

Facile synthesis of stable cubic mesoporous silica SBA-1 over a broad temperature range with the aid of D-fructose†

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A highly ordered cubic mesoporous silica SBA-1 with enhanced stability towards washing with water has been synthesized simply by adding D-fructose as an auxiliary agent during the synthesis.

The discovery of the M41S family of mesoporous materials has stimulated extensive research in the past decade.¹ Among the various types of mesophases, the SBA-1 cubic (*Pm3n*) structure is very unique because it possesses a cage-type structure with open windows.² Since its three dimensional pore structure promises better catalytic applications, aluminium or other heteroatoms such as V, Mo, Co, and Ti have all been incorporated into SBA-1.^{3,4}

The synthesis of SBA-1 is based on the S⁺X⁻T⁺ templating pathway under strongly acidic conditions and low reaction temperatures, using surfactants with large headgroups such as cetyltriethylammonium bromide (CTEABr). However, the synthesis details were not fully disclosed until the work of Kim and Ryoo.⁵ According to them, the formation of the cubic mesostructure is favored at 273 K, while a hexagonal SBA-3 mesophase is formed above 313 K.

Recently, a new class of periodic mesoporous organosilicas (PMOs) containing organic functional groups inside the channel wall has attracted great interest.⁶ For preservation of functional groups in PMOs, the surfactant can only be removed by solvent extraction, for example, with an acidified mixture of ethanol and water,⁷ because the organic functional groups will be destroyed with calcinations. However, such practice is not easy for SBA-1, since the as-synthesized SBA-1 is known to lose its structure upon washing with water.⁵ To further stabilize the cubic SBA-1 structure, Vinu *et al.*⁸ prolonged the hydrothermal post-treatment at 373 K. However, there was a noticeable structure change from *Pm3n* to a space group with lower symmetry after such treatment. A more direct approach to enhance the stability of SBA-1 will be to increase the reaction temperature during the self-assembly process when the cubic mesostructure is formed. However, this is not feasible with the original procedures.^{2,5}

Herein, we report a successful synthesis of highly ordered SBA-1 materials over a broad temperature range from 273 to 363 K by simply using D-fructose as an auxiliary agent. This is the first report on the successful synthesis of SBA-1 at reaction temperatures higher than 313 K without any phase transformation.

SBA-1 was synthesized by mixing D-fructose (Aldrich, 99%) and HCl with distilled water at room temperature, followed by the addition of tetraethylorthosilicate (TEOS) and then the surfactant CTEABr, synthesized according to previously published procedures,² was added to obtain a homogeneous solution. The resulting mixture, with a molar composition of 1 surfactant : 5 TEOS : 115–460 HCl : 1.3–40.8 D-fructose : 3500 H₂O, was cooled or heated to the desired self-assembly reaction temperature under vigorous stirring for 4 h, followed by hydrothermal post-treatment at 373 K for 1 h. The precipitate was filtered (without washing) and dried at 343 K overnight and denoted as SBA-*T*, where *T* represents the self-assembly reaction temperature. The product yield was in the range of 50 to 60% based on the silica content.

All the as-synthesized SBA-*T* samples, after filtration without washing, showed three well-resolved XRD diffraction peaks in the region of $2\theta = 1.5\text{--}2.5^\circ$ (Fig. 1A), which can be indexed to the (200), (210) and (211) characteristic diffractions of the cubic *Pm3n* mesostructure. The patterns were recorded at the Synchrotron Radiation Research Center of Taiwan with $\lambda = 0.1326$ nm radiation. After calcination, the cubic structure was well preserved. The XRD diffractions of the calcined SBA-*T* samples shifted slightly to lower 2θ values with increasing values of *T*, reflecting a larger unit cell size for samples synthesized at a higher self-assembly reaction temperature (Table 1).

Three ²⁹Si NMR signals at –92, –101, and –110 ppm (Fig. 1B), corresponding to *Q*² (Si(OSi)₂(OH)₂), *Q*³ (Si(OSi)₃(OH)), and *Q*⁴ (Si(OSi)₄) species, were observed for the as-synthesized SBA-*T* samples. An increase in the *Q*⁴ fraction at the expense of both *Q*² and *Q*³ species was observed only when the temperature was higher than 323 K. The ²⁹Si NMR results, as summarized in Table 1, demonstrate that a higher reaction temperature, which is only possible with the addition of D-fructose, does lead to a higher cross-linked silica framework. No ¹³C CPMAS NMR signal associated with D-fructose was observed, suggesting the absence of a sugar moiety inside the SBA-1 sample.

The N₂ sorption isotherms (see ESI†) were similar for all calcined samples under investigation, and showed a large increase at $p/p_0 = 0.15\text{--}0.25$ due to capillary condensation in the mesopores. As seen in Table 1, these samples exhibit a cavity size ranging from 3.4 to 4.0 nm and a BET (Brunauer–Emmett–Teller) specific surface area in the range of 1140 to 1280 m² g^{–1}. The SEM image shows that most particles have a nearly spherical shape and some particles show hexagonal facets, indicating a likely decaoctahedron shape.^{9,10}

The poor stability of SBA-1 is the result of low cross-linkage in the silica framework due to the low reaction temperature.⁵ Since we were able to enhance the cross-linking by increasing the

† Electronic supplementary information (ESI) available: Fig. S1: N₂ adsorption–desorption isotherms of calcined SBA-*T* samples, Fig. S2: ²⁹Si MAS NMR spectra of as-synthesized SBAw/A-H1 and SBAw/P-H2 samples. See <http://www.rsc.org/suppdata/cc/b414786c>

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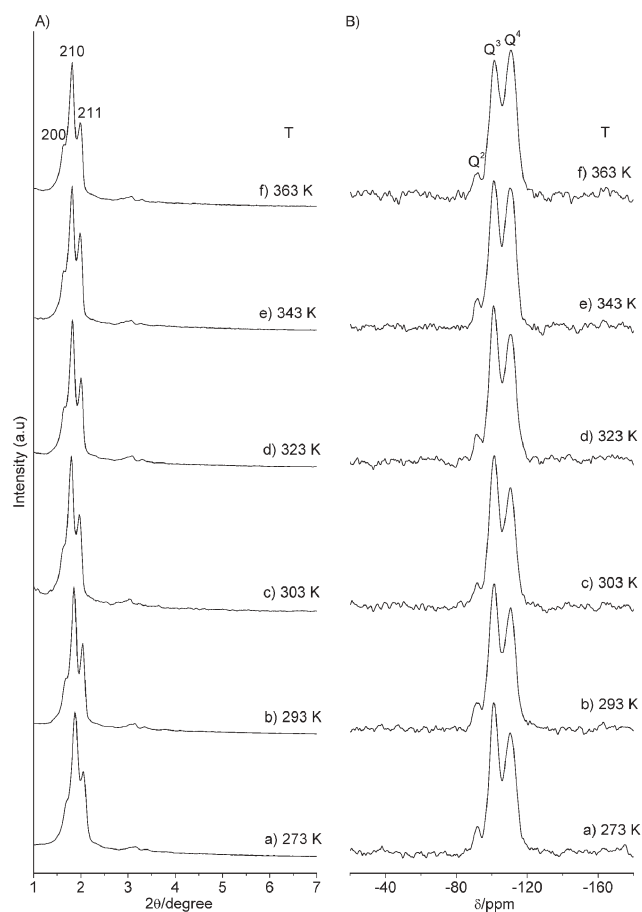


Fig. 1 (A) Powder XRD patterns and (B) ^{29}Si MAS NMR spectra of as-synthesized SBA-*T* samples, prepared with a molar composition of HCl–D-fructose–CTEABr = 230 : 10.2 : 1. The reaction temperature *T* is indicated in the figure.

reaction temperature, the product might be more tolerant to the treatment with water. To verify the proposal, two sets of samples were prepared. The first set of samples, denoted as SBAw/A-H1, was synthesized at a reaction temperature of 343 K for different times (H1 hours) and subsequently hydrothermally post-treated at 373 K for 1 h, as suggested by previous researchers.^{5,8} The second set of samples, denoted as SBAw/P-H2, was prepared by fixing the reaction temperature at 343 K for 4 h, while the time for hydrothermal post-treatment (H2 hours) at 373 K was varied. Each filtrated sample (~0.25 g) was then immediately washed

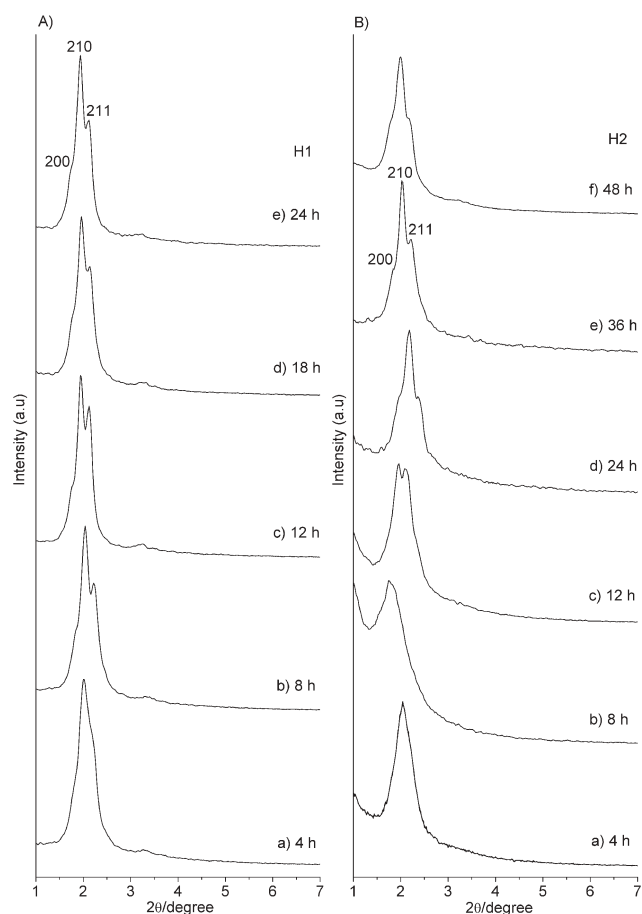


Fig. 2 Powder XRD patterns of as-synthesized (A) SBAw/A-H1 and (B) SBAw/P-H2 samples, respectively. Both samples have been washed with water immediately after synthesis.

with water (0.5 L) and then dried before the powder XRD measurements. Except the one that was prepared at 343 K for only 4 h, the cubic structure of all other SBAw/A-H1 samples was very well preserved (Fig. 2A). The SBAw/A-12 sample also preserved its cubic structure after treatment with an EtOH–HCl mixture. In contrast, as shown in Fig. 2B, only SBAw/P-H2 samples prepared with H2 between 24 and 48 h preserved a certain degree of cubic structure after washing with water, while the structure of others either underwent phase transformation or collapsed. N_2 adsorption measurements also show that SBAw/A-12 exhibits a higher surface area than SBAw/P-48; both samples have values of surface

Table 1 Textural properties and ^{29}Si MAS NMR results of the studied SBA-1 samples

Sample	d_{210} spacing/nm	Lattice parameter a_0 /nm	BET area/m ² g ⁻¹	Mesopore volume/cm ³ g ⁻¹	Cavity size/nm ^a	$Q^4/$ $(Q^3 + Q^2)^b$
SBA-273 K	3.21	7.18	1220	0.59	3.7	0.82
SBA-293 K	3.32	7.43	1265	0.61	3.7	0.86
SBA-303 K	3.47	7.76	1140	0.56	3.4	0.82
SBA-323 K	3.41	7.62	1280	0.63	3.5	0.95
SBA-343 K	3.60	8.06	1185	0.65	4.0	1.06
SBA-363 K	3.64	8.13	1160	0.66	4.0	1.23
SBAw/A-12 ^c	3.48	7.78	1240	0.60	3.7	1.35
SBAw/P-48 ^c	3.34	7.54	1110	0.61	4.0	1.32

^a Calculated according to NLDFT. ^b Deconvolution results from ^{29}Si MAS NMR of the as-synthesized samples. ^c These two samples were washed with water immediately after synthesis.

areas and pore volumes comparable to the SBA-343 K sample, which was not washed with water (see Table 1). ^{29}Si MAS NMR results (see ESI†) also confirm that SBAw/A-H1 samples exhibit a higher degree of cross-linking of the silica framework than the SBAw/P-H2 samples, which is also well correlated with the enhancement of their stability towards washing with water. These results demonstrate that the implementation of a higher reaction temperature, which is only feasible with the addition of D-fructose, is capable of strengthening the cubic SBA-1 structure against washing with water.

In contrast to the conventional synthesis conditions,⁵ the transition of the mesophase from a cubic to hexagonal structure was not observed in the presence of D-fructose, even at a reaction temperature above 313 K. The reason for the preservation of structural ordering at higher temperatures is not clear. It was reported that the aggregation or assembly of D-fructose, D-glucose, and D-maltose could direct the formation of a mesophase in a manner similar to the neutral surfactants under basic or near neutral conditions.¹¹ In the present synthesis route, the high affinity and appropriate hydrophilicity of D-fructose (and/or its derivatives) for the intermediate silicate species might act as a stabilizer for the cubic micelle over a wide range of reaction temperatures.

In conclusion, we have presented for the first time a novel synthesis route for the preparation of well-ordered and stable SBA-1 materials over a broad reaction temperature, by simply using the low-cost and environmentally friendly D-fructose as an auxiliary agent. This strategy offers the opportunity to prepare SBA-1 with enhanced stability towards washing with water, and also shows the potential for the direct synthesis of SBA-1 functionalized with organic groups. Thus, these improvements in the SBA-1 synthesis open new opportunities to facilitate the more widespread use of this unique mesophase in materials research.

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