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KINETIC STUDY OF TEMPLATE REMOVAL OF MCM-41 NANOSTRUCTURED MATERIAL

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Abstract

The siliceous MCM-41 molecular sieve was synthesized starting from a hydrogel with the following molar composition: $4.58SiO_2$:$0.437Na_2O$:1CTMABr:$200H_2O$. The cetyltetramethylammonium bromide (CTMABr) was used as structure template. A kinetic study of template removal after the syntheses was performed by Vyazovkin model-free kinetic method obtaining apparent activation energy of 166±8.2 kJ mol^{-1}.

Keywords: MCM-41, model-free kinetics, pH adjustment, thermogravimetry

Introduction

Since the 90's many researches have been applied in meso- and nanoporous materials field [1–6]. The use of these materials in chemical engineering, chemistry and catalysis has been increasing in the recent years. High surface area, well-defined mesoporous array and possibility of generate surface acidity are potential characteristics of the mesoporous materials. The silica based MCM-41 (MCM=Mobil Crystalline Material) is the main material of the M41S family, discovered by Mobil Company. The formation of the MCM-41 phase occurs according to the liquid crystal template (LCT) mechanism, in which tetrahedral SiO_4 species react with the surfactant template under hydrothermal conditions [3]. A typical preparation of the MCM-41 hexagonal array basically needs a solvent, a template (surfactant molecule) and a silica source. Many papers [7–10] have studied the influence of synthesis variables in the formation of MCM-41 phase. Variables as pH, temperature, time, gel composition and nature of the precursors materials have been of great importance in the production of pure MCM-41 hexagonal phase. After the synthesis the mesoporous materials need a calcination step to remove the template of the pores system. High temperatures favor a rapid cracking and elimination of the template species, however, the ordered

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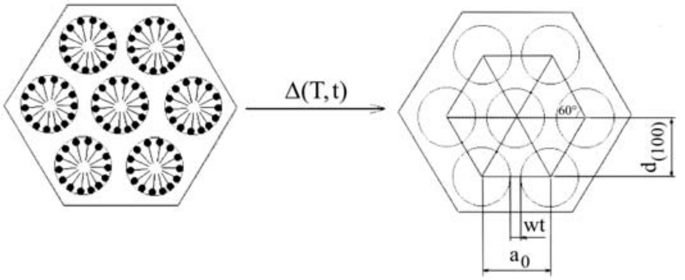


Fig. 1 Schematic representation of the mesoporous array of the MCM-41 before and after the calcination, where (●— – surfactant molecule; *T* – temperature; *t* – time; *wt* – silica wall thickness; $d_{(100)}$ – interplanar distance in the (100) plane and a_0 – mesoporous parameter [9])

silica structure can be destroyed (Fig. 1). The study of the optimal time and temperature to template elimination is an important variable in the final preparation of the MCM-1 material. In this paper thermogravimetry was used to evaluate the monitoring of the pH-adjusted synthesis, as the optimal time and temperature to remove the template of the MCM-41 material after hydrothermal synthesis.

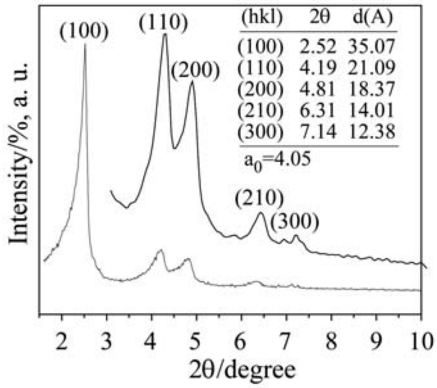
Experimental

SiMCM-41 was synthesized starting from silica gel (Hiedel de Haen, 60-200 mesh, 150 Å), sodium silicate solution containing 18% SiO_2 and 18% Na_2O (Hiedel de Haen), cethyltrimethylammonium bromide (CTMABr, vetec) and distilled water. For the pH adjustment 30% acetic acid in ethanol solution was used. The chemicals were mixed in order to obtain a gel with the following molar composition: $4.58SiO_2$: $0.437Na_2O$: 1CTMABr: $200H_2O$. The procedure used to obtain 2.5 g of calcined MCM-41 was: (*i*) 2.02 g of silica, 1.57 g of sodium silicate and 24.7 mL of water were placed into a 100 mL teflon beaker and stirred at 60°C for 2 h in order to obtain a clear solution; (*ii*) a solution prepared from 3.87 g of cethyltrimethylammonim bromide and 12.3 mL of distilled water was added to the above mentioned mixture and aged for 1 h at room temperature. The hydrogel was placed into 80 mL teflon-lined autoclave and heated at 100°C for four days. Their pH was measured each day and adjusted to 9.5–10. 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 a heating rate of 5, 10 and 20°C min^{-1}. The Vyazovkin [11–13] model-free kinetics was used to evaluate the kinetic parameters relative surfactant decomposition of the MCM-41 material as activation energy, conversion rates and surfactant degradation time as function of temperature.

X-ray diffraction measurement was carried out in Shimadzu (XRD 6000) X-ray equipment using CuK_α radiation in 2θ angle of 1 to 10° with step of 0.01°. For this analysis ca. 100 mg of final material was washed with 25 mL of 2% HCl/EtOH [15] solution and subsequently calcined at 500°C for one hour in nitrogen and for an additional hour in air. The calcination temperature was reached at a heating rate of 5°C min^{-1}.

Results and discussion

The SiMCM-41 material was synthesized by the hydrothermal method [14, 15] using the pH adjustment conform reported elsewhere [15]. The pH value of the synthesis hydrogel was extremely basic (ca. 14). After one day, this value decreased around 11–12. This suggests that the hydroxyl concentration in the synthesized gel decrease 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 9.5–10 during the synthesis [15]. As shown in Fig. 2 the XRD patterns for the studied sample possess a characteristic peak at 2.4°, related to (100) index, and some others in the range from 3 to 7° (their respective *hkl* Miller indices are given in Fig. 2). The XRD patterns of the synthesized samples are similar to those of siliceous MCM-41 materials [16, 17] with mesoporous parameter a_0 of 4.28 nm (sum of pore diameter and the silica wall thickness).



(hkl)	2θ	d(A)
(100)	2.52	35.07
(110)	4.19	21.09
(200)	4.81	18.37
(210)	6.31	14.01
(300)	7.14	12.38

a_0=4.05

Fig. 2 XRD powder pattern of the siliceous MCM-41 material

In literature [16, 17] was previously reported that thermogravimetric analysis of MCM-41 materials (Fig. 3a) after the synthesis in nitrogen atmosphere showed basically three or more mass losses. The mass loss steps are located in the following temperature ranges: *i*) from 30 to 100°C (thermodesorption of physically adsorbed water); *ii*) from 100 to 310°C (surfactant decomposition); *iii*) from 310 to 520°C (residual surfactant decomposition and silanol condensation) and *iv*) from 520 to 860°C (residual silanol condensation). Figure 3b shows a typical DTG curves of the SiMCM-41 material at heating rates of 5, 10 and 20°C min^{-1}.

After the synthesis the next step to obtain the siliceous MCM-41 phase is calcination. In this step the amount will be submitted to effects of the temperature in a dynamic flow of gas (inert gas or oxidant atmosphere). The total removal of the template is the main function of these variables. High temperatures favors a rapid tem-

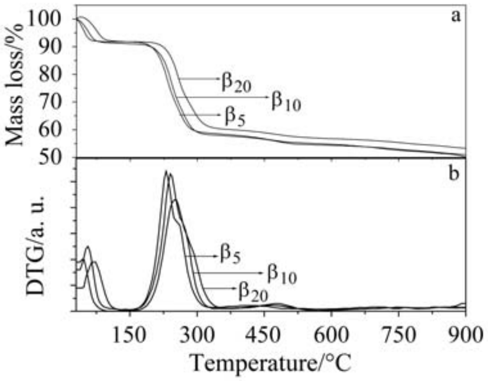


Fig. 3 a – TG curves for unwashed MCM-41 samples synthesized with pH adjustment at different heating rates β_i (i=5, 10 and 20°C min^{-1}) and b – corresponding DTG curves

plate removal, on the other side exceeding can cause the destruction of the MCM-41 structure by the crack of the silicon tetrahedral bonds. Vyazovkin [11–13] developed an integral method of model-free kinetic analysis which as multiple heating rates and allows to evaluate both simple and complex reactions kinetics. The rate of the chemical reactions 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 the respective conversion curves are evaluated from the measured TG curves. For each conversion (α), $\ln(\beta/T_\alpha^2)$ plotted *vs*. $1/T_\alpha$, giving a straight line with slope $-E_\alpha/R$ (Eq. (1)), therefore the activation energy (Fig. 4) is obtained as a function of conversion.

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

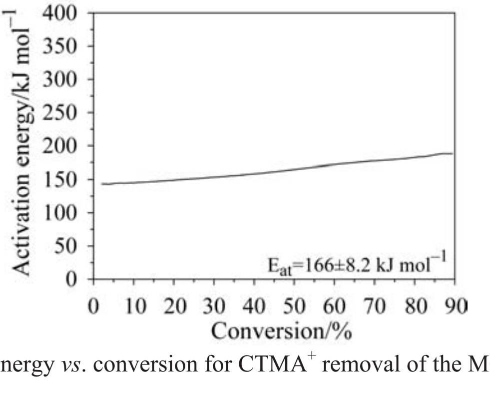


Fig. 4 Activation energy *vs*. conversion for CTMA$^+$ removal of the MCM-41 material

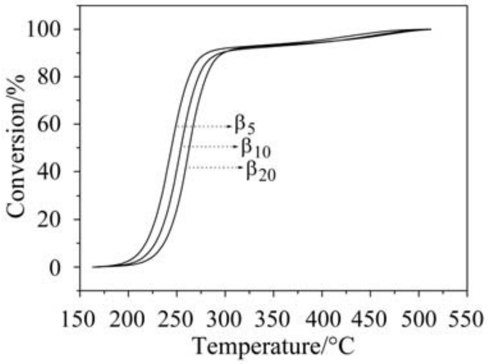


Fig. 5 Conversion curve of the thermogravimetric integral curves for different heating rates β_i (i=5, 10 and 20°C $\min^{-1}$)

The $CTMA^+$ removal of the MCM-41 material was evaluated by thermogravimetry, at heating rates of 5, 10 and 20°C $\min^{-1}$. Figure 5 shows the conversion curves at three different heating rates as a function of temperature.

The activation energy to removal of the $CTMA^+$ species in the range of 5 to 95% of conversion was of 166±8.2 kJ mol^{-1}. Starting the obtained activation energy curve and using the model-free algorithms [11, 12] it is possible to obtain the isoconversion parameters (Table 1). Table 1 shows the predicted values of the temperature removal of the $CTMA^+$ as a function of conversion and time. For example, to remove 95% of the template species in 60 min 334°C is necessary and at the same time to remove 99% 412°C is necessary.

Table 1 Temperature to the removal of $CTMA^+$ of the MCM-41 as a function of time, for different conversions

α/% Time/min	10	30	50	75	90	95	99
0	–	–	–	–	–	–	–
10	200	216	226	241	263	369	444
20	191	207	218	232	254	355	431
30	186	202	213	228	249	347	424
40	183	199	210	224	245	342	419
50	180	196	207	222	243	338	415
60	178	194	205	220	240	334	412
120	170	186	197	212	232	322	400
180	165	181	192	208	227	315	393
240	162	178	189	204	224	310	389
300	160	176	187	202	221	306	385
360	158	174	185	200	219	303	382

Conclusions

Thermogravimetric monitoring of the surfactant removal from the MCM-41 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 Vyazovkin model-free kinetic analysis shows a good alternative to estimate the apparent activation energy to remove template species and to predict conversion and isoconversion parameters.

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