Journal of Thermal Analysis and Calorimetry, Vol. 79 (2005) 493–497

THERMAL ANALYSIS APPLIED TO TEMPLATE REMOVAL FROM SILICEOUS MCM-48 NANOPOROUS MATERIAL

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The MCM-48 siliceous nanostructured molecular sieve was synthesized from a hydrogel, resulting in the following molar composition: $1SiO_2$:$0.25Na_2O$:0.65CTMABr:$60H_2O$. The cetyltrimethylammonium bromide (CTMABr) was used as structure template. Model-free kinetic algorithms were used to study the optimum conditions of template removal and to estimate the apparent activation energy of ca. 178 kJ mol^{-1}.

Keywords: *MCM-48, model-free kinetics, nanostructured molecular sieve, TG*

Introduction

The silica based M41S materials discovered by Mobil Company in the early nineties [1, 2] are very interesting class of nanoporous materials. These materials can be applied as supports, adsorbents and catalysts in the chemical industry. The presence of aluminum in the MCM-48 structure can generate similar superficial acidity to zeolitic materials [3]. The MCM-41 silica whose pore structure consists of hexagonally packed cylindrical channels has been by far the most studied material. Owing to its three-dimensional pore structure, the M41S cubic mesophase, known as MCM-48, may be more advantageous than MCM-41 to catalytic and adsorption properties due to its better accessibility in the pore system [4, 5]. On the basis of X-ray diffraction (XRD) and transmission electron microscopy (TEM) studies, it was shown that MCM-48 materials possess a bicontinuous structure centered on the gyroid minimal surface that divides available pore space into two non-intersecting sub volumes [5]. The formation of the MCM-48 phase occurs according to the liquid crystal template (LCT) mechanism, in which tetrahedral SiO_4 units react with the surfactant template under hydrothermal conditions [2]. A typical preparation of the siliceous MCM-48 material needs basically a solvent, a template (surfactant molecule) and a silica source. Many papers [6–10], have studied the influence of synthesis variables on the formation of MCM-48 phase. Variables such as pH, temperature, time, gel composition and nature of the starting materials have been of a great importance in the production of pure siliceous MCM-48 cubic phase.

After the synthesis of the mesoporous materials a calcination step was needed to remove the CTMA+ species from the pore system and to leave them with accessibility. High temperature favors a rapid cracking and elimination of the template species; however, it can be destroying the ordered silica structure. The study of the optimal time and temperature for template elimination is an important variable in the final preparation of the MCM-48 material. In this paper, thermogravimetry was used to evaluate the optimal time and temperature to remove the template of the MCM-48 material after the hydrothermal synthesis. The Fig. 1 shows the bicontinuous system of pores of MCM-48 (these pores can vary of 10–100 Å in diameter) before and after the calcination. On the left side the presence of the species of CTMA$^+$ micelles can be observed inside of the pores and on the right side the same material with the pores free from the species of CTM$^+$ micelles.

Experimental

The siliceous MCM-48 was synthesized starting from tetraethylorthosilicate (TEOS, Aldrich), sodium hydroxide (Vetec), cethyltrimethylammonium bromide (CTMABr, Vetec) and distilled water. The chemicals were mixed to obtain a gel of the following molar composition: $1SiO_2$:$0.25Na_2O$:0.65CTMABr:$60H_2O$. The procedure used for a sample of 1.12 g of calcined MCM-48 was: (*i*) 4.12 g of TEOS, 0.392 g of NaOH and 10.48 g of water were placed in a 100 mL teflon beaker and stirred at 60°C for 2 h in order to get a clear liquid; (*ii*) a solution prepared from 4.694 g of cethyltrimethylammonium bromide and 10.98 g of dis-

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1388–6150/$20.00

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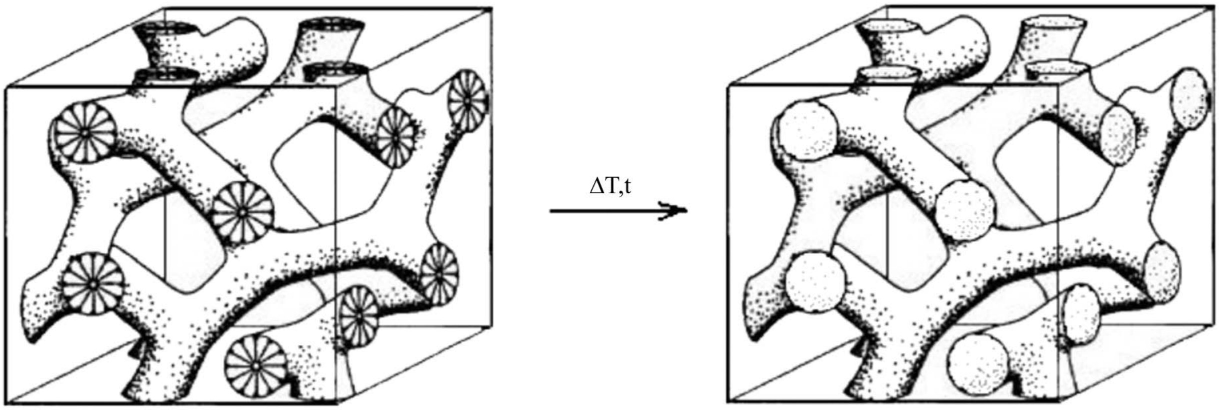

Fig. 1 Schematic representation of the three-dimensional pore structure of the MCM-48 before and after the calcination adapted of [4]

tilled water was added to the mixture (*i*) and aged for 30 min at room temperature. The hydrogel was placed into 45 mL teflon-lined autoclave and heated at 100°C for three days. The pH was measured each day and adjusted to 9–10 with a solution of acetic acid of 30% of concentration. Last day the sodium acetate (Carlo Erba) was added in the 1:3 molar proportion of CH_3COONa/CTMABr in order to stabilize the silica [14]. Thermogravimetric analysis was carried out in Mettler equipment, TGA/SDTA-851 model, using nitrogen as gas carrier flowing at 25 mL min^{-1}. The samples as-synthesized were heated from room temperature up to 900°C, at the heating rate of 5, 10 and 20°C min^{-1}. The Vyazovkin [11–13] model-free kinetics was used to evaluate the kinetic parameters of surfactant decomposition of the MCM-48 material, i.e. the activation energy and the conversion rates of surfactant degradation as the functions of temperature and time.

X-ray diffraction measurement was carried out in Shimadzu (XRD 6000) X-ray equipment using CuK_α radiation in the 2θ angle range of 1 to 10° with steps of 0.01°. For this analysis ca. 100 mg of the final material was washed with 25 mL of 2% HCl/CH_3CH_2OH [14] solution and subsequently calcined at 450°C for 1 h in nitrogen and for an additional hour in air flow of 80 mL min^{-1}. The calcination temperature was reached at a heating rate of 10°C min^{-1}. FT-IR spectra were obtained in a BOMEM equipment model MB100. Scanning electron microscopy (SEM) was obtained in a Philips XL30-ESEM microscope.

Results and discussion

pH values during synthesis

The siliceous MCM-48 material was synthesized by the hydrothermal method using the pH adjustment conforming to that reported elsewhere [14]. The initial pH value of the synthesized hydrogel was extremely basic (ca. 14). After one day, this value decreased to about 11–12. This suggests that the hydroxyl concentration in the synthesized gel decreases during the hydrothermal process due to self-assembly of the silica species. In order to control the self-assembly process, the pH was successively adjusted and maintained about 9–10 [14].

XRD

As shown in Fig. 2 the XRD patterns for the studied sample indicate characteristic peaks at 2θ of 2.62°, related to (211) Miller index, 3° related to (220) index and some others in the range from 3.5 to 6° at 3.97, 4.21, 4.73, 4.93, 5.16 and 5.42° with its respective indexes of (321), (400), (420), (332), (422) and (431) confirming the presence of a cubic mesophase of the three dimensional pore structure. The XRD patterns of the synthesized samples are similar to those of siliceous MCM-48 materials presented in [15, 16].

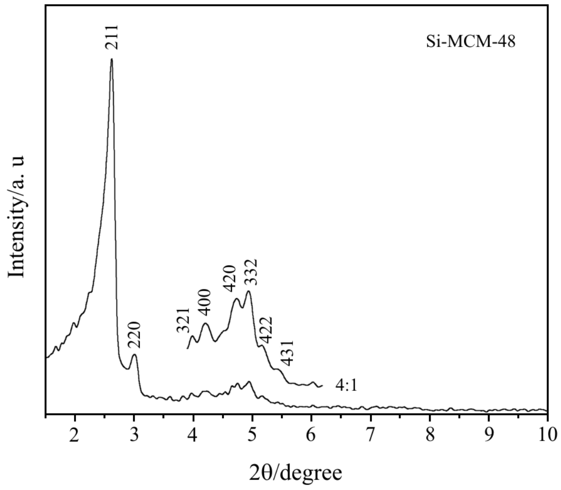

Fig. 2 XRD powder pattern of the siliceous MCM-48 material

Thermal analysis

In [14, 17] it was previously reported that thermogravimetric analysis of MCM-41 and MCM-48 materials (Fig. 3a) after the synthesis in nitrogen

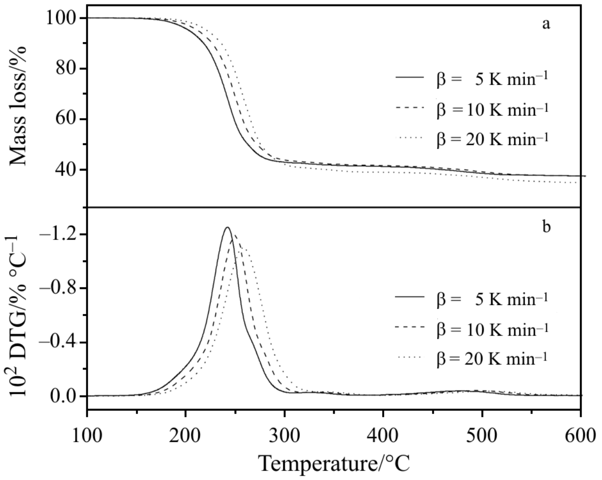

Fig. 3 a – TG curves for unwashed MCM-48 sample synthesized with pH adjustment, obtained at different heating rates β_i=5, 10 and 20°C min^{-1} and b – corresponding DTG curves

atmosphere show basically four or more values of the mass loss. The steps of mass loss are located in the following temperature ranges: *i*) from 30 to 100°C (thermodesorption of physically adsorbed water); *ii*) from 100 to 300°C (surfactant decomposition); *iii*) from 300 to 520°C (residual surfactant decomposition and silanol condensation) and iv) from 520 to 800°C (residual silanol condensation). Figure 3b shows typical DTG curves of the siliceous MCM-48 material at heating rates of 5, 10 and 20°C min^{-1}.

Kinetic evaluation

After the synthesis the next step to obtain the siliceous MCM-48 phase is the calcination. In this step the product is heated to the given temperature in the gas flow. The total removal of the template is mainly function of these variables. High temperature favors a rapid template removal, but a temperature excess can cause the destruction of MCM-48 structure. Vyazovkin [11–13] developed an integral method of model-free kinetic analysis which at multiple heating rates allows to evaluate both simple and complex reactions kinetics. The rate of the chemical reactions depends of the conversion (α), temperature (T) and time (t). The analysis is based on the isoconversion principle, which states that at a constant conversion the reaction rate is a function of the temperature only. In the typical experiment it is necessary to apply at least three different heating rates (β) and the respective conversion curves are evaluated from the measured TG curves. For each conversion (α), $\ln(\beta/T_\alpha^2)$ plotted *vs*. $1/T_a$, gives a straight line with slope $-E_\alpha/R$ (Eq. (1)), therefore the activation energy (Fig. 4) is obtained.

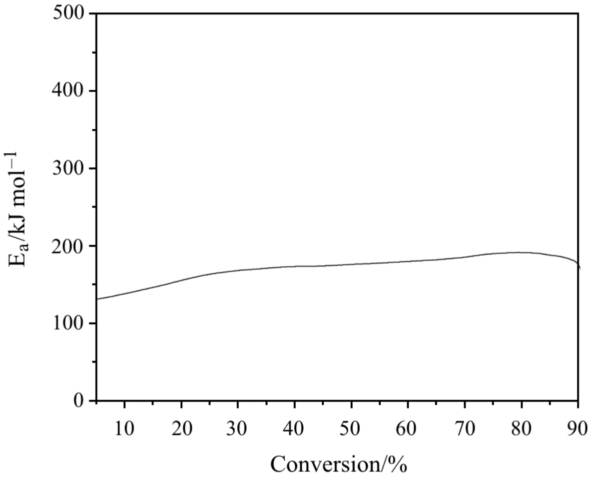

Fig. 4 Activation energy *vs*. conversion for CTMA$^+$ removal from the MCM-48 material

$$\ln \frac{\beta}{T_\alpha^2} = \ln\left[\frac{Rk_0}{E_\alpha g(\alpha)}\right] - \frac{E_\alpha}{RT_\alpha} \qquad (1)$$

The CTMA$^+$ removal of the MCM-48 material was evaluated by thermogravimetry, at heating rates of 5, 10 and 20°C min^{-1}. The Fig. 5 has shown the conversion curves at three different heating rates as function of the temperature.

The activation energy of the removal of CTMA$^+$ species was of 178±8.5 kJ mol^{-1} in the conversion range of 5 to 95%. Applying the obtained activation energy and using the model-free algorithms [11, 12] it was possible to get the isoconversion parameters (Table 1). The Table 1 shows the predicted values of the temperature of removal of the CTMA$^+$ as the function of the conversion and time. Thus e.g. to remove 95% of the template species in 90 min it is necessary to

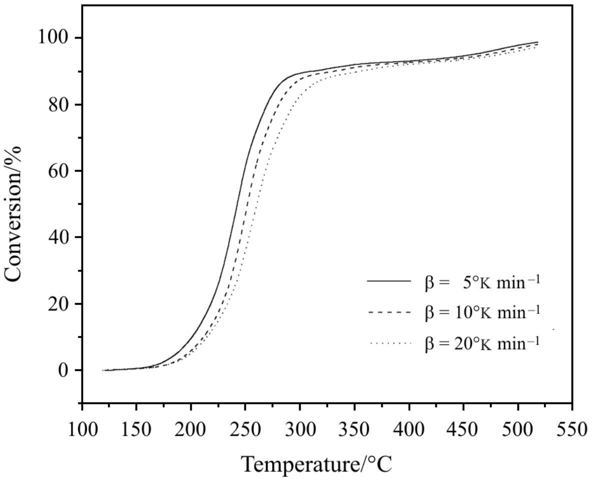

Fig. 5 Conversion curve of the thermogravimetric integral curves for different heating rates β_i=5, 10 and 20°C min^{-1}

Table 1 Temperature of removal of $CTMA^+$ from the siliceous MCM-48 as the function of time, for different conversion values

Time/min	α/%						
	10	30	50	70	90	95	99
10	184	211	225	238	293	428	481
20	177	204	216	228	272	414	469
30	173	199	211	223	260	407	461
40	171	196	208	219	253	401	456
50	168	164	205	216	247	397	452
60	167	192	203	213	242	394	449
70	165	190	202	211	238	391	446
80	164	189	200	209	235	389	444
90	163	188	199	208	232	387	442
100	162	187	198	206	229	385	440
110	161	186	197	205	227	383	439
120	160	185	196	204	225	381	437

reach 387°C and at the same time to remove of 99% the necessary temperature is 442°C. These values are comparative with values found for SiMCM-41 [18] and AlMCM-41 [19].

FTIR analysis

In order to evaluate the efficiency of the calcination process FTIR analysis was done with the aim to observe elimination of the $CTMA^+$ groups from the nanostructured materials [20]. Figure 6 shows the FTIR spectrogram of the siliceous MCM-48 material before and after its calcination. It can be observed that the $CTMA^+$ was fully removed from the mesoporous structure of the MCM-48. The spectra show the following vibration bands: 3750–3250 cm^{-1} hydroxyl groups on mesoporous structure; 3000–2850 cm^{-1} as stretching of C–H bonds of CH_2 and CH_3 groups on $CTMA^+$ species; 1466–1460 cm^{-1} as asymmetric deformation of CH_3-R bond, 1475–1470 cm^{-1} as deformation of CH_2 bond; and 1490–1480 cm^{-1} as asymmetric deformation of group methyl (CH_3–N^+); 1260–1240 cm^{-1} as asymmetric Si–O stretching; 1200–1000 cm^{-1} as internal asymmetric Si–O–Si stretching; 965–955 cm^{-1} as asymmetric CH_3–N^+ stretching and 850–800 cm^{-1} due to symmetric Si–O stretching. The structure of silica of MCM-48 possesses a potential load that after the calcination process can adsorb physically water (ca. 5%) of the atmosphere as observed in 1700–1550 cm^{-1}.

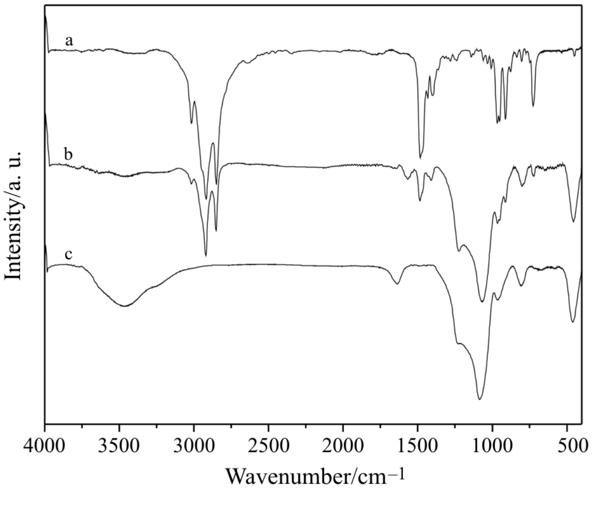

Fig. 6 FTIR spectra of the siliceous MCM-48 material; a – CTMABr; b – SiMCM-48 uncalcined and c – SiMCM-48 calcined

SEM analysis

In agreement with the XRD analysis in the Fig. 2 that shows typical peaks of pure siliceous MCM-48 phase, the Fig. 7 shows typical SEM of SiMCM-48 material. The particles presented dimensions in the range of 1–2 μm with similar forms of small plates, some interlinked ones. In agreement with Cheng and colla-

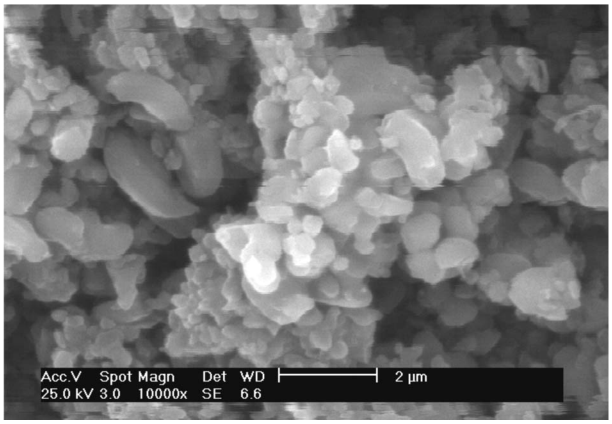

Fig. 7 SEM image for the SiMCM-48 sample with magnification of 10000×

borators [21] the growth of crystals in mesoporous materials can happen with formation of that structure type with crystals in the form of perfect hexagonal plates (ideal case), imperfect and irregular hexagonal plates (realistic case) and in other cases with shapes similar to rice grains.

Conclusions

The use of thermogravimetry in the monitoring of the $CTMA^+$ removal from the MCM-48 molecular sieve at different heating rates represents a good technique to obtain a high quality material after calcination. Under non-isothermal conditions, in which the sample was heated at three different and constant heating rates, the model-free kinetic analysis shows a good alternative to estimate the apparent activation energy of removal of the template species and prediction of the conversion and isoconversion parameters.

Acknowledgements

The authors acknowledge the support from the Agência Nacional do Petróleo (PRH/ANP-14), FINEP / CTPetro and Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq Process Number 300291/1993-0).

References

1 X. S. Zhao, G. Q. Lu and G. J. Millar, Ind. Chem. Res., 35 (1996) 2075.
2 J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Schmitt, C. T. W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, Y. B. Higgins and I. L. Schelenker, J. Am. Chem. Soc., 114 (1992) 10834.
3 A. O. S. Silva, M. J. B. Souza, J. M. F. B. Aquino, V. J. Fernandes Jr. and A. S. Araujo, J. Therm. Anal. Cal., 75 (2004) 699.
4 A. Sayari, Stud. Surf. Sci. Catal., (1996) 102.
5 A. Sayari, J. Am. Chem. Soc., 122 (2000) 6504.
6 W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, J. Am. Chem. Soc., 114 (1992) 10834.
7 A. S. Araujo, V. J. Fernandes Jr. and S. A. Veríssimo, J. Therm. Anal. Cal., 59 (2000) 649.
8 M. Kruk, M. Jaroniec, M. L. Penha and F. Rey, Chem. Mat., 12 (2002) 4434.
9 I. I. Gnatyuk, G. A. Puchkovskaya, Yu. G. Goltsov, L. A. Matkovskaya and M. Drozd, J. Therm. Anal. Cal., 62 (2000) 365.
10 A. S. Araujo, J. M. F. B. Aquino, M. J. B. Souza and A. O. S. Silva, J. Solid State Chem., 171 (2003) 371.
11 S. Vyazovkin and V. Goryachko, Thermochim. Acta, 194 (1992) 221.
12 S. Vyazovkin and A. I. Lesnikovich, Russ. J. Phys. Chem., 62 (1988) 2949.
13 S. Vyazovkin and C. A. Wright, Thermochim. Acta, 340 (1999) 53.
14 S. A. Araujo, M. Ionashiro, V. J. Fernandes and A. S. Araujo, J. Therm. Anal. Cal., 64 (2001) 801.
15 J. C. Vartuli, K. D Schmitt, C. T. Kresge, W. J. Roth, M. E. Leonowicz, S. B. Mccullen, S. D. Hellring, J. S. Beck, J. L. Schlenker, D. H. Olson and E. W. Sheppard, Chem. Mat., 6 (1994) 2317.
16 A. Sayari, Stud. Surf. Sci. Catal., 102 (1996) 1.
17 H. Landmesser, H. Kosslick, W. Storek and R. Fricke, Solid State Ionics, 101 (1997) 271.
18 M. J. B. Souza, A. O. S. Silva, J. M. F. B. Aquino, V. J. Fernandes Jr. and A. S. Araujo, J. Therm. Anal. Cal., 75 (2004) 693.
19 A. S. Araujo, V. J. Fernandes Jr., M. J. B. Souza, A. O. S. Silva and J. M. F. B. Aquino, Thermochim. Acta, 413 (2004) 245.
20 D. C. Calabro, E. W. Valyocsik and F. X. Ryan, Microp. Mesop. Mat., 7 (1997) 243.
21 C. F. Cheng, H. He, W. Zhou and J. Klinowski, Chem. Phys. Lett., 244 (1995) 177.