PREPARATION OF MCM-48 MESOPOROUS MOLECULAR SIEVE INFLUENCE OF PREPARATION CONDITIONS ON THE STRUCTURAL PROPERTIES

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Mesoporous MCM-48 molecular sieves were synthesized using cetyltrimethylammonium bromide (CTAB) as template and tetraethylorthosilicate (TEOS) as silica source. In order to investigate the influence of synthesis condition on the structural properties of MCM-48 obtained, the samples were characterized by X-ray diffraction (XRD), nitrogen adsorption-desorption and scanning electron microscopy (SEM). The results showed that the preparation conditions influenced the properties of MCM-48 silica. This silica showed spherical morphology with a specific average surface area of 1000 m^2/g.

1. Introduction

From the first discovery of this new family of mesoporous sieves by Mobil scientists in 1992, a great interest was targeted on their properties. This M41S material including MCM-41, MCM-48 and MCM-50 have attracted attention mostly in separation and catalysis [1]. M41S materials possess especially large and uniform well-defined pores whose diameter can be varied in the range of approximately 15-100Å. Large channels form these materials with very regular pore openings ordered in different arrays hexagonal (MCM-41), cubic (MCM-48) and lamellar (MCM-50) [2]. This mesoporous molecular sieves exhibited good catalytic behavior in many reactions such as cracking, isomerization, alkylation, hydrogenation, hydroxylation and carbonylation etc. This family of mesoporous sieve can be used in environmental analysis for adsorption and separation [3, 4], as a support material for catalyst [5-7] and template for production of nanostructured carbon [8].

Due to their strong acidity and high hydrothermal stability, composite molecular sieves with bi-pore structure have some potential applications in fine chemical and petrochemical industries [9]. Among this M41S family, MCM-48 is a three-dimensional channel system. MCM-48 has severable advantages compared to other members of M41S family; this can be exemplified by its behavior in catalytic application showing less diffusion limitations making them more resistant to pore blocking [2]. Usually, mesoporous MCM-48 molecular sieves are synthesized by hydrothermal method in basic medium. The synthesis of MCM-48 required relatively long reaction time and rigorous conditions.

Gaydhankar et al. [10] synthesized MCM-41 and MCM-48 using three different source of silica: fumed silica (99% SiO_2) ethyl silicate (40% SiO_2) and silica sol (40% SiO_2). The nature of the silica seems to influence the structural development, textural stability and morphological properties. The type of silica source was found to control the magnitude of the wall thickness and in turn the structural stability of highly ordered of MCM-48 material. Taralkar et al. [2] have indicated that synthesis time is a crucial parameter, which influences the unit cell parameter. Zhao et al. [9] found that the addition of fluoride ions can improve the ordering of the mesoporous phase in the composite. Wang et al. [11] added SO_4^{2-}, NO_3^-, or Cl^- into synthesis system to reduce

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reaction time and to enhance the stability of MCM-48. Thus, the purpose of this work was to describe systematic and comparative studies on synthesis of mesoporous MCM-48 molecular sieves, varying different synthesis parameters, such as stirring time and temperature.

2. Experimental

2.1. Chemicals used

Cetyltrimethylammonium bromide CTAB (98%, Aldrich) was used as the structure directing agent and tetraethyl orthosilicate TEOS (98%, Aldrich) as source of silica. Deionized water, ethanol C_2H_5OH (99,2% Chemical) and aqueous ammonia solution NH_4OH (20% Chemical) were used as reagents for the synthesis.

2.2.MCM-48 synthesis

In a typical synthesis of mesoporous MCM-48 molecular sieve, 5.2 g CTAB were added to 240 ml of deionized water and 100 ml of ethanol under stirring. After the solution turned clear, 24 ml of aqueous ammonia solution was added to the system and it was allowed to mix for 5 min. After that, 7.2 ml TEOS were poured into the solution immediately under vigorous stirring. Stirring was continued for 15 h at room temperature. The solid product was recovered by filtration and dried at room temperature over night. The dried materials were calcined at 560^0C for 6 h in order to remove the surfactant molecules.

2.3.Characterization

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractmeter with CuKα radiation in the 2θ range of 1°-10° at scanning rate of 1°/min. N_2 sorption isotherms at 77 K were recorded with an automatic Quantachrome Autosorb Gas Sorption system. BET surface and pore distribution were determined from the desorption isotherms. The morphology of the sample was examined using a scanning electron microscope Quanta.

3. Results and discussion

3.1. Influence of stirring time during synthesis

Mesoporous MCM-48 silica were prepared under magnetic stirring at 2h, 9h and 15h respectively, to explore the optimum synthesis conditions to obtain silica with high ordered mesostructure.

The XRD patterns of MCM-48 materials calcined at different temperatures (520^0C, 560^0C and 600^0C) are shown in figure 1. All the samples calcined at 560^0C showed two major diffraction peaks, which correspond to the planes (211), (220). For all calcined samples, the d spacing values for the plane decreased as calcinations temperature increased conclusion mentioned also in other research [12]. The samples synthesized at short reaction time 2 h showed the greatest decrease. Their structure is not well defined when the synthesis time is short (in this case 2h). The temperature of 520^0C is not proper to complete the define mesoporous structure. This behavior indicates that when reaction time increased the structure is more define and stable. According to the same researchers, a longer stirring time is required to promote the silica condensation. Also, the sample synthesized at 15 h revealed a high-ordered structure combine with the formation of MCM-48 silica.
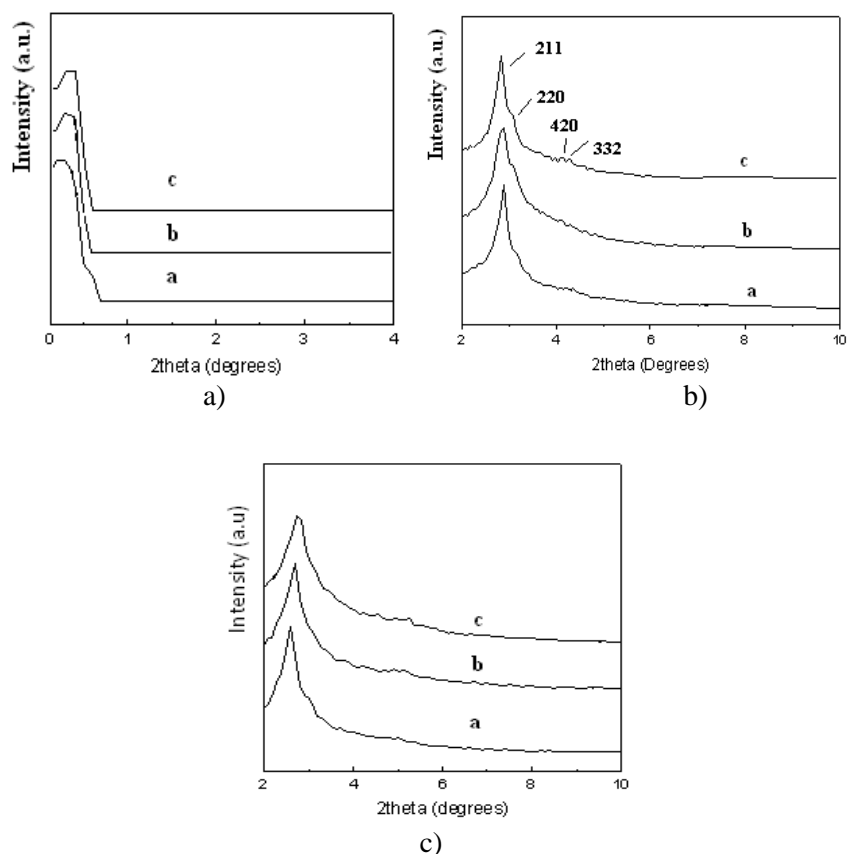
a)

b)

c)

Fig.1. XRD patterns of calcined MCM-48 synthesized at different stirring preparation time:
a. *2h b. 9h and c. 15 h. Calcination temperatures (a) 520^0C (b) 560^0C (c) 600^0C*

3.2. Nitrogen adsorption-desorption

The nitrogen adsorption-desorption isotherms and pore size distribution of some MCM-48 silica synthesized at different conditions are presented in figure 2. The isotherms are type 4 and also present a condensation step in the relative pressure range of 0.2-0.3 which is correlated with capillary condensation in the channels of the mesoporous sieve. All sample showed an average pore diameter under 2.5 nm.

The BET surface area, the pore volume and average pore size is presented in table 1. High specific surface area (1028.95 m^2/g) was obtained for the sample with synthesis time 15 h. It is worth mentioned that the synthesized MCM-48 at room temperature was stable under calcinations at high temperature for 6 h.

Table 1. Surface properties of the catalysts.

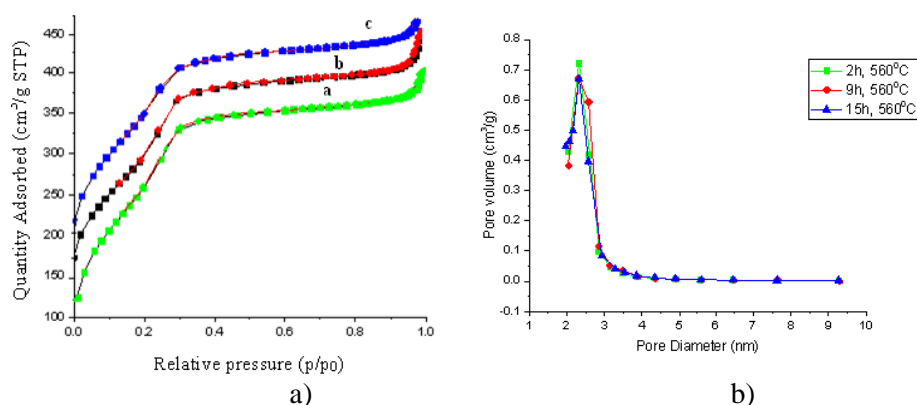| Sample	Synthesis time (h)	Calcination temperature (^0C)	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
MCM-48	2h	560^0C	946.60	0.61	2.58
MCM-48	6h	560^0C	958.71	0.62	2.61
MCM-48	15h	560^0C	1028.95	0.69	2.68

Fig.2. Nitrogen adsorption-desorption isotherms and pore size distribution for MCM-48 synthesized at different stirring time (a) 2h (b) 9h and (c) 15 h and calcinations temperature 560^0C

3.3. Thermal stability

In order to investigate the thermal stability of the synthesized MCM-48 with 15 h reaction time, the mesoporous sieve was treated at different calcinations temperature. We mentioned that the samples were kept 6 h at the corresponding temperature.

From figure 3 it can be seen that when MCM-48 was treated at 520^0C the structure was not define justifying the necessity of a higher temperature. However, at temperatures of 560^0C and 600^0C no significant changes were observed in the XRD patterns. Therefore MCM-48 prepared at room temperature has a defined thermal stability upon $520-540^0C$.
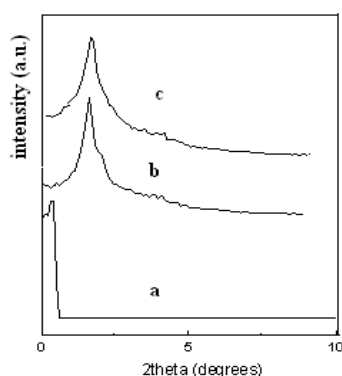

Fig.3. XRD patterns of calcined MCM-48 at a temperature of (a) 520^0C (b) 560^0C and (c) 600^0C.

3.4. Morphology studies

Scanning electron microscopy (SEM) is used to determine the particle shape, particle morphology and particle size distribution of samples.

The SEM micrographs of the mesoporous MCM-48 sieve are shown in figure 4. From the figures we clearly notice that the MCM-48 silica has spherical morphology. These spheres are uniform with sizes 200 nm. As literature mentioned [12] this spherical particle morphology may be due to the presence of ammonium hydroxide.
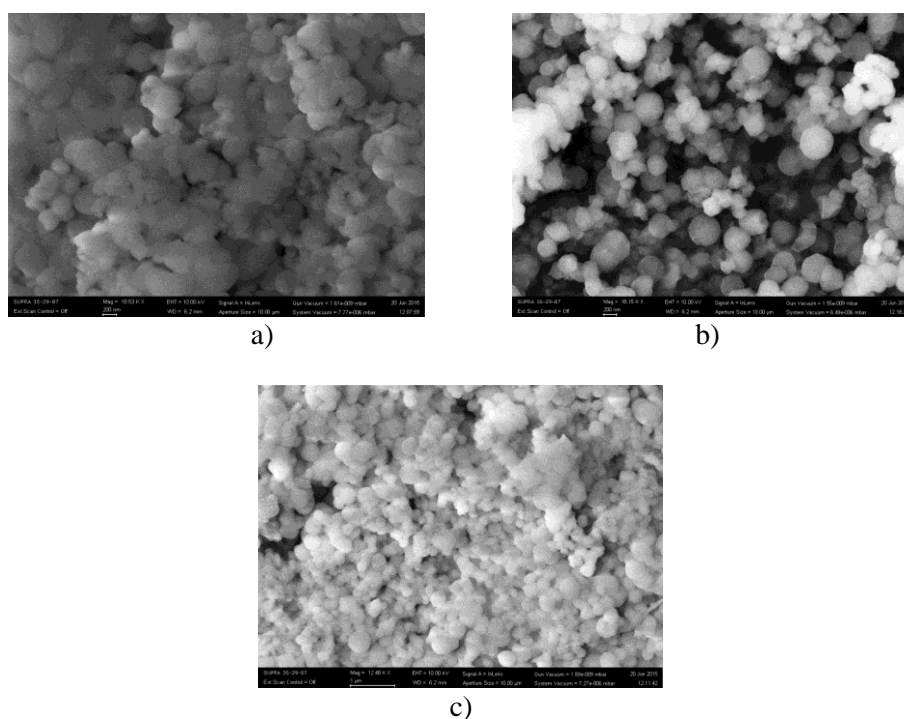
a)

b)

c)

Fig.4. Scanning electron micrographs of the MCM-48 synthesized at different calcination temperature (a) 520^0C (b) 560^0C and (c) 600^0C at synthesized time stirring of 15 h.

4. Conclusions

MCM-48 molecular sieve was successfully synthesis in different conditions and characterized by XRD, SEM and nitrogen adsorption-desorption analyses. The influence of synthesis variables as stirring time and calcination temperature on the structural properties of MCM-48 was investigated. According to the characterization results a reaction time of 15 h is correlated to obtain MCM-48 silica with higher thermal stability. These MCM-48 molecular sieves present a uniform size and spherical morphology with a surface area between 1028.96-946.60 m^2/g. Based on the results obtained and shape uniformity, MCM-48 silica itself or metal impregnated provide good activity for application in catalyzed processes.

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