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TEMPLATE TRANSFORMATIONS IN PREPARATION OF MCM-41 SILICA

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Template transformation in MCM-41 material during thermal treatment under different conditions was investigated on the basis of thermogravimetry (TG-DTA), X-ray diffraction (XRD) and positron annihilation lifetime spectroscopy (PALS). Micelle templated silica was prepared using C18 trimethylammonium bromide. The pore structure of MCM-41 samples obtained after removal of the surfactant in air, argon flow and vacuum was analyzed on the basis of the adsorption isotherms of nitrogen at 77 K and XRD experiments. The TG-DTA experiments confirm the mechanism of the template removal known from literature. However, the sequence of the processes during thermal treatment of as-synthesized sample and temperature of transformations depended strongly on the presence of oxygen and the heating rate. The main template degradation took place below 573 K and was independent of the kind of atmosphere above the sample. Residual carbonaceous species are removed from pores and the external surface of MCM-41 silica upon heating to 823 K by combustion or evaporation. The latter process as well as translocation of liquid-like products of template degradation from the pore interior to external surface was confirmed by PALS experiment in vacuum.

Keywords: *MCM-41, template removal, thermogravimetry, PALS*

Introduction

Mesoporous silica materials of MCM-41 type characterized by a highly ordered pore structure attracted during the last ten years increasing interest. Intensive studies of these materials were prompted by the possibilities of their application as specific sorbents, host materials for biologically active substances or supports for many active species in catalysis [1–6].

The quality and degree of ordering of the hexagonally arranged uniform cylindrical pores as well as the adsorption properties of MCM-41 silica material depend on the method of removal of the organic template from as-synthesized sample. The most common method used for removing of the organic core filling silica framework is calcination at 823–873 K in air. In these conditions total degradation of organic template occurs. This process is intensively studied using thermogravimetric techniques including sample controlled thermal analysis (SCTA) [7–10]. After thermal treatment in the indicated temperature interval on the internal surface of MCM-41 silica these remain products of pyrolysis of the template. Organic traces are detectable even above 1073 K [11]. Thus the final MCM-41 silica, independently of the applied method for template removal, always contains traces of carbonaceous species influencing the hydrophobicity of silica surface. Our earlier investigations indicated that prolonged heating of the calcined sample in oxygen flow at 823 K changed substantially the adsorption properties of silica surface which becomes more homogeneous and less hydrophobic [12]. It should be mentioned that high temperature treatment for many hours modifies the structural properties of silica material as well as the concentration of surface silanols which condense forming siloxane bridges [13–16].

Many efforts have been devoted to organic template removal by extraction with different solvents, i.e. ethanol, ethanol/HCl or water/ethanol mixtures [17–19].

The removal of the alkyl chains of the surfactant can be accomplished by using ozone without calcination [20, 21]. This reaction is exothermic and must be carefully controlled. The final material from ozonolysis has larger pores, a narrower pore size distribution, lower external surface area and greater degree of condensation of silica than the calcined material. Meretei *et al*. [22] investigated structural consequences of template removal using oxygene, ozone, N_2O and NO_2 as oxidation agents. Ozone was the most active at lower temperature (423 K) and the treatment was less destructive than burning off the template in oxygen. The same effect is observed in the case of nitrogen oxides.

Recently we studied organic template removal by heating the as-synthesized sample at a rather low temperature (~520 K) in vacuum from MCM-41 silica synthesized with octadecyltrimethylammonium bromide as the templating agent [23, 24]. The final product had the same structural properties as those prepared by classic methods. The elemental analysis of

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the emptied in vacuum and calcined samples indicated that both evacuated samples contained some amount of carbon. However, carbon contamination markedly decreased to 5.5% for samples heated up to 523 K in vacuum to 2.6% for calcined at 823 K, compared to silica with pores filled with the template (26.7%). For both evacuated samples the presence of nitrogen was not determined.

The present paper deals with some aspects of the mechanism of template removal in different conditions. Temperature programming desorption experiments supplemented with low temperature nitrogen adsorption, X-ray diffraction and positronium annihilation lifetime spectroscopy provide additional information on the physical and chemical processes occurring when as-synthesized MCM-41 silica sample is thermally treated. The results are compared with those presented in the current literature.

Experimental

Material

Pure silica MCM-41 materials were prepared following the synthesis procedure reported previously [25]. MCM-41 material was synthesized, using tetraethyl orthosilicate (TEOS) as silica source, octadecyltrimethylammonium bromide (C18TMAB) as a template and ammonia as the catalyst. The final surfactant-silica mesophase was filtered, washed with distilled water and dried at 323 K. Two portions of as-synthesized samples designated MCM-41(18) were next calcined at 823 K in air and argon atmosphere. The calcined samples were termed MCM-41(18)air and MCM-41(18)Ar, respectively.

Methods of analysis

Nitrogen adsorption/desorption isotherms were measured at 77 K on ASAP 2010 volumetric adsorption analyzer Micromeritics (Norcross, GA). For calculation of the pore size of MCM-41 mesoporous materials the BJH method was applied [26]. The specific surface areas of the investigated samples were evaluated using the standard BET method for the adsorption data in a relative pressure p/p_0 range from 0.04 to 0.25. The total pore volume was estimated from a single point adsorption at the relative pressure of about 0.99. The primary mesopore volumes were estimated for $p/p_0 \approx 0.5$ (the end of the first step on the adsorption isotherms).

Template removal was conducted by calcination in either air or argon flow. TG and DTA curves were measured with Setaram Setsys 16/18 instrument, using standard platinum crucibles and sample size of ~10 mg. The samples were heated at a rate of 2.5 K min^{-1} from room temperature to 873 K in air or argon flow of 0.6 $\text{dm}^3\ \text{h}^{-1}$. Prior to TG-DTG and DTA experiment the as-synthesized MCM-41(18) sample was dried at 323 K for 12 h until the mass became constant. Part of the raw silica material was calcined in air using Derivatograph C (MOM, Hungary) equipped with so-called quasi-isothermal programme (QI).

X-ray diffraction measurements were performed using DRON-3 X-ray apparatus (SSSR) with CuK_α tube and Ni filter. X-ray patterns of the investigated samples were obtained by measuring the number of impulses within a given angle over 10 s. The measurements were taken every 0.02°.

Positronium annihilation measurements (PALS method) and the data processing were done as described in [27]. In PALS experiment the temperature was changed stepwise by 10 K, the duration of one step was 3 h.

Results and discussion

The TG, DTG and DTA data for MCM-41(18) sample calcined in air and argon are shown in Figs 1 and 2, respectively. The upper parts of these figures illustrate the mass loss *vs*. temperature, TG curves and appropriate differential DTG curves. The bottom parts present DTA curves.

In the case of air calcination, four maxima on the mass loss curve can be observed. The first at the initial stage of calcination below 373 K is associated with water desorption and represents about 2.4% mass loss. The next two peaks can be ascribed to Hoffman elimination reaction – a large contribution to the mass loss (about 29%) and combustion of carbon species – a lower contribution (about 14%). Recently, Kleitz *et al*. carried out in situ studies of template removal by calcination of mesostructured ordered silicas by combining X-ray diffraction, thermogravimetry and mass spectroscopy [7, 8]. These investigations confirm a stepwise mechanism of the template removal for MCM-41 samples synthesized with *n*-alkyltrimethylammonium surfactants. According to the results presented in [8] the first small step on TG curve represents desorption of physically bonded water (298–423 K), the next step between 273–523 K is usually assigned to Hoffman degradation resulting in the formation of the trimethylamine and hydrocarbon chain. The exothermic step within the temperature range 523–573 K originates from the carbon chain fragmentation and oxidation process producing CO_2 and H_2O. The final oxidation above 573 K causes burning-off of the organic compounds and coke formed during earlier pyrolysis and desorption of organic products. Additional maxima on DTG curve appearing in some experiments for C18MCM41 above 673 K are usually ascribed to condensation of the surface OH groups and formation of siloxane bridges.

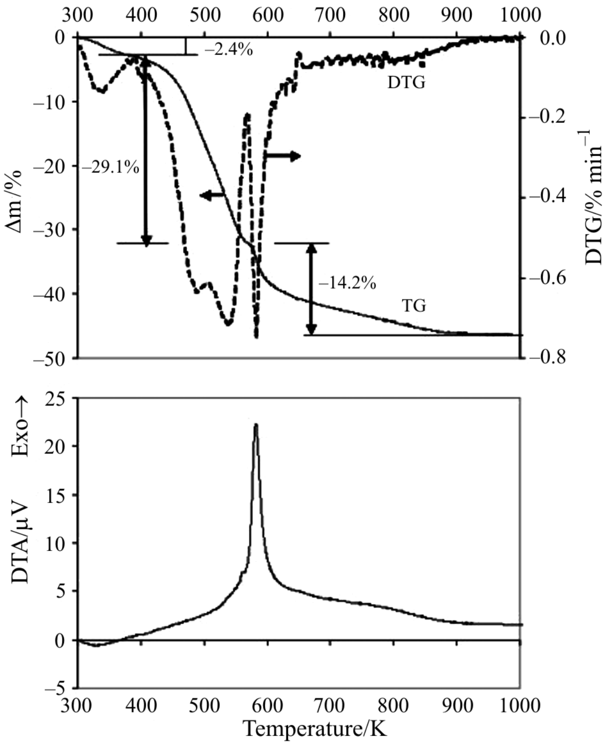

Fig. 1 TG-DTA measurements performed on MCM-41(18) in air atmosphere

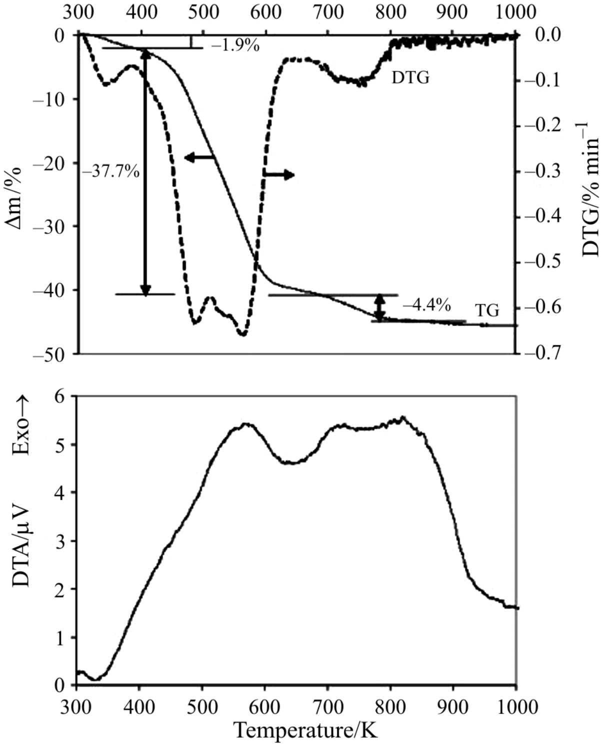

Fig. 2 TG-DTA measurements performed on MCM-41(18) in argon atmosphere

A change of reflection intensities and evolution of *d*-spacing for MCM-41silica in X-ray diffraction are also observed during calcination. From these studies it follows that the main structural parameters are stabilized after heating to 523 K, and up to this temperature a pronounced shrinkage of hexagonal structure of silica skeleton takes place [7, 8].

In general one can say that TG-DTA results presented in Fig. 1 illustrate the mechanism of template degradation in air according to the previous investigations. In the case of the present experiment the major exothermic (DTA curve) process during calcination in air occurs between 563 and 603 K and is represented by a well defined step on TG curve. This peak may be assigned to the combustion of the remaining carbonaceous species and deposited carbon or coke. The location of this peak can slightly change *vs.* the heating rate applied. For faster heating the temperature at the peak maximum is shifted towards higher temperature. At a heating rate of 2° min^{-1} the DTA peak is located at ~560 K [15], for 2.5° min^{-1} heating rate (our experiment) this peak maximum appears at 581 K, and for 5° min^{-1} heating rate at 614 K [8]. The temperature shift is caused probably by kinetic effect connected with diffusion of gaseous products from the pore interior to pore exterior [28].

It should be noted that the total mass losses recorded in air and argon atmosphere are identical. However, mass losses at above 573 K occur at different temperatures. In the absence of oxygen above the sample, exo- and endothermic effects on DTA curves are less pronounced. In Fig. 2 the ordinate was stretched by a factor of four compared to Fig. 1. However, the first distinct maximum on DTA curve appears in both cases at about 573 K.

For the sample heated in argon atmosphere in a higher temperature interval 673–793 K, there appears an additional step on TG curve characterized by a small endothermic effect on DTA curve. The mass loss within this temperature range can be ascribed to desorption of some carbonaceous species or condensation of surface silanols. Kleitz *et al.* observed a similar peak for calcination in air. The intensity of this effect increases when the alkyl chain of the templating agent increases from C12 to C18 [8]. In our case this peak disappeared for calcination in air. However, the three remaining peaks were identical with those presented it [8]. The presence of the observed transformation in the sample heated above 673 K in argon should be rather ascribed to desorption of products of the surfactant degradation than condensation of surface silanols. According to the results of Ek *et al.* [14] condensation of silanols is a continuous process which takes place within a wide temperature range 523–1523 K without sharp transformations at the particular temperature. Thus, the mass loss above 673 K (~4.4%) (Fig. 2) should be rather ascribed to desorption of thermal degradation products.

As it was mentioned earlier, for argon experiment the major part of the surfactant is removed by exothermic decomposition when 38% mass loss is observed. An additional small but clearly visible endothermic process between 573–693 K appears when the sample mass is practically stable. The observed effect can be explained by translocation of residual quasi-liquid products from pore interior to pore openings. Thermal treatment without burn-off process can lead to the formation of a distinct amount of liquid products of surfactant degradation in pores of MCM-41 silica. Thus, even at higher temperatures pores are partially filled with these organic species.

Structural changes of a partially decomposed template within pores at increasing temperature can be seen in positron annihilation experiment [27]. Application of positron annihilation spectroscopy (PALS) for registration of changes in the template structure indicates that in vacuum before chemical degradation of surfactant molecules some restructurization inside the pores begins by splitting the cylindrical micelle template into smaller parts and appearance of free volumes between them. One can imagine that in the conditions applied in our experiments the template exhibits some properties of the liquid. The results of PALS experiment performed for as-synthesized MCM-41(18) sample are shown in Fig. 3.

For MCM-41 with C18 template under study at ~420 K a positronium lifetime component ≈20 ns appears (curve b in Fig. 3). That lifetime corresponds to the gaps in the template structure ≈2 nm in size; already at ~463 K this component disappears (as well as the component typical of a continuous template, curve a). In the same temperature range the component 100 ns (curve c in Fig. 3) related to the escape of positronium from empty pores begins to grow. The existence of 20 ns component is an evidence of breaking the micelle into fragments with empty spacing between them.

The as-synthesized sample and samples after thermal treatment with emptied pores were tested by the liquid nitrogen adsorption/desorption method. Respective isotherms are shown in Fig. 4. As seen, the isotherms for samples calcined in air and argon are close each other. It means that the degree of surfactant removal is in both cases very similar. The isotherms for silica with evacuated surfactant exhibit well-developed steps in a relative pressure p/p_0 range 0.3 to 0.4, which is characteristic of capillary condensation within ordered primary pores. The second condensation step suggests the presence of wider pores which should be ascribed to secondary interparticle pores. Adsorption/desorption isotherm for initial silica with the template filling the pores is much lower and without a condensation step characteristic of primary mesopores.

In Table 1 the parameters characterizing the pore structure of the investigated samples are summarized. In the raw material a small specific surface area derived from the nitrogen adsorption data is related to large free volumes which can be ascribed to the voids between grains. However, for both evacuated samples the values of S_{BET} are very similar.

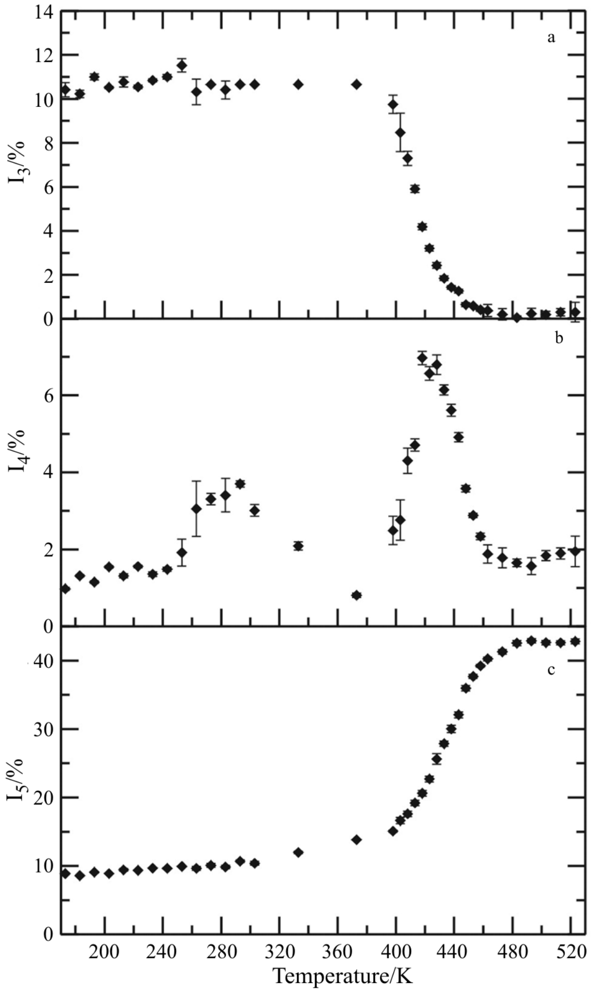

Fig. 3 Positron annihilation data. Intensities of various *ortho*-Ps components as a function of temperature: a – ≈4 ns, *o*-Ps inside micelle body; b – ≈20 ns, *o*-Ps in the gaps between micelle fragments; c – ≈100 ns, *o*-Ps escaped from empty pores to outside and *o*-Ps on the outer grain surface

The results of X-ray diffraction experiments for the samples investigated are shown in Fig. 5. It can be seen that the XRD patterns show quite a good resolution for (100) and (110) diffraction peaks. Both MCM-41 samples after temperature treatment exhibit a similar d_{100} value. For template removal in argon, the intensity of the (100) reflection is slightly decreased. However, for both calcined samples d_{100} spacing is much smaller in comparison to the as-synthesized sample, which is caused by shrinkage of the silica framework at higher temperatures. These changes coincide with those found in pore size distributions (PSD) derived from nitrogen adsorption data. Pore size distributions calculated by BJH method [26] for samples under study from the desorption branch of the nitrogen iso-

Table 1 Structural parameters of silica samples investigated

Sample	S_{BET}/ $m^2\ g^{-1}$	V_{prim}/ $cm^3\ g^{-1}$	R_{prim}/ nm	d_{100}/ nm
MCM-41(18)	101	–	–	4.90
MCM-41(18)air	1132	0.71	1.52	4.40
MCM-41(18)Ar	1273	0.91	1.45	4.28

therm are presented in Fig. 6. Both PSDs for thermally treated samples are practically identical.

As seen in Table 1, the temperature treatment of MCM-41 up to 873 K in argon atmosphere and the absence of the oxidation agent, i.e. oxygen, is also efficient for surfactant removal. Moreover, the pore structure of the final product is almost identical with the pore structure of the sample calcined in air.

It is interesting to test if some processes occurring during pyrolysis and Hoffman degradation take place at constant temperature. The presence of the steep segments appearing on TG curves presented in Figs 1 and 2 suggests some isothermic processes during calcination. Thus, thermogravimetric experiment was repeated for the same as-synthesized sample in quasi-equilibrium conditions. This unique heating mode is possible using Derivatograph C (MOM, Hungary) equipped with so-called quasi-isothermal programme (QI) [29]. The sample was placed in a platinum crucible of labyrinth type. This type of crucible guarantees the formation of self-generated atmosphere above the sample. The QI programme regulates automatically the heating rate according to sample transformations. Due to large mass loss, exceeding a fixed mass loss level, the isothermal conditions are established. This effect was observed earlier for desorption of liquids from pores of various materials [30].

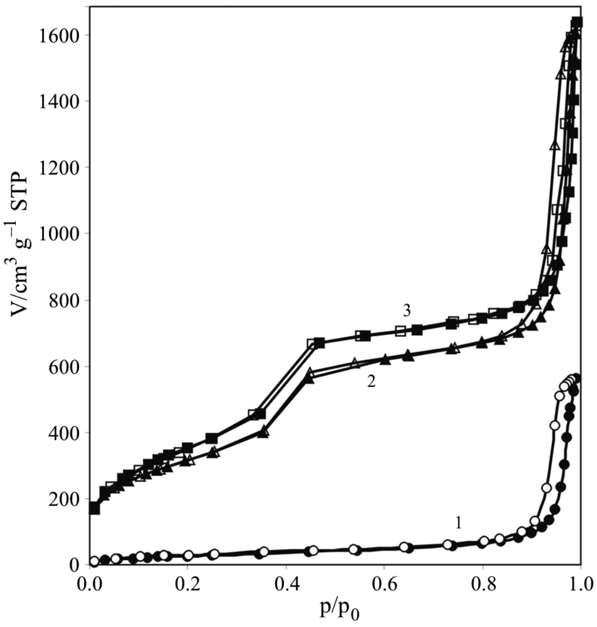

Fig. 4 Nitrogen adsorption/desorption isotherms for silicas: 1 – MCM-41(18), 2 – MCM-41(18)air, 3 – MCM-41(18)Ar

Figure 7 shows TG and DTA curves for as-synthesized MCM-41(18) sample. The TG curve illustrates continuous mass loss *vs*. increasing temperature with three poor visible steps and inflection points corresponding to ~370, ~520 and ~660 K. The initial mass loss is accompanied by endothermic effect. However, the process at higher temperatures is exothermic. A large peak on DTA curve within the temperature range 623–723 K can be ascribed to oxidation of residual carbonaceous species and their conversion to CO_2. Oxidation in static conditions without air flow takes place at relatively higher temperatures. The first step on TG curve represents water desorption. It should be noted that no isothermic processes were registered within the whole temperature range at 0.5 K min^{-1} heating rate. The extended TG curve along temperature axis without sharp steps suggests that various processes which take place during calcination, i.e. Hoffman elimination of tri-

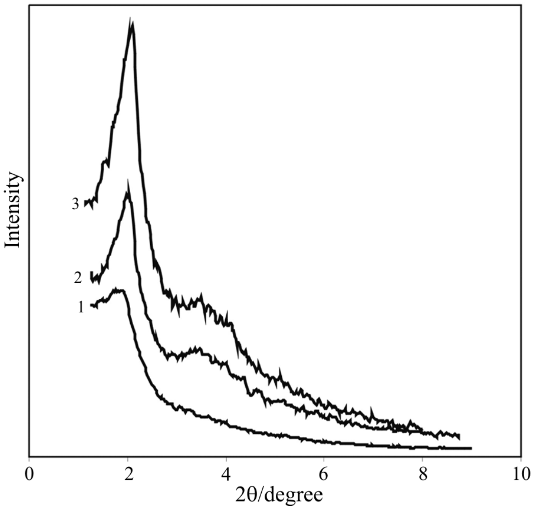

Fig. 5 X-ray diffraction patterns for silicas: 1 – MCM-41(18), 2 – MCM-41(18)air, 3 – MCM-41(18)Ar

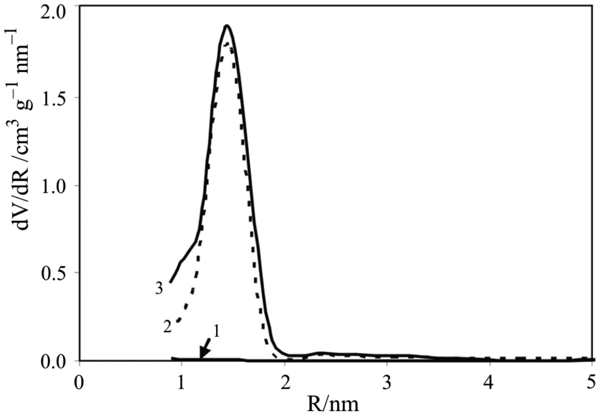

Fig. 6 Pore size distributions for silicas: 1 – MCM-41(18), 2 – MCM-41(18)air, 3 – MCM-41(18)Ar

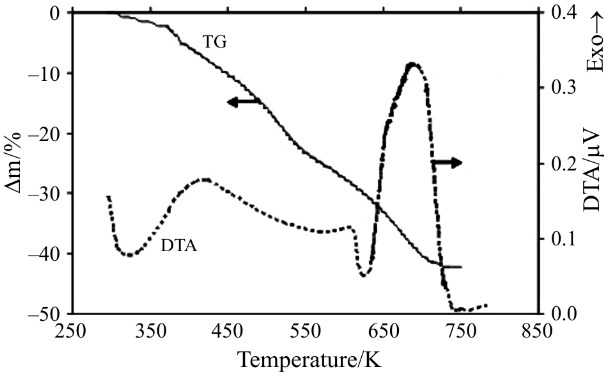

Fig. 7 TG-DTA measurements performed on MCM-41(18) in air atmosphere using quasi-isothermal program

methylamine, carbon chain fragmentation and oxidation of different fragments of hydrocarbon chain overlap.

Conclusions

Template removal by calcination is accompanied by several physical and chemical processes. The sequence of the chemical processes which take place during calcination in air is well established and widely described in literature. The results presented in this paper are in good agreement with the previous results for template removal in air. However, temperature conversion for the successive stages of template removal is dependent on the applied heating rate. Slow temperature increase facilitates secondary adsorption of products on highly developed surface area of silica. In this connection the temperatures for a given process are not precisely determined. Thermal treatment of an as-synthesized sample in argon atmosphere is sufficiently efficient for removal of organic templates. The obtained MCM-41 silica materials exhibit the same structural and chemical properties as in the case of calcination in air. Chemical degradation of surfactant molecules is accompanied by translocation of liquid-like products from the pore interior to pore exterior. These processes are of endothermic character. Due to overlapping of the above mentioned processes TG-DTA curves do not exhibit isothermal transformations during degradation of the template.

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