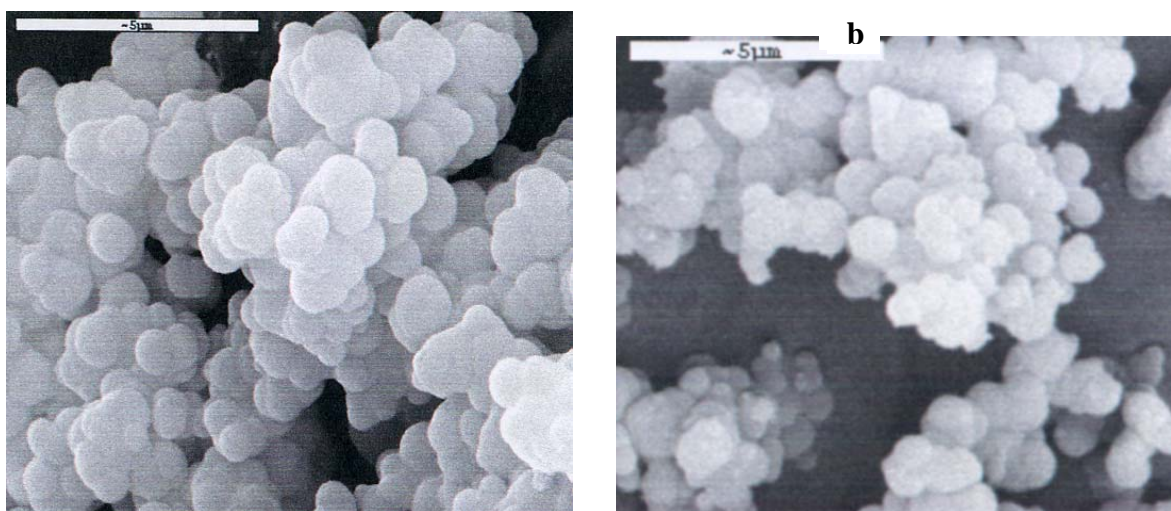


Figure 2: SEM micrographs of MCM-41 samples: (a) MCM-41 obtained at pH 11, in autoclave at 125°C , for 12h; (b) MCM-41 obtained after loading 3% MoO_3

It is observed that the $x \text{ (wt.\%)} \text{MoO}_3/\text{MCM-41}$ catalysts obtained by precursor solution impregnation method exhibit better performance

in ethylbenzene dehydrogenation reaction compared with the ones obtained by solid-state thermal spreading. This maybe is interpreted

that in impregnation process, the precursors and the solvents have diffused into the pores of MCM-41 support, and then the solvent was eliminated in calcinations, the precursors were decomposed and formed catalytic phase onto internal surface of pores. With small concentration of MoO₃, in the case of 3 wt.% MoO₃, this catalytically active phase has been formed under the form of nanostructure monolayer in interaction chemical with surface of the pores resulting decrease of pore size increasing MoO₃ content. This explanation may observe on SEM micrograph of MCM-41 sample loading 3wt.% MoO₃ (Fig. 2b). In the same time, the catalyst sample of 3wt.% MoO₃/MCM-41 (I) gave the best performance compared with the others: 6wt.% MoO₃/MCM-41(I) and 9wt.% MoO₃/MCM-41(I). Thus, when MoO₃ loading increases, the aggregation of nanoparticles conducted to the bigger particles blocking the diffusion of reagent molecules into the pores of MCM-41 support, so resulting conversion of ethylbenzene decreased (see table1). The x wt.% MoO₃/MCM-41 (S)** (x = 3; 6; 9) catalysts obtained by solid-state thermal

spreading exhibit conversion not high, may be due to the MoO₃ small particles could not expand on internal pores surface of MCM-41 support in calcination process at 550°C.

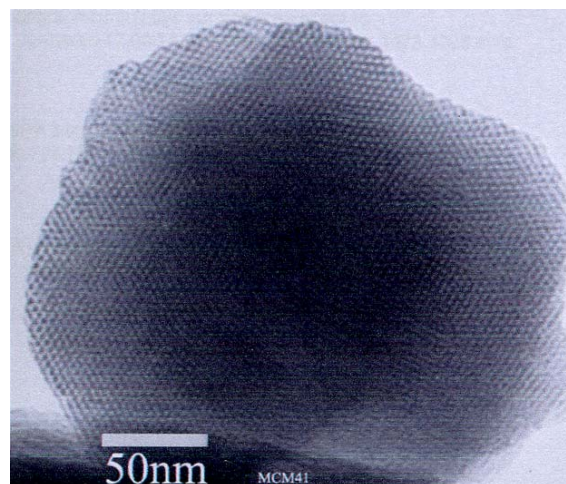


Figure 3: TEM micrograph of MCM-41 obtained at pH 11, in autoclave at 125°C, for 12h

Table 1: Results of ethylbenzene dehydrogenation reaction to styrene over x (wt.%) MoO₃ supported-MCM-41 catalysts, at 500°C, space velocity 1.86h⁻¹

Catalyst	Ethylbenzene conversion, %	Selectivity in styrene, %	Yield, %
3% MoO ₃ /MCM-41 (I)*	25.43	84.18	21.40
6% MoO ₃ /MCM-41 (I)*	24.96	81.60	20.37
9% MoO ₃ /MCM-41 (I)*	24.67	78.67	19.41
3% MoO ₃ /MCM-41 (S)**	9.56	40.62	3.88
6% MoO ₃ /MCM-41 (S)**	11.71	36.85	4.31
9% MoO ₃ /MCM-41 (S)**	11.88	35.48	4.21

*: Catalysts obtained by precursor solution impregnation method

** : Catalysts obtained by solid-state thermal spreading of MoO₃, at 550°C, for 6h.

IV - CONCLUSIONS

MCM-41 support material was synthesized from silicic source Si(OC₂H₅)₄, template CTAB in autoclaving at 125°C, pH 11 for 12h and eliminated the template at 550°C for 4h. MCM-41 obtained exhibited a surface area BET of

809m²/g, pore volume 0,67cm³/g and pore size of 33.03 Å.

The loading MoO₃ on the MCM-41 supports was conducted following two maners: precursor solution impregnation and solid-state thermal spreading. The catalysts obtained by precursor solution impregnation method

exhibited a better performance in ethylbenzene dehydrogenation reaction compared with the ones by solid-state thermal spreading one wherein the 3(wt.%) MoO₃/MCM-41 (I) catalyst gave the best performance.

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