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Temperature removal of templating agent from MCM-41 silica materials

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Abstract

Temperature programmed desorption coupled with mass spectrometry, FT-IR spectroscopy with photoacoustic (PA) detector have been applied to investigate organic template degradation during thermal treatment of as synthesized MCM-41 silica. Micelle templated silica was prepared using C18 trimethylammonium bromide. The processes accompanying the template transformations were investigated in argon flow and mixed oxygen–helium atmosphere. Template removal appears to be completely different in the inert gas atmosphere and at the presence of oxygen. The results obtained for as synthesized sample were compared with those for calcined sample in air and additionally thermally treated in oxygen flow. Spectroscopic data indicate the presence of a variety of chemical species on silica surface after template removal. Additional oxidation of calcined sample leads to elimination of most organic functional groups and increase of siloxane bridges as a product of surface silanols condensation.

Keywords: MCM-41; Template degradation; TPD; TPO; MS; FT-IR/PAS

1. Introduction

Mobil catalytic materials of number 41 (MCM-41) belongs to the family of periodic mesoporous molecular sieves discovered by Beck et al. in the beginning of 1990s [1,2]. These materials are synthesized using micelles of a surfactant as an organic template with an addition of an inorganic silica source. The cylindrical micelles in the solution at the presence of e.g. ammonia as catalyst become covered with silica layer about 1 nm thick. The surfactant micelles are thus encapsulated in silica skeleton. The pore size is adjustable by changing the alkyl chain length and hydrothermal treatment of final product. The micellar core can be removed by calcination at high-temperature creating in this way porous silica with hexagonally arranged cylindrical channels. Investigations of surfactant removal presented in many papers have shown that degradation of the surfactant at higher temperature occurs by a stepwise mechanism [3–5]. The essential part of organic template is decomposed during thermal treatment to 200–300 °C. However, organic traces are detectable by ^{13}C solid state NMR even above 700 °C [6]. Our earlier investigations indicate that complete removal of carbon deposits requires a long-time high-temperature treatment of an as-synthesized sample in oxygen. Thermal treatment in inert argon atmosphere at 580 °C is efficient for removal of main part of organic template. However, silica sample prepared in these conditions still contains some amount of carbon species [7,8].

It has been widely realized that MCM-41 have found potential applications as catalysts [9–13], adsorbents, materials for microelectronics [14] and as hosts for various organic agents including those biologically active. The potential usefulness of MCM-41 mesoporous materials in above mentioned applications reflect their structural properties i.e., controllable pore size at high uniformity, narrow pore size distribution and exceptionally high pore volumes. The nature of MCM-41 makes it essential to employ a combination of methods in investigation their synthesis and properties. This in-

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cludes, among many others, temperature programming techniques [12] and infrared (IR) spectroscopy [15–18]. Various IR spectroscopy techniques have been widely employed as a useful complementary method in structural research on molecular sieves. However, very seldom photoacoustic spectroscopy (FT-IR/PAS) is applied for this purpose [19–21].

As it was mentioned above final stage of MCM-41 silica preparation is connected with removal of organic template from pore interior. Pore emptying is realized usually by calcination at 550 °C. At so high-temperature surface hydroxyls present on amorphous silica are destroyed. Some amount of silanols condenses forming siloxane bridges. Hence, silica surface becomes more hydrophobic in comparison to silica gel surface obtained by classical sol–gel method. For example silanol numbers at 550 °C for amorphous Si-40 silica gel and MCM-41 are 1.4 and 0.84 (OH nm^{-2}), respectively [22]. Moreover, after calcination some traces of carbon remain on silica surface [2,5,23].

Removal of organic template by calcination is mostly often conducted in air or in oxygen. To eliminate the matrix at lower temperature, the solvent extraction [24] or supercritical CO_2 extraction [25] may be used. Moreover, calcination can be conducted in the presence of ozone or nitrogen oxides [26].

Thermal and hydrothermal stability is a crucial parameter for the practical application of MCM-41 materials. Very important factor is quality i.e. geometrical regularity of final silica [27]. On the other hand chemical properties of these materials are modified by incorporation of various heteroatoms into silica framework or postsynthesis silylation [28]. Any modification process may be applied successfully if silica surface does not contain carbon deposits. Hence, there are many studies devoted to the improvement of template removal. From the viewpoint of catalysis it is important to study the mechanism of template degradation at different conditions and simultaneous changes of silica surface properties.

The aim of the present paper is to study the evacuation of various chemical species confined within the pores of the host silica material during thermal decomposition of template.

2. Experimental

2.1. Materials

MCM-41 raw material was synthesized using octadecyltrimethylammonium bromide (C18TAB; Sigma-Aldrich). The preparation procedure followed the method described in the literature [29]. Tetraetoxysilane (TEOS; Aldrich, 98%) was used as silica source. Prior to the experiments a part of raw MCM-41 sample was calcined in air at 550 °C, another part was calcined and then heated to 550 °C for 5 h in an oxygen stream in order to eliminate the carbon deposits left after calcination in static conditions. The remainder of the initial sample was dried at 60 °C and used without further thermal treatment, thus the micellar filling was entirely preserved.

The following notation is used for these samples. The raw sample dried at 60 °C is denoted MCM-41-AS, calcined sample and heated additionally in oxygen stream are designated as MCM-41-CA and MCM-41-OX, respectively.

2.2. Methods

Nitrogen adsorption measurements were carried out using an ASAP 2405 volumetric analyzer (Micrometrics, Norcross, CA). The specific surface areas S_{BET}, were calculated using the BET method for the adsorption data in a relative pressure range p/p_0 from 0.05 to 0.25. Pore size and pore size distributions were determined using the BJH procedure [30]. Parameters characterizing pore structure of MCM-41 samples are given in Table 1 [8].

Pore radii given in Table 1 corresponds to the peak of pore size distribution PSD calculated for first inflection point on desorption isotherm of nitrogen, i.e. at $p/p_0 \approx 0.4$.

Temperature programming studies were conducted with AMI-1 (Altamira Instruments) coupled on-line with mass spectrometer (MS) HAL201RC (HIDEN Analytical) by heated stainless steel capillary. Samples (0.05 g) were placed on the quartz wool (RESTEK #20790) inside the flow quartz reactor (i.d. = 10 mm). Initially, at room temperature (RT) samples were washed with argon (99.995 BOC) additionally deoxidized by MnO/SiO_2 trap or washed in 5 vol.% of O_2 in He mixture (Praxair). Flow rate of gas was 30 cm^3/min. A temperature controller maintained the reactor temperature within 1 °C and provided linear temperature programming. Samples were heated with the linear temperature programming 10 °C/min up to 800 °C. After achievement of fixed temperature they were cooled quickly to RT in flow of the same gas, and passed to the additional investigations. In a similar way were prepared samples for spectroscopic analysis applying ramp of temperature 3 °C/min. With the help of mass spectrometer were recorded the changes of signal of selected ions, e.g.: $m/z = 2$, 14, 16, 17, 18, 28, 30, 32, 44, 59, 96.

The FT-IR/PAS spectra were recorded by means of a Bio-Rad Excalibur 3000MX spectrometer equipped with photoacoustic detector MTEC300 (in the helium atmosphere in a detector) over the 4000–400 cm^{-1} range at the resolution of 4 cm^{-1} and maximum source aperture. The spectra were normalized with reference to MTEC carbon black standard. A stainless steel cup (diameter 10 mm) was filled with powder samples (thickness < 6 mm). Interferograms of 1024 scans were averaged for each spectrum.

Table 1
Parameters characterizing pore structure of examined samples

Sample	S_{BET} (m^2/g)	R_{p} (nm)
MCM-41-CA	1132	1.52
MCM-41-OX	1190	1.45

3. Results and discussion

Large surfactants molecules of templating agents like, bromides or chlorides of quaternary amines under treatment at high-temperature are decomposed into various products. The mechanism of template degradation depends strongly on external atmosphere above the sample and mainly on the presence of oxygen [8]. However, the final MCM-41 silica obtained after calcination in air as well as argon exhibit almost identical structural properties. In the case of thermal treatment of as-synthesized MCM-41 in inert atmosphere it is possible to avoid very intensive exothermic processes connected mainly with combustion of carbon species present in pores. The local overheating may change the chemistry of silica surface through condensation of surface silanols and formation siloxane bridges. On the other hand chemical processes are accompanied by endothermic desorption as well as evaporation of liquid products of surfactant degradation. Some structural transformations of organic template in pores during calcination were detected by positronium annihilation lifetime spectroscopy [7].

Analysis of template degradation products with the help of MS is relatively a difficult task. In the ionization chamber of the MS aliphatic amines can undergo fragmentation consisting on the break-up process of C–C bond in β position in relation to nitrogen, what reveals in $CH_2{=}NH_2^+$ ion formation ($m/z = 30$). On the other hand, aliphatic hydrocarbon chain can undergo subsequent fragmentation with the creation of CH_2^+ ions. Ions $m/z = 30$ are characteristic for nitrogen oxide, too. Their formation can be indicated by the decrease of oxygen signal ($m/z = 32$) or considerably weaker signals $m/e = 14$. The ions $m/z = 18$ are characteristic for water. The ion $m/z = 17$ is connected with fragmentation of water or can be an indication of ammonia formation. In a similar way, the presence of $m/z = 2$ ion may indicates fragmentation of H_2O or decomposition of other organic molecules. The formation of CO_2 can be confirmed by the appearance of signal originating from the presence of $m/z = 44$ ions (as well as $m/z = 28$, 16). Ions $m/z = 58$, 59 can be resulted from fragmentation of aliphatic amine or may indicate the presence of the trimethylamine $N(CH_3)_3$ formed in the reaction of Hoffman degradation.

In Fig. 1 there are sets of temperature-programming results conducted in oxidative atmosphere as well as in the inert gas. Analysis of presented curves for as-synthesized MCM-41-AS sample testifies, that the template removal in the oxidative atmosphere is a complex process. At the initial stage of sample heating the removal of physically adsorbed water and CO_2 is observed. Similar effects are described in the literature on the basis of TG-DTA experiments [5].

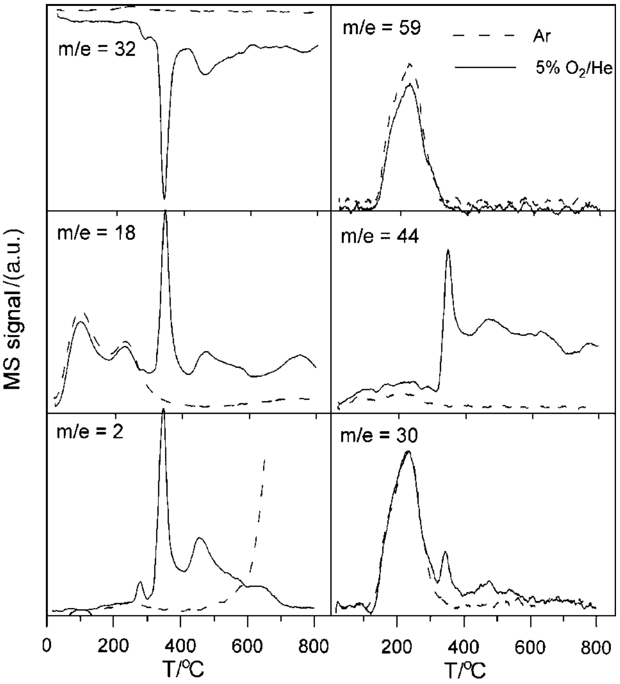

Fig. 1. Mass spectra for thermally treated MCM-41-AS silica in oxidative and inert gas atmosphere.

After crossing 100 °C the level of signal for ions $m/z = 30$, 58, 59 increases. This could be resulted from template desorption and/or its decomposition into amine group (Hoffman degradation of the template), creation of trimetylamine as well as suitable unsaturated hydrocarbon. The small decrease of oxygen observed within temperature range 100–300 °C suggests possibility of the partial oxidation of hydrocarbons and amines with the formation of: CO_2, H_2O and NO_x. Kleitz et al. [4,5] on the ground of the TG-DTA investigations observed within this temperature range the endothermic effect which may be assigned to elimination reaction of the trimetylamine head group and evaporation of alkene ($C_{16}H_{32}$) [31]. The appearance at higher temperatures exothermic effects are connected with the partial oxidation and the degradation of hydrocarbons. The treatment at the temperature above 250 °C leads to intensification of the oxidation processes and thermal degradation of hydrocarbons. Simultaneously some amount of hydrogen is evolved. This was confirmed by the presence of maxima located at 350 °C for CO_2, H_2, H_2O, as well as maximum of oxygen consumption. Regardless of reactor walls heating on its cooler part there was observed formation of liquid drops. Initially they were colorless but some time later they become more and more dark brown. After cooling down the reactor it was affirmed that deposit formed had a dense consistence and a part of it was difficult to remove. It can be stated, that decomposition curves characterize not only changes which undergo directly in the examined sample but also (especially in region of higher temperatures) processes connected with the fragmentation of hydrocarbons chains. This observation can be of a great practical importance. The inappropriate construction of devices for calcination process can causes that desorption is restricted and condensation of decomposition products becomes more favorable.

The presence of the great amount of oxygenation products formed during calcination of silica materials in oxidative atmosphere testifies the large intensity of these processes. It was suggested, that substantial amount of steam as well as strong exothermic effects can negatively influence on the structure and surface properties of the obtained material [15]. In our investigations we affirmed, that during thermal treatment of samples with the template (MCM-41-AS) in an atmosphere of inert gas, the initially observed transformations were similar to those which takes place at the presence of oxygen. Elimination of H_2O and CO_2 is observed within a similar temperature range. Recorded peaks have similar shape and size confirming that desorbed water is physically bonded. Kleitz et al. [4] suggest that water evolved between RT and ∼250 °C originates from silica skeleton transformations. In XRD experiments the intensity of the (1 0 0) reflections increases strongly up to this temperature and next maintains practically constant. However, on the decomposition curves recorded in Ar atmosphere did not appear maxima for NO_x, CO_2, H_2O, and O_2, which are characteristic for oxidizing processes. In both cases thermal treatment at ∼400 °C leads to a complete deammoniation of the sample. The presence of maxima for hydrogen, confirming thermal degradation of hydrocarbons, was observed at considerably higher temperatures.

Next it was intended to analyze simultaneously the oxygen consumption, appearance of surfactant decomposition species and accompanying energetic effects. Energetic characterization of the above mentioned processes during thermal treatment in argon and oxygen are clearly visualized by differential thermal curves DTA [8]. Differential thermal analyzes were performed in air or argon flow of 0.6 dm^3/min. DTA curves presented in Fig. 2 for as-synthesized sample are very different.

A strong exothermic effect for thermal treatment of sample in oxidizing atmosphere appears at ∼300 °C and illustrates burn-off to burning of organic template. In argon atmosphere exothermic effects are less pronounce and extended continuously along temperature axis. Maximum on DTA curve measured in air corresponds very well to peaks representing oxygen consumption and liberation of H_2O, CO_2 and H_2 on MS spectra in Fig. 1.

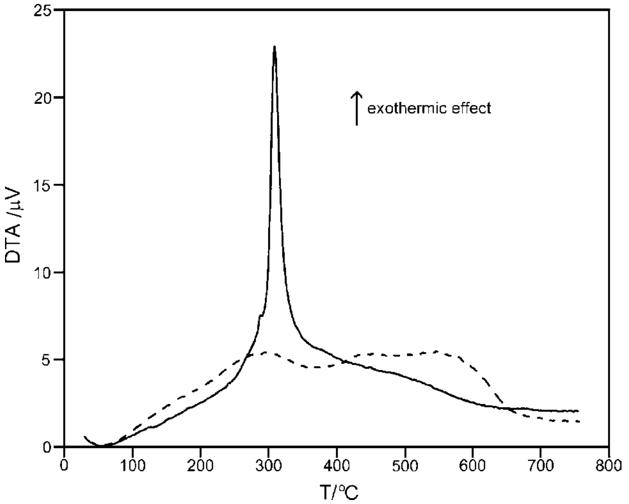

Fig. 2. DTA curves for MCM-41-AS thermally treated in air (solid line) and oxygen (dashed line).

It should be mentioned that similarly to the experiments conducted in an oxidative atmosphere, in the cooler part of the heated reactor there was observed formation of liquid colorless drops. They do not turn brown even at the temperature 800 °C (measurements were led in the same manner as described above). After cooling down the reactor it was affirmed that deposit formed had a dense, colorless (partly white) consistence.

The presence of oxygen favors the complex processes of the oxidative destruction of hydrocarbons formed after subtraction of the amine functional group.

In the next set of experiments MCM-41-CA and MCM-41-OX samples after calcination in air and oxygen were compared. The samples prior to experiment were exposed to air and next used without further pretreatment. Fig. 3 illustrates the comparison of the course of mass spectra for the studied samples.

At the low-temperature range it was possible to observe differentiated ions levels corresponding to formation of water and carbon dioxide. Sample calcined in an oxygen (MCM-41-OX) exhibit two desorption stages. First one is observed within temperature range from RT to 150 °C and suggests the presence of the weak interactions of H_2O and CO_2 with siliceous material. For MCM-41-OX sample additional intensive peak *m*/*e* = 18 appears below 100 °C. It can be observed, that maximum of water desorption for MCM-41-AS appears at higher temperature. Maxima corresponding to water desorption for calcined and oxidized sample are much lower and located at lower temperature. This shift may indicate stronger

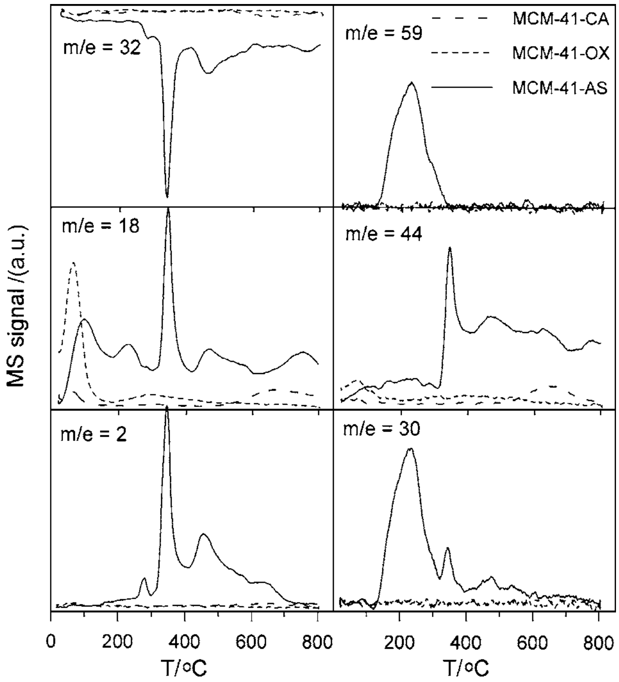

Fig. 3. Comparison of the course of the MS spectra for the studied samples.

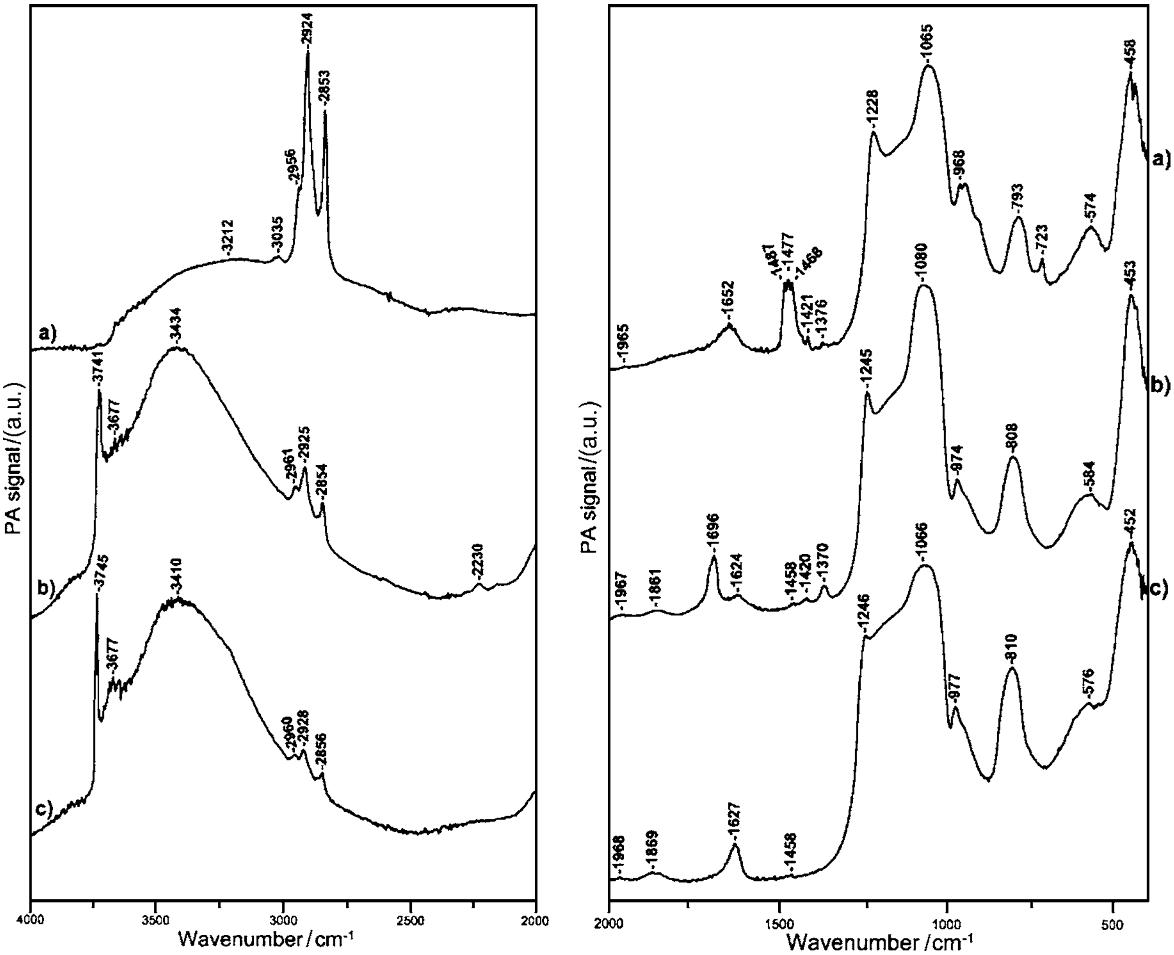

Fig. 4. FT-IR/PAS spectra of the studied samples: (a) MCM-41-AS, (b) MCM-41-CA, (c) MCM-41-OX.

interaction between water and silica supported with surfactant molecules. However, two peaks corresponding to removal of water from raw material disappear. It means that first peak represents physically adsorbed water. The second water desorption peak is located between 200 and 500 °C. Desorption of molecules in this temperature range is very small and serve the presence of considerably stronger bounded water. In case of MCM-41-CA sample the low-temperature maxima are considerably weaker, and the maxima for temperature interval 200–500 °C are hardly perceptible. This indicates considerably weaker H_2O and CO_2 interactions with silica surface. Moreover, broad CO_2 maximum occurred within temperature range 500–800 °C range and decrease of oxygen testify about burning of coke residuals. With regard to the position of this maxima and shape of the band make possible to state, that in the sample there are present coke species deposited on siliceous support. The smaller adsorption of H_2O and CO_2 from air could be explained as the partial blocking of the silica surface by coke remainders and consequently its higher hydrophobicity. Spectroscopic investigations confirm this effect.

Photoacoustic spectroscopy (PAS) measures a sample's absorbance spectrum directly with a controllable sampling depth and with little or no sample preparation. Among others key features of PAS are that it is non-destructive, non-contact, insensitive to surface morphology, and is capable of measuring spectra of all types of solids without exposure to air or moisture [32].

In Fig. 4 the FT-IR/PAS spectra of the respective MCM-41 samples are depicted.

The well resolved vibration band at about 3740 cm^{-1} is assigned to the isolated terminal silanol groups [15]. An additional shoulder at 3677 cm^{-1} in MCM-41-CA and MCM-41-OX sample may be attributed to hydrogen-bonded terminal hydroxyl groups SiOH$\cdots$OSi hydrogen bridges in the wall [33]. The broad band in the range 3700–3000 cm^{-1} is the O–H stretch and the bending of physisorbed water. The geminal and the associated terminal silanol groups exhibit a broad band where the maximum is centered at ~3550 cm^{-1} [34]. In case of MCM-41-AS sample this band is covered by the band of physisorbed water. Thus, the isolated terminal silanol groups are not detected. Primary infrared bands related to the silica framework are the asymmetric and symmetric stretch of Si–O–Si at ~1070 and ~808 cm^{-1}, respectively [13]. The increase of intensity of the bands due to symmetric Si–O stretching vibrations around 800 cm^{-1}, and decrease of the intensity of the vibrational bands at ∼1240 cm^{-1} for MCM-41-OX reflect the formation of additional siloxane bridges as compared to MCM-41-CA. The band at about 450 cm^{-1} is assigned to the Si–O bending vibration. The band at ∼576 cm^{-1} is a preliminary criterion for the formation of ordered network solids [18].

The surfactant bands (with different intensities) are present in all samples. The spectrum of MCM-41-AS sample has absorption peak at ∼1477 cm^{-1} which is assigned to CH_3–N^+ deformation band. Bands at ∼1620 cm^{-1} present in all samples are assigned to the R–NH_3^+ group of a protonated amine. This is a result of decomposition of the template [29]. Samples MCM-41-AS and MCM-41-CA have peaks at 1420 and ∼1370 cm^{-1} which are assigned to C–N and C–H bands, respectively. The lack of these bands in case of MCM-41-OX sample may be explained by removing a significant part of the template during calcination in oxygen. It can be confirmed by decreasing the intensity of peaks at about 2956, 2924 and 2853 cm^{-1} and originated from the template, which are assigned to –CH_3 and –CH_2-deformation bands (sample MCM-41-AS and MCM-41-OX, respectively). The intensity of lower band located at 2283 cm^{-1} (MCM-41-CA sample) may be assigned to acetonitrile formed during calcination in the air, derived from the template and adsorbed on silanol groups of silica [17]. Moreover, in the case of MCM-41-CA sample there can be found a band located at 1696 cm^{-1}, which is attributed to C=O vibration. The summary of recorded spectroscopic data is presented in Table 2 [13,15,18,35].

Fig. 5 shows two spectra of MCM-41-AS sample after TPD in the atmosphere of inert gas (Ar) with two different heating rates: 3 °C/min, up to 600 °C and 10 °C/min, up to 800 °C, respectively.

The peaks responsible for –CH_3 and –CH_2-groups in template almost disappear after heat treatment at 800 °C. Lower temperature (600 °C) is not sufficient for total removal of the template. Temperature treatment decreases the intensity of peaks responsible for the template. However, inert atmosphere is also not favorable for total removal of the organics. Some carbon-like species may remain in pores of MCM-41 even after high-temperature treatment.

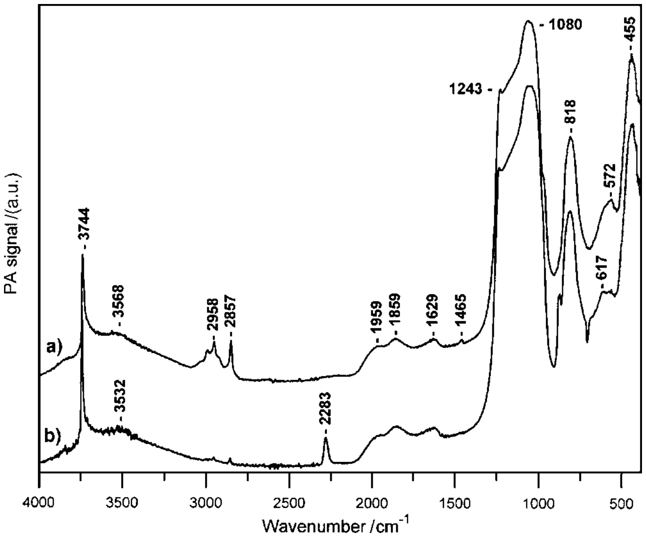

Fig. 5. Spectra of MCM-41-AS sample for TPD in the argon atmosphere: (a) thermal treatment up to 600 °C, (b) thermal treatment up to 800 °C.

Table 2
Assignments of selected bands in IR spectra of MCM-41 samples

Wavenumber (cm^{-1})			Assignment
MCM-41-AS	MCM-41-CA	MCM-41-OX	
3035	–	–	C–H stretching
2956	2961	2960	asCH_3
2924	2925	2928	asCH_2
2853	2854	2856	sCH_2 + sCH_3
1965	1967	1968	C–H
–	1861	1869	C–H
–	1696	–	C=O
1652	1624	1627	R–NH_3^+
1487	–	–	CH_3
1477	–	–	H_3C–N^+
1468	1458	1458	–CH_2 or CH_3-deformation bending
1420	1420	–	C–N
1376	1370	–	C–H
723	–	–	N–H

as – asymmetric and s – symmetric stretch.

Spectra of all samples after TPO process (up to 500 °C) are very similar (not shown).

There are still present bands corresponding to non-removed template, although weaker than after TPD process. It may indicate, that oxygen atmosphere allows elimination of the main part of the template below 500 °C.

4. Conclusions

The phenomena occurred during calcination of silicaceous materials of MCM-41 type in order to template removal in oxidative or inert gas atmosphere, in the region of low-temperatures (<250 °C) are similar. Desorption of water, carbon dioxide as well as desorption and decomposition proceed in a similar ranges of temperature, and with a comparable intensity. Heating of the materials in higher temperatures causes the degradation of organic molecules. The presence of oxygen favors the different degradation processes, mainly oxidation to H_2O, CO_2 and NO_x. Thermal treatment in the inert gas atmosphere favors the processes of hydrocarbons break-up (gradual dehydrogenation). It is possible, that in the case of the inappropriate choosing of the parameters of the process (e.g., too quick temperature change) the strong assembling of the coke remainders. The use of pure oxygen leads to more efficient removal of organics. The small coke residuals, removable above 600 °C, can modify surface properties of the siliceous materials, what has an influence on their sorptive or catalytic properties.

Choosing the right conditions of the template removal, i.e. of suitable calcination temperature and/or heating rate, gas flow, the concentration of oxidative agent, mass of the samples, and also appropriate construction of calcination device are the key synthesis conditions having an influence on the final properties (chemical and textural) of mesoporous silica materials.

References

[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710–712.

[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. Shepparol, S.B. McCullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834–10843.

[3] M.J. Hudson, P. Trens, in: K.K. Unger, G. Kreysa, J.P. Baselt (Eds.), Studies in Surface Science Catalysis, vol. 128, Elsevier, Amsterdam, 2000, pp. 505–513.

[4] F. Kleitz, W. Schmidt, F. Schuth, Micropor. Mesopor. Mater. 44–45 (2001) 95–109.

[5] F. Kleitz, W. Schmidt, F. Schuth, Micropor. Mesopor. Mater. 65 (2003) 1–29.

[6] M.T.J. Keene, P.L. Llewellyn, R. Denoyel, R.D.M. Gougeon, R.K. Harris, J. Rouquerol, in: M.M.J. Tracy, B.K. Marcus, M.E. Bisher, J.B. Higgins (Eds.), Proceedings of the 12th International Zeolite Conference, vol. II, MRS, Warrendale, USA, 1999, pp. 779–786.

[7] R. Zalewski, J. Wawryszczuk, J. Goworek, A. Borowka, T. Goworek, J. Colloid Interf. Sci. 262 (2003) 466–473.

[8] J. Goworek, A. Borowka, R. Zalewski, R. Kusak, J. Therm. Anal. Calorim. 79 (2005), in press.

[9] M.L. Pena, A. Dejoz, V. Fornes, F. Rey, M.I. Vazquez, J.M. Lopez Nieto, Appl. Catal. A 209 (2001) 155–164.

[10] A. Galernau, D. Desplantier-Giscard, F. Di Renzo, F. Fajula, Catal. Today 68 (2001) 191–200.

[11] R. Wojcieszak, S. Monteverdi, M. Mercy, I. Nowak, M. Ziolek, M.M. Bettahar, Appl. Catal. A 268 (2004) 241–253.

[12] M. Hunger, U. Schenk, M. Breuninger, R. Glaser, J. Weitkamp, Micropor. Mesopor. Mater. 27 (1999) 261–271.

[13] R.K. Rana, B. Viswanathan, Catal. Lett. 52 (1998) 25–29.

[14] W. Zhou, J.M. Thomas, D.S. Shephard, B.F.G. Johnson, D. Ozkaya, T. Maschmayer, R.G. Bell, Q. Ge, Science 280 (1998) 705–708.

[15] A. Corma, V. Fornes, M.T. Navarro, J. Perez-Pariente, J. Catal. 148 (1994) 569–574.

[16] H. Landmesser, H. Kosslick, W. Storek, R. Fricke, Solid State Ionics 101–103 (1997) 271–277.

[17] J. Janchen, H. Stach, M. Busio, J.H.M.C. van Wolput, Thermochim. Acta 312 (1998) 33–45.

[18] T. Gavrilko, I. Gnatyuk, G. Puchkovska, Yu. Goltsov, L. Matkovskaya, J. Baran, M. Drozd, H. Ratajczak, Vibr. Spectrosc. 23 (2000) 199–206.

[19] M.S. Wong, D.M. Antoelli, J.Y. Ying, Nanostruct. Mater. 9 (1997) 165–168.

[20] M.S. Morey, J.D. Bryan, S. Schwarz, G.D. Stucky, Chem. Mater. 12 (2000) 3435–3444.

[21] M.M. Mohamed, J. Colloid Interf. Sci. 265 (2003) 106–114.

[22] S. Ek, A. Root, M. Peussa, L. Niinisto, Thermochim. Acta 379 (2001) 201–212.

[23] A.S. Araujo, M. Jaroniec, Thermochim. Acta 363 (2000) 175–180.

[24] D. Kumar, K. Schumacher, C. du Fresne von Hohenesche, M. Gruen, K.K. Unger, Colloids Surf. A: Phys. Eng. Aspects 187–188 (2001) 109–116.

[25] X.-B. Lu, W.-H. Zhang, J.-H. Xiu, R. He, L.-G. Chen, X. Li, Ind. Eng. Chem. Res. (Commun.) 42 (2003) 653–656.

[26] E. Meretei, D. Mehn, J. Halasz, I. Kiricsi, Solid State Phenom. 90–91 (2003) 79–84.

[27] M. Kruk, M. Jaroniec, Y. Sakamoto, O. Terasami, R. Ryoo, Ch.H. Ko, J. Phys. Chem. B 104 (2000) 292–301.

[28] R. Ryoo, S. Jun, J. Phys. Chem. B 101 (1997) 317–320.

[29] M. Gruen, K.K. Unger, A. Matsumoto, K. Tsutsumi, in: B. McEnaney, J.T. Mays, J. Rouquerol, F. Rodriguez-Reinoso, K.S.W. Sing, K.K. Unger (Eds.), Characterization of Porous Solids IV, The Royal Society of Chemistry, London, 1997, pp. 81–89.

[30] E.P. Barrett, L.G. Joyner, P.P. Halenda, J. Am. Chem. Soc. 73 (1951) 373–380.

[31] M.T.J. Keene, R.D.M. Gougeon, R. Denoyel, R.K. Harris, J. Rouquerol, P.L. Llewellyn, J. Mater. Chem. 9 (1999) 2843–2850.

[32] K.H. Michaelian, Photoacoustic Infrared Spectroscopy, Wiley, Hoboken, NJ, 2003.

[33] H. Eckert, J.P. Yesinowski, L.A. Silver, E.M. Stolper, J. Phys. Chem. 92 (1988) 2005.

[34] H.P. Boehm, Adv. Catal. 16 (1966) 179–226.

[35] G. Socrates, Infrared Raman Characteristic Group Frequencies. Tables and Charts, 3rd ed., Wiley, Chichester, 2001.