

Synthesis and characterization of periodic mesoporous organosilicas from bridged organosilanes in the presence of mixed salts

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Abstract

A simple but effective synthetic pathway to periodic mesoporous organosilicas (PMOs) has been put forward in this article. The novelty of the present preparative route lies in that, for specific examples, highly ordered ethane- and benzenesilica PMOs can be facilely prepared in the presence of an inorganic salt pair within a wide compositional range, where no addition of mineral acids was necessary. Most of interest is that crystal-like pore walls were observed for the large-pore benzenesilica PMO promoted by this novel system, which has rarely been reported for copolymer-assembled organosilicas, even though the degree of molecular order is not as perfect as those benzenesilicas prepared under basic conditions utilizing cationic surfactants as template. Characterization results based on a series of techniques indicated that both inorganic salts are important for the assembly of ordered mesostructures under the present system, and a plausible formation mechanism deduced from the “salt-assisted” concept as previously reported for mesoporous nonsiliceous materials was discussed.

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1. Introduction

The strategy of synthesis of periodic mesoporous organosilicas (PMOs) is based on the hydrolysis and condensation, in the presence of supramolecular aggregates of long-chain surfactants severing as structure-directing agents, of bis(trialkoxysilyl)alkylsilanes such as $(R'O)_3Si-R-Si(R'O)_3$, in which the organic moiety ($-R-$) is double functionalized with two trialkoxysilyl groups $(-Si(R'O)_3)$ [1–6]. The main properties featured by these materials are highly ordered structures and uniform pore size distributions within a framework formed by a homogeneous distribution of organic fragments and inorganic oxides. Compared to their inorganic counterparts, these organic–inorganic hybrid materials offer unique advantages and diverse applications, which are closely associated with the properties of the organic polymers as such tunable interfacial and physicochemical properties by easily varying the organic-spacer-groups of the organosilica precur-

sors. Because of their ordered and uniform porosity, this kind of materials is very interesting for applications such as catalysis, separation, chromatography, low- k devices or host–guest chemistry.

Up to date, many kinds of organic bridging groups have been successfully incorporated into the corresponding PMO materials, from small aliphatic spacers to aromatic and large heterocyclic ones including for instance methylene [7,8], ethane [4,6,9–16], ethylene [5,17,18], thiophene [19,20], thioether [21–23], benzene [24–27], toluene [28], 2,5-dimethylbenzene [28], *p*-xylene [29], 1,4-divinylbenzene [30,31], biphenyl [32,33], 4-phenylether-/4-phenylsulfide [34] and isocyanurate [35] and so on. Very recently, the syntheses of bi- and multifunctional PMOs are another hot research direction because a proper selection of these groups allows one to design functional nanocomposites for specific catalytic and environmental application objectives [36–45].

In comparison with the common basic synthesis pathways using ionic alkylammonium surfactants as templates, an alternative promising route to PMO materials under acidic conditions employing nonionic oligomeric or triblock

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copolymers as structure-directing agents was much more desirable, because of the well-known advantages of neutral surfactants as such diversity and versatility [46]. Thus, it was possible to obtain PMO materials with a high degree of mesostructural order, high specific surface areas and larger pore sizes. However, in contrast to the extensive study and well-controlled basic synthesis route to PMOs, the development of PMO materials via nonionic-surfactant-templating strategy is relatively limited, particularly for large pore-sized ones templated by block copolymers [1].

Currently, there is a quest for large-pore PMOs from the point of view of immobilization and encapsulation of large molecules; therefore, the development of the synthesis method is closely related to their forthcoming applicability. Although great effort has been spent on the preparation of SBA-15-type PMOs, in most cases these products were either poorly ordered [11,47] or it was necessary to carry out the synthesis under somewhat critical conditions of high acid or surfactant concentrations [12,14,47]. Even though a novel low-acid-concentration pathway has been recently reported, the synthesis range is limited as the authors described [16,48]. Therefore, the exploration of alternative effective synthesis method may be an interesting task to the synthesis of highly ordered SBA-15-like PMOs, which is one of the main aims of the present work. Undoubtedly, it has been well established that the report of PMO materials in 1999 is one of the most recent innovations in the field of ordered mesoporous materials [1,49], and most of interest is the successful synthesis of PMOs with crystal-like pore walls in case of ethylene- [17,18], 1,4-/1,3-benzene- [24,26,27,50], 1,4-divinylbenzene- [30,31] as well as biphenyl-bridged [32,33] organosilicas. However, with limited exception [51,52], all these attractive materials can only be directly prepared under basic conditions using cationic templates [1,24] or post-treatment of P123-templated materials with alkaline solutions [53]. That is, only two reports can be found in the literature on the direct synthesis of SBA-15-like PMOs with distinct crystal-like property templated by copolymer surfactant [51,52].

Recently, we reported highly ordered Zr-containing PMO (ZrPMO) with different Zr/Si ratios by employing $\text{ZrOCl}_2\text{-NaCl}$ combination as a promoting agent by simply adjusting the molar ratio of the zirconium species to the organosilica precursor, where no addition of mineral acids was necessary. A plausible assembly mechanism based on the synergistic effect of both “nonhydrolyzable” (NaCl) and “hydrolyzable” (ZrOCl_2) inorganic salts was discussed in detail, where the “salting out” effect and self-generated acidity from both inorganic salts, respectively, were believed to be key factors for the formation of ordered SBA-15-type ZrPMO materials under the synthesis condition. Following our previous works [14,15,54], a much facile synthesis pathway to prepare ordered SBA-15-type PMOs using “salt-assisted” self-assembly concept [55] was presented in this article. Employing triblock copolymer

Pluronic P123 as template, two series of standard aliphatic and aromatic organic group bridged products as ethane- and benzenesilicas were easily prepared in the presence of NaCl/ FeCl_3 salt pair within a wide synthesis range, without using any acid during the synthesis procedure. We found that the present salt combination is quite interesting, since highly ordered PMOs can be synthesized and also there is indication of the appearance of crystal-like pore walls in the benzenesilicas. To the best of our knowledge, this observation has rarely been reported for SBA-15-like benzenesilicas prepared under acidic conditions, even though the crystal-like pore walls of the present benzenesilica is not highly perfect as those obtained using cationic surfactants under basic conditions [24].

2. Experimental procedures

2.1. Chemicals

Bis(trimethoxysilyl)ethane (BTME, 96%), 1,4-bis(triethoxysilyl)benzene (BTEB, 96%), iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 98%), and triblock poly(ethylene oxide)-*b*-poly(propylene oxide)-*b*-poly(ethylene oxide) copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123, $M_w = 5800$) were purchased from the Aldrich-Sigma company. All chemicals were used as received without further purification.

2.2. Synthesis

Ethane- and benzene-bridged mesoporous materials were synthesized from BTME and BTEB in the presence of NaCl/ FeCl_3 pair without addition of any mineral acids. Keeping NaCl/Si ratio constant at 4 and 2, respectively, for ethane- and benzene-bridged products, structurally ordered SBA-15-type PMOs can be facilely synthesized by tuning the Fe/Si ratios between 0.01 and 0.2. In a typical synthesis for ethanesilica, 1.5 g of P123, 3.5 g of NaCl and predetermined amount of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ were dissolved in 50 g of deionized water and stirred for 4 h at a fixed temperature 40 °C. Then, 1.96 mL BTME was added to the solution and stirred for 24 h at the same temperature. The molar ratio of the reactants is $\text{BTME/P123/H}_2\text{O/NaCl/FeCl}_3 \cdot 6\text{H}_2\text{O} = 1:0.034:400:8:0.02 \sim 0.4$. The solution along with the precipitate was then transferred to an autoclave and hydrothermally treated by putting in an 80 °C oven for another 48 h. The product was filtered and extracted two times with pure ethanol (100 mL) and HCl (3 mL conc. HCl) at 60 °C for 6 h to remove P123 template according to the reported methods [1,14,56]. The final PMO products were collected by filtration and dried in air at room temperature.

The synthesis procedure for benzenesilicas using BTEB as precursor is entirely similar to the ethanesilica as described above only except with the different molar composition, here the ratio is $\text{BTEB/P123/H}_2\text{O/NaCl/FeCl}_3 \cdot 6\text{H}_2\text{O} = 1:0.034:400:4:0.02 \sim 0.4$.

2.3. Characterization

Small-angle X-ray scattering (SAXS) measurements were performed using synchrotron X-ray source of Pohang Accelerator Laboratory (PAL, Korea): Co $K\alpha$ ($\lambda = 1.608 \text{ \AA}$) radiation with an energy range of 4–16 keV (energy resolution $\Delta E/E = 5 \times 10^{-4}$, photo flux = 10^{10} – 10^{11} ph/s, beam size $< 1 \text{ mm}^2$). Powder X-ray diffraction (XRD) patterns were collected on a Rigaku RINT-2200 diffractometer with Cu $K\alpha$ radiation (40 kV, 30 mA) from 5° to 70° in 0.02° steps at a scan speed of $1^\circ (2\theta) \text{ min}^{-1}$. Transmission electron microscopy (TEM) images were obtained by a JEOL2010 electron microscope with an acceleration voltage of 200 kV. The powder samples for TEM measurements were suspended in ethanol, ground in a mortar, and then loaded onto the Cu grids with holey carbon films. Scanning electron microscopy (SEM) images were recorded on a JEOL6400 microscope operating at 10 kV, and the samples were coated with gold. Nitrogen sorption isotherms of samples were obtained by a Quantachrome's Quadrasorb SI analyzer at -196°C . Before the measurements, the samples were degassed at 120°C for 12 h in vacuum. The Brumauer–Emmett–Teller (BET) surface area was calculated using experimental points at a relative pressure of $P/P_0 = 0.05$ – 0.25 . The total pore volume was calculated by the N_2 amount adsorbed at the highest P/P_0 for each sample ($P/P_0 = 0.99$). The pore size distribution was calculated from the adsorption branches by Barrett–Joyner–Halenda (BJH) method. The micropore area and volume were calculated by the t -plot method using experimental points at a relative pressure of $P/P_0 = 0.10$ – 0.20 . ^{13}C cross polarization (CP) and ^{29}Si MAS NMR spectra were obtained on a Bruker DSX400 spectrometer at room temperature with a 4 mm zirconia rotor spinning at 6 kHz (resonance frequencies of 79.5 and 100.6 MHz for ^{29}Si and ^{13}C CPMAS NMR, respectively; 90° pulse width of 5 μs , contact time 2 ms, recycle delay 3 s for both ^{29}Si and ^{13}C CPMAS NMR).

3. Results and discussion

3.1. Ordered ethane-bridged SBA-15 type PMOs

For ethanesilica as an example, various preparation conditions, as shown in Table 1, have been investigated to

prove the importance of the inorganic salt pair. Fig. 1 shows the SAXS patterns of the samples synthesized with and without salt pair in the aqueous system. Interestingly, all SAXS patterns of the solvent-extracted ethanesilicas prepared with the aid of NaCl/FeCl₃ salt pair exhibit at least three discernible reflections. Following previous studies [57], the three basal reflections can be indexed as (100), (110) and (200) peaks of a typical hexagonal ($p6mm$) mesoporous materials, clearly indicating that highly ordered SBA-15-like PMO materials could be facilely prepared with the employed synthesis conditions, over the wide range of Fe/Si molar ratio from 0.01 to 0.1 while keeping the amount of NaCl constant with the NaCl/Si ratio at 4 (Fig. 1d–f). In contrast, no distinct reflection peaks can be observed for the samples synthesized from the systems in the absence of FeCl₃/NaCl salt pair (Fig. 1a–c). The results strongly illustrate the synergic effect of both salts on the assembly of ordered PMO materials.

The nitrogen sorption isotherms of corresponding ESx materials synthesized in the presence of salt pair are shown in Fig. 2. All samples exhibit isotherms resembling type IV with a nearly parallel H1 hysteresis loop [57]. This strongly suggests the presence of uniform cylindrical pores in these materials, in accordance with the two-dimensional (2-D) hexagonal pore structures revealed by the SAXS data. Correspondingly, the pore size distributions of these samples clearly display a quite uniform pore structure; nearly no difference can be found from those reported studies on the SBA-15-like PMOs synthesized by other pathways [8,14]. The total pore volumes, micropore volumes, pore diameters and BET surface areas are also summarized in Table 1. All periodic ethanesilicas possess typical structural properties of the SBA-15 type materials as large surface area and pore volume and a considerable amount of micropores [46,57]; these observations are comparable to those SBA-15 type ethanesilicas prepared under strong acidic conditions [11,12,14]. However, no distinct relationship can be found between the preparation conditions and structural properties of these samples synthesized with the present synthesis conditions.

Consistent with the results of the SAXS and the physisorption measurements, respectively, TEM images of the ES1 ethanesilica viewed along different directions

Table 1
Preparation conditions and structural parameters of PMOs synthesized using NaCl/FeCl₃ pair

Sample ^a	NaCl/Si	FeCl ₃ /Si	S_{BET}^b (m^2/g^{-1})	V_p^c ($\text{cm}^3/\text{g}^{-1}$)	D^d (nm)	V_{micro}^e ($\text{cm}^3/\text{g}^{-1}$)
ES1	4	0.1	716	0.8	8.1	0.13
ES2	4	0.05	905	1	10	0.18
ES3	4	0.01	794	0.78	8.3	0.2
BS1	2	0.1	647	0.58	5.3	0.22

^aES and BS for ethane- and benzenesilica, respectively.

^bMultipoint surface area calculated at relative pressure of $P/P_0 = 0.05$ – 0.25 .

^cTotal pore volume determined by the N_2 amount adsorbed at the highest P/P_0 (0.99).

^dCalculated from the adsorption branches by the BJH method.

^eCalculated by t -plot method using experimental points at relative pressure of $P/P_0 = 0.10$ – 0.20 .

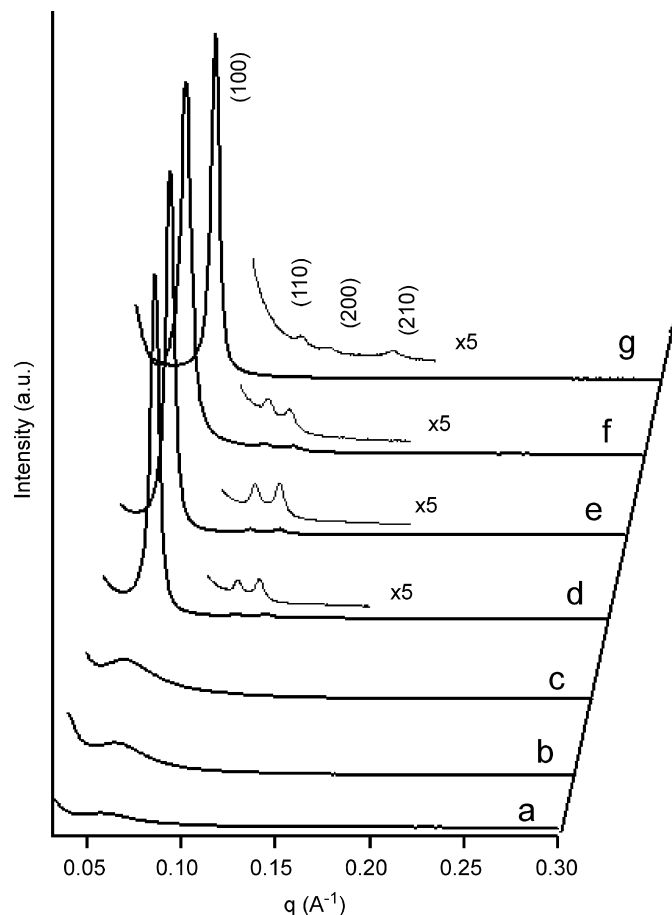


Fig. 1. SAXS patterns of the samples synthesized with various conditions from ethane-bridged (a–f) and benzene-bridged (g) organosilica precursors. (a) Na/Si = 0, Fe/Si = 0; (b) Na/Si = 4, Fe/Si = 0; (c) Na/Si = 0, Fe/Si = 0.05; (d) ES1; (e) ES2; (f) ES3; (g) BS1 (see Table 1).

further confirm the 2-D hexagonal arrangements of well-defined mesopores with a high degree of mesostructural ordering (Fig. 3a and b). Actually, there is no distinct difference between this observation and those for P123-templated ethanesilicas synthesized under various conditions as such salt-assisted acidic synthesis [14,58] or lyotropic liquid crystal templating [12] pathway, again confirming the crucial role of this salt pair in this system, entirely similar to those reported Na(K)Cl/HCl pairs used for the synthesis of large-pore PMOs [14,58]. However, no interesting macroscopic morphology could be observed for this sample (supplementary information Fig. S1a). Irregular particles were dominant through the whole image, which is greatly different from those reported SBA-15-like materials obtained from strong acidic or KCl-assisted acidic systems where wheat-like aggregations [57] or monodisperse short rods [58] were commonly observed.

The ^{13}C cross-polarization (CP) and ^{29}Si MAS NMR spectra were used to clarify the basic structural unit in the ES1 sample prepared from the highest Fe/Si ratio in this work (Fig. S2). The ^{13}C CP MAS and ^{29}Si NMR spectra of the extracted material clearly demonstrated that all of the Si atoms in the ES1 sample are bonded covalently to carbon atoms and the whole framework consists of $\text{SiO}_{1.5}\text{CH}_2\text{CH}_2\text{SiO}_{1.5}$ structural units.

The framework composition of the representative ES1 (and BS1) sample was analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) technique. The Fe content in the final samples is completely negligible, only 0.8 ppb was detected in the ES1 ethanesilica (0.5 ppb for BS1). Comparing with the Fe/Si molar ratio of 0.10 in the synthesis mixture, we can come to the conclusion that the framework of the mesoporous organosilicas

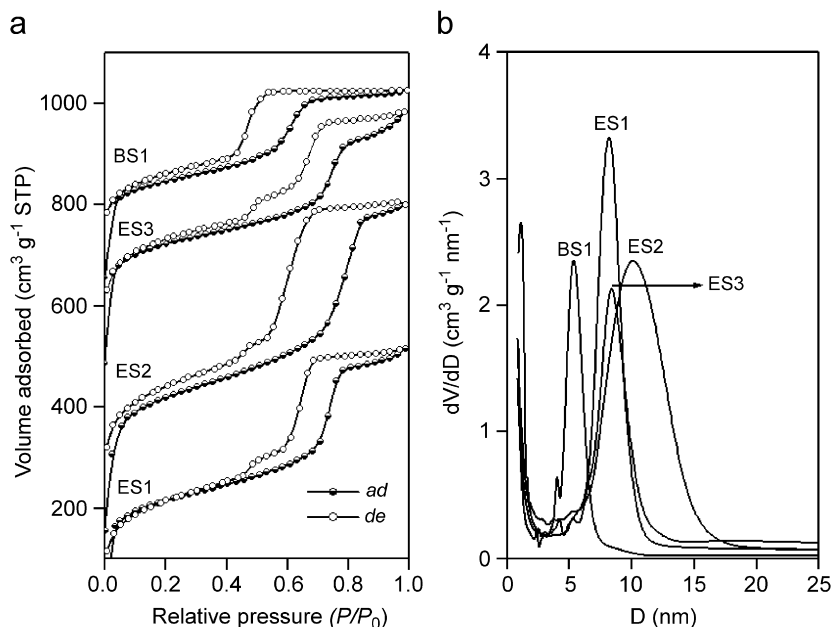


Fig. 2. Nitrogen sorption isotherms (a) and BJH pore size distributions (b) of the studied PMOs.

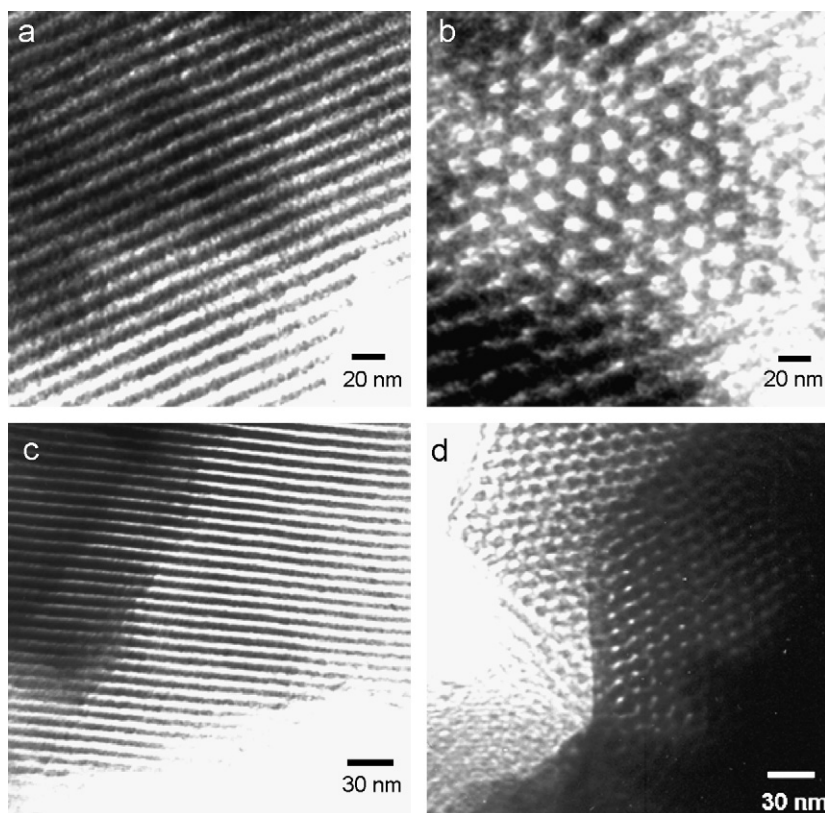


Fig. 3. TEM images of the ESI (a, b) and BS1 (c, d) PMOs viewed perpendicular (a, c) or parallel (b, d) to the pore axes.

synthesized under the present conditions is totally free of metals, which is well consistent with the reported results for organosilicas prepared in the presence of other inorganic salts [14,54,59]. In fact, we did find that there was a visual color change before and after the extraction process, that is, light yellow powdery sample entirely became a white one after two times extraction, indicating the metal species could be easily washed away. In short, highly ordered SBA-15-like ethanesilicas can be facily prepared in the presence of $\text{FeCl}_3/\text{NaCl}$ without being contaminated by the inorganic salts.

3.2. Ordered benzenesilicas with partly crystal-like pore walls

In contrast to BTME, BTEB, bearing a much more hydrophobic and larger benzene-bridging group, requires a little bigger steric space and stronger interaction with the copolymer surfactant to be assembled into an ordered mesophase. As expected, highly ordered benzenesilicas can also be easily prepared from this system within wide reaction compositions, similar to those studied ethanesilicas. As shown in Fig. 1(g), SAXS pattern of a solvent-extracted benzenesilica clearly exhibits four well-defined peaks, attributable to the (1 0 0), (1 1 0), (2 0 0) and (2 1 0) reflections of the hexagonal space group [57], indicating that a highly ordered SBA-15-like organosilica was successfully prepared. Nitrogen sorption isotherms of the sample display a typical type IV adsorption isotherm of

mesoporous materials with a type H1 hysteresis loop (Fig. 2, BS1), which is similar to the aforementioned ethanesilicas and other P123-templated materials [57,58]. In comparison with other ethanesilicas, the capillary condensation step of the sample not only locates at relatively lower pressure but also totally finishes within a fairly narrowed relative pressure range, indicating a smaller but much more uniform distribution of the pore size. Indeed, a quite narrower and smaller pore size distribution calculated from the similar adsorption branch using the BJH method is observed for the sample (Fig. 2). As listed in Table 1, the BET surface area and total pore volume calculated are $647 \text{ m}^2/\text{g}$ and $0.58 \text{ cm}^3/\text{g}$, respectively. In addition, the micropore volume calculated from the t -plot method for this PMO material is $0.22 \text{ cm}^3/\text{g}$, which is slightly larger than that for other ethanesilicas prepared with the same inorganic salt pair.

TEM images of the PMO material recorded along different zone axes further confirm a highly ordered hexagonal mesostructure, which is similar to those observations for other SBA-15-like organosilicas or silicas (Fig. 3c and d) [57,58]. In combination with the SAXS and N_2 sorption data, it is clear that structurally ordered hybrid benzenesilica could be easily synthesized from this synthesis system. Besides this, similar to above ethanesilicas, no interesting morphology were observed for this SBA-15-like benzenesilica (see Fig. S1(b)).

In Fig. 4, the ^{29}Si MAS NMR spectrum of the present hybrid benzenesilica includes three distinct signals at -62 ,

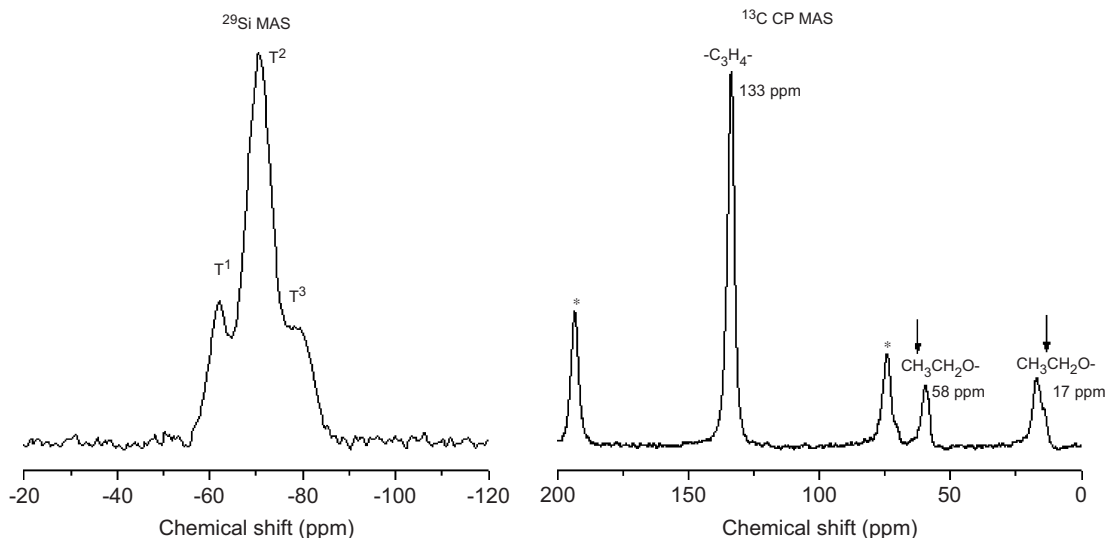


Fig. 4. ^{29}Si and ^{13}C MAS NMR spectra of the extracted BS1 benzenesilica (** denotes the side bands due to the phenylene carbon).

–71 and –78 ppm, assigned to the Si species covalently bonded to carbon atoms of $\text{T}^1[\text{Si}(\text{C}(\text{OH})_2(\text{OSi}))]$, $\text{T}^2[\text{Si}(\text{C}(\text{OH})(\text{OSi})_2)]$ and $\text{T}^3[\text{Si}(\text{C}(\text{OSi})_3)]$, respectively, clearly confirming the full framework linkage of these bridging organic groups, and this observation is consistent with the results reported before [25]. The absence of SiO_4 species such as $\text{Q}^3[\text{Si}(\text{OH})(\text{OSi})_3]$ and $\text{Q}^4[\text{Si}(\text{OSi})_4]$, which produce signals between –90 and –120 ppm, indicates that no carbon–silicon bond cleavage of the BTEB precursors occurred during this mild synthesis, in accordance with that for ethanesilicas. Comparatively, the T^3/T^2 peak intensity ratio of this sample is somewhat smaller than that observed for the aforementioned ethanesilica, and this may be attributed to the different inductive and steric effects of the bridging groups between them. The ^{13}C NMR spectrum includes a main signal at 133 ppm along with several small peaks from the ethoxy groups and tiny residual copolymer surfactant. The combined results of NMR analysis clearly reveal that the mesoporous framework is a conveniently crosslinked network of $\text{SiO}_{1.5}\text{C}_6\text{H}_4\text{SiO}_{1.5}$ structural units [24,25].

As aforementioned, the discovery of periodic benzene-bridged organosilicas with crystal-like pore walls is a breakthrough in the field of ordered mesoporous materials [1,24]. However, so far only two literatures can be found for ordered crystal-like benzenesilicas directly synthesized via acidic synthesis pathway [51,52]. How about this synthesis system? Actually, it is totally unexpected that a distinct peak at $2\theta = 12^\circ$ due to the 0.76 nm periodicity is observed for the present benzenesilica (Fig. 5a), clearly indicating the appearance of molecular arrangement in the walls similar to those reported for Ph-HMM organosilicas [24,26], even though the intensity of this reflection is not as intense as that for those counterparts prepared under basic conditions. However, in comparison with the results for the SBA-15-like benzenesilicas with partly crystal-like pore walls prepared through post-treatment of the parent

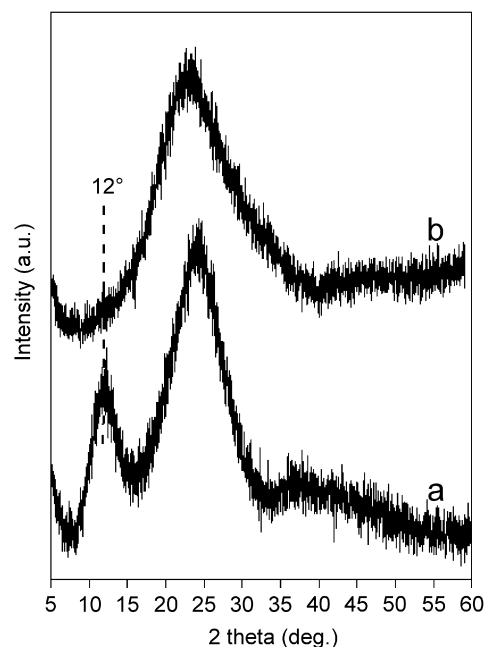


Fig. 5. Wide-angle XRD patterns of the extracted (a) and calcined (b) BS1 benzenesilica.

amorphous ones with alkaline solution [53], this reflection due to the phenylene group arrangement within the pore walls is more clear, and also this direct synthesis is much simple. Being treated in air at 550°C for 6 h, the peak totally disappeared (Fig. 5b), manifesting that it is really due to the presence of obvious molecular arrangement of phenylene groups [24]. The detailed formation process is not yet clear at this stage, which however should be closely associated with the specific synthesis conditions. Actually, it is found that, even without NaCl in the system, entirely similar wide-angle XRD analysis result can still be observed (Fig. S3), thus revealing the importance of the ferric salt in this synthesis. In contrast, no distinct

molecular-scale periodicity could be observed if ferric salt were replaced by HCl for the synthesis, which has been clearly confirmed by previous reports [1,25,53]. Further study is needed to understand on the actual reason for the development of molecular-scale periodicity from the present synthesis system.

Our results have shown that, even without additional acids, highly ordered hexagonal PMOs can be easily prepared using the NaCl/FeCl₃-assisted synthesis strategy. Following previous studies [46,55], it is proposed that both salts can independently behave as a well-understood micellization-promoting agent [46,60] (lower the critical micelle concentration and the temperature of a copolymer surfactant) and a “catalyst” [46] for the hydrolysis and condensation of the silica precursors by the self-generated acidity from the hydrolysis of ferric salt. Indeed, the self-generated acidity, even though the ferric salt amount in this system is quite small, is enough for the sol–gel processing of the bridged organosilanes due to their easier hydrolysis and condensation features in comparison to conventional TEOS or tetramethoxy orthosilicate (TMOS) [8], even which can also be facilitated by this proposal to assemble ordered mesostructures [61–63]. In fact, this mechanism in nature is somewhat similar to the reported “salt-assisted” concept for those mesoporous nonsiliceous materials, where the appropriate acidity self-adjusted by the inorganic precursors is a key factor for the whole synthesis [46]; inorganic metallic chlorides are considered as relatively strong “acids” since a certain amount of acid is generated in the synthesis gels. Meanwhile, with the well-known “salting-out” function [55,60], sodium chloride can effectively facilitate the formation of ordered organosilicas.

4. Conclusion

The synergistic effects of both inorganic salts of NaCl and FeCl₃ on the synthesis of PMOs templated by copolymer surfactant P123 under no additional acid conditions were systematically studied. Not only can highly ordered ethane- and benzenesilica PMOs be prepared but also the development of partially crystal-like pore walls in the phenylene-bridged PMO can be distinctly observed, which has rarely been reported for benzenesilica PMOs templated by copolymer surfactants. A plausible “salt-assisted” mechanism was discussed, and this simple concept based on the self-generated acidity from the system for the hydrolysis and condensation of the organosilanes was a key factor. Finally, well-ordered PMOs can be facily synthesized with the aid of “salting effect” of NaCl salt, clearly indicating the important effect of both salts on the assembly process of ordered PMO materials.

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Appendix A. Supplementary information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2007.11.011.

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