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Published on Web 10/14/2006

Temperature-Programmed Microwave-Assisted Synthesis of SBA-15 Ordered Mesoporous Silica

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Abstract: The currently available microwave technology permits the development and implementation of a temperature-programmed microwave-assisted synthesis (TPMS) of ordered mesoporous silicas (OMSs). Unlike in previously reported syntheses of OMSs, in which only the final hydrothermal treatment was carried out under microwave irradiation, this work takes advantage of the existing capabilities of modern microwave systems to program the temperature and time for the entire synthesis of these materials. To demonstrate the flexibility of the proposed microwave-assisted synthesis, besides programming two consecutive steps involving initial stirring of the gel at a lower temperature and static hydrothermal treatment at a higher temperature, we explored the possibility of temperature programming of the latter step. A major advantage of microwave technology is the feasibility of temperature and time programming, which has been demonstrated by the synthesis of one of the most popular OMSs, SBA-15, over an unprecedented range of temperatures from 40 to 200 °C. Since the synthesis of OMSs has not yet been explored and reported at temperatures exceeding 150 °C, this work is focused on the SBA-15 samples prepared at higher temperatures (such as 160, 180, and even 200 °C). These SBA-15 samples show better thermal stability than those synthesized at commonly used temperatures either under conventional or microwave conditions. Moreover, a partial decomposition of the template during high-temperature microwave-assisted syntheses does not compromise the formation of well-ordered SBA-15 materials. This study shows that the simplicity and capability of temperature and time programming in TPMS allows one not only to tune the adsorption and structural properties of OMSs but also to easily screen a wide range of conditions in order to optimize and scale-up their preparation as well as to significantly reduce the time of synthesis from days to hours.

Introduction

Since the discovery of ordered mesoporous silicas (OMSs),[1−3] this class of nanomaterials has become an important part of nanoscience.[4−13] OMSs are very attractive materials due to their high surface areas, large volumes of ordered mesopores (pores with diameters between 2 and 50 nm), and diverse morphology. Since 1992,[1,2] numerous methods have been elaborated for the synthesis of OMSs (see several review articles[4−13] and references therein), aiming at the reduction of time, energy, and cost without sacrificing the quality of the materials. Among these methods, the microwave-assisted synthesis of OMSs has gradually gained popularity (see published reviews[14−16] and references therein) because microwave irradiation assures a rapid and homogeneous heating of the entire sample, enhances reaction rates, facilitates formation of uniform nucleation centers, and is energy efficient and environmentally friendly.[14−19] Other advantages of microwave technique include its capability to screen a wide range of experimental conditions (such as time and temperature) and to easily scale-up the synthesis of OMSs.[19] Although in-depth theoretical and practical knowledge of microwave interactions with matter is still at an initial stage of development, there is a great interest in the microwave-assisted synthesis of nanomaterials due to the aforementioned advantages of this method.

To date, microwave irradiation has been used only to carry out the hydrothermal treatment,[15,20−31] which is the final stage

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10.1021/ja065345h CCC: $33.50

of the OMS synthesis, and to perform the template removal.[32] This strategy has been employed for surfactant-templated OMSs such as MCM-41 and MCM-48,[20,21] as well as for block copolymer-templated OMSs such as SBA-15 (2-D hexagonal, *P*6*mm* symmetry),[23−25] SBA-16 (3-D body-centered cubic, *Im*3*m* symmetry),[26] FDU-1 (face-centered cubic, *Fm*3*m* symmetry),[27] and other related materials.[28−30] Despite the numerous reports on the microwave-assisted synthesis of OMSs,[15−32] the further development of this area is somewhat hindered by the fact that the structural properties of the reported OMS samples synthesized under microwave irradiation are often inferior to those of OMSs obtained in a conventional way.

In general, a typical supramolecular-templated synthesis of OMSs (excluding template removal) can be considered as a two-step process: the first step—involving the self-assembly of silica and template species—occurs under vigorous mechanical or magnetic stirring at a lower temperature (between 25 and 50 °C), and the second step (hydrothermal treatment)—involving the mesostructure expansion and consolidation of siliceous pore walls—is usually performed under static conditions at a higher temperature (between 80 and 120 °C). Many attempts have been made to control experimental conditions in both synthesis steps as well as to optimize their temperature and duration.[32−40] So far, the so-called microwave-assisted synthesis of OMSs has been carried out by performing the first step under conventional conditions (which often takes about 1 day) and the second step under microwave irradiation.[15,20−31] In the case of the conventional synthesis, the reacting mixture is transferred to a sealed autoclave and kept in a regular oven for an extended period of time, from several hours to a few days. Therefore, one-batch, uninterrupted synthesis of OMSs with initial stirring but without the necessity of transferring the reacting mixture would be desirable because of a better possibility to strictly control the synthesis conditions.

Here we propose performing the entire synthesis (self-assembly process and hydrothermal treatment) of OMSs, specifically SBA-15 materials, under microwave irradiation by taking advantage of the existing capabilities of modern microwave systems to program the time and temperature of consecutive steps. This approach, somewhat similar to the method used for growing zeolite crystals under microwave conditions,[41,42] simplifies the preparation of OMSs, reduces its total time from days to hours without sacrificing the quality of the product, and permits an easy programming of the time and temperature of consecutive synthesis steps. Therefore, we propose to name this method "temperature-programmed microwave-assisted synthesis" (TPMS). Since modern microwave systems have the capability to handle several samples at the same time as well as to significantly reduce the time needed for their synthesis, we were able to synthesize a large series of SBA-15 samples over a wide range of temperatures and times. Namely, the SBA-15 samples were synthesized over a temperature range from 40 to 200 °C (with temperature steps of 20 °C) and a time range from 3 to 15 h.

Note that, besides some syntheses of OMSs performed at elevated temperatures (120−150 °C),[43−47] preparation of typical OMSs above 150 °C (conventional or microwave-assisted) has yet not been reported, except for OMSs prepared using fluorocarbon surfactants as templates.[48−51] Therefore, in this work we focus on SBA-15 materials synthesized at higher temperatures (such as 160 and 180 °C) because they are high-quality samples from the viewpoint of adsorption properties and structural ordering and they show much better thermal stability than their counterparts prepared in a conventional way. Under microwave conditions, good-quality SBA-15 samples can be obtained in as little as 3 h, which represents a significant time reduction in comparison to the conventional synthesis. A detailed comparison of the proposed and conventional protocols for the preparation of OMSs is presented in the Supporting Information, Scheme S1, which shows several advantages of TPMS over conventional synthesis.

Experimental Section

Materials. SBA-15 samples were synthesized under acidic conditions using poly(ethylene oxide)−poly(propylene oxide)−poly(ethylene oxide) triblock copolymer ($EO_{20}PO_{70}EO_{20}$, Pluronic P-123, BASF) as a template and tetraethyl orthosilicate (TEOS, Aldrich) as a silica source. The molar composition used was analogous to that reported elsewhere:[52] 1 TEOS:0.0167 P123:190 H_2O:5.82 HCl. The entire synthesis, including low-temperature initial gel formation under vigorous stirring and subsequent hydrothermal treatment, was carried out in

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a microwave oven (microwave-accelerated reaction system, MARS5, 2450 MHz frequency, CEM Corp.), equipped with optional magnetic stirring, with ESP-1500 Plus and RTP-300 Plus pressure and temperature sensors, respectively. The QC RTP "ramp to temperature" control method and a maximum power of 300 W were selected for all the syntheses (see ref 53 for details related to the MARS5 system). Immediately after mixing TEOS with the prepared acidic solution of the template, the resulting homogeneous mixture was promptly (before any observable precipitation) divided into equal parts and transferred into microwave-compatible high-pressure Teflon vessels (XP-1500, containing magnetic rods), which were subsequently positioned inside the microwave oven. It is noteworthy that, under the conditions used (silica source, temperature, pH), the precipitation (visible clouding of the reaction mixture) is relatively slow and occurs usually within 15−30 min after addition of TEOS. Therefore, the reaction mixture was transferred to the microwave oven before the start of the precipitation in order to perform this process under microwave irradiation. For each microwave synthesis, the temperature and time were selectively programmed, and the first step was conducted with fast stirring (option 3 in MARS5) at 40 °C for 2 h. Subsequently, the temperature was ramped during 5−10 min to the selected level in the range from 40 to 200 °C, at which the process was continued without stirring for various periods of time from 30 min to 12 h (second step). Since both steps were carried out under microwave irradiation, the synthesis was uninterrupted, unlike in the previously used methods.[10−15] The resulting as-synthesized composites were filtered, washed with deionized water, and dried overnight at 80 °C. After subsequent calcination at 540 °C, the resulting materials were denoted as MS*x*-*y* (where *x* and *y* refer to the temperature in °C and time in hours of the hydrothermal process (second step). For example, MS180-3 denotes the SBA-15 sample prepared under microwave irradiation at 40 °C with stirring for 2 h and at 180 °C without stirring for 3 h and subsequently calcined at 540 °C.

Several SBA-15 samples (denoted as PS*x*, where *x* stands for the initial temperature of hydrothermal treatment) were prepared under microwave irradiation using a three-step temperature−time program. The main difference in the syntheses of MS*x*-*y* and PS*x* samples is in the hydrothermal treatment process; the latter, after initial stirring at 40 °C for 2 h, were subjected to a two-step hydrothermal treatment at either 160 or 180 °C for 1 h (to expand the mesopores and to initiate the structure consolidation) and at 100 °C for 6 or 12 h (to condense the silica walls and stabilize the structure at milder conditions). For example, PS160 refers to the calcined (at 540 °C) SBA-15 material that was prepared entirely under microwave irradiation: initially at 40 °C with stirring for 2 h, next at 160 °C without stirring for 1 h, and subsequently at 100 °C for 6 h.

For comparison, a series of the SBA-15 samples (denoted OS*x*-*y*, where *x* and *y* stand for the temperature and time of hydrothermal treatment) were prepared in a conventional oven at the same temperatures as the corresponding MS*x*-*y* samples. For example, OS160-3 denotes the calcined SBA-15 sample synthesized at 40 °C with traditional vigorous mechanic stirring for 2 h,[33] which after its transfer to a Teflon-lined autoclave was kept in a conventional oven at 160 °C for 3 h. In order to monitor the thermal stability of SBA-15, the selected samples were calcined at higher temperatures and denoted as MS*x*-*y*-C*T*, PSx-C*T*, or OS*x*-*y*-C*T*, where *T* stands for calcination temperature in °C. For example, MS180-3-C1000 denotes the MS180-3 sample calcined at 1000 °C instead of 540 °C, and PS160-C900 denotes the PS160 sample calcined at 900 °C. All calcinations, including the high-temperature ones, were conducted for 6 h at the specified temperature at a heating rate of 3 deg min^{-1} (temperature ramp and the first 3 h of calcination were done in flowing nitrogen, and the remaining 3 h of this process was performed in flowing air). To avoid the structural degradation of OMSs during microwave synthesis at higher temperatures, it is recommended to set a relatively low maximum power in the MARS5 program, specifically 300 W. This power was sufficient to achieve and control the desired temperature (up to 200 °C) in up to six vessels containing the SBA-15 synthesis mixture, and it was mild enough to cause no structural damage (which is the main concern in the microwave-assisted synthesis). Moreover, to achieve a good reproducibility of the samples, it is crucial to use the same volume of the reacting gel in each microwave vessel.

Hazardous Issues in Microwave Synthesis. The microwave system (MARS5) has built-in safety features that are described in detail (along with multiple safety notes and warnings) in the operation manual. Nevertheless, it is important to additionally point out that, during microwave-assisted high-temperature syntheses, the sealed vessels contain superheated solutions and need to be handled with proper precautions, especially during their removal from the microwave oven. The vessel holders are made of a material that does not undergo intensive heating under microwave irradiation, and they can be quite safely held, even if the reacting solution (inside the Teflon lining) is very hot (e.g., about 200 °C). However, special precaution is always required when operating vessels under high pressure and with hot content, during and after the high-temperature reaction (including the ones performed in the classical oven). Moreover, before each vessel can be safely opened, it is necessary to allow it to cool (usually for about 0.5−1 h), and then, in the case of microwave vessels, prior to the opening, the pressure needs to be released from each vessel using a built-in vent.

Measurements. Nitrogen adsorption/desorption isotherms were measured at −196 °C using Micromeritics ASAP 2010 and ASAP 2020 volumetric adsorption analyzers. Before adsorption measurements, each sample was outgassed under vacuum for at least 2 h at 200 °C.

Room-temperature powder X-ray diffraction (XRD) data were collected on a PANalytical X'Pert Pro multipurpose diffractometer using Cu Kα radiation and a proportional detector. Programmable divergence slits and programmable anti-scatter slits were employed to achieve performance at the lowest angles. The multipurpose sample stage (MPSS) was used to scan the samples in 0.02° 2θ steps with counting time of 25 s per step.

Calculations. Adsorption and structural parameters for the samples studied were determined from nitrogen adsorption data collected at −196 °C. The BET specific surface area was evaluated from adsorption data in the relative pressure range of 0.04−0.2.[54,55] The total pore volume was estimated from the amount adsorbed at the relative pressure of 0.99.[55] The volume of complementary pores (i.e., pores with widths smaller than the diameter of ordered mesopores) was obtained by integration of the pore size distribution (PSD) in the range up to ∼4 nm. The pore size distribution for each SBA-15 sample was calculated from the adsorption isotherm branch using the improved KJS method,[56] which is based on the BJH algorithm for cylindrical mesopores.[57] Although the KJS method is based on the BJH algorithm,[57] it provides a better assessment of PSD than the latter because it uses the statistical film thickness and the pore width−condensation pressure relation established for a series of hexagonally ordered OMSs.[56,58] The pore width at the maximum PSD was used to characterize the size of ordered mesopores.

Results and Discussion

Microwave-Assisted Synthesis of SBA-15 with Two Temperature Steps. Shown in Figure 1 are nitrogen adsorption isotherms measured at −196 °C and the corresponding XRD patterns for a series of the SBA-15 samples synthesized by

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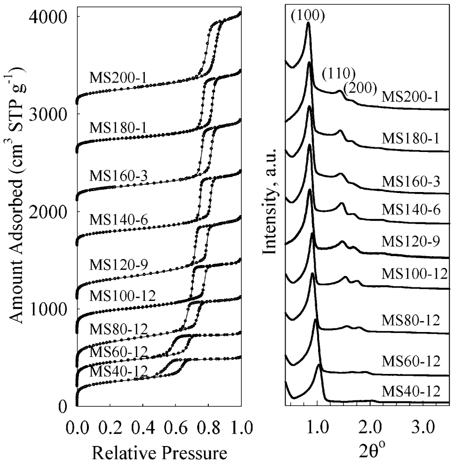

Figure 1. Nitrogen adsorption−desorption isotherms at −196 °C, together with the corresponding small-angle X-ray diffraction patterns for a series of the SBA-15 samples synthesized under microwave irradiation at various temperatures (40−200 °C) for an optimal duration of the hydrothermal treatment (1−12 h). For clarity, the isotherm curves (starting from MS60-12) are vertically offset by 200, 400, 750, 1100, 1650, 2100, 2600, and 3100 cm^3(STP) g^{-1}, respectively.

varying the time and temperature of microwave irradiation (see Supporting Information, Scheme S2a). Each sample of this series was synthesized entirely under microwave irradiation by using a two-step process: initial magnetic stirring of the polymer−TEOS mixture at 40 °C for 2 h, followed by static hydrothermal treatment at the specified temperature and time. Figure 1 shows nitrogen adsorption isotherms for the SBA-15 samples subjected to the hydrothermal treatment at different temperatures from 40 to 200 °C (with 20 °C increments) for a period of time that led to a good-quality sample; the time of this treatment was gradually reduced from 12 to 1 h with increasing temperature.

As can be seen from Figure 1, the samples studied feature type IV adsorption isotherms with the H1-type hysteresis loop.[55] The capillary condensation step shifts gradually in the direction of higher relative pressures, and its height increases with increasing temperature of the hydrothermal treatment, which reflects an increase in the pore width and pore volume. At the same time, the BET specific surface area and the volume of complementary pores are progressively reduced (see Table 1). Nitrogen adsorption isotherms and XRD patterns (Figure 1) and the corresponding PSD curves (Figure 2), as well as basic adsorption and structural parameters summarized in Table 1, show that the microwave-assisted synthesis affords SBA-15 samples with tunable adsorption properties. These samples are highly ordered (their XRD patterns often have five reflections, which satisfy the rules for a *P*6*mm* symmetry group) and feature narrow PSD curves (except for the MS200-1 sample), as shown in Figure 2. Their pore widths, estimated at the maximum of the PSD curves, can be tuned from 6.7 nm (MS40-12) to as high as 11.4 nm (MS200-1). However, in the case of the SBA-15 samples synthesized at somewhat extreme temperatures (40 and 200 °C), the PSD curves are wider, indicating smaller pore size uniformity.

In the case of the SBA-15 samples synthesized at temperatures below 120 °C, their PSD curves feature two distinct peaks: the first one, located in the pore width range below 4 nm, indicates the presence of small complementary pores (mainly micropores), and the second one represents ordered mesopores. The presence of small complementary pores in the siliceous walls of SBA-15 will not be discussed here because it is well-documented in the literature.[59−62] In contrast, the first peak on the PSD curves for the SBA-15 samples synthesized above 120 °C is not visible, indicating the lack of small complementary pores (about 2 nm). In addition, the left side of the PSD curves shows a small tailing, indicating the presence

Table 1. Adsorption and Structural Parameters for the SBA-15 Samples Studied, Calculated from Nitrogen Adsorption Isotherms at −196 °C and Small-Angle XRD Data[a]

sample	S_{BET}, m^2/g	V_t, cm^3/g	V_c, cm^3/g	*w*, nm	d_{100}, nm
		Figure 1			
MS40-12	875	0.77	0.24	6.7	8.48
MS60-12	889	0.85	0.23	7.3	9.04
MS80-12	930	1.10	0.21	8.3	9.60
MS100-12	822	1.15	0.15	9.2	10.11
MS120-9	727	1.28	0.06	9.6	10.21
MS140-6	510	1.16	0	10.4	10.14
MS160-3	523	1.27	0	10.5	10.09
MS180-1	492	1.28	0	10.8	10.22
MS200-1	508	1.42	0	11.4	10.42
		Figure 3			
MS160-1	474	1.16	0	10.7	10.15
MS160-3	523	1.27	0	10.5	10.09
MS160-6	547	1.22	0	10.2	10.20
MS160-8	551	1.28	0	10.4	10.19
MS160-10	414	1.24	0	11.4	10.48
		Figure 4			
MS100-6-C540	836	1.16	0.15	9.0	9.89
MS100-6-C900	469	0.67	0.08	8.0	8.88
MS100-6-C1000	175	0.26	0.05	6.6	8.00
MS160-3-C540	523	1.27	0	10.5	10.09
MS160-3-C900	494	0.98	0.01	9.2	9.54
MS160-3-C1000	392	0.70	0.03	8.1	-
MS180-3-C540	508	1.29	0	10.7	9.88
MS180-3-C900	478	1.19	0	10.4	9.89
MS180-3-C1000	338	0.80	0.02	10.1	9.71
		Figure 5			
MS160-3	523	1.27	0	10.5	10.09
MS160-3-C900	494	0.98	0.01	9.2	9.53
PS160	552	1.26	0	10.3	10.35
PS160-C900	471	1.06	0.01	9.8	9.55
		Figure 6			
PS180	534	1.34	0	11.0	10.32
PS180-C900	409	1.00	0	9.8	-
		Figure 7			
MS180-1	492	1.28	0	10.8	10.22
MS180-1-C900	405	0.67	0	9.9	-
MS180-3	508	1.29	0	10.7	9.88
MS180-3-C900	478	1.19	0	10.4	9.89
OS180-1	957	1.16	0.22	8.7	-
OS180-1-C900	431	0.58	0.06	7.5	-
OS180-3	703	1.32	0.05	10.1	-
OS180-3-C900	481	0.91	0.04	9.2	-
		Figure 8			
st40-2h	908	0.64	0.24	4.6	-
Mst40-2h	789	0.64	0.21	5.7	8.81
MS100-10m	734	0.65	0.18	6.7	8.24
MS100-6	836	1.16	0.15	9.0	9.89

[a] S_{BET}, BET specific surface area; V_t, single-point pore volume; V_c, volume of complementary pores, which was estimated by integration of the pore size distribution (PSD) below 4 nm; *w*, pore width at the maximum PSD; d_{100}, spacing value for the 100 XRD peaks (for some samples, XRD data were not recorded).

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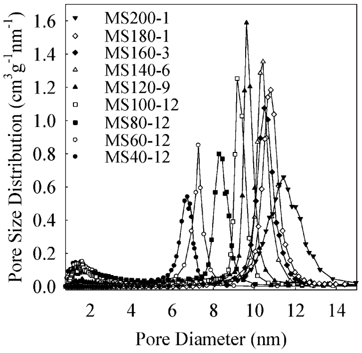

Figure 2. Pore size distributions for the SBA-15 samples synthesized entirely under microwave irradiation using various temperatures (40−200 °C) and times (1−12 h) for the hydrothermal treatment; these distributions correspond to the nitrogen adsorption isotherms shown in Figure 1.

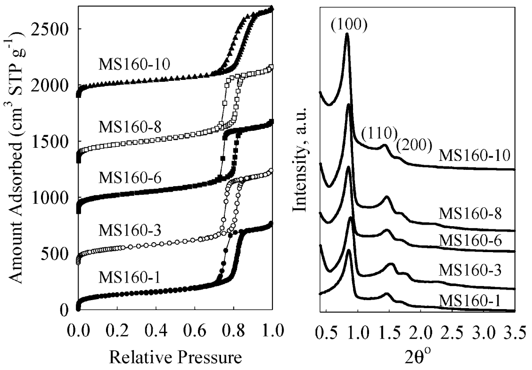

Figure 3. Nitrogen adsorption−desorption isotherms at −196 °C, together with the corresponding small-angle X-ray diffraction patterns for the SBA-15 samples synthesized by using an initial fast stirring in the microwave oven at 40 °C for 2 h, followed by hydrothermal treatment under microwave irradiation at 160 °C for 1, 3, 6, 8, and 10 h, respectively. For clarity, the isotherms for MS160-3, MS160-6, MS160-8, and MS160-10 are vertically offset by 400, 870, 1320, and 1900 cm^3(STP) g^{-1}, respectively. The corresponding pore size distributions are presented in the Supporting Information (Figure S1).

of larger complementary pores in these samples, which makes them attractive for the nanocasting synthesis of ordered carbons, inorganic oxides, and related materials (see published reviews[63,64] and references therein).

To show the effect of the time of hydrothermal treatment under microwave irradiation, Figure 3 presents nitrogen adsorption isotherms and the corresponding XRD patterns for a series of the SBA-15 samples subjected to the hydrothermal treatment at 160 °C for different periods of time from 1 to 10 h; the corresponding PSDs for these samples are shown in the Supporting Information (Figure S1). As can be seen from Figures 3 and S1, good-quality SBA-15 samples are obtained if duration of hydrothermal treatment at 160 °C is less than 10 h; the PSD curve for the sample prepared at 10 h is quite broad. Even 1 h of hydrothermal treatment is sufficient to get a good sample, although the optimal time for this treatment seems to be between 3 and 6 h. These data show that microwave-assisted synthesis at high temperatures reduces the total time to 3−5 h (e.g., MS160-1 was obtained in just 3 h, including the initial 2 h of stirring at 40 °C).

Since the stability of SBA-15 samples synthesized under microwave irradiation (including those prepared at temperatures higher than 150 °C) has not yet been reported, here we present the thermal stability of the samples prepared at 160 and 180 °C in comparison to that of a sample obtained at 100 °C. Nitrogen adsorption isotherms and the corresponding PSD and XRD curves are shown in Figure 4 for the aforementioned samples calcined at 540 (typical calcination conditions), 900, and 1000 °C. As can be seen from this figure, the samples synthesized in the microwave oven at high temperatures show better thermal stability than those prepared at 100 °C. This effect is clearly visible for the MS180-3 sample, which retained a good structural ordering even after calcination at 1000 °C. For comparison, calcination of the MS100-6 sample at 1000 °C led to a significant deterioration of the mesoporous structure.

High-temperature synthesis also affects the morphology of the SBA-15 materials, as shown in the Supporting Information (Figure S2). The samples synthesized in the temperature range from 100 to 160 °C possess rope-like morphology, while those prepared at 180 °C are in the form of discoid particles.

Microwave-Assisted Synthesis of SBA-15 with Three Temperature Steps. In order to explore the flexibility of temperature and time programming under microwave conditions, we performed some syntheses by using three temperature steps instead of two as discussed above. It is was shown elsewhere that longer hydrothermal treatment is beneficial for the structure consolidation.[34] However, if this treatment is performed above 150 °C, its longer duration may lead to structure deterioration (see Figure 3). In order to take advantage of high-temperature synthesis and simultaneously avoid structure deterioration, we used a two-step hydrothermal treatment in addition to the initial stirring of the reacting mixture at 40 °C for 2 h. An illustration of this temperature-programmed hydrothermal treatment is shown in the Supporting Information (Scheme S2b). It involves a short hydrothermal treatment at high temperature (e.g., for 1 h at 160 or 180 °C) to expand the pore size and consolidate the structure, which is further continued under milder conditions (e.g., for 6 h at 100 °C).

To illustrate the temperature-programmed hydrothermal treatment, Figure 5 shows nitrogen adsorption isotherms and the corresponding PSD curves (insets) for two SBA-15 samples, MS160 and PS160, prepared by using one-step and two-step hydrothermal treatments, respectively. As can be seen from this figure, both types of samples calcined at 540 and 900 °C are similar. However, a comparison of the PSD curves (insets in Figure 5) shows that the thermal stability of PS160 is slightly better. This suggests that a prolonged hydrothermal treatment at 100 °C, preceded by a short high-temperature treatment, is beneficial for the consolidation of the structure, which was initially expanded at high temperature. Another illustration of this synthesis approach is shown in Figure 6, which presents nitrogen adsorption isotherms and the corresponding PSD curves for the PS180 sample calcined at 540 and 900 °C.

Comparison of the SBA-15 Samples Obtained by Microwave-Assisted and Conventional Syntheses. Figure 7 shows nitrogen adsorption−desorption isotherms at −196 °C and the corresponding PSD curves for the SBA-15 samples synthesized at 180 °C under microwave and conventional conditions. Since it is difficult to directly compare conventional synthesis with that performed under microwave irradiation, which accelerates the synthesis process, two durations of the hydrothermal treatment at 180 °C were analyzed, specifically 1 and 3 h.

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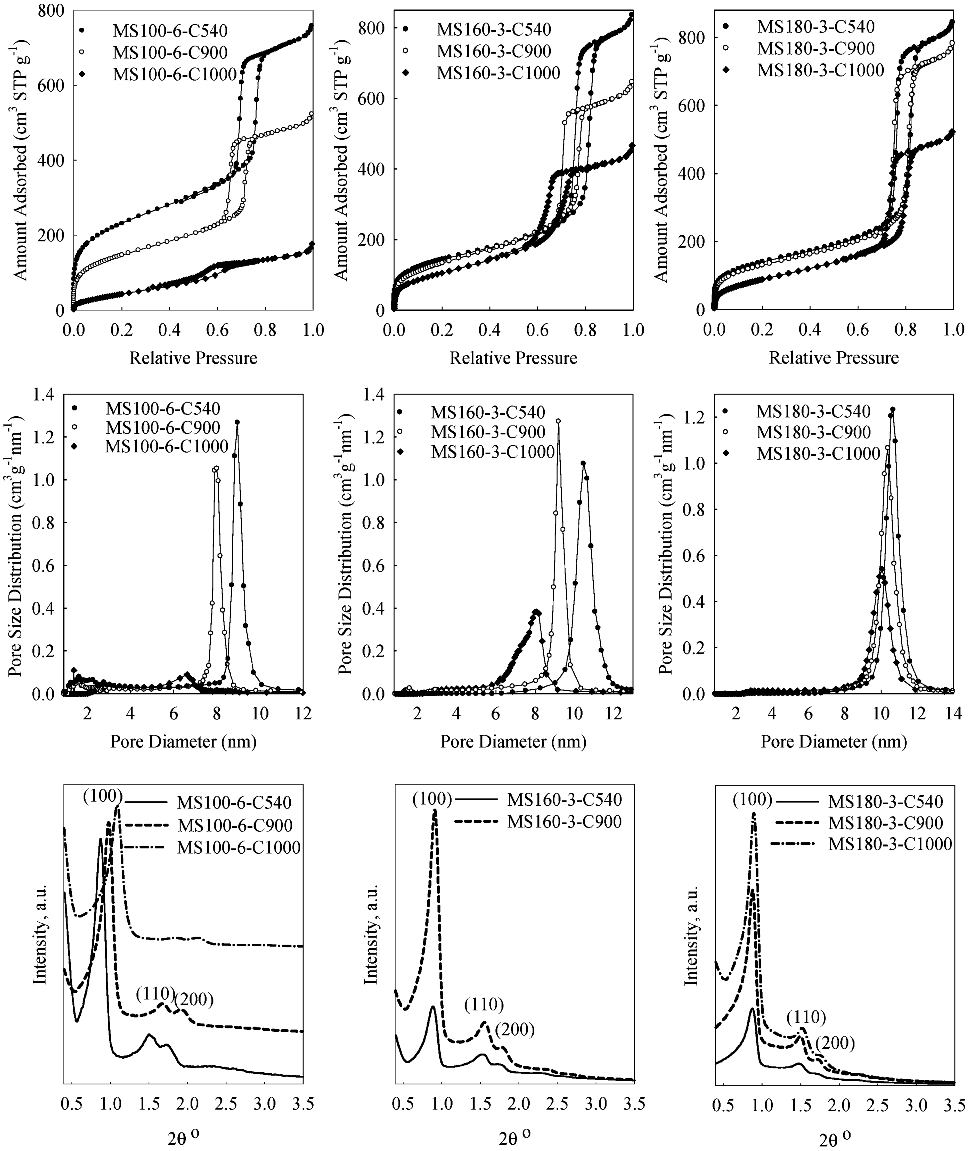

Figure 4. Comparison of the thermal stability of the SBA-15 samples prepared by using hydrothermal treatment under microwave irradiation at 100, 160, and 180 °C. Panels from top to bottom show nitrogen adsorption isotherms, pore size distributions, and small-angle XRD patterns for the samples calcined at 540, 900, and 1000 °C.

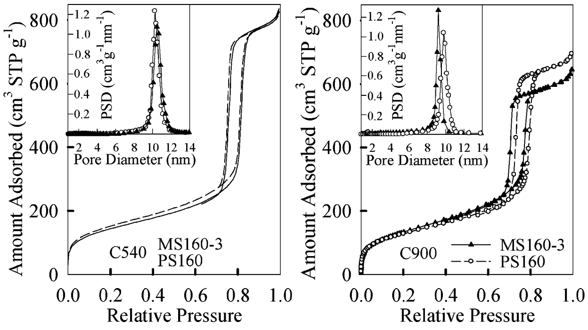

Figure 5. Nitrogen adsorption−desorption isotherms at −196 °C for the MS160 and PS160 samples synthesized by employing one-step (3 h at 160 °C) and two-step (1 h at 160 °C and 6 h at 100 °C) hydrothermal treatment, respectively, and calcined at 540 and 900 °C. The insets show the corresponding pore size distributions.

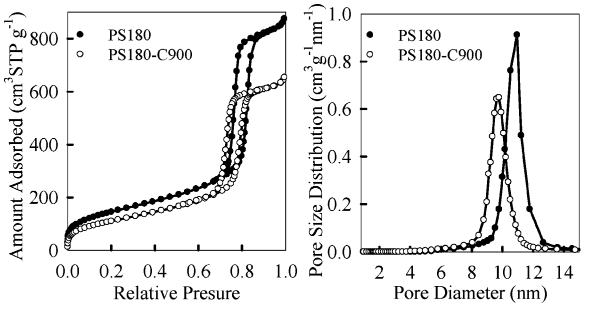

Figure 6. Nitrogen adsorption isotherms at −196 °C and the corresponding pore size distributions for the SBA-15 samples prepared entirely under microwave conditions using two-step hydrothermal treatment (180 °C for 1 h and 100 °C for 6 h) and calcined at 540 and 900 °C.

The conventional SBA-15 samples studied (OS180) possess much higher surface areas (∼700−950 m^2 g^{-1}) than the corresponding MS180 samples. The surface area of the latter is reduced to ∼500 m^2 g^{-1} due to the absence of small complementary porosity, mainly micropores. For instance, the OS180-1 sample exhibits quite a large volume of pores below 4 nm (mainly micropores) and a large BET specific surface area. However, after prolonged hydrothermal treatment at high temperature, these quantities are reduced. In contrast, the

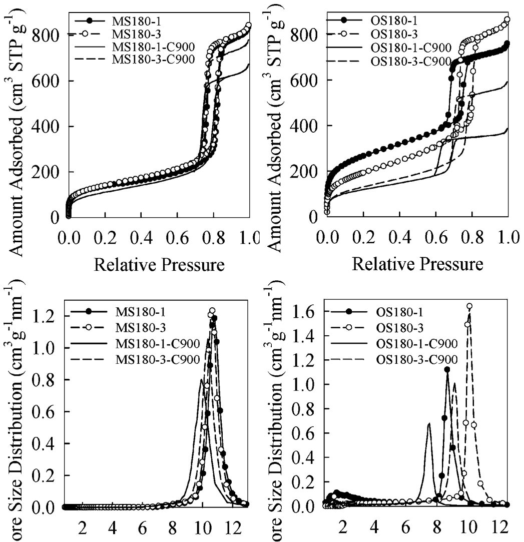

Figure 7. Nitrogen adsorption−desorption isotherms at −196 °C (top panel) and the corresponding PSD curves (bottom panel) for the SBA-15 samples synthesized at 180 °C under microwave (MS180 samples) and conventional (OS180 samples) conditions and calcined at 540 and 900 °C.

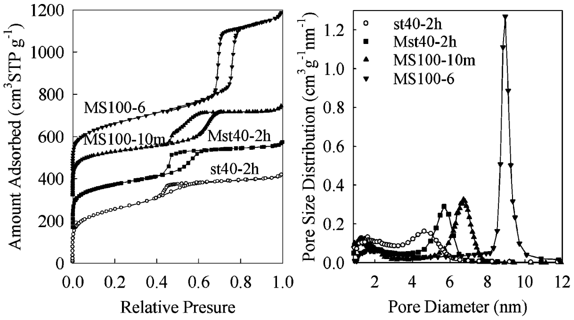

Figure 8. Nitrogen adsorption−desorption isotherms at −196 °C and the corresponding PSD curves for the SBA-15 samples prepared by stirring the reacting mixture at 40 °C for 2 h under conventional (st40-2h sample) and microwave (Mst40-2h sample) conditions. Adsorption isotherms are also shown for the latter sample exposed to 10 min and 6 h of hydrothermal treatment at 100 °C. The isotherm curves for Mst40-2h, MS100-10m, and MS100-6 are vertically offset by 150, 320, and 420 cm^3(STP) g^{-1}, respectively

samples obtained at high temperatures under microwave irradiation exhibit a large volume of primary mesopores and a smaller BET surface area (∼500 m^2 g^{-1}). Therefore, their thermal stability is enhanced because of the negligible volume of small complementary pores, and consequently, the structure shrinkage is significantly reduced. This effect is clearly visible in Figure 7, which shows that the PSD curves for the MS180 samples (prepared at 180 °C under microwave irradiation) calcined at 540 and 900 °C do not change significantly; however, this change is quite significant for the corresponding samples prepared in a conventional oven. Also, calcination of the conventional SBA-15 samples at 900 °C causes a more pronounced reduction of the total pore volume.

Effect of the Initial Step in the SBA-15 Synthesis. This step is usually performed under vigorous stirring of the reacting mixture close to room temperature. To show the importance of the initial step in the synthesis of SBA-15, a couple of samples were prepared by stirring the reacting mixture at 40 °C for 2 h under conventional (st40-2h sample) and microwave (Mst40-2h sample) conditions for comparison with two samples obtained by exposing the latter sample to 10 min and 6 h of hydrothermal treatment at 100 °C (MS100-10m and MS100-6, respectively). Nitrogen adsorption isotherms and the corresponding PSD curves are shown in Figure 8. As can be seen from this figure, the initial stirring of the reacting mixture under microwave irradiation accelerates the self-assembly process, which results in a much better sample than the corresponding one stirred in a conventional way (see adsorption isotherms and PSDs for the Mst40-2h and st40-2h samples). Of course, exposure of the former sample to the microwave−hydrothermal treatment, even for a short period of time, improves its adsorption and structural properties significantly.

Conclusions

This study shows that microwave-assisted synthesis of SBA-15 has several advantages: (i) it provides an easy way to program and control the temperature and time of the synthesis, (ii) it accelerates the entire synthesis by reducing its time from days to hours, (iii) it permits the synthesis of samples at high temperatures, which have larger pore widths and better thermal stability than those obtained under conventional conditions, and (iv) most importantly, this method permits a fine-tuning of the sample properties by varying the temperature and time of the synthesis. Thus, if microwave irradiation is appropriately used, it not only can reduce significantly the time of OMS synthesis but also, when combined with temperature programming, can provide well-ordered materials with highly consolidated frameworks and very good thermal stability.

Since modern microwave systems permit an almost immediate rise to the desired temperature with uniform heat distribution, this method is promising for the synthesis of various ordered nanoporous materials. Because the programming and implementation of experimental conditions such as temperature and time in these systems is very easy, numerous recipes for the syntheses of various materials can be created and examined.

Acknowledgment. This research is partially supported by the National Science Foundation under grant CTS-0553014. The authors thank the Saint-Gobain Research Laboratory in Stow, OH, for SEM measurements.

Supporting Information Available: Figures showing pore size distributions and SEM images, and schemes with information about microwave-assisted synthesis and experimental conditions used. This material is available free of charge via the Internet at http://pubs.acs.org.

JA065345H