

## Highly Stable Mesoporous Materials

### High-Temperature Generalized Synthesis of Stable Ordered Mesoporous Silica-Based Materials by Using Fluorocarbon–Hydrocarbon Surfactant Mixtures\*\*

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The hydrothermal stability of mesoporous materials is currently of great interest because of this requirement for potential applications.<sup>[1,2]</sup> A number of successful examples of mesoporous materials with good hydrothermal stability were reported recently,<sup>[1–9]</sup> for example, an ordered hexagonal SBA-15 with thicker pore walls,<sup>[3]</sup> vesicle-like MSU-G materials with a high SiO<sub>4</sub> cross-linking,<sup>[4]</sup> disordered KIT-1,<sup>[5]</sup> and stable mesoporous aluminosilicates from a grafting route<sup>[6]</sup> and from a preformed solution of “zeolite seeds”.<sup>[7–9]</sup> Notably, these mesostructured materials are prepared at room temperature or relatively low temperatures (80–150 °C). This is quite different from the higher temperatures (150–220 °C) used for the syntheses of many microporous zeolites or phosphates

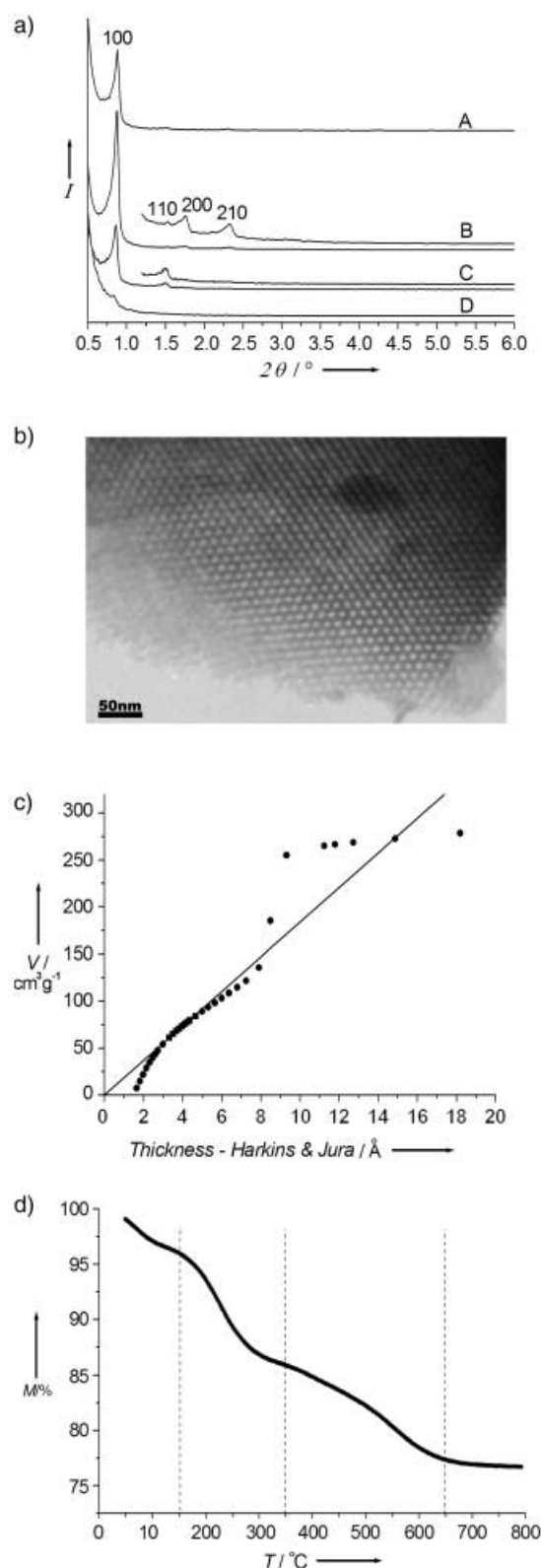
because the surfactant molecules are not able to direct the mesoporous structure formation due to the unfavorable conditions for micelle formation at the higher temperatures.<sup>[10,11]</sup> In some cases, the large-chain surfactants will even decompose at temperatures greater than 150 °C. As with silica-based materials, a critical factor in increasing hydrothermal stability is to have more silica condensation on the pore walls,<sup>[4,6]</sup> but low synthetic temperatures result in imperfectly condensed mesoporous walls with large amounts of terminal hydroxyl groups that make the mesostructure unstable, especially under hydrothermal or steam conditions.<sup>[1]</sup> It can be expected that the level of silica condensation will be enhanced by increasing the crystallization temperature. As suggested above, the strategy of using higher crystallization temperature for the synthesis of mesoporous materials may require special surfactants that can be used as template at high temperature. Fluorocarbon surfactants are a kind of stable surfactant, which are widely used at high temperatures (> 200 °C). However, due to the rigidity and strong hydrophobicity of the fluorocarbon chains,<sup>[12]</sup> fluorocarbon surfactants are not suitable as templates for the preparation of well-ordered mesoporous materials. We demonstrate herein that when a fluorocarbon surfactant (C<sub>3</sub>F<sub>7</sub>O(CF<sub>2</sub>CF<sub>2</sub>O)<sub>2</sub>CF<sub>2</sub>CONH(CH<sub>2</sub>)<sub>3</sub>N<sup>+</sup>(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>CH<sub>3</sub>I<sup>−</sup>, FC-4) is mixed with a triblock copolymer surfactant (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>, Pluronic P123) to form a surfactant mixture and this mixture is used as the template, highly ordered mesoporous silica-based materials with unusual hydrothermal stability, designated JLU-20, are successfully synthesized in strong acidic media at high temperatures (160–220 °C).

The X-ray diffraction (XRD) pattern of calcined JLU-20 (Figure 1aB) shows four clearly well-resolved peaks that can be indexed as the (100), (110), (200), (210) diffractions associated with the *p6mm* hexagonal symmetry with a lattice constant *a* = 118 Å. In contrast, ordered mesostructured silica cannot be formed by high temperature crystallization in the absence of FC-4 (Figure 1aD). Figure 1aA and Figure 1aB shows that the unit cell of JLU-20 does not contract during calcination at 650 °C for 5 h and demonstrates its excellent thermal stability (Table 1). This may be attributed to the pore wall of JLU-20 being fully condensed even prior to calcination, as clarified by NMR (Figure 3). In particular, JLU-20 is much more hydrothermally stable than SBA-15.<sup>[3]</sup> Upon hydrothermal treatment in boiling water for 80 h, JLU-20 remains well-ordered with clear XRD peaks associated with the *p6mm* hexagonal symmetry (Figure 1aC), whereas SBA-15 loses most of its mesostructure (Table 1).

Transmission electron microscopy (TEM) images (Figure 1b, Figure 2) of calcined JLU-20 show well-ordered hexagonal arrays of mesopores with 1D channels and further confirm that JLU-20 has a 2D hexagonal (*P6mm*) mesostructure. Interestingly, JLU-20 has continuous zigzag mesoporous channels that can be as long as 6 μm (Figure 2), much longer than in conventional SBA-15.<sup>[3]</sup> Such continuous ultralong channels have not been reported before and may be related to the high crystallization temperature. Additionally, during observations by TEM, unlike most ordered mesoporous materials that are extremely vulnerable to heating and electron radiation,<sup>[14]</sup> JLU-20 was not damaged even under

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**Figure 1.** a) XRD patterns of as-synthesized JLU-20 (curve A), calcined JLU-20 (B), JLU-20 treated in boiling water for 80 h (C) and as-synthesized sample prepared with the same procedure as JLU-20 except for the absence of FC-4 in the initial reaction mixture (D). b) TEM image of calcined JLU-20 taken in the [100] direction. c)  $N_2$  adsorption isotherm  $t$ -plots of calcined JLU-20. d) Thermogravimetry curve of JLU-20.

relatively strong current density for a long time. This is another indication that JLU-20 has unusual stability.

The  $^{29}\text{Si}$  MAS NMR spectrum of the as-synthesized JLU-20 provides direct evidence of the extent of silica condensation. JLU-20 is primarily made up of fully condensed  $Q^4$  silica units ( $\delta = -112$  ppm) with a small contribution from incompletely cross-linked  $Q^3$  ( $\delta = -102$  ppm) as deduced from the very high  $Q^4/Q^3$  ratio of 6.5, while no  $Q^2$  units were observed (Figure 3A). In contrast, SBA-15 has typical peaks correspond to  $Q^2$ ,  $Q^3$ , and  $Q^4$  silica species, and the ratio of  $Q^4/Q^3 + Q^2$  is 1.9 (Figure 3B, Table 1), thus suggesting the presence of large amounts of terminal hydroxy group in the framework. To our knowledge, JLU-20 has the highest degree of silica condensation among all kinds of mesoporous silica materials except for the vesicle-like MSU-G that has a similarly high-degree  $\text{SiO}_4$  cross-linking.<sup>[4]</sup> In that case, however, MSU-G has a poorly ordered mesostructure (analogous to the  $L_4-L_3$  intermediate structure) and no textural properties of the hydrothermally treated MSU-G, such as surface area and pore volume, was shown to justify its high hydrothermal stability.

The  $N_2$  adsorption isotherms (Figure 4, Table 1) further indicate the ultra-high stability of JLU-20. For example, after hydrothermal treatment in boiling water for 80 h, there is only a decrease in BET surface area of 7% (from  $300 \text{ m}^2 \text{ g}^{-1}$  to  $278 \text{ m}^2 \text{ g}^{-1}$ ) for JLU-20, whereas it is 68% (from  $1005 \text{ m}^2 \text{ g}^{-1}$  to  $320 \text{ m}^2 \text{ g}^{-1}$ ) for SBA-15. Furthermore, the isotherm of the treated JLU-20 sample is still a typical IV isotherm (Figure 4aB), which implies the good maintenance of the uniform mesopores. Its pore size distribution curve (Figure 4bB) is as sharp as the untreated sample (Figure 4bA). In contrast, the treated SBA-15 shows a poor isotherm (Figure 4aD) with an indiscernible pore size distribution (Figure 4bD). Correspondingly, the primary mesopore volume (BJH adsorption cumulative pore volume of pores between 20 and  $250 \text{ \AA}$  diameter) of JLU-20 reduces by only 5% from  $0.46 \text{ cm}^3 \text{ g}^{-1}$  to  $0.44 \text{ cm}^3 \text{ g}^{-1}$ , while that of SBA-15 reduces by 30% from  $1.44 \text{ cm}^3 \text{ g}^{-1}$  to  $1.03 \text{ cm}^3 \text{ g}^{-1}$  (Table 1). Another example of the stability of JLU-20 is that when it was steamed with 100% water vapor at  $800^\circ\text{C}$  for 2 h, there was a limited effect on the structural integrity of JLU-20, whereas the mesostructure of SBA-15 is completely destroyed by the same treatment (Table 1).

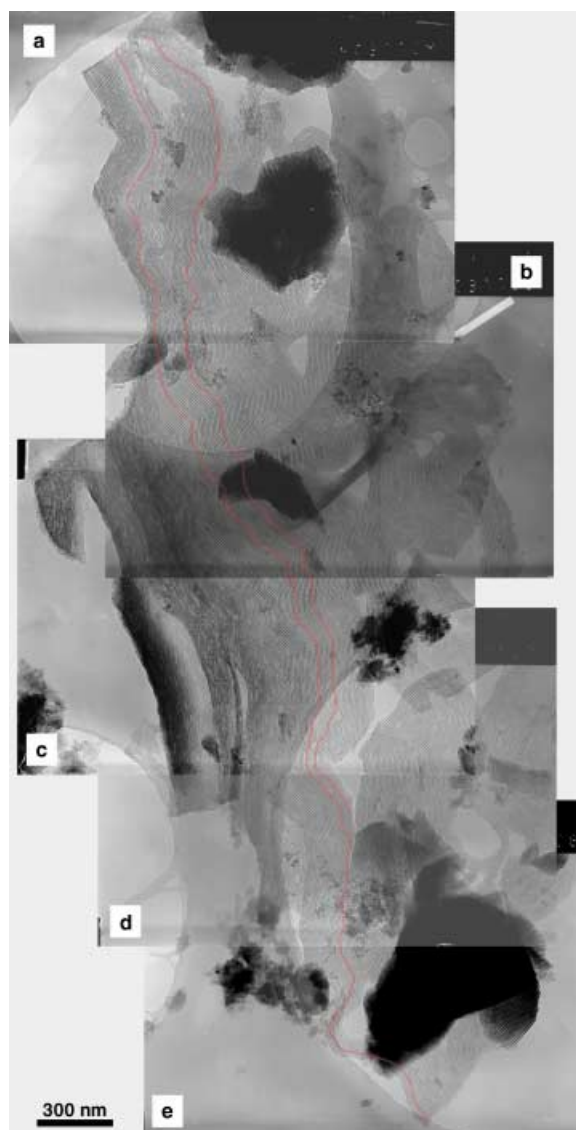
From XRD and  $N_2$  adsorption data, the wall thickness and mesopore size of JLU-20 are calculated to be  $55 \text{ \AA}$  and  $62 \text{ \AA}$ , respectively, and those of SBA-15 are  $43 \text{ \AA}$  and  $78 \text{ \AA}$ , respectively (Table 1). It is proposed that besides complete silica condensation, the thick wall and large wall thickness/pore size ratio of JLU-20 are favorable factors for its great stability, which also results from the high-temperature of the synthesis.<sup>[6c]</sup>

It is worth noting that as-synthesized JLU-20 has a relatively low surface area ( $300 \text{ m}^2 \text{ g}^{-1}$ ) and pore volume ( $0.46 \text{ cm}^3 \text{ g}^{-1}$ ) when compared with SBA-15. It was reported that SBA-15 has a specific surface area and pore volume that are far too large for a material with approximately uniform cylindrical (or hexagonal) pores, and there may be a large number of micropores in the wall.<sup>[13]</sup> However, JLU-20 strictly fulfills the fundamental relation between the structural

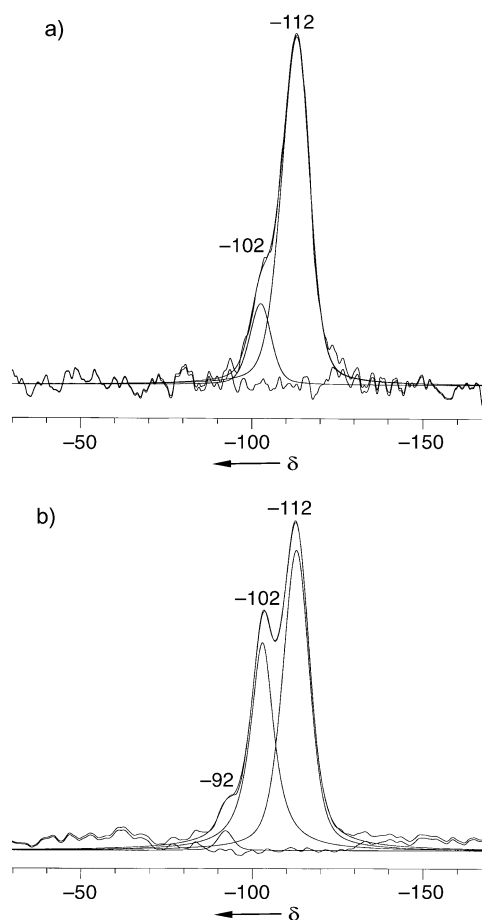
**Table 1:** Properties of the samples before and after hydrothermal and steaming treatment.<sup>[a]</sup>

Sample	$d(100)$ [Å]	Pore size [Å]	Wall thickness [Å]	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ] <sup>[d]</sup>	Surface area [m <sup>2</sup> g <sup>-1</sup> ]	$Q^4/Q^3 + Q^2$	$wSV^{-1}$
JLU-20	101					6.5	
calcined	101	62	55	0.46	300		4.0
treated <sup>[b]</sup>	101	66	51	0.44	278		4.2
treated <sup>[c]</sup>	95	65	45	0.32	225		4.5
SBA-15	110					1.9	
calcined	105	78	43	1.44	1005		5.4
treated <sup>[b]</sup>				1.03	320		
treated <sup>[c]</sup>				0.35	214		

[a] Pore size distributions and pore volumes determined from N<sub>2</sub> adsorption isotherms at 77 K and the wall thickness was calculated as: thickness =  $a - \text{pore size}$  ( $a = 2d_{(100)}/3^{1/2}$ ). Because SBA-15 was rendered amorphous after the hydrothermal or steaming treatment, there are no  $d(100)$  values, pore sizes and wall thickness for the treated SBA-15 samples given in this table. [b] Treated in boiling water for 80 h. [c] Treated with 100% water vapour at 800 °C for 2 h. [d] The pore volume here is the primary mesopore volume (BJH adsorption cumulative pore volume of pores between 20 and 250 Å diameter).

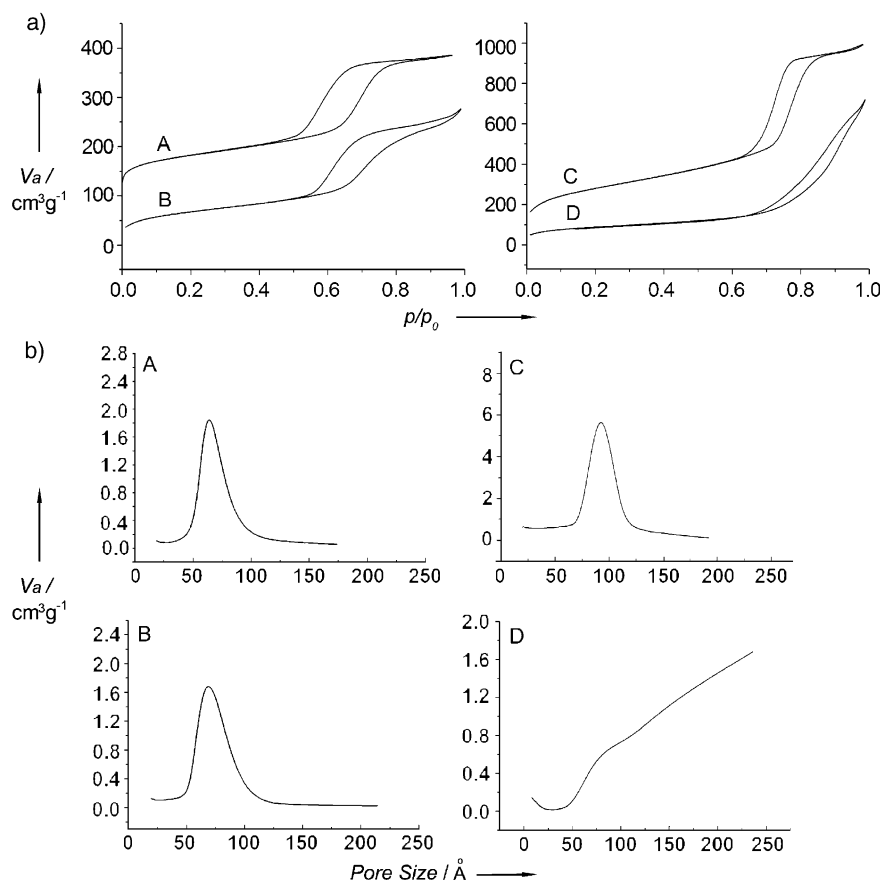


**Figure 2.** TEM image of calcined JLU-20 taken in the [110] direction. The ordered region is so large that five photos (a–e) had to be taken. The five images are arranged in succession to completely show the continuous ultra-long channels, two of which are marked by red lines for clarity.



**Figure 3.** <sup>29</sup>Si NMR spectra of as-synthesized a) JLU-20 and b) SBA-15.

parameters for materials with uniform pores of simple cylindrical geometry:  $wSV^{-1} \approx 4$  ( $w$ ,  $S$ , and  $V$  denote pore size, surface area and pore volume, respectively).<sup>[13]</sup> This suggests that unlike SBA-15, JLU-20 is free of micropores in the mesoporous walls, which is confirmed by N<sub>2</sub> adsorption isotherm  $t$ -plots (Figure 1c). Based on reported proposals regarding the formation of micropores in SBA-15,<sup>[13]</sup> we surmise that the elimination of micropores in JLU-20 may be



**Figure 4.** N<sub>2</sub> adsorption/desorption isotherms (a) and pore size distributions (b) of calcined samples before and after treatment in boiling water for 80 h: A) JLU-20 (before); B) JLU-20 (after); C) SBA-15 (before) and D) SBA-15 (after). Isotherms A and C have been offset by 100  $\text{cm}^3 \text{g}^{-1}$  along the vertical axis for clarity.

related to the increased hydrophobicity of the triblock copolymer surfactant in high-temperature synthesis. In the absence of micropores in the wall and the presence of a thicker wall with higher density, the relatively low values of surface area and pore volume in the case of JLU-20 is reasonable.

Due to the relatively low surface areas of JLU-20, the remaining surface area of JLU-20 is not more than that of SBA-15 after the hydrothermal treatments. However, JLU-20 has a much better ability to keep the integrity of its well-ordered mesostructure in hydrothermal conditions as shown above. Thus, in many applications where a well-ordered mesostructure (or uniform mesopores) instead of a large surface area plays the most important role (such as shape-selected catalysis, adsorption, separation, and host-guest chemistry), JLU-20 is a better candidate.

The thermogravimetric analysis curve of as-synthesized JLU-20 (Figure 1 d) shows that the total weight loss of JLU-20 is about 25 % and occurs in three steps: 5 % weight loss at 50–150 °C arising from water desorption, 10 % weight loss at 150–350 °C arising from P123 decomposition and 10 % weight loss at 350–650 °C arising from FC-4 decomposition. This result suggests that there are two kinds of surfactants in nearly equal quantities in the as-synthesized JLU-20 and is confirmed by

the results of elemental analysis. It is possible that FC-4 and P123 are entangled with each other to form a mixed micella rather than forming micella in the aqueous solution separately. Evidence for this is provided by the fact that the mixture of P123 and FC-4 has a lower value of the critical micelle concentration (CMC) than either P123 or FC-4.<sup>[15–17]</sup> When a silica source is added into the synthesis system, hydrolyzed Si species can interact with P123 and FC-4 through  $\text{S}^0(\text{H}^+)\text{X}^-\text{I}^+$  and  $\text{S}^+\text{X}^-\text{I}^+$  routes respectively to form the mesostructure.<sup>[18–19]</sup> Although part of the P123 surfactant may decompose during high-temperature crystallization, FC-4 successfully preserves the mesostructure from collapse because of its special stability towards high temperatures. It is noted that disordered mesoporous silica with a BET surface area of 256  $\text{m}^2 \text{g}^{-1}$  is obtained if only FC-4 (without P123) is used for the synthesis. This may be because the fluorocarbon surfactant by itself tends to assemble into small-sized micella instead of periodic long-range ordered micella due to the rigidity and strong hydrophobicity of the fluorocarbon chain.<sup>[12]</sup>

The complete silica condensation and high stability of JLU-20 should be attributed directly to the high-temperature of the synthesis rather than other reasons, such as the fluorocarbon surfactant. If JLU-20 is prepared at 100 °C instead of at 190 °C, it shows no difference in both structural properties (such as surface area, pore volume,  $Q^4/Q^3$  ratio) and stability with conventional SBA-15 although FC-4 is used. However, the use of the fluorocarbon surfactant allows full condensation by a high-temperature synthesis. This method is not limited to the combination of FC-4 with P123, and many mixtures of hydrocarbon and fluorocarbon surfactants can be used if they effectively form a regular mixed micella in solution with suitable interactions between the chosen surfactant and inorganic species. Moreover, a high-temperature synthesis can also be extended to neutral or basic media with suitable surfactants. This method may open a door for the preparation of a series of ordered mesoporous materials with various mesostructures such as 2D hexagonal  $P6mm$ , cubic  $Ia3d$ , cubic  $Pm3n$ , and cubic  $Im3m$ . For example, mesoporous silica with cubic  $Im3m$  symmetry has been obtained recently by using the surfactant mixture of FC-4 and triblock copolymer F127 as a template and the resulted material is more hydrothermally stable than its counterpart prepared at low temperature, SBA-16. As catalyst supports, cubic mesoporous materials, for example, SBA-16 and MCM-48, have the

advantage of 3D structures that lead to better transport and therefore it is of great importance to improve the hydrothermal stability of these materials.

Additionally, we have successfully introduced heteroatoms (active sites in catalysis) such as Al and Ti into the mesoporous wall of JLU-20 by a "pH-adjusting" method<sup>[20]</sup> and preformed zeolite TS-1 nanoclusters,<sup>[8c,9]</sup> respectively. Both of these exhibit much higher hydrothermal stabilities than pure silica JLU-20, which will be separately discussed in near future.

### Experimental Section

In a typical synthesis, FC-4 (1.2 g) and P123 (0.4 g) were dissolved in a mixture of H<sub>2</sub>O (20 mL) and HCl (10 M, 5 mL), followed by the addition of 2.4 mL of tetraethyl orthosilicate (TEOS). After the mixture was stirred at 40 °C for 20 h, it was transferred into an autoclave for further condensation. The crystallization temperature was slowly increased to 190 °C over 10 h and maintained there for 30 h. The product was collected by filtration, dried in air and calcined at 650 °C for 5 h to remove the surfactant template. This product is denoted as JLU-20. The SBA-15 sample was synthesized at 40 °C for 20 h and then heated at 100 °C for 2 days following the procedure reported by Zhao, Stucky and co-workers.<sup>[3]</sup>

X-ray diffraction patterns were obtained with a Siemens D5005 diffractometer by using Cu<sub>Kα</sub> radiation. Transmission electron microscopy experiments were performed on a JEM-200CX electron microscope (JEOL, Japan) with an acceleration voltage of 200 kV. The nitrogen adsorption and desorption isotherms at the temperature of liquid nitrogen were measured using a Micromeritics ASAP 2010M system. The samples were outgassed for 10 h at 300 °C before the measurements. <sup>29</sup>Si NMR spectra were recorded on a Varian Infinity plus 400 spectrometer, fitting the samples in a 7 mm ZrO<sub>2</sub> rotor, spinning at 8 kHz. A Perkin-Elmer TGA 7 unit was used to carry out the thermogravimetric analysis (TGA) in air at a heating rate of 20 °C min<sup>-1</sup>.

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