Journal of Thermal Analysis and Calorimetry, Vol. 87 (2007) 1, 217–222

MESOPOROUS MICELLE TEMPLATED SILICA WITH INCORPORATED C_8 AND C_{18} PHASE

J. Goworek[1*], *W. Stefaniak*[1], *Agnieszka Kierys*[1] *and Mariola Iwan*[2]

[1]Maria Curie-Skłodowska University, Department of Adsorption, M. Curie-Skłodowska sq. 3, 20-031 Lublin, Poland
[2]Maria Curie-Skłodowska University, Department of General Chemistry, M. Curie-Skłodowska sq. 3, 20-031 Lublin, Poland

Mesoporous silica material of MCM-41 type was synthesized by co-condensation of highly concentrated octyltriethoxysilane (OTEOS), octadecyltriethoxysilane (ODTEOS) and tetraethoxysilane (TEOS). The obtained hybrid materials were characterized using XRD, TG-DSC and low temperature adsorption/desorption of nitrogen. It was shown that the applied method of synthesis allows to obtain silica of MCM-41 type with a high degree of hydrocarbon saturation.

Keywords: *DSC, hybrid silicas, MCM-41, TG, XRD*

Introduction

Silica materials of MCM-41 type of hexagonal symmetry, characterized by highly ordered pore structure, attract increasing attention [1, 2]. Due to high specific surface and high total pore volume these mesoporous silicas can be used as specific sorbents, host materials for biologically active substances or support for many active species in catalysis, especially dedicated to oxidation reaction, reduction or dehydrogenation reactions [3–9].

After the classical synthesis procedure, the internal surface of MCM-41 silica is covered with silanol groups and Si–O–Si bridging oxygen atoms in the pore walls. Thus surface polarity of MCM-41 sample is comparable to that of amorphous silica gel [10–12]. However, for specific applications in catalysis or separation methods inorganic–organic hybrid materials using the micelle template mechanism are synthesized. Numerous procedures are described in literature and there are many different methods for preparation of periodic mesoporous organo-silica [13–20].

One way of preparing these materials is surface silylation which improves the hydrothermal stability of MCM-41 material due to enhanced surface hydrophobicity [21–23].

Another very effective method for obtaining the modified silica materials is based on the sol–gel method, which involves hydrolysis and co-condensation of silica precursor tetraethoxysilane (TEOS) with an organosilane precursor e.g. organo-trialkoxysilane. As a result, the organo-functionalised silica material is prepared. Surface properties of these materials depend significantly on character of incorporated organic group e.g. alkyl-trialkoxysilane, 3-aminopropyltriethoxysilane (ATES), allyltrimethoxysilane (ATMS), 3-sulphanylpropyl trimethoxysilane (SPTMS), etc. [18–20]. It should be noted that in most cases modifying agents exhibit the presence of relatively short linear alkyl chains containing 2–4 carbon atoms. Due to low thermal stability of periodic mesoporous organo-silicas, the removal of surfactant template without destruction of organic species imprinted into the silica framework is commonly carried out by means of alcohol-aided extraction.

Adsorption of various substances on siliceous MCM-41 is widely discussed in many papers. However, sorption properties of as-synthesized MCM-41 with the pores filled with organic template are rarely investigated. MCM-41 silica containing the template in the pore interior can sorb appreciable amount of hydrocarbon as well as other organic species.

It is surprising that the as-synthesized MCM-41 samples with the template in pores exhibit very low nitrogen adsorption similar to non-porous material, but simultaneously adsorb significant amount of hydrocarbons [24]. The sorption mechanism is probably caused by solubilization of hydrocarbon in the confined hydrocarbon ligands but not adsorption on the silica surface.

In the present paper the investigations of MCM-41 with the incorporated hydrocarbon (C_8) and (C_{18}) group are reported. The co-condensation of tetraethoxysilane and organo (C_8 or C_{18})-triethoxysilane in the presence of the surfactant micellar template was used for preparation of organosilica material of highly hydrophobic character and high hydrocarbon contamination. The high concentrations of organosilane modifiers were used in the synthesis at the expense of the regularity of hexagonally arranged pore structure. The structural parameters of MCM-41(C_8) and MCM-41(C_{18}) after re-

---

[*] Author for correspondence: jgoworek@hermes.umcs.lublin.pl

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

moval of organic species were compared with those for pure siliceous MCM-41.

Experimental

Synthesis of materials

The synthesis of organo-silica-materials with incorporated alkyl chains silicas was accomplished using the procedure described in [25] with the use of octadecyltrimethylammonium bromide (Aldrich) as a structure directing agent (surfactant). As silica source tetraethoxysilane (TEOS) (Aldrich), octadecyltriethoxysilane (ODTEOS) (Aldrich) and octyltriethoxysilane (OTEOS) (Aldrich) were used. The last two above mentioned silicas allow to introduce during the co-condensation process C_8 and C_{18} ligands into the silica framework. The obtained materials are designated as MCM-41(C_8) and MCM-41(C_{18}), respectively. Surfactant forming the template was dissolved in deionised water to give a 0.055 mol dm^{-3} solution and 9.5 g of aqueous ammonia (POCh, Poland) were added into the solution while stirring. TEOS and OTEOS (or ODTEOS) of the total amount of 0.05 moles and the molar ratio 4:1, respectively, were added slowly to this solution and stirred at 323 K for 1 h. The resultant solid products were filtered and washed with hot distilled water and dried in air at 363 K for 24 h. In the case of MCM-41 sample only TEOS was used.

Template removal from MCM-41, MCM-41(C_8) and MCM-41(C_{18}) was carried out by extraction at 363 K. To investigate the effectiveness of template removal by propanol, part of each sample was not propanol extracted and washed only with water.

About 1 g of as-synthesized material was combined with 50 cm^3 of propanol and refluxed in soxlet for 12 h. Afterwards the product was isolated by filtration and dried at 333 K for 24 h. Part of the as-synthesized materials was placed in a porcelain crucible and calcinated in air at 823 K for 8 h.

Methods

Nitrogen adsorption

Nitrogen adsorption measurements at 77 K were carried out using an ASAP2405 analyzer (Micromeritics, Norcross, USA). Nitrogen adsorption was used to measure the Brunauer–Emmett–Teller (BET) surface area and pore size. The pore size distribution (PSD) was calculated from the desorption branches of isotherms using the standard Barrett–Joyner–Halenda (BJH) procedure [26]. The pore volumes were estimated from the amount adsorbed at the relative pressure at the end of first condensation step on the adsorption isotherms.

X-ray diffraction

X-ray diffraction (XRD) patterns were measured on a DRON-3 (USSR) powder diffractometer using CuK$_\alpha$ radiation. X-ray patterns were obtained by measuring the number of impulses within a given angle over 10 s. The measurements were taken every 0.02°.

Thermogravimetric analysis

Thermogravimetric experiments were conducted in air. TG, DTG and DSC curves were measured with a Setaram Setsys 16/18 instrument, using a standard platinum crucible and the sample mass of ~10 mg. The samples were heated at a rate of 5 K min^{-1} from room temperature to 873 K in air flow of 0.6 dm^3 h^{-1}. Prior to the TG-DTG and DSC experiment the as-synthesized MCM-41 samples were dried at 353 K for 12 h until the mass became constant.

Results and discussion

Nitrogen adsorption isotherms were measured for the as-synthesized, extracted with propanol and calcined samples.

Low temperature adsorption/desorption isotherms for these samples are shown in Figs 1–3. Parameters characterizing pore structure of these materials are summarized in Table 1.

Generally one can say that the adsorption of N_2 on the as-synthesized samples is very low and confirms that mesopores are inaccessible for nitrogen and in the adsorption process only external surface of microparticles of MCM-41 takes place.

The largest adsorption of nitrogen is demonstrated for purely siliceous MCM-41 calcined and ex-

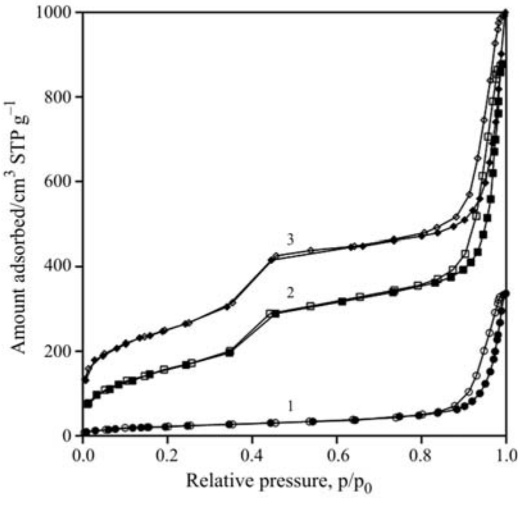

Fig. 1 Nitrogen adsorption/desorption isotherms at 77 K for MCM-41 silica: 1 – as-synthesized, 2 – extracted with propanol, 3 – calcined. Open points – adsorption, filled points – desorption

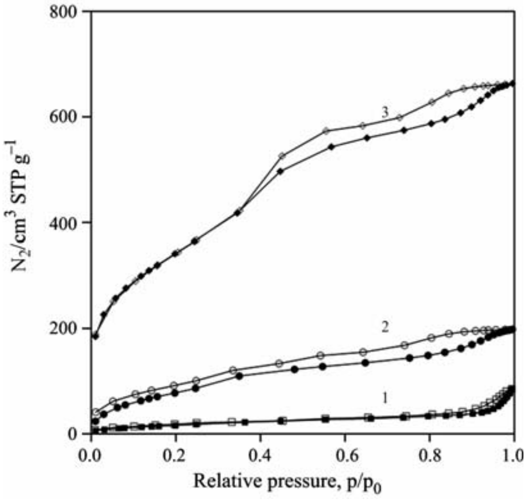

Fig. 2 Nitrogen adsorption/desorption isotherms at 77 K for MCM-41(C_8) silica: 1 – as-synthesized, 2 – extracted with propanol, 3 – calcined. Open points – adsorption, filled points – desorption

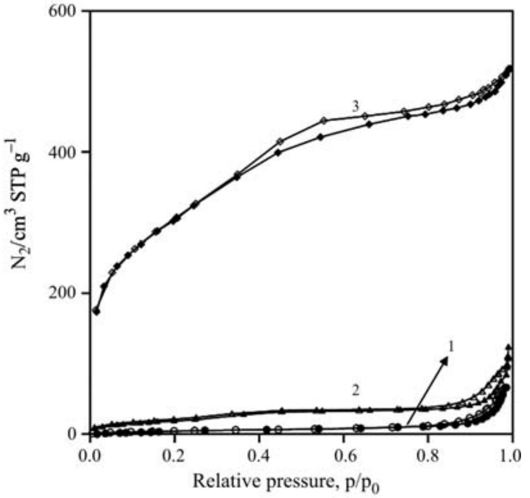

Fig. 3 Nitrogen adsorption/desorption isotherms at 77 K for MCM-41(C_{18}) silica: 1 – as-synthesized, 2 – extracted with propanol, 3 – calcined. Open points – adsorption, filled points – desorption

tracted with propanol. The adsorption isotherms of nitrogen for this sample featured well resolved inflection at the partial pressure $p/p_0 \approx 0.3–0.4$ demonstrating the existence of uniform mesopore channels.

The presence of hysteresis loop in the high relative pressure region indicates the presence of secondary mesopores or macropores attributed to the interparticle voids. The resulting isotherm can be classified as a type IV according to the IUPAC classification.

However, the adsorption isotherm for MCM-41(C_{18}) after extraction is comparable with those for as-produced sample and exhibit the shape characteristic rather of nonporous sample. It means that in this case template removal by soxlet extraction with propanol is ineffective. A similar effect was observed for the same sample extracted with methylene chloride and ethanol. Elimination of template by extraction is larger for the MCM-41(C_8) sample. However, adsorption is not reversible in the whole pressure range. This effect testifies that substantial part of template is still present in the pores. After thermal treatment of the same sample at 823 K in air (Fig. 1) one can observe appearance of porosity, however the shape of N_2 adsorption/desorption isotherms is different in comparison to pure MCM-41. Compared with the isotherms for the MCM-41 samples the capillary condensation step of calcined MCM-41(C_{18}) sample is less pronounced, indicating the less ordered porous structure. The adsorption/desorption isotherms for MCM-41(C_8) exhibit two inflections above p/p_0= 0.35. Moreover, adsorption of nitrogen is not reversible within a wide range of relative pressure.

It should be mentioned that during calcination of modified samples the organic surfactant template as well as C_8 and C_{18} ligands incorporated into the silica framework during co-condensation are destroyed and evacuated.

The desorption branches of nitrogen isotherms provide useful information about the uniformity of pores in the investigated samples. Pore size distributions (PSDs) derived from the desorption data for MCM-41(C_8) and MCM-41(C_{18}) are presented in Figs 4 and 5.

The pore size distribution curve for calcined MCM-41(C_{18}) exhibits practically one well resolved peak whose maximum is located at R_{peak}=1.5 nm indicating that calcination causes pore emptying and degradation of C_{18} ligands. For the same sample after

Table 1 Parameters characterizing the porous structure of investigated materials

Parameter	Materials						
	MCM-41			MCM-41(C_8)		MCM-41(C_{18})	
	1	2	3	2	3	2	3
$S_{BET}/m^2\ g^{-1}$	106	1042	1214	293	1225	59	1084
$V_p/cm^3\ g^{-1}$	0.06	0.75	0.93	0.24^a	0.85^a	0.04^a	0.57^a
R_{peak}/nm	–	1.8	1.5	1.8	1.5	1.5	1.5

V_p – pore volume of primary pores from nitrogen adsorption at p/p_0=0.5,
[a]total pore volume, 1 – as-synthesized, 2 – extracted with propanol, 3 – calcined

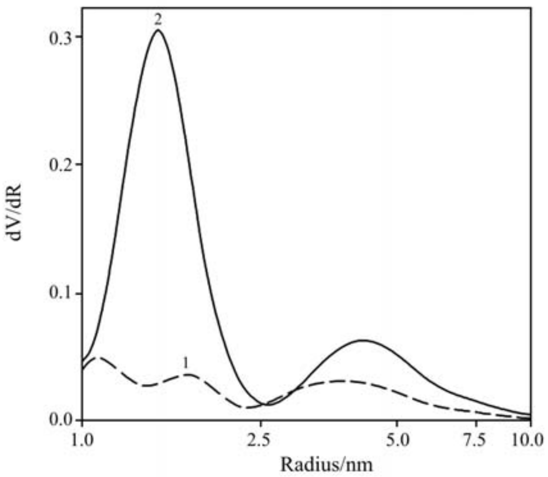

Fig. 4 Pore size distributions for MCM-41(C_8) silica: 1 – extracted with propanol, 2 – calcined

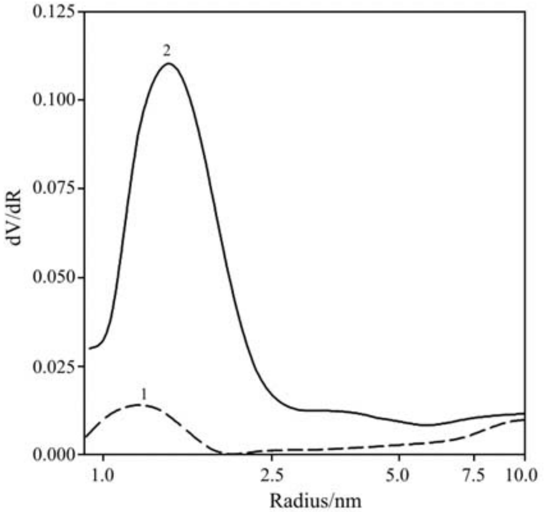

Fig. 5 Pore size distributions for MCM-41(C_{18}) silica: 1 – extracted with propanol, 2 – calcined

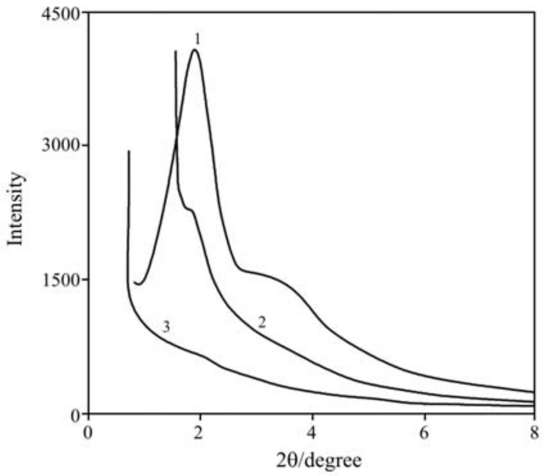

Fig. 6 XRD patterns for calcined: 1 – MCM-41, 2 – MCM-41(C_8), 3 – MCM-41(C_{18})

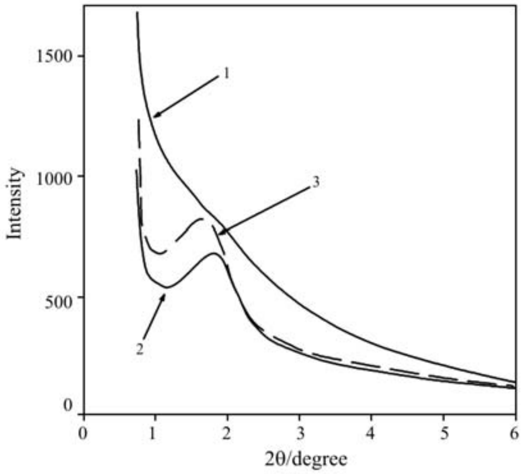

Fig. 7 XRD patterns for MCM-41(C_{18}): 1 – calcined, 2 – as-synthesized, 3 –extracted with propanol

propanol extraction we observe a small peak corresponding to the primary pores which testifies that only small part of these pores is emptied. Partial destruction of pore ordering for MCM-41(C_8) and total destruction for MCM-41(C_{18}) after calcination is confirmed by the XRD patterns measured for the investigated samples.

Figure 6 shows the XRD patterns for the mesoporous silica sample prepared with OTEOS and ODTEOS along with the pattern of the sample prepared in the absence of organosilica agent (curve 1).

Figure 7 shows the XRD patterns for the mesoporous silica sample prepared with ODTEOS. The XRD patterns of as-synthesized and extracted sample MCM-41(C_{18}) (curves 2 and 3) exhibit only one reflection of low intensity which can be indexed as (100) assuming hexagonal symmetry. Smaller intensity of the XRD reflection in this case is caused by a contrast matching between the silica framework and the pore interior filled with the surfactant template.

It can be seen that the pattern of the calcined sample MCM-41(C_{18}) is different from that of the initial material. The (d_{100}) peak disappears after calcination indicating that the ordered pore structure collapse.

Next experiments were devoted to thermal decomposition of various organic species present in the as-synthesized sample obtained by co-condensation of TEOS and octyl- or octadecyltriethoxysilane. The decomposition of organics for non-modified MCM-41 was also investigated. The thermogravimetric curves TG, DTG and DSC for MCM-41, MCM-41(C_8) and MCM-41(C_{18}) silicas are presented in Figs 8–10. For all investigated samples at temperature of up to 423 K physisorbed water and water confined in the silica material are desorbed, resulting in small mass loss. Above 423 K mass loss indicates decomposition of alkyl chains. The results present in Figs 8–10 confirm a stepwise mechanism of template removal for the MCM-41 samples synthesized with *n*-alkyltrimethyl ammonium surfactant [27–30].

At higher temperatures MCM-41 shows two distinct TG steps and consequently two DTG peaks – the first wide peak of bimodal character at about 473–523 K originating from large mass loss and the second representing small mass loss at about 573 K. The step between 473–523 K is usually assigned to Hoffman degradation resulting in the formation of the trimethylamine and hydrocarbon chain. The exothermic peak 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 the burn-off of organic compounds and coke formed during pyrolysis. For MCM-41(C_8) and MCM-41(C_{18}) we observe also two mass loss steps: the first at about 483 K and the second above 553 K. It should be mentioned that the MCM-41(C_{18}) sample contains relatively small amount of template and some amount of C_{18} phase. Relatively lower template contamination in MCM-41(C_8) and MCM-41(C_{18}) results in the lower first step on the TG curve in comparison to the MCM-41 sample. Consequently, the process below 523 K is less exothermic as compared to pure MCM-41. However, the exothermic combustion at about 573 K is larger for the imprinted silica samples. It means that the substantial part of organics (template+C_8 or C_{18} ligand) is evacuated at higher temperature.

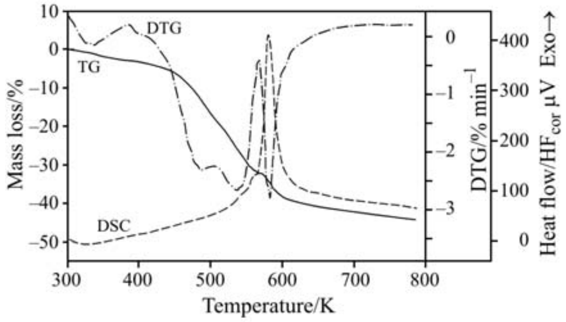

Fig. 8 TG, DTG and DSC curves for MCM-41 as-synthesized

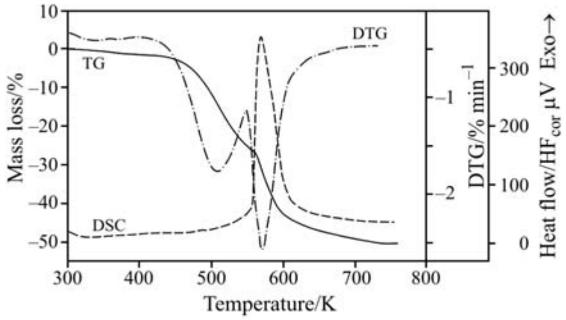

Fig. 9 TG, DTG and DSC curves for MCM-41(C_8) as-synthesized

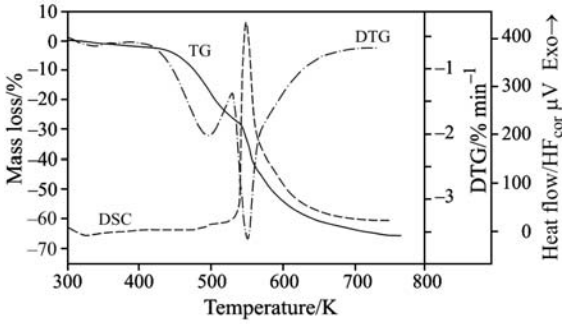

Fig. 10 TG, DTG and DSC curves for MCM-41(C_{18}) as-synthesized

The shape of thermogravimetric curves suggests a different mechanism of burn-off process for these samples. For MCM-41(C_8) and MCM-41(C_{18}) one can observe markedly higher total mass loss in comparison to MCM-41 silica, 56, 67 and 46%, respectively. During calcination in air, either surfactant or imprinted hydrocarbon phase (octane or octadecyl) is destroyed and next removed from the sample. As a result, we obtain loose particles of silica with emptied pores. It may be assumed, that the difference of mass loss for both samples corresponds to destruction and evacuation of C_8 or C_{18} radicals. Thus, from the mass loss difference it may be calculated that about 10% of C_8 and 21% of C_{18} chain are incorporated into the silica skeleton.

All above described experiments indicate that condensation of (TEOS and OTEOS) or (TEOS and ODTEOS) on the micellar template is a complex process. During framework formation, TEOS is preferentially cross-linked due to its higher rate of hydrolysis and condensation. In the successive stages of synthesis OTEOS or ODTEOS are condensed on the surface of the existing silica network. Finally, the primary particles represent the ordered phase with C_{18} alkyl chains inside and outside silica cylinders.

It is usually assumed that organic ligands are oriented towards the micelle interior with the silica head groups located on the external surface of template. These groups condense with TEOS finally producing classical hexagonal array. It is possible that C_8 or C_{18} groups dissolve partially in the hydrophobic region of the surfactant micelle in the initial stage of the assembly process. As it was stated earlier [24, 31] as-synthesized MCM-41 can sorb significant amounts of hydrocarbons even with the surfactant residing in the pore channels. Hence, these groups may be assumed as pore expanders. The formation of supramolecular aggregates is favoured by the hydrophobic interactions of surfactant hydrocarbon chains. Thus, rather wider mesopores should be expected in the terminal material of hexagonal structure. On the other hand, it is worth noting that the external, polar surface of micellar cylinder additionally coated by the condensed silica originating from TEOS is a barrier for hydrophobic C_8 or C_{18} ligands of silane which confines their penetration into the micelle interior. In that case the essential structure of silica product should be stable during calcination and surfactant should be removed simultaneously with C_8 or C_{18} groups during thermal treatment. Our results indicate a diverse mechanism of organo-functionalized silica formation. From the presented results one may conclude that both processes mentioned above, i.e. formation of mixed organo-silica walls of pores and penetration of micelle structure by C_8 or C_{18} ligands, take place simultaneously during synthesis. However, due to a large difference of hydrolysis and condensation for TEOS and OTEOS or ODTEOS, condensation of TEOS on the micellar template is a dominant process at the beginning of mesophase formation.

Conclusions

Summing up our investigations, one can state that co-condensation of TEOS and siloxane with octyl and octadecyl ligands makes it possible to prepare mixed organo-silica material of MCM-41 type with the incorporated long chain ligands in the silica framework. Hydrocarbon ligands are located within the walls of silica material as well as in the micellar template. Thus, template removal using extraction is practically impossible. Total removal of organics is possible by calcination. After thermal treatment the organo-silica material exhibits uniform mesopores characteristic of MCM-41 and some amount of larger pores. Moreover, after calcination of MCM-41 silicas with C_8 and C_{18} ligands the hexagonal arrangement of silica pores observed for the as-synthesized sample collapse. It indicates that part of hydrocarbon ligands is located between the cylindrical channels as organic deposits. The thermal destruction of organic moieties causes that silica structure becomes less ordered and more heterogeneous.

It would be advisable to investigate the adsorption properties of synthesized materials of high contamination of hydrocarbon species. The adsorption of hydrocarbon adsorbates should be enhanced in the case of synthesized material in comparison to the as-synthesized MCM-41 silica.

References

1 C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, Nature, 359 (1992) 710.
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. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, J. Am. Chem.Soc., 114 (1992) 10834.
3 I. V. Kozhernikov, A. Sinnema, R. J. J. Jansen, K. Panin and H. van Bekkum, Catal. Lett., 30 (1999) 241.
4 X. Feng, G. E. Fryxell, L.-Q. Wang, A. Y. Kim, J. Liu and K. H. Kemner, Science, 276 (1997) 923.
5 C. Baleizao, B. Gigante, D. Das, M. Alvaro, H. Garcia and A. Corma, Chem. Commun., (2003) 1860.
6 A. Taguhi and F. Schuth, Microporous Mesoporous Mater., 77 (2005) 1.
7 Y. Shin, J. Liu, L.-Q. Wang, Z. Nie, W. D. Samuels, G. E. Fryxell and G. J. Exarhos, Angew. Chem. Int. Ed., 39 (2000) 2702.
8 K. V. Katok, V. A. Tertykh, S. Ya. Brichka and G. P. Prikhod'ko, J. Therm. Anal. Cal., 86 (2006) 109.
9 F. S. M. Sinfrônio, A. G. Souza, M. G. Santos Ieda, V. J. Fernandes Jr., Cs. Novák and Zs. Éhen, J. Therm. Anal. Cal., 85 (2006) 391.
10 R. Denoyel, M. T. J. Keene, P. L. Llewellyn and J. Rouquerol, J. Therm. Anal. Cal., 56 (1999) 261.
11 S. A. Araujo, M. Ionashiro, V. J. Fernandes and A. S. Araujo, J. Therm. Anal. Cal., 64 (2001) 801.
12 M. J. B. Souza, A. O. S. Silva, J. M. F. B. Aquino, V. J. Fernandes and A. S. Araujo, J. Therm. Anal. Cal., 79 (2005) 493.
13 C. Sanchez and F. Ribot, New J. Chem., 18 (1994) 1007.
14 D. J. Macquarrie, Chem. Commun., 16 (1996) 1961.
15 S. L. Burkett, S. D. Simms and S. Mann, Chem. Commun., 11 (1996) 1367.
16 M. H. Lim, C. F. Blanford and A. Stein, J. Am. Chem. Soc., 119 (1997) 4090.
17 L. Mercier and T. J. Pinnavaia, Chem. Matter., 12 (2000) 188.
18 Ch. E. Fowler, S. L. Burkett and S. Mann, Chem. Commun., (1997) 1769.
19 J. Shah, S.-Su. Kim and Th. J. Pinnavaia, Chem. Commun., (2004) 572.
20 S. R. Hall, Ch. E. Fowler, B. Lebeau and S. Mann, Chem. Commun., (1999) 201.
21 X. S. Zhao and G. Q. Lu, J. Phys. Chem. B, 102 (1998) 1556.
22 X. S. Zhao, G. Q. Lu and X. Hu, Microporous Mesoporous Mater., 41 (2000) 37.
23 K. A. Koyano, T. Tatsumi, Y. Tanaka and S. Nakata, J. Phys. Chem. B, 101 (1997) 9436.
24 J. C. Vartuli, A. Malek, W. J. Roth, C. T. Kresge and S. B. McCullen, Microporous Mesoporous Mater., 691 (2001) 44.
25 M. Grün, K. K. Unger, A. Matsumoto and K. Tsutsumi, Characterization of Porous Solids IV, B. McEnaney, J. T. Mays, J. Rouquerol, F. Rodriguez-Reinoso, K. S. W. Sing and K. K. Unger, Eds, The Royal Society of Chemistry, London 1997, p. 81.
26 E. P. Barrett, L. G. Joyner and P. H. Halenda, J. Amer. Chem. Soc., 73 (1951) 373.
27 F. Kleitz, W. Schmidt and F. Schüth, Microporous Mesoporous Mater., 44–45 (2001) 95.
28 F. Kleitz, W. Schmidt and F. Schüth, Microporous Mesoporous Mater., 65 (2003) 1.
29 J. Ryczkowski, J. Goworek, W. Gac, S. Pasieczna and T. Borowiecki, Thermochim. Acta, 434 (2005) 2.
30 J. Goworek, A. Borówka, R. Zaleski and R. Kusak, J. Therm. Anal. Cal., 79 (2005) 555.
31 L. Mercier and Th. J. Pinnavaia, Chem. Mater., 12 (2000) 188.

DOI: 10.1007/s10973-006-7811-z