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THERMOGRAVIMETRY APPLIED TO CHARACTERIZATION OF SBA-15 NANOSTRUCTURED MATERIAL

Ana Carla S. L. S. Coutinho[1]*, Solange A. Quintella*[1]*, A. S. Araujo*[1*]*, Joana M. F. Barros*[1]*, Anne M. G. Pedrosa*[1]*, V. J. Fernandes Jr.*[1] *and M. J. B. Souza*[2]

[1]Federal University of Rio Grande do Norte, Department of Chemistry, 59078-970 Natal, RN, Brazil
[2]Federal University of Sergipe, Department of Chemical Engineering, 49.000-000 São Cristovão, SE, Brazil

Nanoporous silica with narrow pore size distribution has attracted increasing attention as a novel material for separations and reactions involving large molecules. SBA-15 has been synthesized in an acidic medium using a triblock copolymer as template. In this work, the SBA-15 was synthesized by the hydrothermal treatment at 373 K for 48 h, of a gel with the following overall molar composition: 1.0TEOS:0.017P123:5.7HCl:193H$_2$O, where TEOS is tetraethyl orthosilicate and P123 is poly(ethylene oxide, propylene oxide and 1,4-dioxane). The obtained material was characterized by thermogravimetry, X-ray diffraction, infrared spectroscopy and BET surface area. A kinetic study using the model free model was accomplished in the stage of decomposition of the template (P123). The obtained value of the apparent activation energy was ca. 131 kJ mol^{-1}.

Keywords: *model-free kinetics, SBA-5, thermogravimetry*

Introduction

Since mesoporous molecular sieves such as hexagonally ordered MCM-41 were discovered by Mobil Corporation Scientists in 1992 [1, 2], surfactant-templated synthetic procedures have been extended to include a wide range of compositions, and a variety of conditions have been developed for exploiting the structure-directing functions [3]. In 1998, the so-called SBA-15 materials, characterized by thicker silica walls, have been prepared in an acidic medium using neutral triblock copolymers as template (Pluronic, triblock copolymer, poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide), $EO_xPO_yEO_x$, BASF) [3–5]. It has a more regular structure and a thicker channel wall than MCM-41, resulting in much higher thermal stability.

Figure 1 shows the three main components of a mesostructured hybrid (template, inorganic and solvent), connected by their binary relationships. This gives a first-order general picture of the important variables [6]. Alexandridis and coworkers established correlations between the cosolvent polarity and its location within each block, or the different interfaces [7, 8]. Using the solvent-polymer-cosolvent phase diagram, it is possible to design different mesostructures. The inorganic monomers or polymers can swell one of the blocks; therefore, the polarity of the inorganic species should affect the final mesostructure.

In the current work, the SBA-15 mesoporous molecular sieve was synthesized by the hydrothermal treatment using tetraethyl orthosilicate (TEOS) as source of silica, Pluronic P123–poly(ethylene oxide)–poly(propylene oxide)–poly(1,4-dioxane) as a template, hydrochloric acid and water. The obtained material was calcined, and then characterized by TG analysis, XRD and infrared spectroscopy. A kinetic study using the Vyazovkin model free kinetics [9–11] was accomplished in the stage of decomposition of the template (P123). The thermogravimetry was the main technique used for characterization of the SBA-15 material.

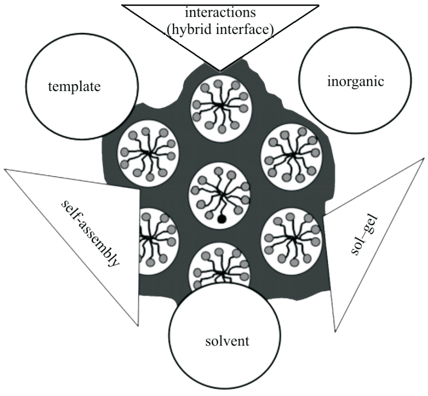

Fig. 1 Scheme of the main relationships between the solvent, the template and the inorganic center [6]

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* Author for correspondence: asa-ufrn@usa.net

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Springer, Dordrecht, The Netherlands

Experimental

The chemicals used to synthesize SBA-15 were triblock copolymer (Pluronic P123)–poly(ethylene oxide)–poly(propylene oxide)–poly(ethylene oxide)–$EO_{20}PO_{70}EO_{20}$ from BASF Co. (M_{av}= 5750 g mol^{-1}) as a template, hydrochloric acid fuming 37% p.a. from Merck, distilled water and tetraethyl orthosilicate (TEOS) from Aldrich. The reactants were mixed in order to obtain gel of the following molar composition: 1TEOS:0.017P123:5.7HCl:193H_2O [3–5]. For the synthesis, the P123 copolymer was firstly dispersed in HCl and water, under stirring at 35°C. After complete dissolving of P123, the TEOS was added to the dispersion. The mixture was aged by 24 h, in order to obtain a homogeneous gel. The reaction mixture was hydrothermally treated under autogeneous pressure at 373 K for 48 h. The resulting products were filtered, washed with distilled water and a solution of 2% HCl/EtOH, and dried at room temperature [12]. The calcination was carried out at 500°C for one hour under nitrogen and an additional hour in air. The calcination temperature was reached at a heating rate of 10°C min^{-1}.

TG measurements for uncalcined samples were carried out in flowing nitrogen on a TGA/SDTA 851 (Mettler) in the temperature range from 30 to 900°C with heating rates of 5, 10 and 20°C min^{-1} and nitrogen flow rate of 25 mL min^{-1}. TG analyses were used to study kinetics properties of uncalcined material, in the stage of decomposition of the template (P123). The Vyazovkin [9–11] model-free kinetics was used to evaluate the kinetics parameters relative template decomposition (P123) as activation energy, conversion rates and surfactant degradation time as function of temperature.

XRD measurement was carried out in Shimadzu (XRD 6000) X-ray equipment using CuK_α radiation in 2θ angle of 0.5 to 5 with step of 0.01°. FTIR spectra were acquired from KBr pellets using a Bomen MB102 Series Spectrophotometer. BET surface area was measured using nitrogen adsorption at 77 K, on an ASAP 2010 (Micromeritics).

Results and discussion

As shown in Fig. 2 the XRD patterns for the studied sample (a) as-synthesized SBA-15 and (b) washed and calcined SBA-15 possess three characteristic peaks at 0.86, 1.48 and 1.71° for (a) and 0.85, 1.64 and 1.70° for (b), related to (100); (110) and (200) Miller index respectively, characteristics of siliceous SBA-15 materials [3, 13, 14]. The XRD patterns showed that the samples present mesoporous parameter *d*(100)=10.2 nm; a_0=11.8 nm for (a) and *d*(100)=10.4 nm and a_0=12.0 nm for (b). The specific surface area for the washed and calcined SBA-15 sample was determined according to the standard Brunauer–Emmett–Teller (BET) method [15] and pore size distributions by Barrett–Joyner–Halenda (BJH) algorithm [16]. The results were: surface area=655 m^2 g^{-1}; total pore volume=0.84 cm^3 g^{-1}; pore size (D_p)=7.5 nm and pore width (W_T)=4.5 nm.

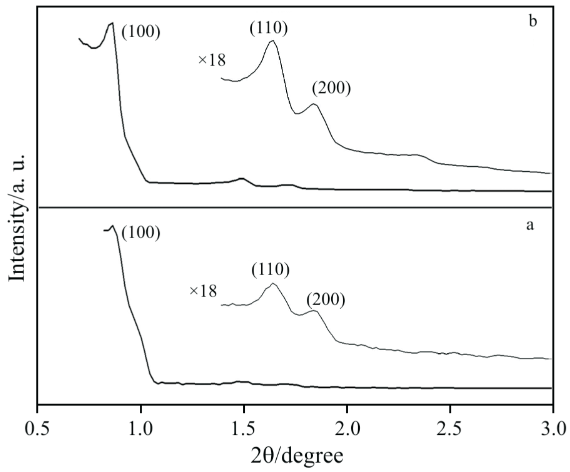

Fig. 2 XRD powder pattern of the siliceous SBA-15 materials a – as-synthesized SBA-15 and b – washed and calcined SBA-15

TG analysis of silica SBA-15 provides information about the mass loss steps of the uncalcined SBA-15 sample. The mass losses steps are located in the following temperature ranges: *i*) from 30 to 100°C as thermodesorption of physically adsorbed water; *ii*) from 100 to 450°C as P123 decomposition and *iii*) from 450 to 600°C as residual P123 decomposition and water from silanol condensation. Both TG curves show analogous behavior, which is characteristic for uncalcinated SBA-15-type materials. The P123 removal of the SBA-15 material was evaluated by TG at heating rates of 5, 10 and 20°C min^{-1}. Figure 3 shows the mass loss curves at three different heating rates as function of the temperature and its respective derivates.

Template removal, on the other side exceeding can cause the destruction of SBA-15 structure by the crack of the silicon tetrahedral bonds. Vyazovkin [9–11] developed an integral method of model-free kinetic analysis which as multiple heating rates and allows evaluating both simple and complex reactions kinetics. The rate of the chemical depends on the conversion (α), temperature (*T*) and time (*t*). The analysis is based on the isoconversion principle, which states that a constant conversion of the reaction rate is only a function of temperature. In a typical experiment it is necessary to obtain at least three different heating rates (β) and respective conversion (α), $\ln(\beta / T_\alpha^2)$ plot-

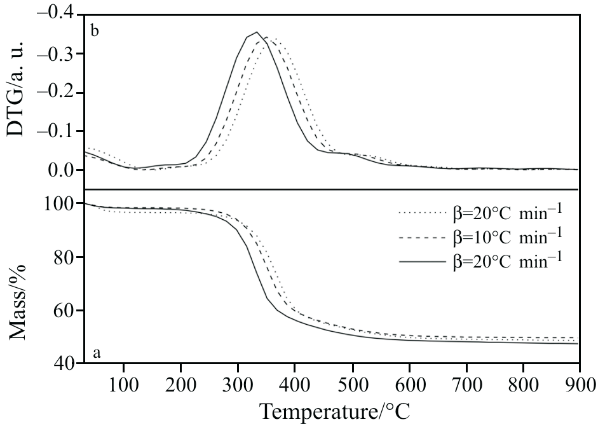

Fig. 3 a – TG curves for unwashed SBA-15 sample at different heating rates and b – corresponding DTG curves

ted *vs*. $1/T_\alpha$ giving a straight line with slope equivalent to $-E_a/R$, therefore the activation energy (Fig. 4) is obtained as a function of conversion. The theory is based on the assumption that the reaction rate is:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=k\mathrm{e}^{-\mathrm{E/RT}}f(\alpha) \tag{1}$$

and that the activation energy $E(\alpha)$ is constant for a certain value of conversion α (iso-conversional method). Taking the reaction rate Eq. (1), presented as $f(\alpha)$ and dividing by the heating rate $\beta=\mathrm{d}T/\mathrm{d}t$:

$$\frac{\mathrm{d}\alpha}{\mathrm{d}t}=kf(\alpha)\Rightarrow\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\frac{k}{\beta}f(\alpha) \tag{2}$$

where $\mathrm{d}\alpha/\mathrm{d}t$=reaction rate ($\mathrm{s}^{-1}$); k=velocity constant (s^{-1}); α=conversion; β=heating rate ($\mathrm{K\ s}^{-1}$).

Substituting k on Eq. (2) by the Arrhenius equation ($k=k_0\mathrm{e}^{-\mathrm{E/RT}}$) and rearranging gives:

$$\frac{1}{f(\alpha)}\mathrm{d}\alpha=\frac{k_0}{\beta}\mathrm{e}^{-\mathrm{E/RT}}\mathrm{d}T \tag{3}$$

The integration of the Eq. (3) up to conversion α (at the temperature T) gives:

$$\int_0^\alpha\frac{1}{f(\alpha)}\mathrm{d}\alpha=\frac{k_0}{\beta}\int_{\mathrm{T_0}}^{\mathrm{T}}\mathrm{e}^{-\mathrm{E/RT}}\mathrm{d}T \tag{4}$$

where

$$\int_0^\alpha\frac{1}{f(\alpha)}=g(\alpha)$$

Considering that E/RT on Eq. (4) is much bigger than 1, the temperature integral can be approximated by:

$$\int_{\mathrm{T_0}}^{\mathrm{T}}\mathrm{e}^{-\mathrm{E/RT}}\mathrm{d}T\approx\frac{R}{E}T^2\mathrm{e}^{-\mathrm{E/RT}} \tag{5}$$

Substituting Eq. (5) on Eq. (4), rearranging and applying the logarithm, gives:

$$\ln\frac{\beta}{T_\alpha^2}=\ln\left[\frac{Rk_0}{E_\alpha g(\alpha)}\right]-\frac{E_\alpha}{R}\frac{1}{T_\alpha} \tag{6}$$

Equation (6) is defined as a dynamic equation, which is used for the determination of the activation energy (E_a) for all conversion values (α). The conversion curves are presented in the Fig. 5.

From thermogravimetry, applying the model free kinetics at multiple heating rates, was possible to determine the activation energy relative to triblock copolymer P123 decomposition from the mesopores of the SBA-15. The activation energy to removal of the P123 species in the range of 5 to 80% of conversion was of 131.2±7.1 kJ mol^{-1}.

Starting of the obtained activation energy curve and using the model-free algorithms [9–11] is possible to obtain the isoconversion parameters. Table 1 shows the predicted values of the temperature removal of the P123 as function of the conversion and time. As example to remove 95% of the template species in 120 min is necessary 431°C and at the same time to remove of 99% is necessary 468°C.

FTIR spectra of as-synthesized; washed with water and 2% HCl/EtOH solution and washed with water and 2% HCl/EtOH solution and calcinated SBA-15

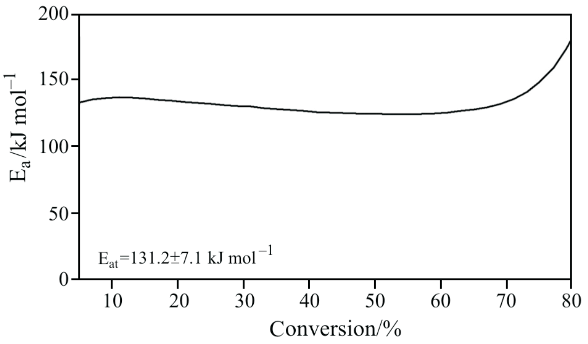

Fig. 4 Activation energy (E_a) *vs*. conversion for P123 removal of the SBA-15 material

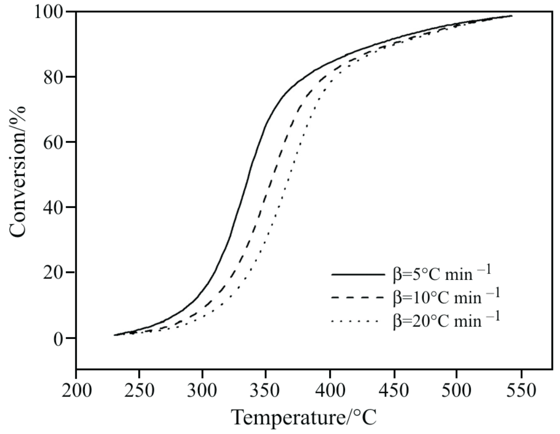

Fig. 5 Conversion curves from the integral of DTG at different heating rates

Table 1 Temperature to removal of P123 of the SBA-15 material as function of the time, for different conversions

Time/min	Conversion/%						
	10	30	50	70	90	93	99
10	269	299	316	335	411	456	491
20	257	285	300	319	402	449	485
30	250	277	291	310	397	445	481
40	245	271	285	304	394	442	478
50	242	267	280	300	391	440	476
60	239	264	277	296	389	438	474
70	236	261	274	293	388	437	473
80	234	259	271	290	386	435	472
90	232	256	269	288	385	434	471
100	231	255	267	286	384	433	470
110	229	253	265	284	383	432	469
120	228	251	263	282	382	431	468

(Fig. 6) are dominated by the asymmetric Si–O–Si stretch at 1085 cm^{-1} with a shoulder at 1220 cm^{-1}. The symmetric stretch occurs at 800 cm^{-1}, while the band at 460 cm^{-1} is assigned to the Si–O–Si bending mode. The band at 960 cm^{-1} can be assigned to the Si–OH vibrations generated by the presence of defect sites. The band centered at 3500 cm^{-1} can be assigned to the O–H vibrations corresponding to the silanol groups. The spectra for the as-synthesized SBA-15 (Fig. 6a) and the washed with water and 2% HCl/EtOH solution (Fig. 6b) indicate the presence of Pluronic 123 structure-directing agent as evidenced by the strong C–H vibrations in the 2810–3015 cm^{-1} region and the C–O–C vibrations at 1370 and 1460 cm^{-1} [17, 18].

The results presented in this paper show the potentialities of the isoconversion method in the estimate of time and temperatures necessary in the degradation of template species from the pores of SBA-15 and other related materials [19, 20].

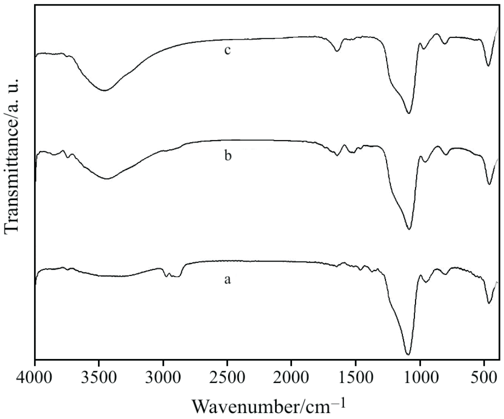

Fig. 6 FTIR spectra of the SBA-15 materials where a – as-synthesized, b – washed with water and 2% HCl/EtOH solution and c – washed with water and 2% HCl/EtOH solution and calcined

Conclusions

The thermogravimetric monitoring of the P123 removal from the SBA-15 material at different heating rates represents a good technique to preview the temperature and time for calcinations, in order to obtain a high quality material. Under non isothermal conditions, in which the sample was heated at three different and constant heating rates, the Vyazovkin model-free kinetic analysis shows a good alternative to estimate the apparent activation energy to removal of template species and prediction of the conversion and isoconversion parameters.

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References

1 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, J. B. Higgins and J. L. Schlenker, J. Am. Chem. Soc., 114 (1992) 10834.
2 C. T. Kresge, M. E. Leonowicz, J. S. Beck, J. C. Vartuli and W. J. Roth, Nature, 359 (1992) 710.
3 D. Zhao, J. Feng, Q. Hou, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. Stucky, Science, 279 (1998) 548.
4 P. Yang, D. Zhao, D. Margolese, B. Chmelka and G. Strucky, Nature, 396 (1998) 152.
5 T. Yamada, H. Zhou, K. Asai and I. Honma, Mater. Lett., 1 (2002) 3538.

6 G. J. A. A. Soler-Illia, E. L. Crepaldi, D. Grosso and C. Sanchez, Curr. Opin. in Colloid and Interface Sci., 8 (2003) 109.
7 R. Ivanova, P. Alexandridis and B. Lindmann, Colloids Surf. A, 41 (2001) 183.
8 R. Ivanova, P. Alexandridis and B. Lindmann, Adv. Colloid Interfare Sci., 351 (2001) 89.
9 S. Vyazovkin and A. I. Lesnikovich, Russ. J. Phys. Chem., 62 (1988) 2949.
10 S. Vyazovkin and V. Goryachko, Thermochim. Acta, 194 (1992) 221.
11 S. Vyazovkin and C. A. Wright, Thermochim Acta, 340 (1990) 53.
12 S. A. Araujo, M. Ionashiro, V. J. Fernandes and A. S. Araujo, J. Therm. Anal. Cal., 64 (2001) 801.
13 D. Zhao, Q. Huo, J. Feng, B. F. Chmelka and G. D. Stucky, J. Am. Chem. Soc., 120 (1998) 6024.
14 Y. J. Han, J. M. Kim and G. D. Stucky, Chem. Mater., 12 (2000) 2068.
15 S. Brunauer, P. H. Emmett and E. Teller, J. Amer. Chem. Soc., 60 (1938) 309.
16 E. P. Barrett, L. J. Joyner and P. P. Halenda, J. Amer. Chem. Soc., 73 (1951) 373.
17 D. Coutinho, A. O. Acevedo, G. R. Dieckmann and K. J. Balkus Jr., Microporous Mesoporous Mater., 1249 (2002) 1.
18 G. Calleja, R. van Grieken, R. García, J. A. Melero and J. Iglesias, J. Molecular Catalysis: Chemical, 182–183 (2002) 215.
19 M. J. B. Souza, A. O. S. Silva, V. J. Fernandes Jr. and A. S. Araujo, J. Therm. Anal. Cal., 79 (2005) 425.
20 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.

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