Optimization of MCM-48 synthesis using factorial design

(Otimização da síntese do MCM-48 usando planejamento fatorial)

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Abstract

MCM-48 mesoporous materials were hydrothermally synthesized according to the 2^2 factorial design by varying the crystallization time and temperature of the synthesis gel, and characterized by means of X-ray diffraction analysis and adsorption of N_2. In the crystallization temperature and time conditions used, specific areas between 924 to 1102 $m^2.g^{-1}$, pore volumes between 0.015 to 0.087 $cm^3.g^{-1}$ and pore diameters between 3.2 to 4.0 nm were obtained. It was observed that for the syntheses performed at high temperature, the crystallization time should be reduced so that the material structure is formed.
Keywords: MCM-48, 2^2 factorial design, crystallization temperature and time.

Resumo

O material mesoporoso MCM-48 foi sintetizado hidrotermicamente de acordo com o planejamento fatorial 2^2, variando-se a temperatura e o tempo de cristalização do gel de síntese, e caracterizado através de análise por difração de raios X e adsorção de N_2. Nas condições de temperatura e tempo de cristalização utilizadas, foram obtidas áreas específicas entre 924 a 1102 $m^2.g^{-1}$, volumes de poros entre 0,015 a 0,087 $cm^3.g^{-1}$ e diâmetros de poros entre 3,2 a 4,0 nm. Observou-se que, para as sínteses realizadas com temperatura elevada, deve-se reduzir o tempo de cristalização para que a estrutura do material seja formada.
***Palavras-chave**: MCM-48, planejamento fatorial 2^2, temperatura e tempo de cristalização.*

INTRODUCTION

The family of mesoporous silica molecular sieves designated as M41S with pore diameters between 2.0 and 10 nm is of considerable interest for various applications [1]. Depending on the synthesis conditions, different phases may be obtained, such as the hexagonal MCM-41, cubic MCM-48, as well as the MCM-50 lamellar compound. The MCM-48 molecular sieve has a cubic structure indexed in the Ia3d space group, having two continuous interpenetrating networks of chiral channels separated by an inorganic wall which follows a minimal surface gyroid. The three-dimensional open pore MCM-48 increases the number of interactions between reagents and catalytic sites, resulting in a higher activity and resistance to block pores [2-4]. The MCM-48 has proven to be efficient for applications in adsorption, catalysis, chromatography, and gas separation, among others.

The synthesis parameters used for mesoporous materials can give different characteristics to the material, so the choice of these parameters is of fundamental importance for improving materials to be applied in different areas [5]. The variations in temperature and reaction time influence the specific area, volume and pore diameter. The factorial design 2^n is used to obtain the best operating conditions in a system under study, carrying out this way fewer experiments and detecting interactions of important factors. The first step of this method consists in modeling that is done by adjusting the mathematical model to the experimental results obtained by factorial design [6-18]. It is added to the factorial design repeats in the central point in the experimental section, in order to establish a measure of pure error and stabilize the variance of the response. After this step, you can move along the adjusted response surface in order to locate regions fulfilling conditions of interest, calculating its extreme points. The aim of this study was to use the statistical analysis of the experiments associated with response-surface methodology to evaluate and optimize the

hydrothermal synthesis parameters of time and temperature in the formation of MCM-48, especially in the specific area, volume and pore diameter.

EXPERIMENTAL

Experimental design: the full factorial design 2^2 with triplicate central point was used to build the matrix of experiments. Seven experiments were performed, three of them repetitions at the central point. Table I shows the variables used in the design and combinations of upper (+) and lower (–) levels, and central point (0) for the variables used. The coefficients of the mathematical model were obtained after the analysis of the effects. The surfaces responses were obtained after evaluation of the mathematical model by ANOVA (analysis of variance).

Table I - Experimental matrix for MCM-48 synthesis.
[Tabela I - Matriz experimental para síntese de MCM-48.]

Experiment	Temperature (°C)	Time (h)
I	100 (–)	24 (–)
II	150 (+)	24 (–)
III	100 (–)	72 (+)
IV	150 (+)	72 (+)
Central point	125 (0)	48 (0)
Central point	125 (0)	48 (0)
Central point	125 (0)	48 (0)

Hydrothermal synthesis of MCM-48: the preparation of solid mesoporous MCM-48 type was performed using the hydrothermal method, following procedure described in [19] with the necessary adaptations, as reported in [20]. TEOS (Sigma-Aldrich) were used as the source of silicon, NaOH (Vetec) as the source of sodium, CTMABr (Vetec) as structural conductors and distilled water as the solvent. The molar chemical composition of the synthesis gel was obtained using the following formula: $0.25Na_2O$-$1SiO_2$-$0.55CTMABr$-$100H_2O$. The general synthesis procedure consisted in preparing a solution, without pH control, containing the driver structure and sodium hydroxide in the amount of water required for the synthesis. The solution was subjected to stirring at 50 °C to solubilize the structural conductors. The source of silicon (TEOS) was added and the solution remained stirring at 50 °C for 40 min. The material was transferred to a Teflon autoclave, which was jacketed by stainless steel. The reaction temperature and time were used according to the matrix of experiments for MCM-48 synthesis shown in Table I. The obtained material was calcined under synthetic air at 550 °C for 2 h.

Characterization: the synthesized samples were analyzed by X-ray diffraction (Shimadzu XRD, 7000) and the angle range used between 1° and 10° in order to verify the formation of hexagonal mesoporous structure; physical adsorption characterization with N_2 (Quantachrome Nova 2000) was used to evaluate the specific area (BET method), such as volume and pore size distribution (BJH method). The material presented better textural characteristics in that design was synthesized and used as adsorbent by [20] for the capture of CO_2.

RESULTS AND DISCUSSION

Figs. 1 and 2 show the X-ray diffraction (XRD) patterns of the calcined and uncalcined synthesized samples, obtained from the experimental matrix of Table I. The temperature adversely interacts with the crystallization time of the synthesis gel; this means that when moving from higher levels of both temperature and time simultaneously (150 °C for 72 h), there is no MCM-48 structure formation. Therefore, for high-temperature synthesis, one should reduce the reaction time so that the material structure is formed. In the syntheses performed at lower temperature levels and higher and lower levels of crystallization time, there was MCM-48 structure formation. The textural properties of synthesized samples such as surface area, pore volume and diameter, mesoporous structure parameter and wall thickness are shown in Table II.

Tables III, IV and V show the estimated effects for each factor (crystallization temperature and time) and interactions, as well as the p-value and the coefficients for constructing the mathematical model response to the specific area, pore diameter and pore volume, respectively. For the variable to be considered statistically significant, p-value should be below 0.05 (1-0.95) [6]. The p-values obtained (Table III) show that the variables of crystallization temperature and time did not significantly influence the increase in the specific area of the material and other factors can affect this parameter such as the stoichiometric amount of reagents. Under the crystallization temperature and time conditions used, specific areas were obtained between 924 to 1102 $m^2.g^{-1}$. According to the data in Table IV, it is observed that the p-values obtained are below 0.05, showing that the temperature and crystallization time variables used significantly influence the pore diameter of the synthesized materials. According to the data in Table V, it is observed that the p-values were greater than 0.05, showing that the variables of crystallization time and temperature did not significantly increase the pore volume of the material, as occurred for the specific area parameter.

Through the straight linear adjustment shown in Table IV, a mathematical model for the pore diameter was obtained (Equation A). According to this model, the optimal temperature and crystallization time values of the gel for further synthesis of MCM-48 can be obtained from the significant pore diameter. Its application allows for selecting the combination of maximized levels in getting the best response for every situation.

$$Dp = 3.546 + 0.122.t + 0.112.T + 0.503.t.T \qquad (A)$$

where, t represents the time in h and T the temperature in °C. To analyze the adjustment or reliability of the mathematical model, an analysis of variance (ANOVA) was conducted which shows the p-values (Table VI) for each variable

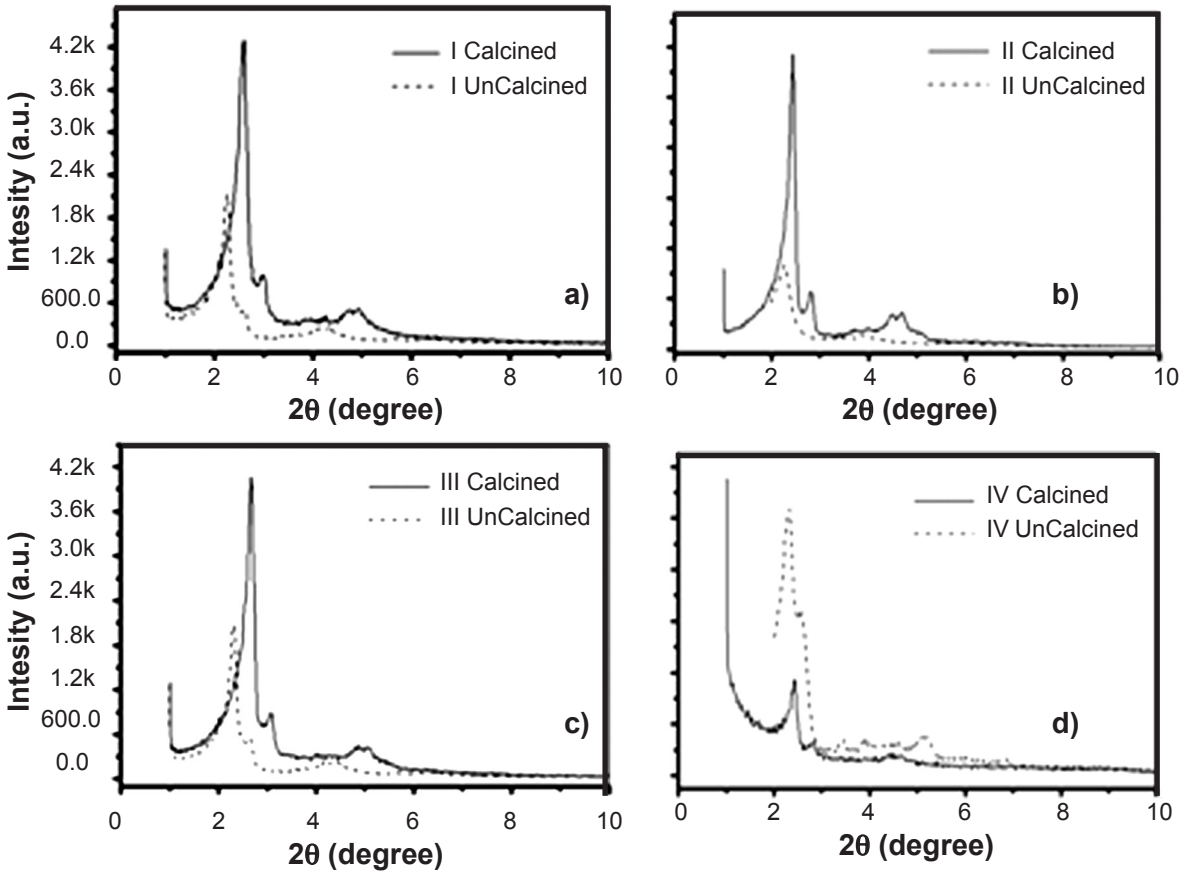

Figure 1: XRD patterns of samples related to experiments I and II, crystallization at 100 and 150 °C during 24 h, and experiments III and IV, crystallization at 100 and 150 °C during 72 h.
[Figura 1: Difratogramas de raios X das amostras referentes aos ensaios I e II, cristalização a 100 e 150 °C por 24 h, e aos ensaios III e IV, cristalização a 100 e 150 °C por 72 h.]

Table II - Textural properties of MCM-48 samples.
[Tabela II - Propriedades texturais das amostras de MCM-48.]

Experiment	a_0 (nm)	S_{BET} ($m^2.g^{-1}$)	Vp ($cm^3.g^{-1}$)	Dp (nm)	W (nm)
I	8.42	1008	0.026	4.03	0.71
II	8.88	924	0.087	3.25	1.23
III	8.64	1010	0.015	3.27	1.16
V	8.20	1080	0.068	3.25	1.06
VI	8.26	1102	0.062	3.27	1.08
VII	8.20	1067	0.065	3.26	1.08

Legend: a_0 - lattice parameter of mesoporous structure ($a_0 = d_{211}\sqrt{6}$), S_{BET} - specific area, Vp - pore volume, Dp - pore diameter, W - wall thickness.

Table III - Estimated effects of variables for the specific area parameter.
[Tabela III - Estimativa dos efeitos das variáveis para o parâmetro área específica.]

Factor	Effect	Standard deviation	p-value	Coefficient
Average	1167.457	49.673	0.00185	1167.457
(1) Time (h)	402.205	157.081	0.12464	201.103
(2) Temperature (°C)	215.806	157.081	0.30320	107.903
1 with 2	300.225	157.081	0.19613	150.113

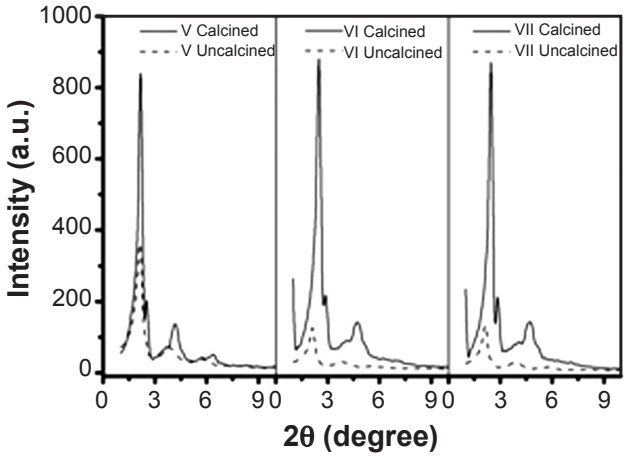

Figure 2: XRD patterns of samples related to experiments V, VI and VII, crystallization at 125 °C during 48 h.
[Figura 2: Difratogramas de raios X das amostras referentes aos ensaios V, VI e VII, cristalização a 125 °C por 48 h.]

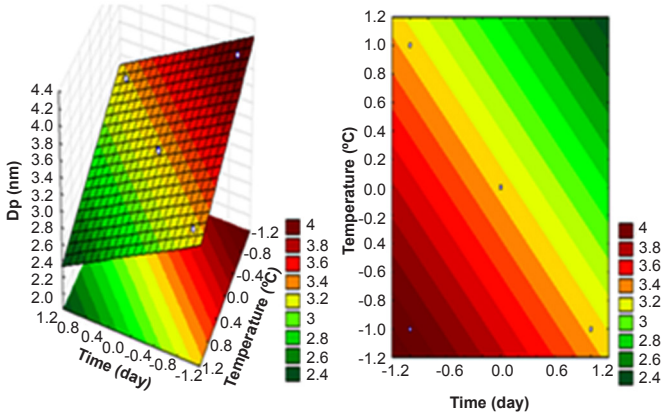

Figure 3: Response surface of the variables time and temperature as a function of Dp (pore diameter).
[Figura 3: Superfície de resposta das variáveis tempo e temperatura em função do Dp (diâmetro de poros).]

Table IV - Estimated effects of variables for the pore diameter parameter.
[Tabela IV - Estimativa dos efeitos das variáveis para o parâmetro diâmetro de poros.]

Factor	Effect	Standard deviation	p-value	Coefficient
Average	3.546	0.0023	0.000000	3.546
(1) Time (h)	0.243	0.0061	0.000618	0.122
(2) Temperature (°C)	0.225	0.0061	0.000722	0.112
1 with 2	1.006	0.0061	0.000036	0.503

Table V - Estimated effects of variables for the pore volume parameter.
[Tabela V - Estimativa dos efeitos das variáveis para o parâmetro volume de poros.]

Factor	Effect	Standard deviation	p-value	Coefficient
Average	0.0575	0.0139	0.0257	0.0575
(1) Time (h)	-0.0391	0.0368	0.3657	-0.0196
(2) Temperature (°C)	0.0332	0.0368	0.4331	0.0166
1 with 2	-0.0278	0.0368	0.5044	-0.0139

Table VI - Analysis of variance (ANOVA) for setting the mathematical model for the pore diameter parameter.
[Tabela VI - Análise da variância (ANOVA) para o ajuste do modelo matemático para o parâmetro diâmetro de poros.]

Source of variance	Quadratic sum	Degree of freedom	Mean square	p-value
(1) Time (h)	0.1744	1	0.1744	0.00021
(2) Temperature (°C)	0.1829	1	0.1829	0.00020
1 with 2	0.0000	1	0.0000	0.95098
Pure error	0.000073	2	0.000037	
Total	0.4972	5		

used for pore diameter results, which showed p-values <0.05. With respect to the value of p, it can be seen that the model is statistically significant, showing that the time and temperature exert significant influence on the MCM-48 synthesis.

After adjusting the model to the values of the experiment results, the response surfaces were obtained in order to verify the conditions for obtaining the MCM-48 with high pore diameter. The response surfaces were constructed for all possible combinations of the variables of temperature and crystallization time. A graph of the optimized response surface

to obtain the best pore diameter conditions is shown in Fig. 3. It can be seen that smaller pore diameters are obtained by higher levels of temperature and time, as can be seen in Table II. It also agrees with the XRD patterns where it was observed that for higher levels of temperature and time, there was no formation of the mesoporous structure. In the crystallization temperature and time conditions used, pore diameters between 3.2 to 4.0 nm were obtained.

CONCLUSIONS

It was observed that temperature interacts negatively with crystallization time when using higher levels of both time and temperature simultaneously. The estimated effects of time and temperature variables showed no significant influence on the increase of the specific area and pore volume of the material; however, it had significant influence on the pore diameter. Through the straight linear fitting it was possible to obtain the mathematical model from the pore diameter of interest, to determine the optimal crystallization temperature and time values of the gel for further MCM-48 hydrothermal synthesis.

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