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Adsorption properties of ordered mesoporous silicas synthesized in the presence of block copolymer Pluronic F127 under microwave irradiation

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Abstract Ordered mesoporous silicas (OMSs) were prepared at different temperatures by using tetraethyl orthosilicate (TEOS) as a silica source, poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (Pluronic F127) as a structure directing agent and sodium chloride as an additive under acidic conditions and microwave irradiation. The small angle X-ray diffraction patterns of these samples indicate the presence of ordered mesopores, while adsorption studies show that they possess high volumes of pores, bimodal pore size distributions and large pore sizes. There is an interesting change in the hysteresis loop of nitrogen adsorption isotherms with increasing temperature of hydrothermal treatment; a delayed desorption characteristic for cage-like mesostructures is observed for the OMS samples treated at 100 and 120 °C, while the hydrothermal treatment at 140 and 160 °C leads to the samples having hysteresis loops characteristic for channel-like materials.

Keywords Mesoporous ordered silica · Microwave-assisted synthesis · Nitrogen adsorption · Cage-like mesostructures · Channel-like mesostructures

Nomenclature

a	unit cell parameter (nm)
S_{BET}	BET specific surface area (m^2/g)
V_c	volume of micropores and interconnecting pores of the diameter below 4 nm (cm^3/g)
V_p	volume of primary pores (cm^3/g)
V_t	single-point pore volume (cm^3/g)
w_{KJS}	mesopore cage diameter calculated by the KJS method (nm)

1 Introduction

A major breakthrough in the area of porous materials was the discovery of ordered mesoporous silicas (OMSs) in 1992 (Kresge et al. 1992; Beck et al. 1992). This important finding opened new perspectives for the development and applications of nanomaterials as well as stimulated further advancements in nanoscience and nanotechnology (Van Der Voort et al. 2008; Ciesla and Schuth 1999; Sayari and Hamoudi 2001; Oye et al. 2001; Stein 2003; Taguchi and Schuth 2005; Cejka and Mintova 2007; Izqierdo-Barba et al. 2008; Ispas et al. 2009; Jaroniec et al. 1998; Nowak et al. 2004; Kruk et al. 2002b). There is a wide interest in OMSs, especially those with organic functionalities, which can be synthesized by using commercially available organosilanes in the presence of structure directing agents such as ionic surfactants (Beck et al. 1992; Asefa et al. 1999; Antochshuk and Jaroniec 1999, 2000; Kruk et al. 2002b; Lim and Stein 1999), neutral surfactants and non-ionic block copolymers (Olkhovyk and Jaroniec 2005b; Grudzien et al. 2006a, 2006b).

Ionic surfactants were used as the first templates to fabricate OMSs (Kresge et al. 1992; Beck et al. 1992; Huo et al. 1994, 1996; Jaroniec et al. 2001; Kruk et al. 1997; Kruk and Jaroniec 1999a, 1999b; Kruk et al. 1999). The most popular surfactant-templated OMSs materials are MCM-41 (Kresge et al. 1992; Beck et al. 1992), FSM-16 (Yanagisawa et al. 1990) and MCM-48 (Beck et al. 1992; Kruk and Jaroniec 1999b; Kruk et al. 1999). MCM-41 and FSM-16 refer to 2D (two-dimensional) ordered honeycomb structure (*P6mm*) consisting of parallel and nonintersecting cylindrical mesopores, while MCM-48 refers to 3D

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(three-dimensional) cubic bicontinuous channel-like structure (*Ia3d*).

The possibility of using non-ionic block copolymers as templates opened new prospects for the development of ordered mesoporous materials (Zhao et al. 1998; Van Der Voort et al. 2008; Ciesla and Schuth 1999; Sayari and Hamoudi 2001; Taguchi and Schuth 2005; Stein 2003). Polymeric templates are inexpensive, environmentally friendly, commercially available, which make them attractive for the synthesis of OMSs. One class of the most popular templates includes non-ionic triblock copolymers Pluronics composed of poly(propylene oxide) hydrophobic and poly(ethylene oxide) hydrophilic blocks. Among them Pluronic 123 ($EO_{20}PO_{70}EO_{20}$; EO and PO denote ethylene and propylene oxides, respectively) has been used to synthesize one of the most popular OMSs, SBA-15, which is a 2D hexagonal structure of parallel mesochannels interconnected by irregular micropores (Zhao et al. 1998; Kruk et al. 2000; Ravikovitch and Neimark 2001; Fulvio et al. 2005; Yang et al. 1999). The available assortment of block copolymers permitted synthesis not only 2D mesomaterials, but also three-dimensional mesostructures such as SBA-16 (Voort et al. 2002; Sakamoto et al. 2000; Wang et al. 2004; Grudzien et al. 2006c; Kim et al. 2004; Zhao et al. 2004) (3D cubic mesostructure with *Im3m* symmetry group; body-centered packing), which can be obtained by using copolymers with longer poly(ethylene oxide) blocks like Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) or FDU-1 (3D face-centered (*Fm3m*) cubic mesostructure) prepared by employing a poly(ethylene oxide)-poly(butylene oxide)-poly(ethylene oxide) triblock copolymer B50-6600 ($EO_{39}BO_{47}EO_{39}$) (Yu et al. 2000; Kruk et al. 2002a; Matos et al. 2003; Grudzien and Jaroniec 2005a, 2005b; Grudzien et al. 2006d; Kruk et al. 2004).

It is noteworthy that the family of cage-like OMSs is very attractive because of their unique structural properties facilitating transport of molecules in the entire 3D arrangement of cages. Namely, each cage in SBA-16 and FDU-1 mesostructures is connected via small apertures with 8 and 12 neighboring cages, respectively. Such 3D mesoporous structures are propitious for immobilization of biomolecules and transport of reactants because of better accessibility of pores than in 2D networks. All these factors make cage-like mesostructures attractive for adsorption, catalysis and related applications (Srivastava et al. 2006; Olkhovyk and Jaroniec 2005a; Zhang et al. 2003; Wu and Bein 1996; Kruk et al. 2002b; Burkett et al. 1996; Gong et al. 2001).

The above cited papers refer to the OMSs obtained by hydrothermal synthesis in conventional oven. An alternative to this approach is the microwave-assisted synthesis, which not only affords good quality OMSs but also is energy and time efficient as well as environmentally friendly (Newalkar et al. 2000; Newalkar and Komarneni 2001, 2002; Fantini et al. 2004; Hwang et al. 2004; Bandyopadhyay and Gies 2005; Park et al. 2004; Tompsett et al. 2006; Celer and Jaroniec 2006; Grabicka and Jaroniec 2009). It is important to mention that the synthesis temperature and pressure are easily programmable in modern microwave instruments, which facilitates screening of a wide range of conditions over relatively short time.

Microwave-assisted synthesis offers many benefits over conventional method and was successfully used for the preparation of various OMSs such as MCM-41 (Wu and Bein 1996; Bandyopadhyay and Gies 2005), MCM-48 (Wu and Bein 1996; Bandyopadhyay and Gies 2005), SBA-15 (Newalkar et al. 2000; Newalkar and Komarneni 2001, 2002), SBA-16 (Hwang et al. 2004), FDU-1 (Fantini et al. 2004) and related mesoporous materials (Tompsett et al. 2006). This method has been used for the synthesis of surfactant-templated OMSs such as MCM-41 and MCM-48 and block-copolymer-templated OMSs such as SBA-15, SBA-16 and FDU-1. It is noteworthy that in the aforementioned reports microwave irradiation was used only in the final step of the synthesis, known as hydrothermal treatment. Recently, the entire synthesis of SBA-15 was carried out under microwave irradiation by using TEOS and Pluronic P123 and by programming temperature and time of the initial self-assembly and hydrothermal treatment steps (Celer and Jaroniec 2006). In contrast to previous attempts, in which microwave system was used only for hydrothermal treatment, Celer and Jaroniec (2006) employed this technique for both steps of the synthesis. This approach permitted to significantly reduce the entire synthesis time from at least 72 hours to even 3 hours and simultaneously, to obtain the well ordered SBA-15 samples with high specific surface area and large pore volume (Celer and Jaroniec 2006). Their work shows new opportunities in the microwave-assisted synthesis of OMSs such as SBA-15, especially in taking advantage of easy programming of the synthesis temperature and time.

Here, the ease of programming temperature and time in the microwave-assisted synthesis is utilized for the preparation of SBA-16, one of the most popular OMSs among cage-like siliceous materials. An extensive series of the samples was obtained under microwave irradiation using temperature-time programming for both steps of the synthesis, self-assembly and hydrothermal treatment. To the best of our knowledge, the microwave technique was barely employed to obtain cage-like mesostructures (Hwang et al. 2004) and its usage was limited only for one step of the process, hydrothermal treatment, whereas the first stage of the synthesis was performed under conventional conditions. Also, the hydrothermal treatment process was carried out to maximum temperature of 120 °C for 30–120 min (Hwang et al. 2004). This synthesis recipe resulted in moderate quality OMSs.

In this study the OMS samples were prepared by using temperature-programmed microwave-assisted synthesis with hydrothermal treatment carried out from 100 to 160 °C. These samples were synthesized using tetraethyl orthosilicate (TEOS) as a silica source and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) block copolymer (Pluronic F127; $EO_{106}PO_{70}EO_{106}$) as a structure directing agent in the presence of sodium chloride at low acid concentrations; note that the OMS samples prepared in the presence of Pluronic F127 at 100 °C are known as SBA-16 cage-like mesostructures (*Im3m* symmetry group). The quality of the resulting OMSs was studied by nitrogen adsorption and powder X-ray diffraction (XRD). The main goal of this study was not only to take advantage of the microwave technique for the synthesis of SBA-16 but also to find out how adsorption and structural properties of this mesostructure change by varying temperature of the microwave-assisted hydrothermal treatment from 100 to 160 °C and its duration from 2 to 36 h. It is shown that when the aforementioned treatment was carried out at 100 and 120 °C the resulting OMSs gave nitrogen adsorption isotherms with delayed desorption characteristic for cage-like mesostructures such as SBA-16, however conducting this treatment at higher temperatures (140 and 160 °C) led to the samples giving adsorption isotherms characteristic for channel-like materials. It is noteworthy that the microwave-assisted synthesis offers not only an easy synthesis of good quality of OMMs, but also permits a significant time reduction, great flexibility in controlling temperature and pressure as well as significant energy and costs savings. All advantages emphasize an enormous potential of the microwave-assisted synthesis and highlight a wide range of opportunities in employing this method for the preparation of various nanomaterials.

2 Experimental

2.1 Chemicals

Poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) used as a structure directing agent was provided by BASF Corporation. Tetraethyl orthosilicate (TEOS) was purchased from Across Organics (98%). Deionized water was obtained by using in-house Ionpure Plus 150 Service Deionization ion-exchange purification system. All reagents were used as received without further purification.

2.2 Microwave-assisted synthesis of OMSs

A series of OMSs was synthesized by self-assembly of tetraethyl orthosilicate (TEOS) as a silica source and poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer (Pluronic F127; $EO_{106}PO_{70}EO_{106}$) as a structure directing agent under microwave conditions. The recipe used was analogous to that reported by Zhao et al. (2004). All samples were prepared by using 2 g of Pluronic F127 polymer and 7.05 g of sodium chloride, which were dissolved in 80 ml of 0.5 M HCl under magnetic stirring at 40 °C. The addition of sodium chloride was used to improve the ordering of silica mesostructures (Grudzien and Jaroniec 2005a; Kraemer et al. 1998; Zhao et al. 1999). After 4 hours of stirring, 8.4 g of TEOS was added dropwise. The resulting mixture was transferred to Teflon vessels, which were installed in microwave oven (MARS 5, CEM Corp.). Both steps of the synthesis, i.e., initial self-assembly and subsequent hydrothermal treatment, were carried out under microwave irradiation. In the first step, the synthesis mixture was stirred using magnetic bars from 2 to 12 h at 40 °C. After this step, magnetic stirring was off and temperature was increased to 100, 120, 140 or 160 °C and kept at this temperature for 1 to 48 h; the exact durations of the initial synthesis step carried out at 40 °C and the hydrothermal treatment performed at higher temperature as well as temperature of the aforementioned treatment are specified in the samples notation. The resulting slurry was filtered, washed with deionized water, and dried in oven at 80 °C. All samples were calcined at 350 °C for 4 h under air atmosphere with the heating rate 5 °C min^{-1}. This calcination was performed in a tube furnace by placing four samples of each series in small quartz boats (Grudzien et al. 2007). The resulting OMS samples were denoted as x–y–z, where x stands for the hydrothermal treatment temperature (100–160 °C), y and z refer to the duration (in hours) of the initial self-assembly at 40 °C and hydrothermal treatment at higher temperature (100–160 °C), respectively.

2.3 Measurements

Nitrogen adsorption measurements were carried out using ASAP 2010 volumetric analyzers manufactured by Micromeritics, Inc. (Norcross, GA). Adsorption isotherms were measured at −196 °C over the interval of relative pressures from 10^{-6} to 0.995 using ultra high purity nitrogen from Praxair Distribution Company (Danbury, CT, USA). All samples were outgassed under vacuum in the port of the adsorption instrument for at least 2 hours at 200 °C prior to each measurement until the residual pressure dropped to 6 or less µm Hg. The Brunauer-Emmett-Teller (BET) surface area (Brunauer et al. 1938) was calculated using adsorption data in the range of 0.05–0.2 p/p_o. The single-point pore volume was estimated at 0.99 p/p_o (Sing et al. 1985). The pore size distributions (PSDs) were evaluated from adsorption branches of nitrogen adsorption isotherms using the improved Kruk-Jaroniec-Sayari (KJS) method (Jaroniec and Solovyov 2006), which employs the Barrett-Joyner-Halenda (BJH) algorithm (Barrett et al. 1951) for cylindrical pores.

For the samples with spherical pores such as SBA-16 this method underestimates the size of primary mesopores about 2 nm. The mesopore diameters were acquired at the maximum of the PSD curve.

The small angle XRD patterns were recorded over a range of $0.40° < 2\theta < 3.50°$ on a PANanalytical Inc. X'Pert Pro (MPD) Multi Purpose Diffractometer with CuKα radiation (0.1540 nm) using an operating voltage of 40 kV and 40 mA, 0.01° step size and 20 s step time. Microscope glass slides were used as sample supports for these measurements. The samples were manually ground prior to the XRD analysis and all measurements were performed at room temperature.

STEM images were taken using a Hitachi HD-2000 Scanning and Transmission Electron Microscope (STEM). For the STEM analysis, a Lacy carbon coated, 200-mesh, copper grid was dipped into the sample suspension (sample in ethanol) and then dried under vacuum prior to analysis. The unit was operated at an accelerate voltage of 200 kV and an emission current of 30 μA.

3 Results and discussion

Nitrogen adsorption isotherms measured at −196 °C for the calcined OMSs are shown in Figs. 1, 2, 3 and 4 together with the corresponding pore size distributions, which were calculated from adsorption branches of nitrogen adsorption isotherms using the improved KJS method, and with small angle powder X-ray diffraction (XRD) patterns. It is noteworthy that each particular series of the OMS samples was obtained by varying temperature and time of microwave irradiation. The first step of the synthesis was performed at 40 °C for 2 to 12 hours. The second step, hydrothermal treatment, was carried out at 100, 120, 140 or 160 °C for 2 to 24 hours. The basic parameters for the samples studied such as the BET specific surface area, the single-point pore volume, the volume of complementary pores, the pore width and the d-spacing are provided in Table 1. Figures 1, 2, 3 and 4 and data summarized in Table 1 show that the temperature and time of microwave irradiation are essential factors that control the adsorption properties of the resulting OMS samples.

Figure 1 shows a complete set of nitrogen adsorption isotherms, pore size distributions and small angle XRD patterns for all OMS samples hydrothermally treated under microwave irradiation at 100 °C. Panels A, B and C contain adsorption isotherms for the samples obtained by stirring at 40 °C for 2, 6 and 12 hours, respectively; each panel shows a series of isotherms referring to different durations of hydrothermal treatment at 100 °C. The BET specific surface area, the volume of complementary pores, single-point total pore volume and mesopore diameter for these samples are summarized in Table 1. As can be seen from Fig. 1, all adsorption isotherms are type IV with a broad hysteresis loop and delayed desorption ending at relative pressure of ∼0.45, which is typical for cage-like mesostructures. The type of the block copolymer used, the shape of hysteresis loop and the corresponding XRD profiles indicate that all samples have the SBA-16-type mesostructure. For these SBA-16 samples the BET specific surface area changes from 626 to 1200 m^2/g, the single-point pore volume varies from ∼0.40 to 0.86 cc/g and the pore diameters are in the range of 6–8 nm with a distinctive tendency to grow with increasing time of the microwave-assisted synthesis. Figure 1 and data in Table 1 show that the duration of the first synthesis step as well as hydrothermal treatment (the second step) is an important factor for the overall quality of SBA-16, especially for the surface area and the volumes of primary (ordered) and complementary pores (the latter include regular small apertures interconnecting ordered spherical cages in SBA-16 as well as irregular fine pores present in the mesopore walls due to the penetration of PEO blocks; Kruk et al. 1999). As regards the duration of the first step at 40 °C, this study indicates that the optimal time is between 2 and 6 h. Although 2 h of initial stirring under microwave irradiation at 40 °C seemed to be sufficient for the synthesis of SBA-16, we preferred to use longer time (6 h) for the synthesis of other series of the samples. However, there was no significant effect on the adsorption parameters of the samples stirred for 12 h.

The duration of microwave-assisted hydrothermal treatment of the SBA-16 samples is extremely important factor. An insufficient time of this treatment leads to lower quality of samples in terms of the surface area, pore volume and other structural properties. For instance, two SBA-16 samples, 100-6-1 and 100-6-24 were obtained under microwave irradiation by stirring for 6 h at 40 °C and hydrothermal treatment at 100 °C for 1 and 24 h, respectively. The total pore volume of the sample hydrothermally treated for 24 h doubled in comparison to that for the sample treated for 1 h only. Also, its BET surface area increased from 684 to 1061 m^2/g, its pore width increased by ∼2 nm, and the volume of complementary micropores enlarged by 40%. This substantial increase in the surface area and total pore volume is caused by significant increase in the complementary porosity due to extended time of microwave treatment at 100 °C; similar effect was observed for the cage-like mesostructures prepared under conventional conditions (Matos et al. 2003). Thus, 24 h microwave-assisted hydrothermal treatment of SBA-16 is too long and may lead to the structure deterioration due to the expansion of complementary porosity. Data listed in Table 1 indicate that ∼6–9 h is an optimal time for microwave hydrothermal treatment of SBA-16.

The PSD curves corresponding to the adsorption isotherms shown in Fig. 1 are bimodal with quite narrow peaks;

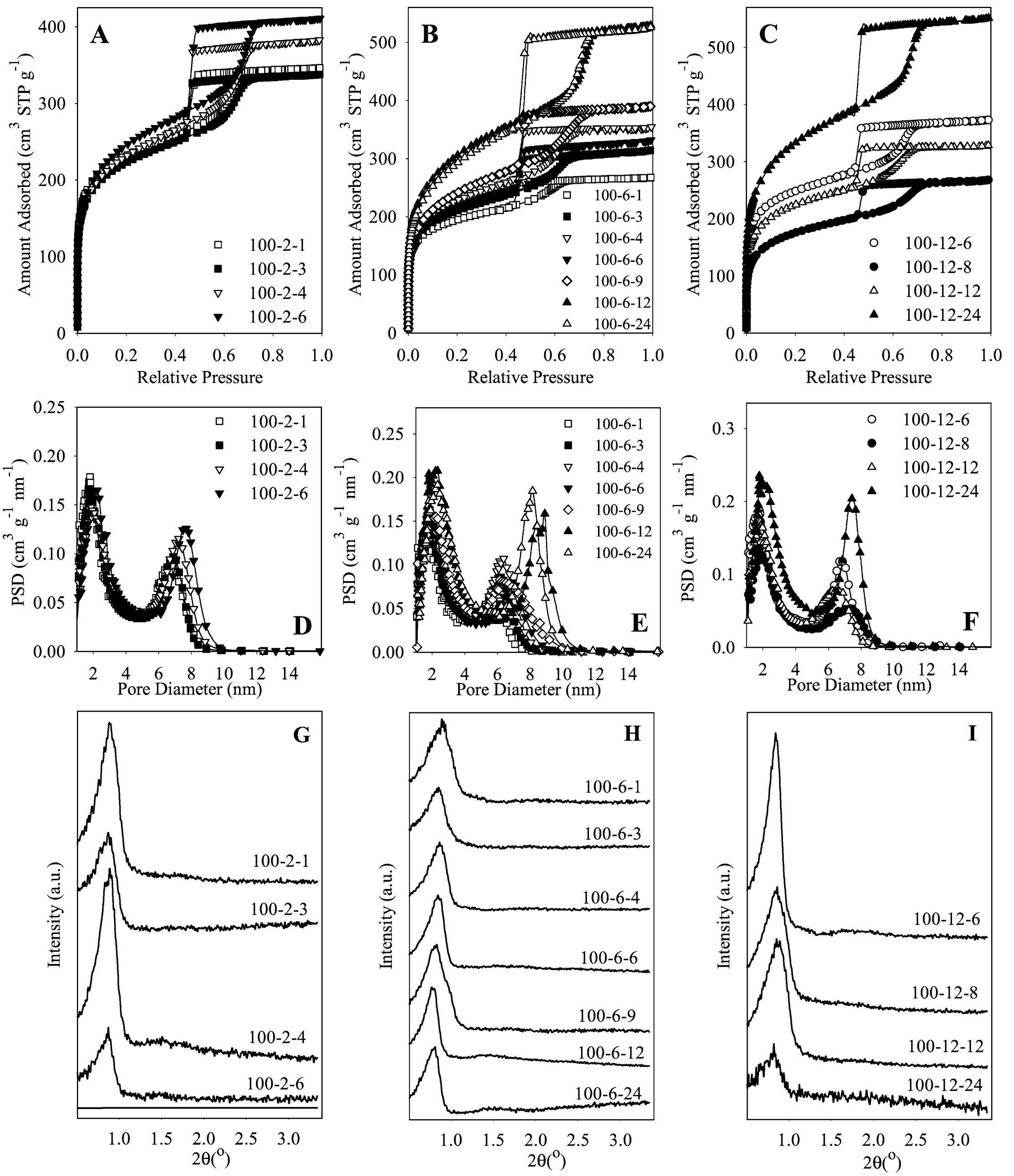


Fig. 1 Nitrogen adsorption isotherms measured at −196 °C (Panels **A**, **B** and **C**) and the corresponding pore size distributions (PSDs) (Panels **D**, **E** and **F**) calculated by the KJS method (Jaroniec and Solovyov 2006) as well as the powder X-ray diffraction patterns (Panels **G**, **H** and **I**) for the ordered mesoporous silicas obtained under microwave irradiation at 40 °C during the self-assembly stage and at 100 °C in the hydrothermal step

one reflecting primary mesopores and other representing complementary pores, which consist of regular apertures and irregular fine pores in the mesopore walls created by penetration of PEO blocks (Kruk et al. 1999). Since hysteresis loops for the isotherms shown in Fig. 1 close at the limiting pressure, the size of pore openings (apertures) is below 5 nm, which is confirmed by location of the first PSD peak. Its maximum is about 2 nm for PSDs shown in Fig. 1. The second PSD peak is located at about 6–8 nm and its position shows some tendency to increase with extending time of hydrothermal treatment. Note that the size of this peak is underestimated about 2 nm (Matos et al. 2003) because the BJH and KJS methods are applicable for cylindrical pores.

Powder X-ray diffraction (XRD) patterns for the above discussed SBA-16 samples are shown in panels G–I of Fig. 1. These XRD patterns show distinct peak at $2\theta \approx 0.85°$

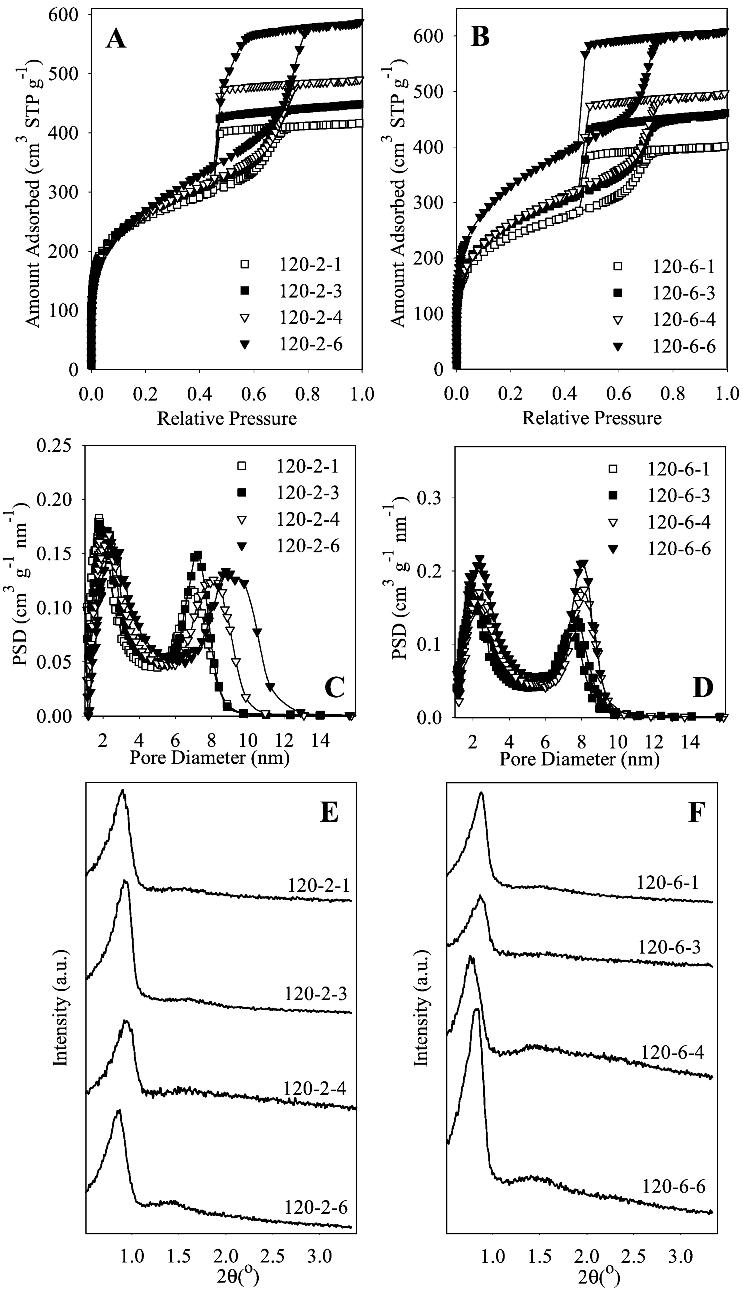
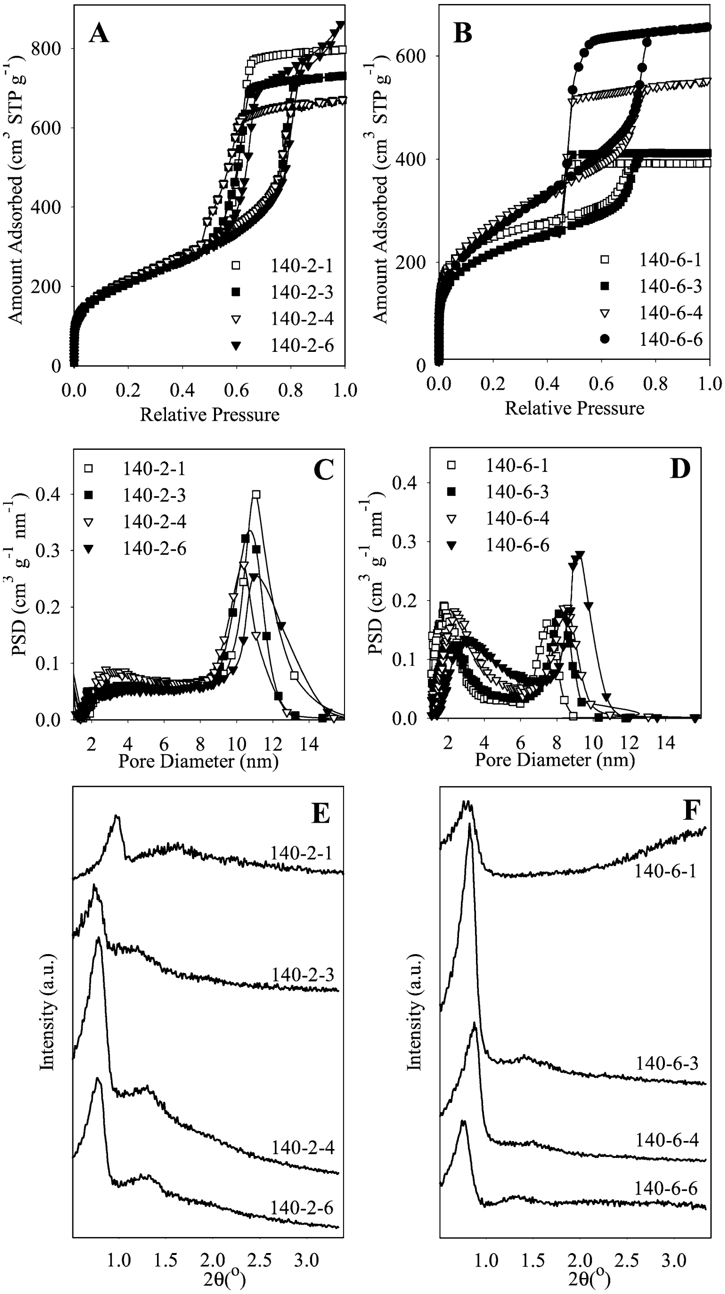


Fig. 2 Nitrogen adsorption isotherms measured at −196 °C (Panels **A** and **B**) and the corresponding pore size distributions (PSDs) (Panels **C** and **D**) calculated by the KJS method (Jaroniec and Solovyov 2006) as well as the powder X-ray diffraction patterns (Panels **E** and **F**) for the ordered mesoporous silicas obtained under microwave irradiation at 40 °C during the self-assembly stage and at 120 °C in the hydrothermal step

attributed to (110) reflection and in some cases further low intensity reflections are visible; poor resolution of the latter reflections is due to limitation of the XRD instrument for recording small angle patterns, especially for cage-like OMSs such as SBA-16. Figure 5 presents the transmission electron microscopy (TEM) and scanning electron microscopy (SEM) images of the selected ordered mesoporous silicas obtained under microwave irradiation at 40 °C followed by hydrothermal treatment at 100 °C (sample 100-12-24) and 120 °C (sample 120-6-6). These images show ordered porosity in the samples studied, which is in agreement with the small angle XRD patterns.

Shown in Fig. 2 are nitrogen adsorption isotherms, PSDs and XRD patterns for the SBA-16 samples obtained by microwave-assisted hydrothermal treatment at 120 °C. Similarly as in the case of hydrothermal treatment at 100 °C, adsorption isotherms shown in Fig. 2 for the samples treated at 120 °C are typical for cage-like OMSs and can be considered as SBA-16 materials. Moreover, there is a similar tendency of increasing the pore volume, surface area and pore width with increasing time of hydrothermal treatment, although the observed changes at 120 °C seem to be slightly smaller than those for the samples treated at 100 °C (Table 1). Analysis of the adsorption parameters for the SBA-16

Fig. 3 Nitrogen adsorption isotherms measured at −196 °C (Panels **A** and **B**) and the corresponding pore size distributions (PSDs) (Panels **C** and **D**) calculated by the KJS method (Jaroniec and Solovyov 2006) as well as the powder X-ray diffraction patterns (Panels **E** and **F**) for the ordered mesoporous silicas obtained under microwave irradiation at 40 °C during the self-assembly stage and at 140 °C in the hydrothermal step



samples prepared at 120 °C under microwave irradiation indicates that 6 h treatment can be too long, especially for the sample initially stirred for 2 h only; in this case desorption branch starts to decrease before 0.45 p/p_o.

In comparison to the SBA-16 samples prepared at 100 and 120 °C under microwave conditions, the OMS samples obtained at higher temperatures (140 and 160 °C) give nitrogen adsorption isotherms with evolving shape of hysteresis loop from H2 type observed for cage-like mesostructures to H1 type characteristic for channel-like materials (Figs. 3 and 4). It is extremely interesting that the aforementioned evolution of the hysteresis loop is more pronounced for the samples initially treated at 40 °C for 2 h. The well-developed H1 hysteresis loops are observed for the samples initially treated at 40 °C for 2 h and hydrothermally treated at 140 or 160 °C for 4–6 h. It seems that the short initial treatment at 40 °C produces less condensed mesostructures, which are more susceptible to structural transformations at higher temperatures. Moreover, the PSD curves (Figs. 3 and 4) for the samples initially treated at 40 °C for 2 h and hydrothermally treated at 140 or 160 °C show less complementary porosity in the range of micropores, which was also observed for the SBA-15 samples synthesized at high temperatures under microwave irradiation (Celer and Jaroniec 2006). This

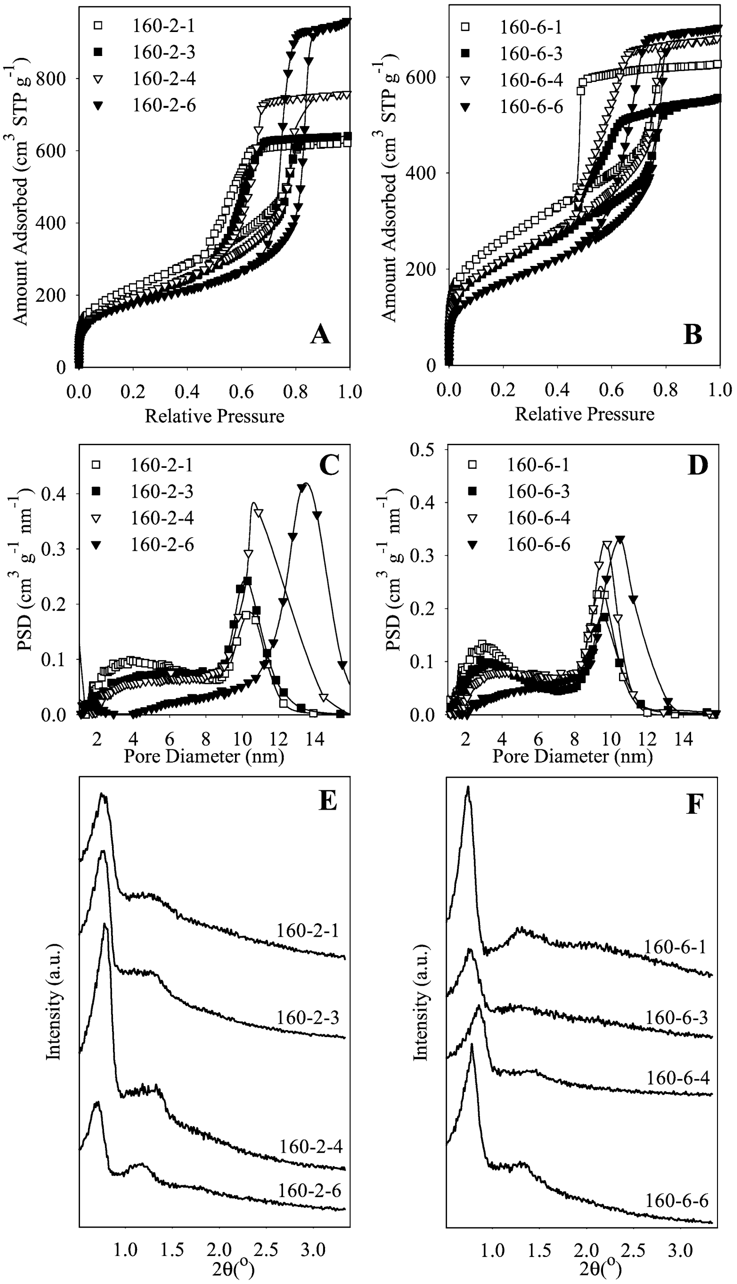


Fig. 4 Nitrogen adsorption isotherms measured at −196 °C (Panels **A** and **B**) and the corresponding pore size distributions (PSDs) (Panels **C** and **D**) calculated by the KJS method (Jaroniec and Solovyov 2006) as well as the powder X-ray diffraction patterns (Panels **E** and **F**) for the ordered mesoporous silicas obtained under microwave irradiation at 40 °C during the self-assembly stage and at 160 °C in the hydrothermal step

effect is especially pronounced for the samples treated at 160 °C; in this case, the surface area is reduced and the pore width and the total pore volume are enlarged with increasing time of hydrothermal treatment. Again, the effect of the pore width expansion seems to be less pronounced for the samples prepared at 140 and 160 °C with longer initial treatment (6 h) at 40 °C. The observed gradual changes in the hysteresis loops for the samples treated at 140 and 160 °C under microwave irradiation are very interesting and suggest structural changes from cage-like to channel-like porous systems.

4 Conclusions

It is shown that the microwave-assisted synthesis affords good quality SBA-16 samples at lower temperatures of hydrothermal treatment (100–120 °C), whereas the treatment at higher temperatures (140–160 °C) may result in the silica mesostructures resembling channel-like porous systems. This structural change seems to be facilitated for the samples exposed to a short stirring (2 h) at 40 °C. Also, this study shows that the microwave-assisted synthesis was successfully used to screen a wide range of temperatures and time in order to establish optimal conditions for the synthe-

Table 1 Adsorption and structural parameters of ordered mesoporous silicas obtained under microwave irradiation

Sample	S_{BET} m^2/g	V_c cm^3/g	V_o cm^3/g	V_t cm^3/g	w_{KJS} nm	d nm
100-2-1	816	0.29	0.22	0.52	6.62	8.4
100-2-3	793	0.28	0.22	0.51	6.78	8.5
100-2-4	830	0.28	0.29	0.59	7.07	8.4
100-2-6	884	0.30	0.32	0.63	7.43	8.6
100-6-1	684	0.22	0.15	0.38	6.02	8.3
100-6-3	745	0.26	0.19	0.47	6.21	8.8
100-6-4	812	0.28	0.24	0.54	6.36	8.6
100-6-6	779	0.27	0.30	0.50	6.80	8.8
100-6-9	866	0.31	0.28	0.61	6.15	9.0
100-6-12	1104	0.39	0.41	0.83	8.32	9.3
100-6-24	1061	0.37	0.43	0.82	7.78	9.2
100-12-6	877	0.30	0.24	0.55	6.77	8.8
100-12-8	626	0.23	0.17	0.41	7.26	8.8
100-12-12	798	0.29	0.20	0.50	6.50	8.5
100-12-24	1200	0.42	0.41	0.86	7.23	9.1
120-2-1	916	0.30	0.32	0.64	6.92	8.4
120-2-3	951	0.32	0.35	0.70	7.08	8.1
120-2-4	951	0.31	0.44	0.77	7.94	9.4
120-2-6	955	0.30	0.60	0.93	8.92	8.7
120-6-1	857	0.29	0.31	0.62	7.23	8.6
120-6-3	942	0.32	0.37	0.72	7.41	8.7
120-6-4	959	0.32	0.44	0.78	7.77	9.5
120-6-6	1191	0.40	0.52	0.95	7.75	8.9
140-2-1	769	0.07	1.16	1.25	9.72	8.9
140-2-3	758	0.09	1.03	1.15	9.36	9.7
140-2-4	798	0.15	0.87	1.06	9.31	9.4
140-2-6	769	0.07	1.10	1.35	9.64	9.4
140-6-1	888	0.31	0.29	0.61	7.24	8.9
140-6-3	787	0.24	0.39	0.64	7.94	8.9
140-6-4	1010	0.33	0.51	0.88	8.11	8.6
140-6-6	953	0.24	0.77	1.04	8.58	9.6
160-2-1	812	0.16	0.79	0.98	9.19	9.7
160-2-3	692	0.08	0.90	1.01	9.24	9.6
160-2-4	710	0.06	1.12	1.20	9.61	9.3
160-2-6	637	0	1.49	1.54	0.92	10.3
160-6-1	953	0.25	0.70	0.98	8.83	9.8
160-6-3	782	0.18	0.64	0.86	8.82	9.6
160-6-4	803	0.12	0.91	1.06	8.92	8.7
160-6-6	631	0.03	1.05	1.11	9.37	9.4

Notation: S_{BET}, BET specific surface area; V_c, volume of the interconnecting pores of the diameters below 4 nm; V_o, volume of ordered pores; V_t, single-point pore volume; w_{KJS}, mesopore diameter calculated by the KJS method (Jaroniec and Solovyov 2006); d, spacing value for the XRD peaks

sis of SBA-16. It is noteworthy that the significant time reduction of the microwave-assisted preparation was achieved in comparison to the conventional method. The duration of this preparation was shortened from 48 hours to 2–6 h for the initial self-assembly and to 6–12 h for hydrothermal treatment in the case of synthesis at 100–120 °C. The resulting

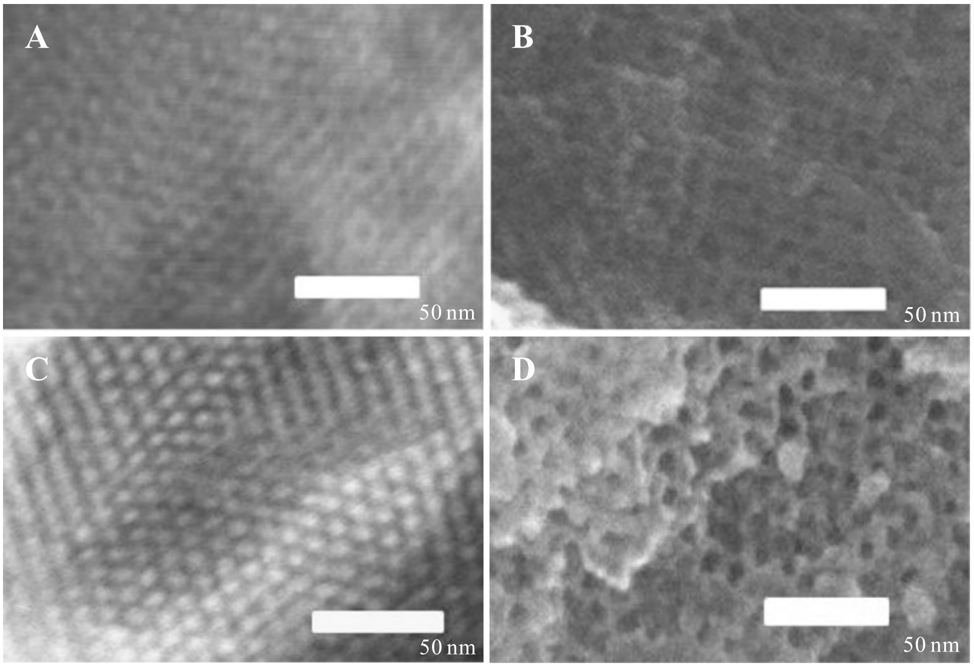


Fig. 5 STEM images of the selected ordered mesoporous silicas obtained under microwave irradiation at 40 °C followed by hydrothermal treatment at 100 °C (sample 100-12-24: panels **A** and **B** show TEM and SEM images, respectively) and 120 °C (sample 120-6-6: panels **C** and **D** show TEM and SEM images, respectively)

materials exhibited high surface area, large pore volume and large pore diameters.

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