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Crucial effect of stirring on the formation of periodic mesoporous organosilicas prepared under salt-mediated conditions

S.-R. ZHAI[a], N. LIU[a], C.-S. HA[b], Q.-D. AN[a,*]
[a] *Faculty of Chemical Engineering and Materials, Dalian Polytechnic University, Dalian 116034, China*
[b] *Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea*

The effect of stirring treatment on the assembly of periodic mesoporous organosilicas (PMO) using 1,2-bis(trimethoxysilyl)ethane as an precursor and triblock copolymer P123 as a template under salt-mediated (NaCl-$ZrOCl_2$) conditions was investigated. It was demonstrated that, according to detailed characterizations, the stirring treatment during the preparation had a great impact on the formation of mesostructures. In contrast to the highly ordered mesoporous ethanesilica with particulate shape, a low-quality mesostructure with platelet-like morphology was clearly observed for the one prepared without stirring, and this observation was rarely reported in previous studies. .

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1. Introduction

Since its first synthesis in 1999 [1-3], periodic mesoporous organosilica (PMO) materials have attracted increasing attention in the field of ordered mesoporous materials. These novel hybrid materials, characterized with the high organic content incorporated within the framework, were synthesized *via* the hydrolysis and condensation of bis-(trialkoxysilyl)alkylsilanes such as $(R'O)_3Si\text{-}R\text{-}Si(R'O)_3$ with the aid of structure-directing agents [1-4]. Fascinating properties featured by these materials include highly ordered structures and uniform pore size distributions within a framework formed by a homogeneous distribution of organic fragments and inorganic oxide. In this regard, PMO materials are promising candidates for applications in the fields of catalysis, selective adsorption, chromatography, low-*k* devices or host-guest chemistry [4-6].

Following our previous studies [7,8], a generalized synthesis pathway to structurally ordered PMO was further developed [9,10]. That is, employing Pluronic P123 as template, series of ethane/benzene-bridged organosilicas could be easily assembled in the presence of inorganic salt pairs within a wide synthesis range and no need of any mineral acids throughout the synthesis. Recently, however, we did find that the stirring treatment during the preparation had a great impact on the formation of hybrid mesostructures. It is interesting that, in contrast to the non-ordered sample with platelet morphology obtained without stirring during the synthesis, a highly ordered ethanesilica with totally different particulate shape was prepared with stirring. This indicates that the dynamic shear flow is of great importance for the formation of hybrid framework, and gives some interesting insights into the growth process of hybrid solids in the proposed synthesis pathway.

2. Materials and experimental method

Bis-(trimethoxysilyl)ethane (BTME, ~96%), Zirconyl chloride octahydrate ($ZrOCl_2 \cdot 8H_2O$, ~99%) and triblock copolymer $EO_{20}PO_{70}EO_{20}$ (Pluronic P123, *M*w = 5800) were purchased from Sigma-Aldrich. All chemicals were used as received.

In a typical synthesis, 1.5 g of P123, 3.5 g of NaCl and a pre-determined amount of $ZrOCl_2 \cdot 8H_2O$ were dissolved in 50 g of deionized water and stirred for 4 h at a fixed temperature of 40°C. Then, 1.96 mL BTME was added to the solution. During this stage, the effect of stirring process was investigated, namely one system was lasted for stirring for 24 h at 40°C and another system was not stirred after addition of BTME at the same temperature. The molar ratio of the reactants is $BTME/P123/H_2O/NaCl/ZrOCl_2 \cdot 8H_2O = 1:0.034:400:8:0.2$. The solution along with the precipitate was then transferred to an autoclave and subjected to a mild hydrothermal treatment at 80 °C for another 48 h. The product was filtered and extracted two times with HCl acidified ethanol (v/v, 3/100) at 60 °C for 6 h to remove the P123 template. The final products were collected by filtration and dried in air at room temperature.

Small-angle X-ray scattering (SAXS) measurements were performed using synchrotron X-ray source of Pohang Accelerator Laboratory (PAL, Korea): CoKα ($\lambda = 1.608$ Å) radiation with an energy range of 4 ~ 16 kev (energy resolution $\Delta E/E = 5\times10^{-4}$, photo flux = $10^{10} \sim 10^{11}$ ph./s, beam size < 1 mm^2). Transmission electron microscopy (TEM) images were obtained by a JEOL2010 electron microscope with an acceleration voltage of 200 kV. Scanning electron microscopy (SEM) images were recorded on a JEOL 6400 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 150 °C for 24 h in vacuum. The Brumauer-Emmett-Teller (BET) surface area was calculated using experimental points at a relative pressure of $P/P_0 = 0.05 \sim 0.25$. The total pore volume was calculated by the N_2 amount adsorbed at the highest P/P_0 for each sample ($P/P_0 = 0.99$). ^{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 CP MAS NMR, respectively; 90° pulse width of 5 μs, contact time 2 ms, recycle delay 3 s for both ^{29}Si and ^{13}C CP MAS NMR).

3. Experimental results and discussion

Fig. 1 shows the SAXS patterns of both samples prepared with and without stirring during the synthesis. It is clear that highly ordered ethane-bridged PMO can be easily prepared from a system consisted of organosilica-P123-H_2O-$ZrOCl_2$-NaCl with stirring after addition of BTME. This is reflected by the distinct (100), (110) and (200) peaks according to a two-dimensional (2-D) hexagonal symmetry (*p6mm*) of the mesostructured materials [7]. In contrast, only a broad reflection without clear index is present for the counterpart sample obtained from the similar system without stirring. This observation indicates that the stirring treatment has a great influence on the formation of hybrid mesostructure.

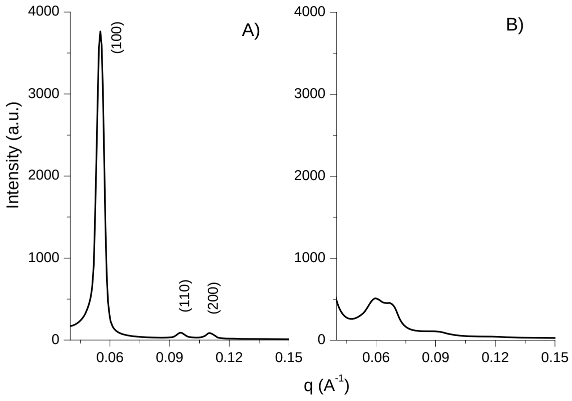

Fig. 1. SAXS patterns of the samples synthesized with (A) and without (B) stirring during the assembly process while keeping other parameters similar.

The structural properties of both samples were further characterized by nitrogen sorption isotherms (Fig. 2). Corresponding to the SAXS results, a type IV isotherm with a nearly parallel H1 hysteresis loop is observed for the ordered sample prepared with stirring. This strongly suggests the presence of uniform cylindrical pores in the material, in accordance with the 2D hexagonal framework revealed by the SAXS result [9,10]. Besides, this sample presents large surface area and total pore volume of 1050 m^2/g and 1.14 cm^3/g. In contrast, the isotherm of the counterpart sample is characteristic of a less-quality mesostructure with decreased adsorption volume, clearly indicating the presence of non-perfect pore structures, which is supported by the much lower surface area and pore volume of 447 m^2/g and 0.46 cm^3/g as compared with the one prepared with stirring. This observation is well consistent with the aforementioned SAXS results (Fig. 1), once again revealing the crucial role of stirring treatment towards the assembly of pore structures.

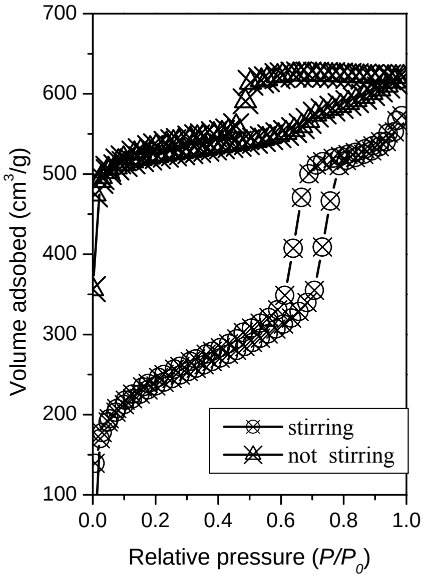

Fig. 2. N_2 sorption isotherms of both samples synthesized with and without stirring during the preparation.

Corresponding to the results of SAXS and sorption measurements, typical TEM images of both samples prepared with and without stirring are shown in Fig. 3. As would be expected, the TEM image of the sample prepared with stirring during the synthesis shows a well-defined arrangement with uniform mesopores. In contrast, the TEM image of the sample synthesized without stirring exhibits a wormhole-like framework structure, similar to the disordered MSU-n materials synthesized under neutral conditions [11], and this observation is in good agreement with its SAXS pattern that only a quite weak reflection is present (see Fig. 1).

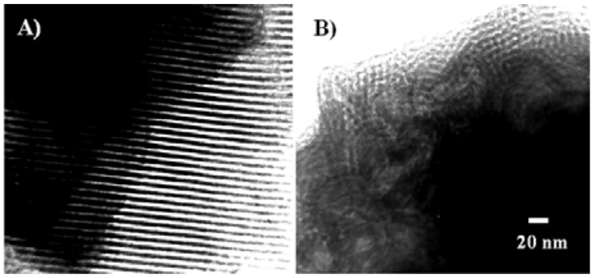

Fig. 3. TEM images of both samples obtained with (A) and without (B) stirring during the synthesis.

Fig. 4 displays the SEM images of both samples prepared with and without stirring during the synthesis. It is clear that the first sample synthesized with stirring is mainly composed of irregular particles or their aggregates without defined morphology, which is greatly different from those reported results that wheat-like fibers or short rods were usually observed for ethanesilicas synthesized under acidic conditions [12,13]. In contrast, the second sample prepared without stirring is nearly consisted of platelet-like particles with smooth surface, and this observation is totally different from that of the first one obtained with stirring during the synthesis; this may be closely associated with the different growth process of the hybrid solids.

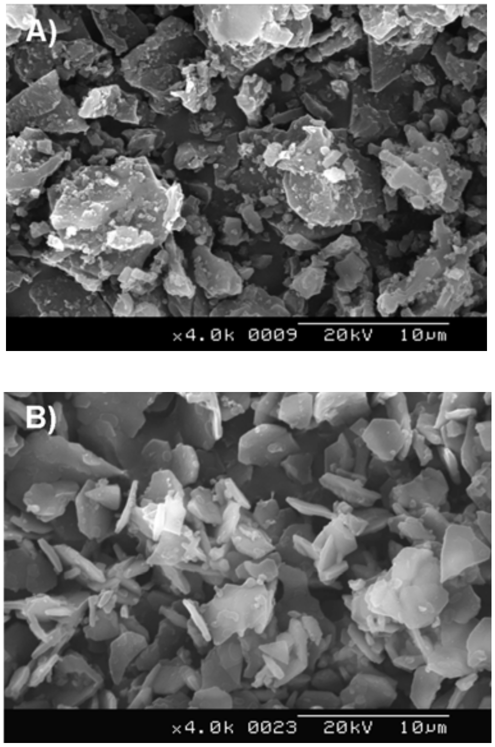

Fig. 4. SEM images of both samples synthesized with (A) and without stirring (B) during the assembly process.

Solid state ^{13}C CP and ^{29}Si MAS NMR technique was used to clarify the basic structural unit in both samples prepared with and without stirring during the synthesis. As shown in Fig. 5, the ^{13}C CP MAS spectra show a strong resonance signal at 5.1 ppm due to the ethane carbons in the framework ($-SiCH_2CH_2Si-$) along with another three weak signals at 17.6, 57.8 and 70.1 ppm, attributable to the carbons from the tiny amount of ethoxy ($-OC_2H_5$) groups exchanged from the extraction process and residual copolymer surfactant [11], respectively.

Next, the ^{29}Si MAS NMR spectra of both samples exhibit two distinct signals at -56.5 and -64.0 ppm, attributable to the T^2 [C-$Si(OH)(OSi)_2$] and T^3 [C-$Si(OSi)_3$] silica species, respectively. Another relatively weak signal at -48.7 ppm is also observed, corresponding to T^1 [C-$Si(OH)_2(OSi)$]Si. The strong intensity for the T^2 and T^3 signals indicates the formation of relatively condensed hybrid frameworks for both samples. The absence of SiO_4 species such as Q^3 [$Si(OH)(OSi)_3$] and Q^4 [$Si(OSi)_4$], which produce signals between -90 and -120 ppm, indicating that no carbon-silicon bond cleavage of the BTME precursors occurred during the synthesis. These combined results clearly demonstrate that all of the Si atoms in both materials are bonded covalently to carbon atoms. It is interesting that no distinct difference in the spectra results can be found between both samples, confirming that both of them possess entirely similar framework compositions, even though their structural properties are greatly different as illustrated by SAXS, sorption, TEM and SEM results.

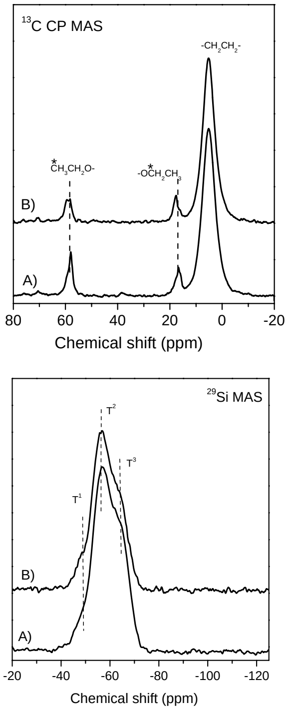

Fig. 5. Solid state ^{13}C CP/^{29}Si MAS NMR spectra of both samples obtained with (A) and without (B) stirring during the preparation process.

As far as the crucial role of stirring on the formation of ordered PMO is concerned, however, possibly it is closely associated with the fairly mild synthetic conditions employed in this study. It is proposed that, if no stirring treatment, the sol-gel kinetics of the organosilica precursor are so slow that the induction time for precipitation is too long to have a favorable effect on the framework structures. Therefore, only less-ordered material was obtained without stirring during the assembly process; meanwhile, a distinct morphological variation was observed between both samples obtained with or without stirring during the synthesis. This result indicates that the shear flow is of great importance for the formation of highly ordered PMO materials in this system due to the mild synthetic conditions, which is greatly different from the earlier work carried out in acidic solutions [12,13].

4. Conclusion

In a word, the crucial role of stirring treatment on the assembly of ethane-bridged PMO prepared by the proposed salt-mediated pathway was demonstrated based on detailed characterizations. It was firstly confirmed that, in contrast to the low-quality hybrid mesostructures obtained without stirring during the synthesis process, highly ordered PMO materials with excellent structural properties could be facilely prepared under mild synthesis conditions along with simple stirring treatment. Meanwhile, the synthesis finished through moderate conditions combined with the structural introduction of organic functional species could be a generalized pathway for various types of hybrid materials with accessible porosity.

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*Corresponding author: anqingda@dlpu.edu.cn