Influence of hydrogel aging temperature in the formation of mesoporous molecular sieve MCM-48

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Usando duas temperaturas distintas de síntese 120°C e 150°C, a peneira molecular mesoporosa de fase cúbica, MCM-48, foi sintetizada hidrotermicamente. Para investigar o efeito da temperatura nas propriedades estruturais dos materiais chamados de MCM-48/120 e MCM-48/150 as amostras foram caracterizadas por difração de raios-X, adsorção-dessorção de nitrogênio e análise termogravimétrica (TG). Ambas as sínteses resultaram na fase cúbica MCM-48, contudo o material sintetizado na maior temperatura mostrou melhores características texturais como maior área superficial, volume e tamanho de poros.

Palavras-chave: Fase MCM-48; efeito da temperatura

Using two temperatures different of synthesis, 120°C and 150°C, mesoporous molecular sieve MCM-48 were hydrothermally synthesized. To investigate the effect of temperature on the structure properties of materials denoted as MCM-48/120 and MCM-48/150 were characterized by X-ray diffraction (XRD), N_2 adsorption-desorption and thermogravimetric analysis (TGA). Both samples resulted in cubic phase MCM-48, however the material synthesized at higher temperature showed better texturais characteristics as the highest surface area, pores volume and size.

Keywords: phase MCM-48; temperature effect

1. INTRODUCTION

Molecular sieves are crystalline solids materials with porosity defined able to differentiate molecules by their dimensions and geometries. The search for molecular sieves with bigger pore diameter aiming its catalytic application with larger dimensions molecules result in the synthesis of the one family mesoporous materials. The MCM-48 is a member of cubic crystalline structure of the family M41S, development by Mobil in 1992 [1]. The interest for these materials are in their versatile structures that presented pores systems one- and three-dimensional with diameter that can be from 15 to 100 Å, besides of their high specifics surfaces areas allowing great dispersion of one active phase [2, 3]. In despite of structural quality advantageous of MCM-41, member more studied in the family M41S, the three-dimensional structure of MCM-48 consisting of two independent and intricately interwoven networks of mesoporous channels is potentially more advantageous for catalytic applications compared with the pores systems one-dimensional, because it favors the diffusion of reactants and products through pores, it being less prone the deactivation [4-7]. The preparation of MCM-48 to require conditions a bit more rigorous of synthesis, variables such as pH, temperature, time, hydrogel composition and nature of starts chemicals, besides template removal conditions has been being of great importance in the production of cubic phase [8-10]. The hydrothermal treatment temperature reduction in the hydrogel aging, it keeping the texturais characteristics this material is one attractive factor of the point of view economic and environmental, since it would reduce in the energetic demand for its production. In the present study was investigated the effect of temperature variation on hydrothermal synthesis of mesoporous materials.

2. MATERIALS AND METHODS

The sample were synthesized through hydrothermal method in according to experimental procedure adapted of Doyle et al. and Souza et al.[11,12] in which was varied the gel aging

temperature in two conditions: 120 and 150°C. The synthesis were accomplished in Teflon flask of 75 mL, being puts in stainless steel autoclaves and then in the oven for hydrothermal treatment. The synthesis of Si-MCM-48 was carried out in a stage, starting from tetraethoxysilane (TEOS) as source of silicon, sodium hydroxide as mineraling agent, hexadecyltrimetthylammonium bromide (CTMABr) as template and distilled water as solvent. The chemicals were mixed to obtain a gel of molar composition: 0,55CTMABr:1,0SiO_2:0,5NaOH:101,4H_2O. In a typical synthesis, about 20 grams of gel was preparing dissolving 1.81g of CTMABr and 0.19g NaOH in 16.45g of water to form a clear solution. Then, 1.88g of TEOS was added in solution drop wise under stirring. The mixture was stirred during 30 minutes at 40°C, being observed the formation of white precipitated. The hydrogel was placed into teflon-lined autoclave and heated at 150°C for 24 hours. After this time, the autoclave was removed in the oven and cooled at room temperature, then was added sodium acetate in the rate of 1:3 (CH_3COONa/CTMABr) in order to stabilize the silica. Then the material was filtered under vacuum, washed with distilled water, dried at 100°C and calcined. This procedure is schematized in Figure 1. The same procedures were adopted for the synthesis in the smaller temperature.

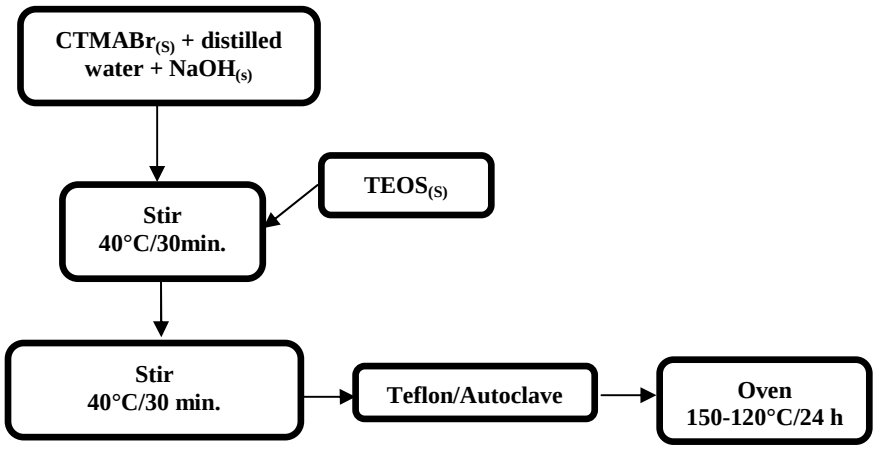

Figure 1. Scheme synthesis procedure of the MCM-48.

The samples were characterized by X-ray diffraction (XRD), N2 adsorption/desorption and thermogravimetric analysis (TGA). X-ray diffraction measurement was carried out in Rigaku (MiniFlex II) X-ray equipment using CuKα radiation in 2θ angle of 1.5 to 10° with step of 0.01°. Nitrogen adsorption and desorption isotherms were performed at 77 K by using a NOVA 1200e analytical system made by Quantachrome Corporation (USA) to determined the physical properties such as pore diameter, pore volume, pore wall thickness and surface area of calcined materials. The specific surface area (SBET) was calculated using the Brunauer–Emmett–Teller BET method for P/P_0 ranged between 0.05 and 0.30. Pore volumes determined by nitrogen adsorption at a relative pressure of 0.99 and pore size distributions from the branch adsorption isotherms by Barrett-Joyner-Halenda (BJH) method. Pore wall thicknesses were estimated with the expression wt = [a_0/3.0919 - Dp/2] for MCM-48 [13]. The thermal properties were carried out in Shimadzu equipment, TGA-50 model, using nitrogen as gas carrier flowing at 40 mL min^{-1}. The samples were heated from room temperature up to 900°C, at a heating rate of 10 °C min^{-1}.

3. RESULTS AND DISCUSSION

The Figure 2, show powder X-ray diffraction patterns of the resultant materials. In two syntheses there was the formation of the cubic phase MCM-48. One intense peak (211) and peaks designed for reflections (321), (400), (420) and (322) which are indexed for *Ia3d* space group. Besides, after calcination, both samples showed better pores ordering. The thermal

treatment increased the intensity of main diffraction peak (211), in which one were shifted a bit larger angles in 2θ, what can be related with a better structural ordered long-range pore.

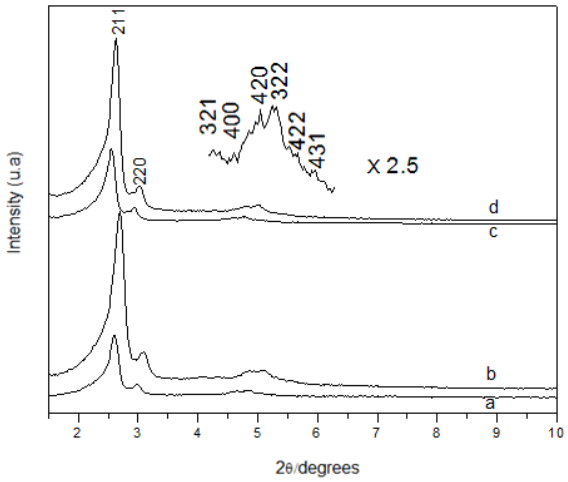

*Figure 2: Powder X-ray diffraction patterns of as-synthesized samples in **a** and **c**; and calcined samples in **b** and **d** for temperature of 120°C, bottom, and 150°C in top.*

The textural characteristics of the samples were determined by nitrogen adsorption-desorption and are showed in Table 1. The results indicate that sample synthesized at 150°C showed better textures properties as higher surface area and pore volume.

Table 1: Samples texturais characteristics of the MCM-48 synthesized at differents temperatures.

Sample	Specific Surface Area BET (m^2/g)	Total Pore Volume BJH (cm^3/g)	Diameter Pore BJH (nm)	Wall Thickness (nm)
MCM-48/ 120ºC	520	0,25	3,6	0,79
MCM-48/ 150ºC	647	0,35	3,6	0,85

In Figure 3, are showed the TG curves for samples MCM-48 as-synthesized, in which it is observed basically three values of mass loss. This stages are localized in the range of 30 to 124°C regarding the desorption of water physically adsorbed, one second loss of 124°C to 336°C attributed to surfactant thermal decomposition and the third loss of 336 to 640°C corresponding to residual surfactant decomposition and groups silanol condensation.

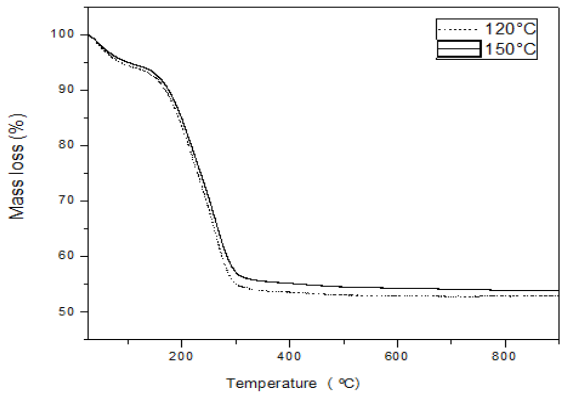

Figure 3: TG curves for uncalcined MCM-48 samples. In the dotted line the synthesis at 120°C; in the continuous line at 150°C.

4. CONCLUSION

The temperature effect study showed that mesoporous material of type MCM-48 can be obtained at lower temperatures than the conventional, this is a factor desirable for hydrothermal synthesis of mesoporous materials, because reduce the cost for production in large-scale. However, for catalytic applications, materials that have better texturais properties such as high surface area, larges pore diameter and volume pore, are highly desirables, mostly when the diffusional limitation of reactants and products is key stage in the process catalytic. Thus, for such applications is more advantageous the use of material synthesized under higher temperature hydrogel aging.

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