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Synthesis monitoring of SBA-15 nanostructured materials

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Abstract The SBA-15 materials were synthesized by the hydrothermal method using tetraethyl orthosilicate as silica source and P123 as template agent. The synthesis process was accomplished varying the time during the hydrothermal processing. For the synthesis monitoring, a small amount of sample was removed at different times, and analyzed by thermal analysis in order to determine the temperature ranges related to water desorption, template decomposition and silanol condensation for the SBA-15 nanostructured materials, as well as to estimate their quality. The samples were characterized by X-ray diffraction, infrared absorption spectroscopy, scanning electron microscopy, BET surface area and pore size distribution. The activation energy relative to decomposition of P123 template was determined from TG curves, using multiple heating rates and applying the model free kinetics. From the obtained data, it is possible to monitor the hydrothermal synthesis of SBA-15 in order to control the properties and conditions to prepare ordered materials.

Keywords Adsorbents · Synthesis techniques · Characterization of properties · Activation · Measurement properties

1 Introduction

Since the discovery of MCM-41 and FSM-16 (Beck et al. 1992; Kresge et al. 1992), a permanent effort is made to develop mesostructured inorganic or hybrid phases, which are potential materials for a variety of applications, in the fields of catalysis, optics, photonics, sensors, separation, drug delivery and adsorption (Soler-Illia et al. 2003). 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 P123, poly(ethylene oxide)-poly(propylene oxide)-poly (ethylene oxide), $EO_xPO_yEO_x$, from BASF). It has a more regular structure and a thicker channel wall than MCM-41, resulting in much higher thermal stability (Zhao et al. 1998a).

Some advantages of neutral non-ionic template used in the SBA-15 synthesis over the ionic ones were immediately noticed: (a) larger inorganic wall thickness, increasing the hydrothermal stability of the mesoporous oxides; (b) easier pore diameter tuning, by varying the type and concentration of the template; (c) easier solvent removal, by solvent extraction, H-bonding interactions between the template and the inorganic framework should be easier to dissociate (Tanev and Pinnavaia 1995; Bagshaw et al. 1995; Boissiere et al. 2000).

Two main processes can be recognized in the formation of the mesophases in the SBA-15 synthesis: one is that the use of block copolymer surfactant creates an organized texture, due to the self-assembly properties of the template. This process results in a microphase separation, which divides the space in hydrophilic and hydrophobic domains. The other is related to the formation of an inorganic network. Condensation reactions will give rise to an extended inorganic network. These can be tuned to take place simultaneously or subsequently as the structure organization proceeds.

In the current work, the SBA-15 mesoporous molecular sieve was synthesized by the hydrothermal treatment using TEOS—tetraethyl orthosilicate, as source of silica; triblock

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copolymer Pluronic P123 as organic template; hydrochloric acid and water. The sample was removed after each step of the synthesis process and analyzed by thermal analysis in order to determine the temperature ranges related to water desorption, surfactant decomposition and silanol condensation for the mesostructure, as well as to estimate their quality. A kinetic study using the *Vyazovkin* model free model (Vyazovkin and Lesnikovich 1988; Vyazovkin and Goryachko 1992) was accomplished in the stage of decomposition of the template (P123).

2 Experimental

The chemicals used to synthesize SBA-15 were triblock copolymer (P123—$EO_{20}PO_{70}EO_{20}$, $M_{av} = 5750\ g\,mol^{-1}$), as structure template; hydrochloric acid, as acidulate; distilled water, as solvent and TEOS, as silica source. The reactants were mixed in order to obtain a reactive hydrogel (Yang et al. 1998). The following overall molar composition used was: 1.0 TEOS: 0.017 P123: 5.7 HCl: 193 H_2O. In a typical procedure to prepare SBA-15 sample, 4.90 g of P123 copolymer was dispersed in solution 28.17 g of HCl and 159.10 g water, under stirring at 35°C. After complete dissolving of P123, 10.65 g of TEOS were added. After the precipitation, a small amount of sample was taken out (SBA-15(Gel) sample). The mixture was aged for 24 hours, in order to obtain an homogeneous gel. Before transferring the reaction mixture for the autoclave, a small amount of sample was taken (SBA-15(0) sample). The reaction mixture was divided in 3 portions and hydrothermally treated under autogeneous pressure at 100°C. To each day of hydrothermal treatment, one sample was collected, and after three days of synthesis, they were assigned as SBA-15(1); SBA-15(2) and SBA-15(3) samples, relative to 1; 2 and 3 days of time of hydrothermal synthesis, respectively. All samples were filtered, washed with distilled water, and dried at room temperature, and then calcined at 500°C for one hour under nitrogen atmosphere and an additional hour in air. The oven was heated at a heating rate of $10°C\,min^{-1}$.

Powder XRD measurements were carried out in a Shimadzu XRD 6000 equipment, using CuKα radiation in the range of 2θ angle from 0.5 to 5 with step of 0.01°. For these analyses, were used *ca.* 100 mg of calcined materials. BET surface area was measured using nitrogen adsorption at 77 K, in a Nova-2000 equipment, from Quantachrome. Prior the nitrogen adsorption, the calcined samples were degassed at 200°C by four hours, in order to activate the pores of the materials. Infrared spectra were acquired using the KBr technique, in a concentration of 5% of material. The equipment used was a FT-IR Bomen MB102 Series Spectrophotometer. The scanning electron micrographics were obtained in order to visualize the morphology of the synthesized material, in a Joel equipment JSM-5610 LV model.

TG measurements for the uncalcined samples were carried out in a TGA/SDTA 851 from Mettler, in the temperature range from 30 to 900°C, heating rates of 5; 10 and $20°C\,min^{-1}$, under nitrogen flowing at rate of $25\ mL\,min^{-1}$. TG analyses were used to study the thermal and kinetics properties of the uncalcined nanostructured materials, in the stage of decomposition of the template (Araujo et al. 2004), and polymers (Polli et al. 2005). In this work, *Vyazovkin* model free kinetics was used to determine the activation energy relative to the decomposition of triblock copolymer P123.

3 Results and discussion

The XRD patterns for the samples obtained after each step of the synthesis process are shown in the Fig. 1. The SBA-15(Gel) and SBA-15(0) samples present similar XRD profiles, evidencing that the silicate groups interact with the P123 copolymer template in a similar way. Otherwise, the SBA-15(1); SBA-15(2) and SBA-15(3) samples present three characteristic peaks in the 2θ range of 0.5 to 2.0°, related to (100); (110) and (200) Miller index, similar to those of siliceous SBA-15 materials (Zhao et al. 1998b). The absence of these peaks in the SBA-15(gel) and SBA-15(0) samples, suggests that the hexagonal structure was not found. Although these two samples do not present a well ordered structure, the calcined materials showed higher surface area (see Table 1). The SBA-15(3) sample presents the more intense peak related to the plane (100), as related to SBA-15(1) and SBA-15(2) samples. However it was observed an inversion in the last two peaks for the SBA-15(1) and SBA-15(2) samples, related to (110) and (200) index, where the sample SBA-15(2) presented the higher ordered hexagonal structure. From the XRD patterns, the samples present mesoporous parameter (a_o) in the range of 11.9 to 12.3 nm.

The specific surface area was determined according to the standard Brunauer-Emmett-Teller (BET) method (Brunauer et al. 1938) and pore size distributions by Barrett-Joyner-Halenda (BJH) algorithm (Barrett et al. 1951). For the hexagonal ordered SBA-15 materials, the BET surface area decreases with the time of synthesis varying from 847 to $631\ m^2\,g^{-1}$; whereas an increasing on the pore size (D_p) from 5.6 to 7.0 nm was observed. The nitrogen adsorption isotherm for SBA-15 material is typically of type IV, as can visualized in Fig. 2, for SBA-15(3). The adsorption properties and mesoporous parameters are summarized in the Table 1.

The FT-IR spectra for the samples and P123 copolymer (Fig. 3) are typically dominated by the Si–O–Si asymmetric stretch at 1085 cm^{-1} with a shoulder at 1220 cm^{-1},

Table 1 Adsorption and mesoporous parameters for the SBA-15 samples obtained during the synthesis process

Sample	Surface area, S_{BET} ($m^2\ g^{-1}$)	Total pore volume V_t ($cm^3\ g^{-1}$)	a_o (nm)*	Pore size D_p (nm)	Pore width, W_t (nm)**
SBA-15(Gel)	701	0.85	–	–	–
SBA-15(0)	808	0.75	–	–	–
SBA-15(1)	847	1.04	12.0	5.6	6.4
SBA-15(2)	663	0.90	11.9	6.4	5.5
SBA-15(3)	631	0.92	12.3	7.0	5.3

*$a_o = 2d_{(100)}3^{1/2}$;
**$W_t = a_o - D_p$

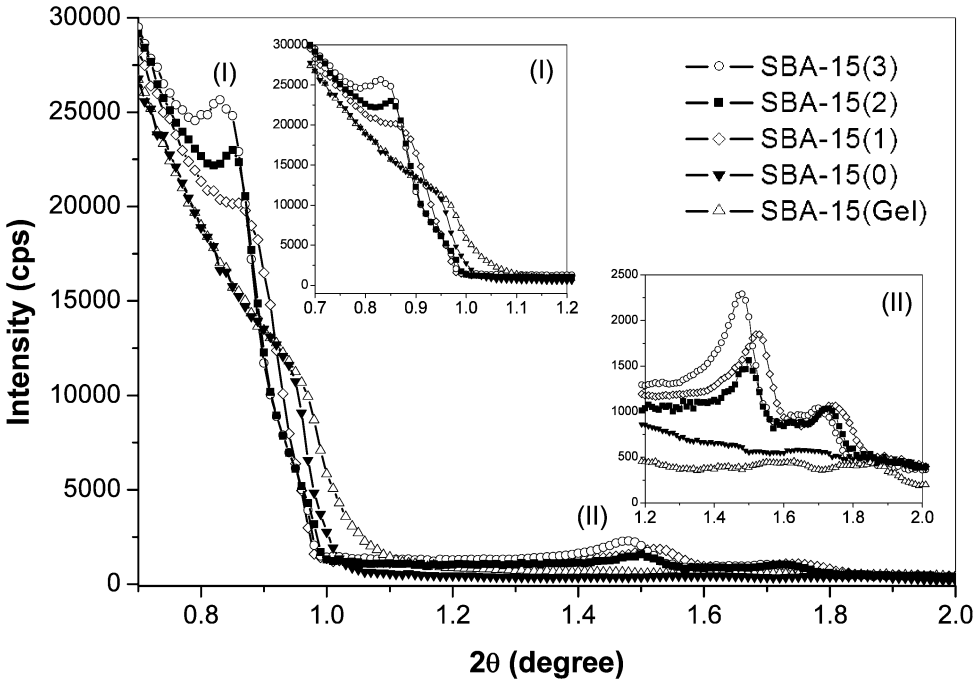


Fig. 1 XRD powder patterns of the siliceous SBA-15 materials, at different synthesis process

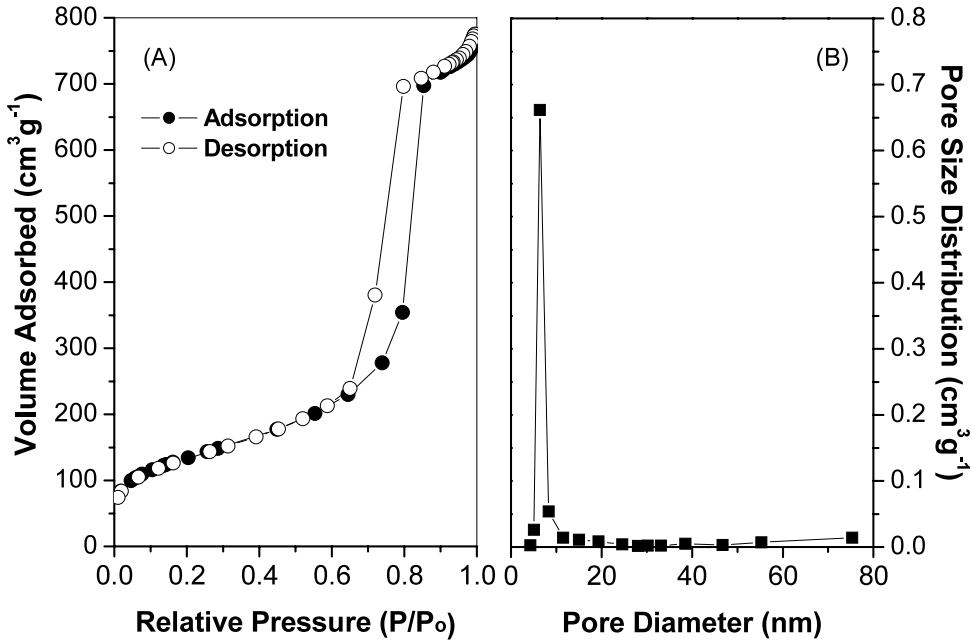


Fig. 2 Nitrogen adsorption–desorption isotherm (**A**) and pore size distribution (**B**) for SBA-15(3)

as shown in the Fig. 2. The symmetric stretch occurs at 800 cm^{-1}, and the band at 460 cm^{-1} was 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} was assigned to the O–H vibrations of the silanol groups. The spectra for the as-synthesized samples indicated the presence of Pluronic 123, which was 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} (Coutinho et al. 2002; Calleja et al. 2002).

The micrographics of the obtained SBA-15(3) material are showed in the Fig. 4. SEM was accomplished in order to observe the morphology of the synthesized sample. For the SBA-15(3) material it was observed a fiber-like structure with micrometric dimensions formed from a linear adhesion of the nodules of sub-micrometric particles. Similar structures have been reported in the literature (Chao et al. 2002; Katiyar et al. 2006), suggesting to be the well organized phase for SBA-15, as observed from XRD and nitrogen adsorption.

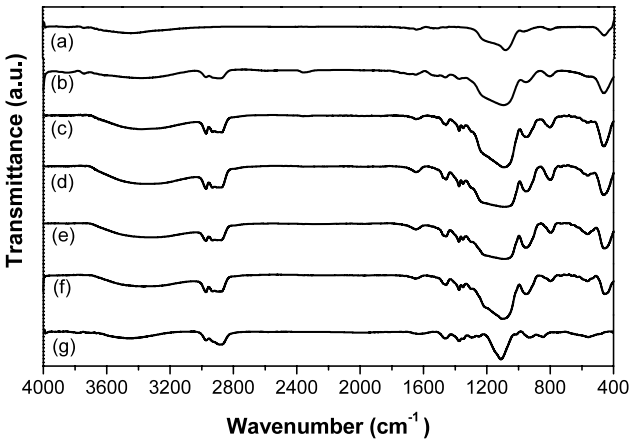


Fig. 3 FT-IR spectra for the studied samples after each stage of the synthesis process and triblock P123 copolymer, where: (*a*) Calcined SBA-15(3); (*b*) SBA-15(3); (*c*) SBA-15(2); (*d*) SBA-15(1); (*e*) SBA-15(0); (*f*) SBA-15(Gel) and (*g*) Pluronic P123

Figure 5 shows the weight losses curves for the obtained materials as function of the temperature and its respective derivates. TG analysis of the materials provides information concerning the weight loss steps of the uncalcined SBA-15 sample. For the SBA-15(1); SBA-15(2) and SBA-15(3) samples, the weight losses steps are located in the following temperature ranges: i) from 30 to 150°C as thermodesorption of physically adsorbed water; ii) from 150 to 450°C as P123 decomposition and iii) from 450 to 600°C as residual P123 decomposition and water from silanol condensation. Both TG and DTG curves present analogous behavior, which is characteristic for uncalcined SBA-15-type materials. Only the SBA-15(Gel) sample presented one step of weight loss, in the range of 100 to 350°C, due to P123 decomposition. The silanol condensation was not observed for this sample. In order to obtain the kinetic parameters for the P123 decomposition from the SBA-15, the uncalcined materials were evaluated by TG at different heating rates, and the activation energies in function of conversion (Fig. 6) were determined applying the *Vyazovkin* model.

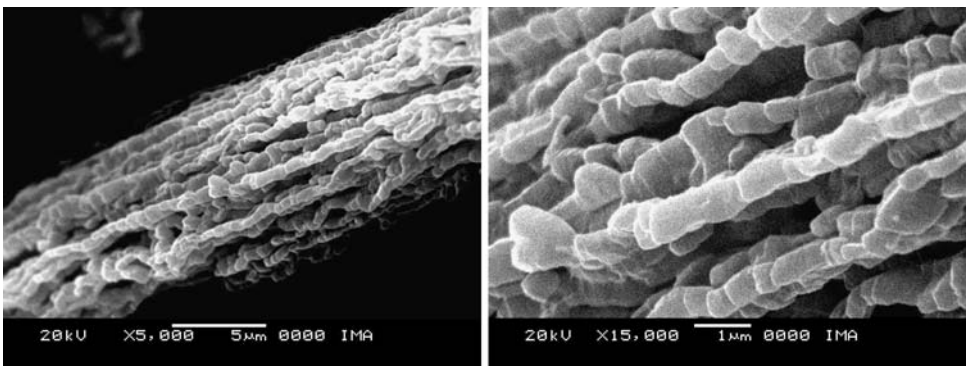
The "*Model Free Kinetic*" is an integral method used for evaluation and determination of kinetic parameters for easy and complex decomposition processes, starting from thermal analysis (TG) experiments at multiple heating rates (Araujo et al. 2004). This method is based on the equation:

$$\frac{d\alpha}{dt} = ke^{-E_a/RT} f(\alpha) \tag{1}$$

where E_a is the activation energy, and k the velocity constant, being E_a constant at a given convention degree, α (iso-conversion method).

In our experiments, the decomposition of the triblock P123 copolymer from the pores of the SBA-15 samples were carried out using thermogravimetry at three multiple heating rates ($\beta = 5$; 10 and 20°C min^{-1}) being the iso-conversion curves calculated from the TG curves of weight losses versus temperature. For each conversion degree (α) it was obtained a graphic of $\ln \frac{\beta}{T_\alpha^2}$ versus $1/T_\alpha$, giving a straight line,

Fig. 4 Scanning electron micrography for the SBA-15(3) sample



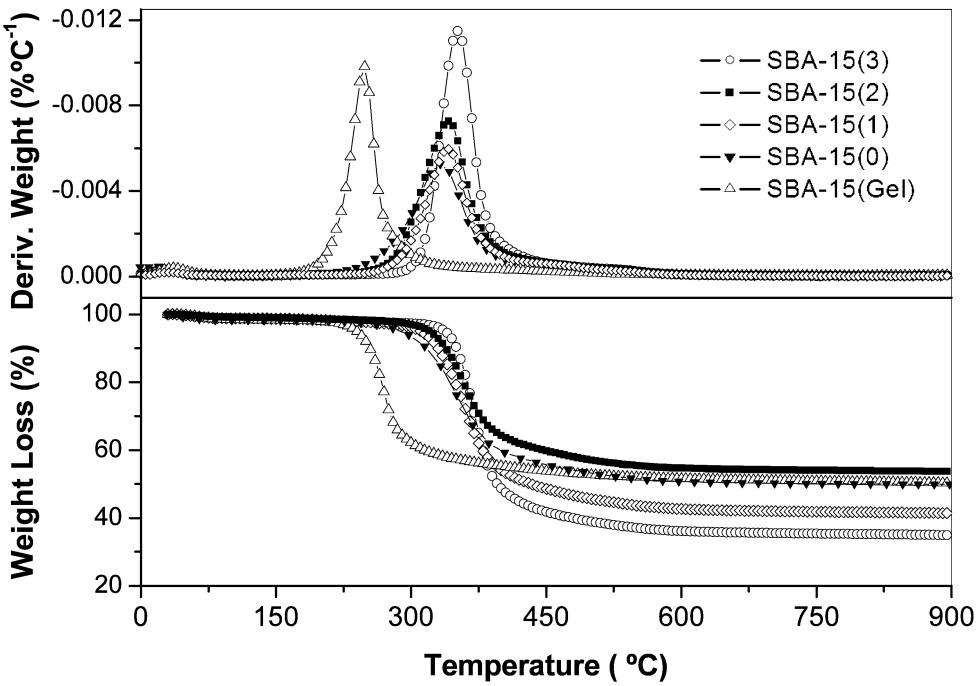


Fig. 5 TG curves for the SBA-15 samples removed after each stage of the synthesis process and corresponding DTG curves (heating rate = 10°C min^{-1}

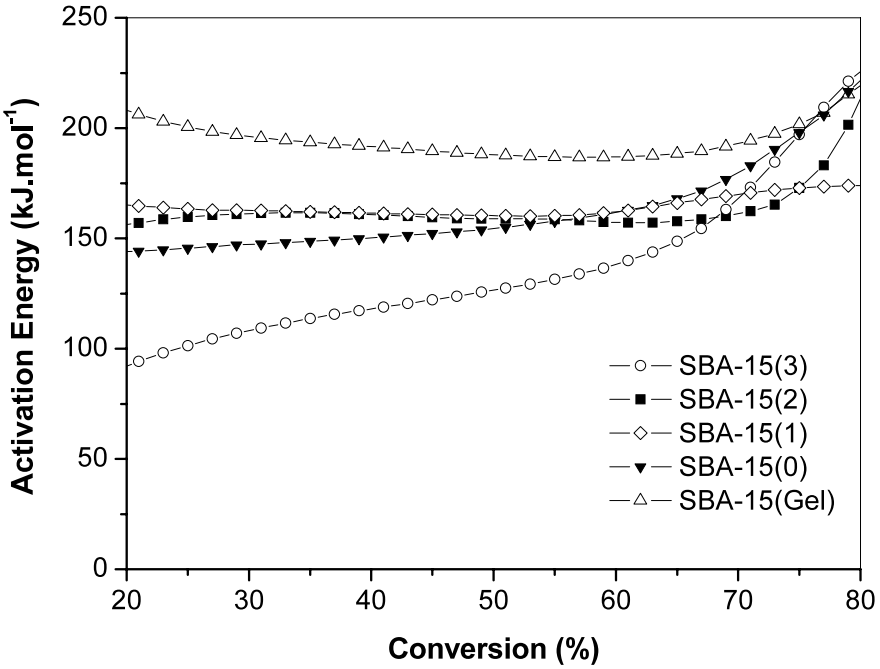


Fig. 6 Activation energy versus conversion for triblock copolymer P123 decomposition for the SBA-15 samples removed after each stage of the synthesis process

with the slope equivalent to $-E_a/R$, where E_a was obtained as a function of the conversion degree. Dividing (1) by the heating rate, $\beta = dT/dt$, a new function of conversion was obtained:

$$\frac{d\alpha}{dt} = kf(\alpha) \rightarrow \frac{d\alpha}{dT} = \frac{k}{\beta} f(\alpha) \tag{2}$$

where $d\alpha/dt$ is the velocity of reaction (s^{-1}); k the velocity constant (s^{-1}); α the conversion; and β the heating rate (K s^{-1}). Substituting the k value in (2), in the *Arrhenius* equation: $k = Ae^{-E_a/RT}$, and reorganizing, then:

$$\frac{1}{f(\alpha)} d\alpha = \frac{k_0}{\beta} e^{-E_a/RT} dT. \tag{3}$$

The integral of (3) up to a conversion degree α, at a given temperature T, gives a $g(\alpha)$ function:

$$\int_0^{\alpha} \frac{1}{f(\alpha)} d\alpha = g(\alpha) = \frac{k_0}{\beta} \int_{T_0}^{T} e^{-E_a/RT} dT. \quad (4)$$

In practical terms, considering that $E_a/2T \gg 1$, the integral of the temperature (right side of (4)) can be approximated to:

$$\int_{T_0}^{T} e^{-E_a/RT} dT \approx \frac{R}{E_a} T^2 e^{-E_a/RT}. \quad (5)$$

Finally, substituting in (4) and the integral of temperature by (5), reorganizing and applying the logarithm, we obtain:

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

Equation (6) is a dynamic equation that was applied for determination of the activation energy for all conversion degree for triblock P123 decomposition in the synthesized SBA-15 samples. The main advantage of the application of the *Model Free Kinetic* is that it is independent of the "*n*" reaction order. Thus, the model represents a very interesting method for determination of the activation energy related to the thermal degradation of the P123 triblock copolymer in the SBA-15 materials. The activation energies to decompose P123 species in the range of 20 to 80% of conversion for the samples were obtained in the range of 100 to 200 kJ mol^{-1} (Fig. 6). The SBA-15(3) sample presented the lower activation energy, while the SBA-15(Gel) sample presented the higher. This is related to the hexagonal structure of the materials, in which highly ordered SBA-15 materials require less energy to decompose the P123 organic template.

4 Conclusions

The obtained results showed a significant variation on the surface properties for the SBA-15 materials evidencing that they present structural flexibility varying the time of synthesis. The use of the hydrothermal treatment process taking out samples at different time was fundamental to study the formation of high-quality SBA-15 structures starting from an amorphous phase, SBA-15(Gel) and SBA-15(0), to a well ordered material, SBA-15(1); SBA-15(2) and SBA-15(3) samples. The XRD, infra-red spectroscopy, nitrogen adsorption (BET, BJH) and TG/DTG technique are satisfactory in the characterization and synthesis monitoring of nanoporous materials. For these three last samples, the surface area decreased from 847, 663 and 631 m^2 g^{-1}, whereas the pore size increased from 5.6, 6.4 and 7.0 nm, respectively, indicating that these properties are directly related with the time of hydrothermal treatment. From thermal analysis, 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. It was observed that the well organized hexagonal SBA-15(3) requires less energy to remove the triblock copolymer P123, than the SBA-15(0), SBA-15(1) and SBA-15(2) samples. TG analysis for the SBA-15(Gel) sample showed only a weight loss, due to P123 decomposition, and the silanol condensation was not observed.

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