Control over Microporosity of Ordered Microporous–Mesoporous Silica SBA-15 Framework under Microwave-Hydrothermal Conditions: Effect of Salt Addition

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The crystallization of ordered microporous–mesoporous silica, SBA-15, has been investigated in the presence of an ionic salt, such as sodium chloride, under microwave-hydrothermal conditions. The crystallization was performed by templating a silica precursor (tetraethyl orthosilicate or sodium silicate) with pluronic123 copolymer ($EO_{20}PO_{70}EO_{20}$; MW 5800) with varied amounts of salt content at 373 K. The crystallized samples were characterized by means of powder X-ray diffraction (PXRD), thermogravimetric analysis (TGA), and nitrogen adsorption–desorption measurements at 77 K. The textural properties of the SBA-15 samples, such as pore volume, pore size, and specific surface area, were found to decrease with an increase in salt concentration. Furthermore, the microporosity of the crystallized samples was found to be a function of the added salt concentration, that is, micropore volume has been found to decrease with an increase in salt concentration. Interestingly, SBA-15 samples crystallized in the presence of higher salt content were found to exhibit a relation between the pore size, pore volume, and specific surface area which is similar to that observed for cylindrical or hexagonal disconnected pores. Such a behavior has demonstrated for the first time that the pore size and microporosity within the pore walls of ordered mesoporous silica SBA-15 can be tuned by means of salt addition under microwave-hydrothermal conditions.

Introduction

Widespread applications of molecular sieves in the fields of separation and catalysis have emphasized the need to search for new structures with new framework compositions.[1] This has resulted in the discovery of the mesoporous molecular silica family (designated as M41S) with ordered arrays of uniform channels with tunable pore size in the range of 20 to 100 Å.[2] This has sparked considerable interest in the synthesis of nanowires[3–5] and in studies related to the behavior of matter in confined geometry[6–8] using these materials as a host. However, poor hydrothermal stability of these materials has restricted their application potential in many areas

of nanotechnology. Thus, attempts are being made to synthesize materials with uniform disconnected channels having good hydrothermal stability and tunable pore size. These attempts have resulted in the synthesis of ordered, hydrothermally stable mesoporous molecular silica, SBA-15, which has been synthesized using a triblock pluronic ($EO_{20}PO_{70}EO_{20}$; MW 5800) copolymer as a template under hydrothermal conditions.[9] This has added an incentive for the development of a wide range of applications in the field of adsorption, catalysis, and advanced materials. Because of this, attempts have been made to prepare Al-, V-, and Ti-substituted SBA-15 framework.[10–15] Surface modification of SBA-15 framework has also been performed via bonding of orgnosilanes,[16,19–21] for heavy metal remediation[17,19–21] sequestration, and controlled release of proteins.[18] Such ma-

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terials have also exhibited facile catalytic properties.[11,12] Furthermore, SBA-15 has also been found applicable as a waveguide and mirrorless laser.[22] It has been successfully employed as a host to prepare mesoporous carbon and metal nanowires and nanoballs.[23–25]

In view of the remarkable application potential of SBA-15 framework, the knowledge of its structural properties has become essential. Recently, several detailed structural elucidation studies[26–28] on SBA-15 have been reported wherein the existence of micropores within the pore walls of SBA-15 has been confirmed. The origin of these micropores is ascribed to the hydrophilic nature of poly(ethylene oxide) (PEO) blocks of the template.[27,28] Because of this, the EO blocks of the templates are expected to be deeply occluded within the silica walls, which upon calcination, are responsible for the generation of microporosity. NMR investigations[29] have also suggested such deep occlusion of EO blocks and X-ray diffraction quantitative measurements[26] have shown the existence of microporous corona around the mesopores of SBA-15 because of occlusion. Owing to the occurrence of such microporosity, the WS/V ratio for SBA-15 framework (where W, S, and V are the mesopore size, mesopore surface area, and mesopore volume, respectively) obtained from nitrogen adsorption–desorption data is often found to vary and remains higher than 4.4 which corresponds to an array of hexagonally packed cylindrical pores of MCM-41 type of material (WS/V = 4.0−4.4).[28] On the basis of these studies, SBA-15 framework has been classified as an array of mesopore−micropore network instead of an array of uniform mesoporous network. In view of these aspects, such a framework cannot be considered as a model porous solid for studies related to the behavior of matter in confined space and as a host for fabrication of nanowires and related areas of nanotechnology. Therefore, it is of utmost importance to synthesize uniform disconnected SBA-15 framework.

To achieve this goal, limited number of attempts have been made which involve both postsynthesis and in-situ synthesis approach. To the best of our knowledge, there are two postsynthesis and one in-situ synthesis approaches. The first postsynthesis approach has suggested the room-temperature treatment at pH = 11[30] while the second approach has recommended the calcination at 1273 K to obtain SBA-15 sample having nitrogen adsorption properties similar to those of uniform hexagonal/circular pore system (MCM-41).[28,31] Furthermore, ethanol/water washing for the crystallized samples is also recommended for reducing the microporosity within the framework.[27] On the other hand, the in-situ approach involves the use of pluronic 104 (BASF) $EO_{17}PO_{58}EO_{17}$, triblock copolymer, and tetraethyl orthosilicate as a template and silica source, respectively.[32] The control over microporosity is achieved by varying synthesis temperature and by an increased silica/polymer molar ratio (60−120) at constant polymer concentration (15.2 g L^{-1}; The polymer concentration used is about 2 times lower than the one used for the synthesis of SBA-15, and the silica/polymer ratio is much higher than the one used for the synthesis of SBA-15, so far[9b]). Considering these facts, efforts need to be focused on the development of new alternatives for controlling the microporosity of the SBA-15 framework. In the present investigation, we report for the first time a rapid in-situ synthesis approach to obtain SBA-15 framework with controlled microporosity, using tetraethyl orthosilicate or sodium silicate (which has been employed successfully for the synthesis of SBA-15[33]) as a silica source by adopting a nonconventional microwave-hydrothermal synthesis route.

The microwave-assisted synthesis of molecular sieves is a relatively new area of research.[34] It offers many distinct advantages over conventional synthesis. They include rapid heating to crystallization temperature because of volumetric heating, resulting in homogeneous nucleation, fast supersaturation by the rapid dissolution of precipitated gels, and eventually a shorter crystallization time compared to conventional autoclave heating.[34] It is also energy-efficient and economical.[34] This method has been successfully applied for the synthesis of several types of zeolites, namely, zeolite A, Y, ZSM-5, MCM- 41, metal-substituted aluminophosphate, and gallophosphate.[34] It has also been successfully applied for the synthesis of mesostructured thiogermanates/germanium sulfides.[35] A rapid synthesis of titanium-substituted MCM-41 molecular sieve has also been reported using the microwave-assisted approach.[36] Recently, we have reported a rapid synthesis of SBA-15 and Ti− and Zr−SBA-15 framework under M−H conditions.[37,38]

In the present study, SBA-15 framework is produced by templating a silica precursor (tetraethyl orthosilicate

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or sodium silicate) with pluronic P123 ($EO_{20}PO_{70}EO_{20}$) in the presence of an ionic salt such as sodium chloride under microwave-hydrothermal conditions at constant silica/polymer molar ratio. The crystallized samples have been characterized with the help of X-ray diffraction, nitrogen adsorption, and thermogravimetric analysis. On the basis of the obtained results, we demonstrate that the control over microporosity of the SBA-15 framework can be achieved using the present in-situ synthesis approach.

Experimental Section

Sample Preparation. SBA-15 samples were prepared using tetraethyl orthosilicate, TEOS, (Aldrich) and sodium silicate (~27% SiO_2, ~14% NaOH, Aldrich) as silica sources. A triblock poly(ethyleneoxide)-poly(propyleneoxide)-poly(ethyleneoxide), ($EO_{20}PO_{70}EO_{20}$; MW 5800, Aldrich) referred to herein after as EO-PO-EO, was used as a structure-directing agent. Typically, a homogeneous solution (1) was prepared by dispersing 1 g of triblock EO-PO-EO in 30 g 2M HCl (J. T. Baker) solution containing requisite amount of sodium chloride under stirring. Similarly, a solution (2) was obtained by mixing 2.22 g sodium silicate solution or 2.375 g tetraethyl orthosilicate with 3.75 g of double-distilled water. Finally, solution (1) was rapidly mixed with solution (2) under vigorous stirring to form a reactive gel with a composition of 1 g (0.17 mmol) polymer: 0.010 mol SiO_2: x mmol NaCl: 0.06 mol HCl: 1.94 mol H_2O (x = 7.7 or 15.5 or 23.3 or 38.8 or 54.4 or 69.9) using sodium silicate as a silica source and 1 g (0.17 mmol) polymer: 0.010 mol SiO_2: x mmol NaCl: 0.06 mol HCl: 44 mmol ethanol: 1.88 mol H_2O (x = 0 or 7.7 or 15.5 or 23.3 or 38.8 or 54.4 or 69.9) using tetraethyl orthosilicate as a silica source. The resultant gel was then stirred overnight at ambient conditions. The gel thus obtained was subjected to microwave-hydrothermal conditions for crystallization under static conditions at 373 K for 2 h. Microwave-hydrothermal synthesis was performed using MARS5 (CEM Corp., Matthews, NC) microwave digestion system as per the method described elsewhere.[37,38]

Characterization. X-ray diffraction patterns were recorded using a Philips X'pert powder diffractometer system with $CuK\alpha$ radiation with a 0.02° step size and 1-s step time over the range $0.5° < 2\theta < 6°$.

The thermogravimetric analysis was performed with a thermal analyzer (TA instruments). Typically, about a 20-mg sample was heated from room temperature to 1273 K with a heating rate of 5 K/min in nitrogen.

The textural properties of the samples were evaluated using nitrogen adsorption/desorption measurements with an Autosorb-1 (Quantachrome) unit. Nitrogen adsorption/desorption isotherms were measured at 77 K after degassing samples below 10^{-3} Torr at 473 K for 4 h. The BET specific surface area (S_{BET}) was estimated using adsorption data in a relative pressure range from 0.04 to 0.2. The external surface area, S_{ex}, total surface area, S_t, primary mesopore surface area, S_p, micropore volume, V_{mi}, and primary mesopore volume, V_p, were estimated using the α_s-plot method, as described elsewhere.[39,40] Amorphous nonporous silica (S_{BET} = 7.0 m²/g, Thiokol) was used as a reference adsorbent. The calculation of mesopore size distribution (PSD) was performed by analyzing the adsorption data of N_2 isotherm using the recently developed KJS (Kruk, Jaroniec, Sayari) approach.[41]The pore diameter corresponding to the maximum of PSD is denoted as W_{KJS}. The statistical film thickness curve used for PSD calculation was estimated using the deBoer approach.[39] The total pore volume, V_t, was

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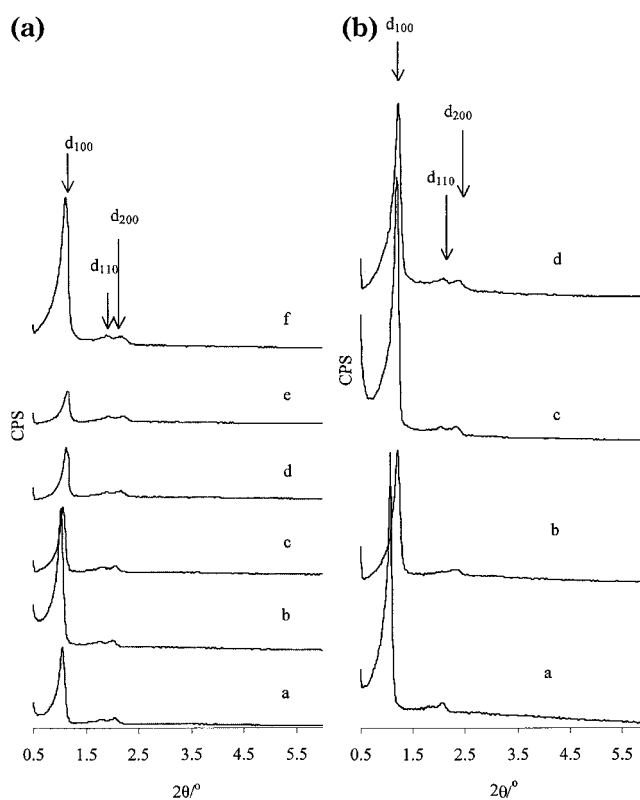
Figure 1. (a) X-ray diffraction patterns for the SBA-15 samples prepared in the presence of (a) 7.7, (b) 15.5, (c) 23.3, (d) 38.8, (e) 54.4, and (f) 69.9 mmol of sodium chloride using sodium silicate as a silica source. (b) X-ray diffraction patterns for the SBA-15 samples prepared in the presence of (a) 0, (b) 7.7, (c) 15.5, and (d) 23.3 mmol of sodium chloride using tetraethyl orthosilicate as a silica source.

estimated from the amount adsorbed at a relative pressure of 0.95.

Results and Discussion

An optimum crystallization time of 2 h has been reported for the preparation of highly ordered SBA-15 molecular sieve under microwave-hydrothermal conditions at 373 K.[37] Hence, all the syntheses were performed for 2 h and crystallized samples were subjected to characterization. The obtained results are discussed in the following sections.

X-ray Diffraction Analysis. Calcined SBA-15 samples prepared in the presence of sodium chloride displayed a well-resolved pattern with a sharp peak in the range of about 0.8–1.1° and two long order weak peaks in the range of about 1.6–2.0° and 1.7–2.3° that matched well with the reported pattern[9b] (Figure 1a, b).

The XRD peaks are indexed to a hexagonal lattice with d(100) spacing corresponding to a large unit cell parameter (a_o). The estimated unit cell parameters for the calcined samples are given in Table 1. The unit cell parameters for samples prepared with sodium silicate as a silica source were found to be almost constant up to the addition of 23.3 mmol of sodium chloride and were found to decrease with further increase in salt content. Interestingly, the wall thickness (t) of the crystallized samples was found to decrease with an increase in salt content up to a level of 54.4 mmol. However, with a further increase of salt content, it was found to increase

Table 1. Structural Parameters for SBA-15 Samples Prepared in the Presence of Sodium Chloride under Microwave-Hydrothermal Conditions[a]

silica source	salt amount (mmol)	$a_o^{\#}$, Å	W_{KJS}, Å	$t,^b$ Å	V_t at p/P = 0.95, cm³/g	V_p, cm³/g	V_{mi}, cm³/g	S_{BET}, m²/g	S_t, m²/g	S_{ex}, m²/g	$(W_{KJS}S_p{}^c)/V_p$
Na−silicate	7.7	95.6	66	29.6	0.67	0.53	0.04	638	610.7	82	6.6
	15.5	98.5	66	32.5	0.67	0.56	0.03	657	608.3	79	6.6
	23.3	94.7	66	28.7	0.63	0.51	0.03	562	539.8	63	6.2
	38.8	90.3	62	28.3	0.47	0.39	0.02	398	393.6	48	5.4
	54.4	88.6	62	26.6	0.47	0.38	0.01	344	340.2	32	5.0
	69.9	90.3	58	32.3	0.44	0.39	∼0	348	341.5	50	4.3
TEOS	0.0	94.8	62	32.8	0.76	0.65	0.04	820	811.8	43	7.3
	7.7	84.2	52	32.2	0.51	0.44	0.02	527	517.4	37	5.7
	15.5	84.2	52	32.2	0.40	0.37	0.01	341	336.1	19	4.4
	23.3	84.2	52	32.2	0.41	0.37	∼0	345	339.2	28	4.4

[a] Syntheses are performed at 373 K for 2 h, $^{\#}a_o = 2/(3)^{1/2} \times d_{100}$. [b] Wall thickness $(t) = a_o - W_{KJS}$. [c] $S_p = S_t - S_{ex}$.
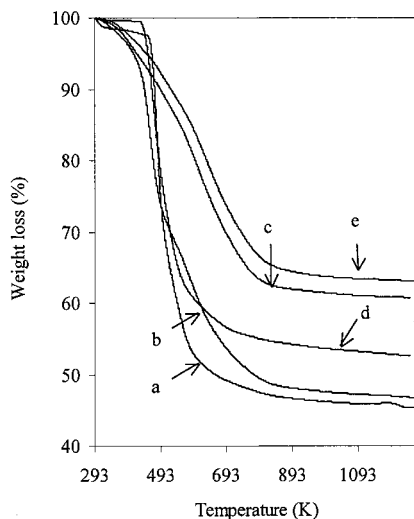

Figure 2. Thermograms for selected SBA-15 samples prepared in the presence of sodium chloride using sodium silicate: (a) 7.7, (b) 38.8, and (c) 69.9 mmol NaCl, and tetraethyl orthosilicate: (d) 0.0 and (e) 23.3 mmol NaCl as a silica source, respectively.

(Table 1). Furthermore, the intensity of the d(100) peak (Figure 1a, f) for the sample obtained in the presence of 69.9 mmol of sodium chloride was found to be much higher than the other crystallized samples. This could be due to the increased crystallinity/uniformity in the SBA-15 framework with an increased salt content. On the other hand, the sample prepared in the absence of sodium chloride using tetraethyl orthosilicate as a silica source was found to have a higher unit cell parameter compared to those prepared in the presence of salt. Furthermore, unit cell parameter and wall thickness for samples prepared in the presence of salt were found to be constant. However, samples obtained with even higher salt content were found to be X-ray amorphous.

Thermogravimetric Analysis. Typical thermograms and weight change derivatives obtained for selected samples are shown in Figures 2 and 3. The as-synthesized samples prepared without addition of any external salts showed a total weight loss of about 50% in the temperature range of 373 and 1273 K with maximum loss occurring at about 483 K (Figure 3, a and d). Such behavior was found to be similar to the one reported under air atmosphere.[9b] This loss can be ascribed to the desorption and decomposition of adsorbed water and polymeric template. Furthermore, a weight loss of about 0.5% at about 1233 K was observed
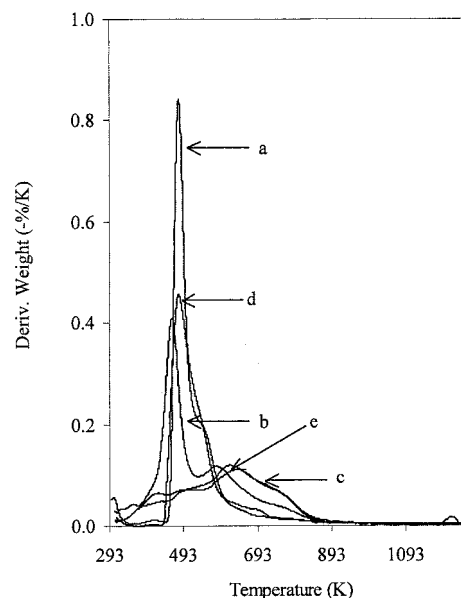

Figure 3. Weight change derivatives for selected SBA-15 samples prepared in the presence of sodium chloride using sodium silicate: (a) 7.7, (b) 38.8, and (c) 69.9 mmol NaCl, and tetraethyl orthosilicate: (d) 0.0 and (e) 23.3 mmol NaCl as a silica source, respectively.

for the sample prepared using sodium silicate as a silica source, which could be due to the release of water through condensation of silanol groups in the silica framework. Such loss was not observed for the sample prepared using tetraethyl orthosilicate as a silica source. Interestingly, the thermal behavior of the samples prepared in the presence of salt was found to be completely different than the one mentioned above, irrespective of the silica source used in their preparation. The samples prepared in the presence of 38.8 and 69.9 mmol of sodium chloride using sodium silicate as a silica source showed a weight loss of about 50% and 39%, respectively, in the temperature range of 373 to 1273 K. Moreover, the maximum weight loss was found to occur in the temperature range of 583 to 610 K and was found to occur at a higher temperature with an increase in salt content (see Figure 3b and 3c). Similarly, the total weight loss for the sample obtained in the presence of 38.8 mmol of salt using tetraethyl orthosilicate as a silica source was found to be about 38% with a maximum loss occurring at about 630 K (Figure 3e). Such a trend has suggested a stronger interaction between the polymeric template and the silica framework of these samples.
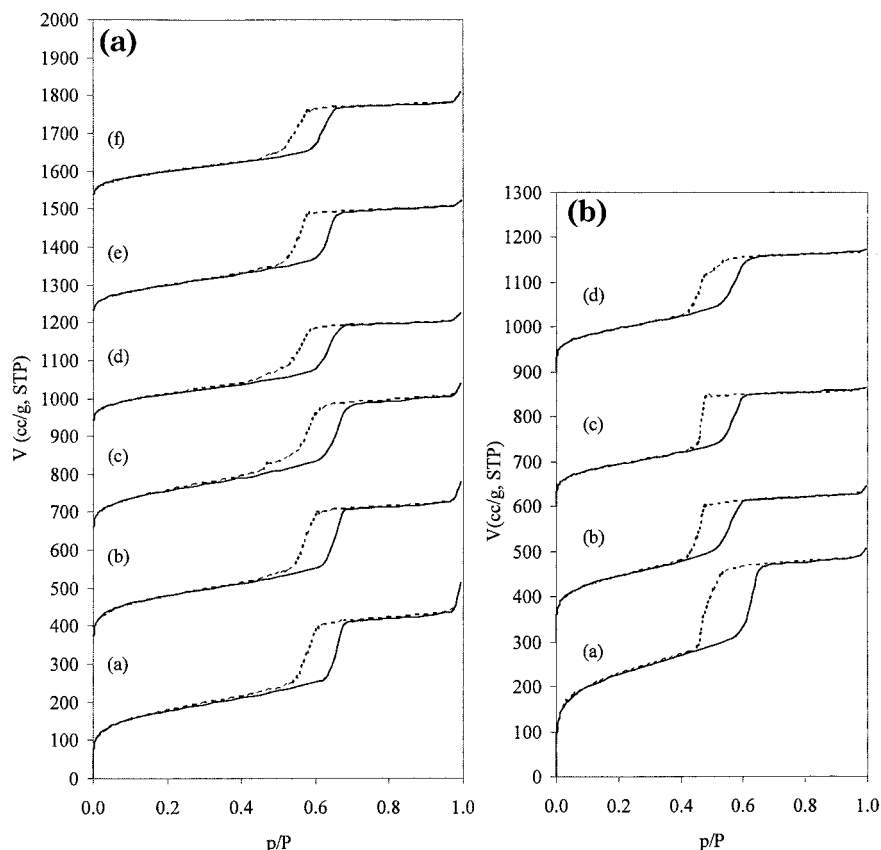
Figure 4. (a) Nitrogen adsorption (—) and desorption (......) isotherms at 77 K for various SBA-15 samples prepared using sodium silicate as a silica source. The adsorption/desorption isotherms for samples prepared with (a) 7.7, (b) 15.5, (c) 23.3, (d) 38.8, (e) 54.4, and (f) 69.9 mmol of NaCl are shifted by 0, 300, 600, 900, 1200, and 1500 cm³ STP/g, respectively. (b) Nitrogen adsorption (—) and desorption (......) isotherms at 77 K for various SBA-15 samples prepared using tetrethyl orthosilicate as a silica source. The adsorption/desorption isotherms for samples prepared with (a) 0, (b) 7.7, (c) 15.5, and (d) 23.3 mmol of NaCl are shifted by 0, 300, 600, and 900 cm³ STP/g, respectively.

Nitrogen Adsorption−Desorption Measurements. Figure 4a and 4b show nitrogen adsorption/desorption isotherms for various SBA-15 samples. The estimated textural parameters such as specific surface area S_{BET}, total surface area, S_t, external surface area, S_{ex}, primary mesopore volume, V_p, micropore volume, V_{mi}, total pore volume V_t, and mesopore size, W_{KJS}, for various samples are compiled in Table 1. The calculated mesopore size distribution based on the KJS approach for each sample is shown in Figure 5a and 5b.

All the nitrogen adsorption/desorption isotherms are found to be of Type IV in nature as per the IUPAC classification and exhibited a H1 hysteresis loop, which is typical of mesoporous solids. However, the hysteresis loops for the samples prepared with tetraethyl orthosilicate (Figure 4b, isotherm b and c) were found to be triangular in shape. Such types of loops have been reported for MCM-41 samples with uniform pore sizes in the range of 40−55 Å.[41] The adsorption branch of isotherm obtained for samples prepared using sodium silicate or tetraethyl orthosilicate as a silica source in the absence of any externally added salt showed a sharp inflection at a relative pressure value of about 0.62. Similarly, the adsorption branches of isotherms for samples obtained in the presence of 15.5, 23.3, 38.8, 54.4, and 69.9 mmol of sodium chloride showed points of inflection at relative pressure values of about 0.62, 0.62, 0.60, 0.60, and 0.58, respectively. On the other hand, a point of inflection at a relative pressure of about

0.52 was noticed for samples prepared with tetraethyl orthosilicate in the presence of 7.7, 15.5, and 23.3 mmol of sodium chloride. This is a characteristic of capillary condensation within uniform pores.[39] The position of the inflection point is clearly related to a diameter in the mesopore range, and the sharpness of these steps indicates the uniformity of the mesopore size distribution.[39] This suggests the reduction in mesopore size of the SBA-15 framework with a higher amount of salt when sodium silicate is used as a silica source. On the other hand, a good match between the points of inflection on the adsorption branch of each isotherm for samples prepared with tetraethyl orthosilicate in the presence of sodium chloride suggests that these samples have similar pore size.

The pore size distribution (PSD) curves shown in Figure 5a for samples prepared with sodium silicate in the presence of 7.7, 15.5, and 23.3 mmol sodium chloride show a narrow pore size distribution with an average pore size of about 66 Å which is found to decrease to about 62 and 58 Å with an increase in salt content. Furthermore, the presence of additional mesopores in the range of 25−50 Å is also noticed for these samples. However, such mesopores are found to be absent in the sample obtained using 69.9 mmol of sodium chloride content. Likewise, a narrow pore size distribution having an average mesopore size of about 62 Å is observed for the sample prepared with tetraethyl orthosilicate in the absence of salt, which decreases to an
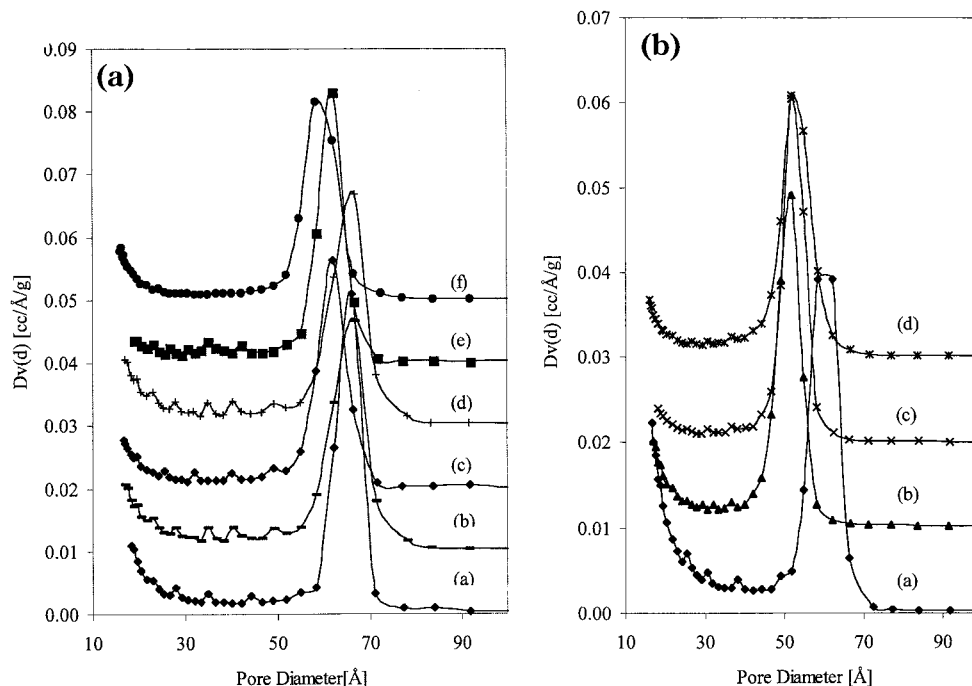
Figure 5. (a) Pore size distribution for various SBA-15 samples with sodium silicate. The PSD curves for samples prepared with (a) 7.7, (b) 15.5, (c) 23.3, (d) 38.8, (e) 54.4, and (f) 69.9 mmol of NaCl are shifted by 0, 0.01, 0.02, 0.03, 0.04, and 0.05 cm^3/Å/g, respectively. (b) Pore size distribution for various SBA-15 samples with tetraethyl orthosilicate. The PSD curves for samples prepared with (a) 0, (b) 7.7, (c) 15.5, and (d) 23.3 mmol of NaCl are shifted by 0, 0.01, 0.02, and 0.03 cm^3/Å/g, respectively.

average mesopore size of about 52 Å with the addition of salt. Additional mesopores having an average size in the range of 20–50 Å are also noticed for the sample prepared in the absence of salt. The density of such mesopores is found to decrease with an increase in salt content.

The textural properties such as specific BET surface area, external surface area, primary mesopore volume, micropore volume, and total pore volume for various SBA-15 samples (Table 1) are found to be dependent on the added salt content. Such an effect is more pronounced when tetraethyl orthosilicate is used as a silica source wherein the textural parameters are found to decrease with an increase in salt content. A similar trend is also observed for the sodium silicate system but at a higher salt content compared to the former one. In addition, the ratio of $W_{KJS}S_p/V_p$ is also found to decrease with an increase in salt content (Table 1) and is found to be about 4.4 for the samples prepared with 69.9 and 15.5 mmol of sodium chloride content when sodium silicate and tetraethyl orthosilicate are used as silica sources. These values are in good agreement with those reported for uniform hexagonal disconnected pore system, namely, MCM-41 (for MCM-41 sample having pore size of about 48 Å, the ratio $W_{KJS}S_p/V_p$ exhibits a value of 4.6[28]). This in turn suggests the crystallization of a uniform hexagonal SBA-15 network with low micropore content using 69.9 and 15.5 mmol of salt content using sodium silicate and tetraethyl orthosilicate as silica sources, respectively, under microwave-hydrothermal conditions. In other words, on the basis of the results obtained, it can be said that a minimum amount of sodium chloride is essential to generate uniformity in the SBA-15 framework in the present experimental conditions. Thus, it can be inferred that the presence of sodium chloride in the reactive gel under microwave-

hydrothermal conditions plays an effective role in controlling the porosity of the framework. This can be judged from the pore size distribution curves obtained for these samples wherein no additional pores between 20 and 30 Å are observed (recently, on the basis of surface modification of SBA-15, the existence of complementary pores in the range of 10–30 Å has been shown which includes both mesopores and micropores[28]). Therefore, it is of utmost importance to understand the role of sodium chloride in the crystallization of SBA-15 framework and has been discussed below.

Role of Sodium Chloride. The present investigation suggests an alternative approach to obtain uniform SBA-15 framework with low micropore content under microwave-hydrothermal conditions in the presence of ionic salt. The addition of salt addition has recently been reported for the generation of macroporosity in mesoporous silica framework.[42] Furthermore, it has been successfully used to control the order and particle size of the nonionically templated silica, MSU-X.[43] On comparing the results obtained in the present study with those reported in the recent study, it can be judged that the addition of salt under microwave-hydrothermal conditions allows structure tuning by altering the gel chemistry.

It has been proposed that the assembly of the mesoporous silica organized by triblock copolymer species in acid media occurs through a (S° H$^+$)(X$^-$ I$^+$) pathway wherein acid anion (X$^-$) is proposed to play a vital role.[9b] Furthermore, the relative times required for silica mesophase precipitation to occur depend on the acid anion and is found to be the shortest in the presence of

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Cl$^-$ anion when used in the form of hydrochloric acid.[9b] The precipitation time is also found to decrease with an increase in Cl$^-$ concentration.[9b] This is indeed observed in the present study with an increase in the added sodium chloride content. In addition to this, sodium chloride is reported to play a role of structure maker during the micellization of PEO−PPO−PEO block copolymers because of its self-hydration through hydrogen bonding.[44] This in turn has been found to lower the copolymer solubility, critical micellar concentration, critical micellar temperature, and cloud point of the copolymer.[44] Recent study has also shown that added sodium chloride develops hydrophobicity in the PPO moieties and reduces hydrophilicity of PEO blocks at ambient conditions thereby favoring the micellization of the block copolymer at relatively lower concentrations than in water at ambient condition.[45] Because of the self-hydration behavior of the added salt, the PEO blocks of the formed silica oligomers and surfactant (micellar) assemblies, in the presence of salt, are expected to have less amount of water than those formed in water at ambient conditions. This in turn suggests a low hydrodynamic volume for the assemblies formed in the presence of salt. Furthermore, PEO blocks of these assemblies have been reported to undergo dehydration with an increase in temperature thus becoming hydrophobic in nature[46] as less polar conformations of ethylene oxide segments are preferred at higher temperatures. Thus, the resulting loss of water at higher temperatures permits the chain to come together. Hence, we believe that the added salt content enhances the formation of the nonpolar environment for the formed micelles because of its structure-making property at ambient conditions and is expected to further enhance as a rapid dehydration of PEO blocks is anticipated under microwave-hydrothermal conditions. In view of this, the crystallization of silica-surfactant assembly, in the presence of salt, is expected to favor the formation of SBA-15 framework having reduced pore size than that formed in the absence of salt under the present conditions. This can be judged from the reduction in the pore size at higher salt content for the sample prepared using sodium silicate as a silica source. Similar behavior is also noticed for the samples prepared using tetraethyl orthosilicate as a silica source. However, the above samples are found to have smaller pore size than those prepared using sodium silicate as a silica source.

Such reduction in the pore size reflects further reduction in the micellar size than that of the micelle formed in aqueous media. This may be due to the increased polarity of the medium as tetraethyl orthosilicate upon hydrolysis is expected to produce 4 mol of ethanol. As a result, polymer chains constituting the micelles are expected to come much closer together compared to those formed in the presence of aqueous medium at ambient conditions. On the basis of the proposed role of sodium chloride, the PEO and PPO chains of the template are expected to be held together with favorable nonpolar conformations of PEO block, which in turn is anticipated to reduce the penetration of the PEO blocks inside the walls of the SBA-15 framework thereby decreasing the microporosity of the framework. The observed trend in the micropore volume is found to further support the role of sodium chloride (Table 1). The crystallization of silica gel type of material at higher salt content observed using tetraethyl orthosilicate could be due to the occurrence of a phase separation behavior for polymer because of the lowering of its cloud point.

In view of this, the obtained trend for the total weight loss in thermogravimetric analysis can be explained. With an increase in hydrophobicity of the PPO and PEO blocks of the micelles formed in the presence of salt, the water content retained by the SBA-15 framework is expected to decrease significantly which in turn would result in the lowering of the total weight loss; this is indeed observed for the samples prepared in the presence of sodium chloride (Figure 2, b, c, e). Furthermore, the higher decomposition temperatures for the polymeric template occluded inside the SBA-15 samples prepared in the presence of salt may be due to stronger interaction between polymer moieties and the hydrophobic silica framework.

Conclusions

In the present investigation, we have illustrated a rapid nonconventional microwave-hydrothermal approach to crystallize SBA-15 with uniform hexagonal channel network with a low content of connecting micropores by controlling the micellar environment with the help of alkali halide salt, namely, sodium chloride using either sodium silicate or tetraethyl orthosilicate as a silica source. On comparison with high-temperature calcination-based postsynthesis approach, the present synthesis route, we believe, is more preferred as the former one has been reported to create nonuniformity in the framework. It is also better than the recently reported in-situ synthesis approach in terms of its cost factor because it can be used with the cheapest source of silica.

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