

Simplified synthesis of micropore-free mesoporous silica, SBA-15, under microwave-hydrothermal conditions†

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Synthesis of micropore-free hydrothermally stable mesoporous silica SBA-15 has been accomplished by templating a silica precursor (sodium silicate/tetraethylorthosilicate) with pluronic123 copolymer (EO₂₀PO₇₀EO₂₀; M.W. 5,800) in the presence of cosolvent (ethanol) using a minimum salt (sodium chloride) content, under microwave-hydrothermal conditions at 373 K in 120 mins.

The disclosure of mesoporous silica SBA-15 sparked considerable interest in the fields of catalysis, separation, and microreactors.¹ However, because of the presence of framework microporosity, such a framework can not be used as a model host to investigate the behavior of matter in confined space.²

Of late, limited synthesis efforts have been made to obtain micropore-free SBA-15 framework by manipulating the synthesis domains such as temperature, surfactant concentration *etc.*³ The use of inorganic ionic salts, especially sodium chloride, during synthesis has also been found to be useful in controlling the framework porosity and tailoring the textural properties of the framework.^{3d} However, a high concentration of salt is found to be essential to achieve this goal. Furthermore, the inorganic salts, when used in high concentrations, have been found to have a significant influence on the synthesis temperature and particle morphology.^{3ef} On the other hand, the use of high concentrations of salts may lead to salt occlusion in the crystallized framework which could impart poor hydrothermal stability in the framework as reported recently.⁴ Hence it is of importance to design a new synthesis approach to achieve control over framework microporosity. In the present communication we report our successful attempt to accomplish this objective by templating SBA-15 framework in manipulated micellar environment in the presence of co-solvent namely ethanol and a minimum amount sodium chloride, under microwave-hydrothermal (M-H)⁵ conditions at 373 K.

Microwave-hydrothermal synthesis of mesoporous silica SBA-15 was performed using the MARS 5 (CEM Corp., Matthews, NC, USA) microwave digestion system. In a typical synthesis, 1.0 g of polymer (P123 M.W. 5800, BASF, NJ, USA) was dispersed in 33.75 g of 2 M hydrochloric acid containing 0/2.02 g of ethanol at ambient conditions. The resultant solution was rapidly mixed with a silica precursor (2.22 g of sodium silicate solution: 27%SiO₂ and 14% NaOH, Aldrich) under vigorous stirring to form a reactive gel having a composition of 1 g P123 : 0.010 mol SiO₂ : 7.7 mmol NaCl : 0.06 mol HCl : 0/44 mmol ethanol : 1.94 mol H₂O. (Note that no external salt has been added in this gel composition, the amount of salt reported is same as that produced from the used silica source). The crystallization of the gel was performed by following the approach described elsewhere.^{5b} The crystallized products were washed with distilled water, dried at 383 K and finally calcined at 813 K in air for 4 h. Thus obtained samples were characterized by X-ray diffraction (XRD), and nitrogen adsorption-desorption measurements at 77 K. 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.⁶ The calculation of mesopore size distribution (PSD) was performed by analyzing the adsorption data of the N₂ isotherm using the recently developed KJS (Kruk, Jaroniec, Sayari) approach⁷ and the pore diameter corresponding to the maximum of PSD was denoted as W_{KJS} .

The X-ray diffraction patterns for SBA-15 samples displayed well-resolved patterns 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.¹ All the samples exhibited a typical type IV adsorption-desorption isotherm during nitrogen adsorption-desorption measurements which is a characteristic of a mesoporous solid (Fig. 1).⁶ The estimated textural parameters from X-ray diffraction and nitrogen adsorption-desorption measurement data are compiled in Table 1. Interestingly, the unit cell parameters and textural properties for the sample crystallized in the presence of ethanol are found to be lower. Furthermore, the ratio of $W_{\text{KJS}}S_p/V_p$ is found to be about 4.0 for this sample. This in turn reflects the crystallization of a uniform hexagonally packed cylindrical pore network of SBA-15, which could have a close structural resemblance with MCM-41. This was further confirmed by the platinum inverse replication method wherein the formation of individual Pt-nanowires having a diameter of about 5.0–6.0 nm is observed (see ESI†).^{8a} Upon comparison with the reported literature data, this result is found to be

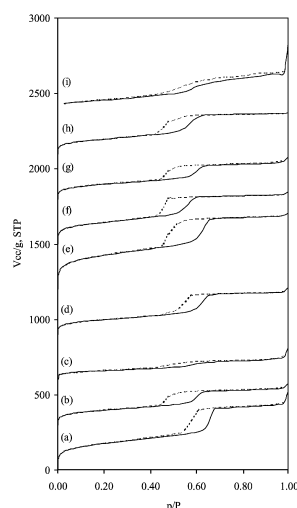


Fig. 1 Nitrogen adsorption (—) and desorption (---) isotherms at 77 K for SBA-15 samples (a) 7.7–0.0, (b) 7.7–44, (c) 7.7–88, and (d) 69.9–0.0^{4d} mmol of NaCl-ethanol prepared using sodium silicate are shifted vertically by 0, 300, 600, 900 ccSTP g⁻¹, and for samples (e) 0.0–44, (f) 7.7–44 and (g) 7.7–88 mmol of NaCl-ethanol prepared using tetraethylorthosilicate as a silica source are vertically shifted by 1200, 1500, and 1800 ccSTP g⁻¹, respectively. Nitrogen adsorption/desorption isotherms for hydrothermally treated samples (h) 7.7–44, and (i) 69.9–0.0 mmol of NaCl-ethanol are shifted vertically by 2100, and 2400 ccSTP g⁻¹, respectively.

† Electronic supplementary information (ESI) available: transmission electron micrographs of Pt-nanowires produced from micropore-free SBA-15 framework. See <http://www.rsc.org/suppdata/cc/b2/b202152h/>

Table 1 Structural parameters for various SBA-15 samples^a

Silica source	Salt-ethanol amount/mmol	$a_0/\text{\AA}$	$W_{\text{KJS}}/\text{\AA}$	$t/\text{\AA}$	V_t at $p/P = 0.95/\text{cc g}^{-1}$	$V_p/\text{cc g}^{-1}$	$V_{\text{mi}}/\text{cc g}^{-1}$	$S_{\text{BET}}/\text{m}^2 \text{g}^{-1}$	$S_t/\text{m}^2 \text{g}^{-1}$	$S_{\text{ex}}/\text{m}^2 \text{g}^{-1}$	$(W_{\text{KJS}}S_p^d)/V_p$
Na-silicate	7.7-0	95.6	66	29.6	0.67	0.53	0.04	638	610.7	82	6.6
	7.7-44	84.5	52	32.5	0.41	0.35	0.00	345	312.2	41	4.0
	7.7-44 ^e	84.2	52	32.2	0.39	0.36	0.00	340	310.8	35	4.0
	69.9-0 ^f	90.3	58	32.3	0.44	0.39	0.00	348	341.0	50	4.3
	69.9-0 ^{ef}	82.5 ^g	—	—	0.30	—	—	172	—	—	—
TEOS	0-44	94.8	62	32.8	0.76	0.65	0.04	820	811.8	43	7.3
	7.7-44	84.2	52	32.2	0.50	0.44	0.02	527	517.4	37	5.7
	7.7-88	84.2	52	32.2	0.42	0.38	0.00	345	339.2	28	4.2

^a Syntheses were performed at 373 K for 2 h. ^b $a_0 = 2/(3)^{1/2} \times d_{100}$. ^c Wall thickness (t) = $a_0 - W_{\text{KJS}}$. ^d $S_p = S_t - S_{\text{ex}}$. ^e Samples were subjected to hydrothermal treatment for 24 h. ^f Ref. 7d. ^g A broad X-ray diffraction peak with decreased peak intensity is observed.

remarkable because external addition of sodium chloride is not required to control the framework porosity as reported previously,^{3d} except when there is *in situ* NaCl generation (7.7 mmol). In order to further investigate the effect of ethanol concentration, the crystallization of a gel with the same composition but with an increased amount of ethanol (88 mmol) was performed. The nitrogen adsorption-desorption isotherm (Fig. 1(c)) for the sample thus obtained did show a distinct condensation step as observed for previous samples. Such an isotherm indicated the formation of a disordered silica structure.

To judge the suitability of a silica precursor, the synthesis was also performed in the presence of sodium chloride using tetraethylorthosilicate as a silica precursor and by employing a gel composition of 1 g P123 : 0.010 mol SiO₂ : x mmol NaCl : 0.06 mol HCl : 44 mmol ethanol : 1.88 mol H₂O; ($x = 0$ or 7.7). For comparison, the concentration of sodium chloride used in the gel formation was kept the same as that produced *in situ* while using sodium silicate as a silica precursor. The reactive gel was prepared as per the method described before and its crystallization was performed under microwave-hydrothermal conditions at 373 K. The crystallized samples were characterized as described earlier. The estimated textural parameters from X-ray diffraction and nitrogen adsorption-desorption measurement data are also compiled in Table 1 and the measured nitrogen adsorption-desorption isotherms are shown in Fig. 1. As seen from Table 1, a low value $W_{\text{KJS}}S_p/V_p$ ratio for the sample obtained in the presence of sodium chloride is also noticed. But the degree of influence was lower as compared to the one observed when sodium silicate was employed as a silica precursor. However, such a ratio was observed to be about 4.0 for a sample which was crystallized from a gel having a composition of 1 g P123 : 0.010 mol SiO₂ : x mmol NaCl : 0.06 mol HCl : 7.7 mmol NaCl : 88 mmol ethanol : 1.88 mol H₂O using TEOS as a silica source. This observed trend further reinforced the ability of ethanol in controlling the framework microporosity for SBA-15 in the presence of a minimum amount of sodium chloride.

Finally, the hydrothermal stability for the present samples was evaluated by exposing the samples to water under reflux conditions for 24 h.^{8b} In order to judge the suitability of the present approach, a micropore-free SBA-15 framework was also assembled by adopting the excess salt route as reported elsewhere.^{3d} Thus obtained samples were characterized by means of X-ray diffraction and the N₂ adsorption method. Interestingly, the mesoporous framework assembled *via* the present methodology was found to have better hydrothermal stability than the one obtained through the excess salt route. The micropore-free sample assembled through high salt content displayed structural degradation (Table 1, Fig. 1(i)). This could be due to base catalyzed hydrolysis of the silica framework due to the presence of sodium ions when used in excess and is found to be in good agreement with the recent report.⁴

These results strongly suggest a specific nature of interaction between ethylene oxide or propylene oxide blocks of the P123 polymer with water in the presence of additives, namely sodium chloride and ethanol. Such interaction is significantly influenced in the presence of sodium chloride.^{3d} The addition of salt also lowers the thermodynamic radius of the formed micelles, which is indeed noticed in the form of the reduction of the unit cell parameter and pore size in the present study. Thus, the rapid dehydration of PEO blocks at elevated temperature under the influence of microwaves coupled with the non-polar environment created by sodium chloride and ethanol means that the formed micelles are expected to have favorable non-polar conformations of PEO blocks. This 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 without further addition of salt.^{3d}

In summary, we have successfully achieved control over microporosity of the SBA-15 framework by manipulating the micellar environment by means of addition of cosolvent and a minimum amount of salt. Such an approach is expected to lead to the formation of a hydrothermally stable micropore-free framework and is also cost effective as it can be practiced with the cheapest source of silica.

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