Supporting information

Testing the limits of zeolite structural flexibility: Ultrafast introduction of mesoporosity in zeolites

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Table S1 Comparison between ultrafast surfactant-templating proceeded using different water contents

Conditions	**Water content**	V_{micro} **(cm^{3}g^{-1}) (<2 nm)**	V_{total} **(cm^{3}g^{-1}) (<8 nm)**	V_{meso} **(cm^{3}g^{-1}) (2–8 nm)**
Parent		0.32	0.41	0.09
1 TO_2: 0.082 CTAB:	21 H_2O	0.15	0.58	0.43
0.10 NaOH: *x* H_2O,	42 H_2O	0.18	0.60	0.41
210 °C, 3 min	63 H_2O	0.20	0.57	0.38

Table S2 Summarized textural properties of parent and treated zeolites

Temperature (°C)	**Time (min)**	**V_{micro} (cm^3g^{-1}) (<2 nm)**	**V_{total} (cm^3g^{-1}) (<8 nm)**	**V_{meso} (cm^3g^{-1}) (2–8 nm)**
Parent		0.32	0.41	0.09
150	0	0.30	0.41	0.11
	1	0.29	0.46	0.17
	2	0.28	0.46	0.18
	3	0.27	0.52	0.24
	5	0.25	0.54	0.30
	10	0.21	0.59	0.37
170	0	0.30	0.41	0.11
	1	0.30	0.48	0.18
	2	0.27	0.51	0.23
	3	0.25	0.53	0.28
	5	0.22	0.59	0.37
	10	0.18	0.59	0.41
190	0	0.30	0.41	0.11
	1	0.27	0.46	0.18
	2	0.26	0.56	0.29
	3	0.22	0.53	0.32
	5	0.20	0.57	0.37
	10	0.17	0.58	0.41
200	0	0.30	0.41	0.11
	1	0.28	0.47	0.19
	2	0.23	0.52	0.29
	3	0.22	0.59	0.37
	5	0.19	0.57	0.39
	10	0.16	0.59	0.43

Table S2 continued

Temperature (°C)	Time (min)	V_{micro} (cm^3g^{-1}) (<2 nm)	V_{total} (cm^3g^{-1}) (<8 nm)	V_{meso} (cm^3g^{-1}) (2–8 nm)
210	0	0.30	0.41	0.11
	1	0.28	0.47	0.19
	2	0.23	0.54	0.30
	3	0.21	0.58	0.38
	5	0.18	0.58	0.40
	10	0.16	0.59	0.43
220	0	0.30	0.41	0.11
	1	0.27	0.50	0.23
	2	0.21	0.54	0.34
	3	0.19	0.57	0.38
	5	0.16	0.57	0.41
	10	0.14	0.54	0.40
260	0	0.30	0.41	0.11
	1/6	0.26	0.43	0.17
	1/3	0.24	0.41	0.17
	1/2	0.24	0.40	0.17
	1	0.21	0.38	0.17
280	0	0.30	0.41	0.11
	1/6	0.23	0.36	0.12
	1/3	0.19	0.31	0.12
	1/2	0.16	0.26	0.11
	1	0.13	0.22	0.09

Table S3. Comparison between ultrafast surfactant-templating proceeded in tube reactors and continuous flow systems

Conditions	**Time (min)**	V_{micro} **(cm^{3}g^{-1})** **(<2 nm)**	V_{total} **(cm^{3}g^{-1})** **(<8 nm)**	V_{meso} **(cm^{3}g^{-1})** **(2–8 nm)**
Parent		0.32	0.41	0.09
Tubular reactor	0	0.30	0.41	0.11
	1	0.28	0.47	0.19
	2	0.23	0.52	0.29
	3	0.22	0.59	0.37
	5	0.19	0.57	0.39
Flow synthesis	0	0.30	0.41	0.11
	1/3	0.29	0.50	0.21
	2/3	0.24	0.55	0.30
	1	0.23	0.54	0.31
	2	0.21	0.59	0.38
	3	0.20	0.56	0.35
	5	0.18	0.59	0.41

Table S4 Textural properties of parent and UST samples used as catalysts in the cracking of 1,3,5-TIPB

Conditions	**Temp. (°C)**	V_{micro} **(cm^{3}g^{-1})** **(<2 nm)**	V_{total} **(cm^{3}g^{-1})** **(<8 nm)**	V_{meso} **(cm^{3}g^{-1})** **(2–8 nm)**
Parent		0.32	0.41	0.09
1 TO_2: 0.082 CTAB:	150	0.28	0.54	0.27
0.14 NaOH: 63 H_2O,	200	0.19	0.54	0.35
batched, 3 min	220	0.17	0.56	0.40

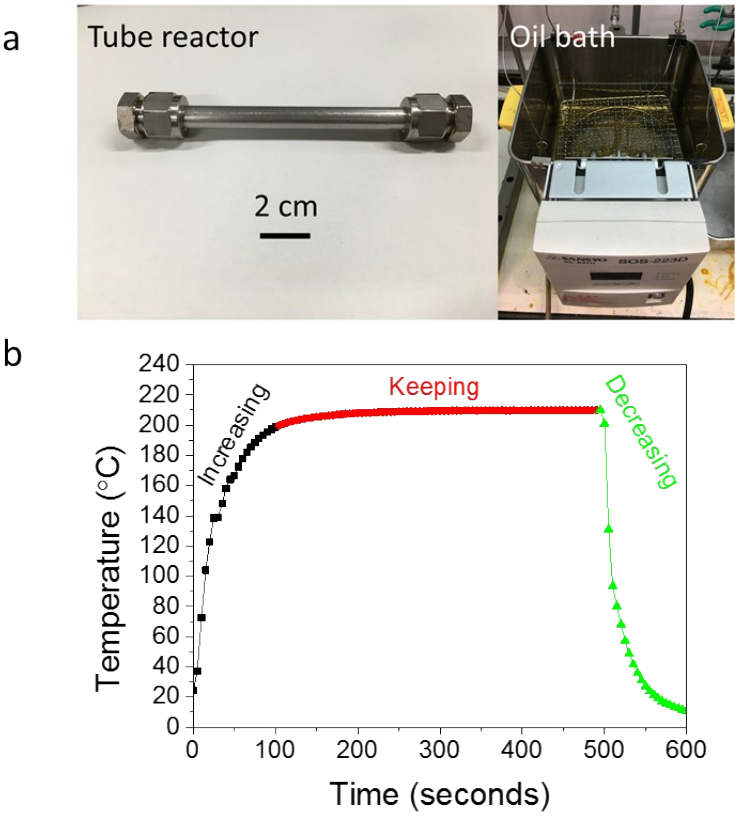

Figure S1 Ultrafast surfactant-templating (UST): a) Photographs of the tube reactor and the oil bath. b) Heating-up and cooling-down curves of the tubular reactor in oil bath and ice water tank, respectively.

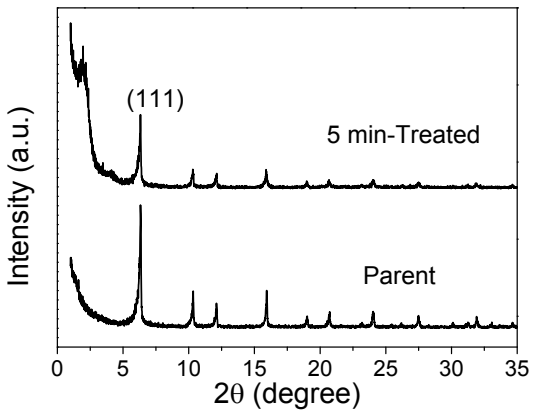

Figure S2. XRD patterns of parent USY zeolite (CBV720, Si/Al=15) and after treatment under 190 °C for 5 min.

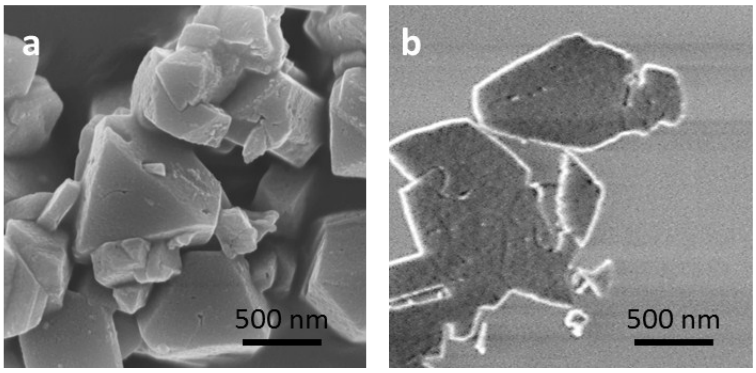

Figure S3 FE-SEM images of UST samples under 190 °C for 2 min. (a) Surface morphology. (b) Inner porous structure clarified after cutting and cross section polishing the sample.

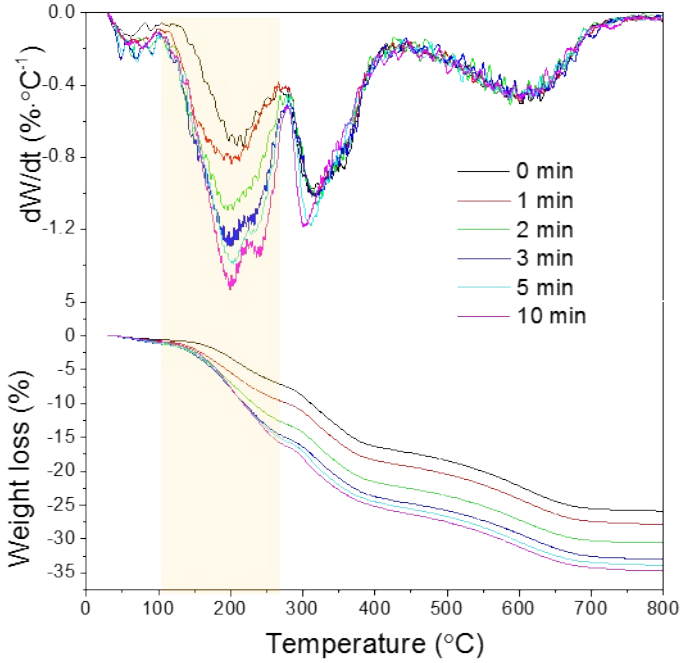

Figure S4. TG-DTG measurements on the treated samples with different periods. Reactant compositions and treating conditions: 1 TO_2: 0.082 CTAB: 0.14 NaOH: 63 H_2O, 190 °C for 1–10 min.

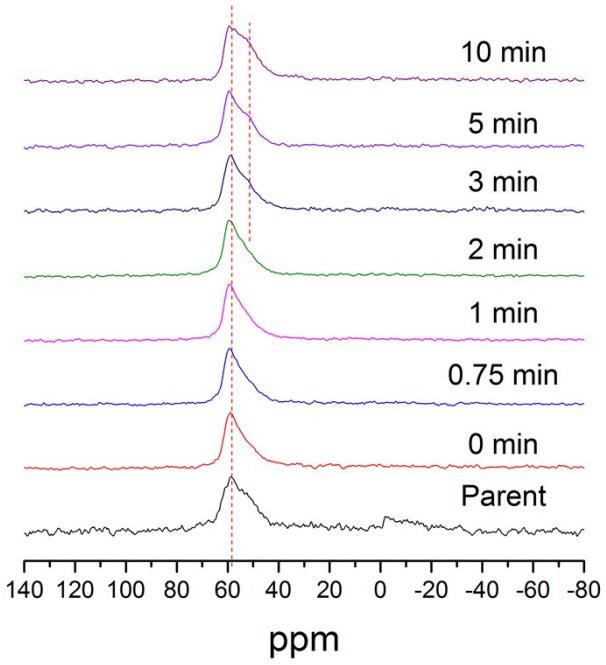

Figure S5. ^{27}Al NMR spectrum of treated samples with different periods. Reactant compositions and treating conditions: 1 TO_2: 0.082 CTAB: 0.14 NaOH: 63 H_2O, 190 °C for 1–10 min.

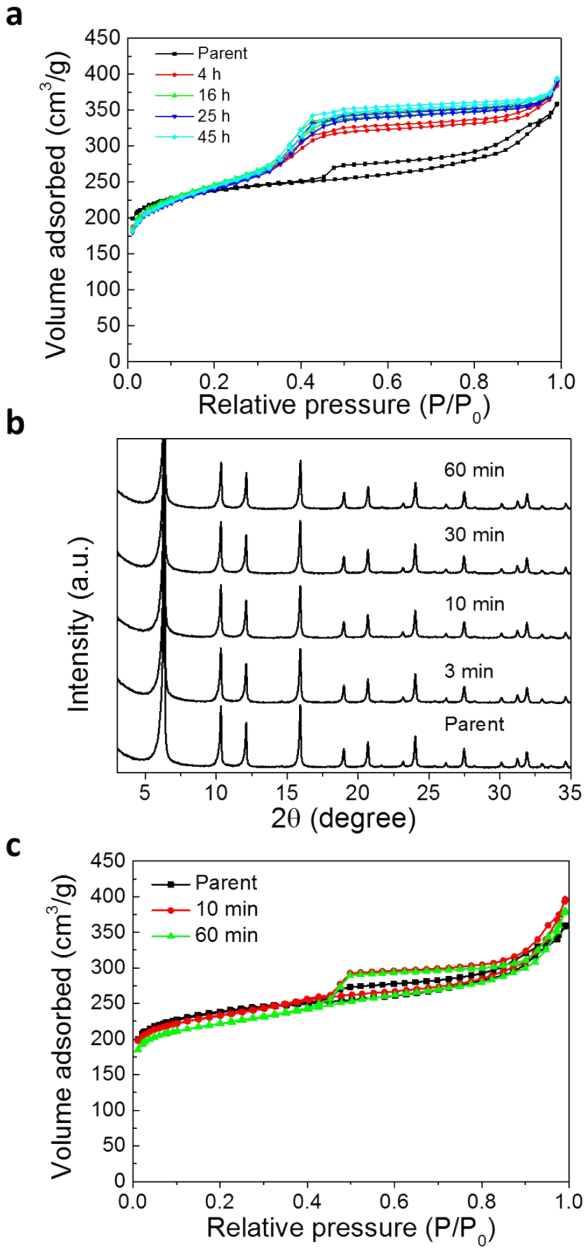

Figure S6. Surfactant-templating using ammonia as a base source: a, nitrogen adsorption isotherms of parent and treated zeolites in autoclave, 150 °C for 4–45 h; b and c, XRD patterns and nitrogen adsorption isotherms of parent and treated zeolites in tubular reactors, 210 °C for 3–60 min. The reaction composition was 1 TO_2: 1.4 NH_4OH: 0.12 CTAB: 210 H_2O. [1]

To investigate how ultrafast surfactant-templating could be realized in such a short period of time, surfactant-templating treatments using ammonia as a base were conducted in autoclaves at 150 °C for 4–45 h (denoted as ST-150-*x* h) or in tubular reactors at 210 °C for 3–60 min (denoted as ST-210-*x*

min), respectively. The synthesis molar composition was 1 TO_2: 0.12 CTAB: 1.40 NH_4OH: 210 H_2O. [14] As shown in **Figure S5a**, for the case of ST-150-*x* h, significant amounts of mesoporosity were formed with a narrow pore size distribution, confirming the efficiency of the surfactant-templating method. However, for the ST-210-*x* min case, which undertook the higher reaction temperature and faster heating rate with the same reaction composition, almost no surfactant-templating effect was observed even after 60 minutes **(Figure S5b, c)**. These observations suggest that fast heating and high temperature treatment, the two usually effective parameters for ultrafast preparation, are not enough for accelerating the surfactant-templating process. Indeed, an effective interaction between alkaline solution and parent zeolite is necessary to achieve the templating effects of the surfactant. With too weak alkalinity, for instance, x_{NaOH} = 0.04 **(Figure 2a)**, new mesopores were hardly formed. An adjustment on the water content also proved that at a higher concentration, the surfactant-templating process takes place faster (**Table S1**). On the other hand, to maintain the integrity of parent zeolite during the base treatment, the protecting effect of the surfactant should be realized which may be a challenge at very high temperatures. It is worth mentioning that in addition to the aforementioned UST conditions (1 TO_2: 0.082 CTAB: 0.14 NaOH: 63 H_2O, 190 °C for several minutes), there are other factors that can accelerate the surfactant-templating of the zeolite: (1) a concentrated reactant mixture with carefully selected alkaline and CTAB concentrations; (2) the temperature of the treatment; (3) reactors featuring fast heating to ensure effective hydrothermal treatment in short periods.

[1] Sachse, A.; Grau-Atienza, A.; Jardim, E. O.; Linares, N.; Thommes, M.; Garcia-Martinez, J., Development of intracrystalline mesoporosity in zeolites through surfactant-templating. *Cryst. Growth Des.* **2017**, *17*, 4289-4305.

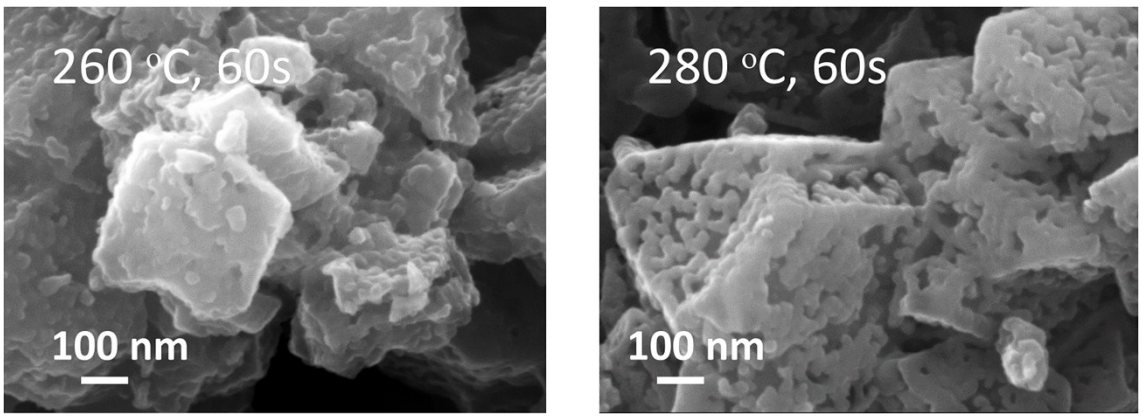

Figure S7. SEM images of treated zeolites under 260 and 280 °C for 60 s with a reactant composition of 1 TO_2: 0.082 CTAB: 0.10 NaOH: 63 H_2O.

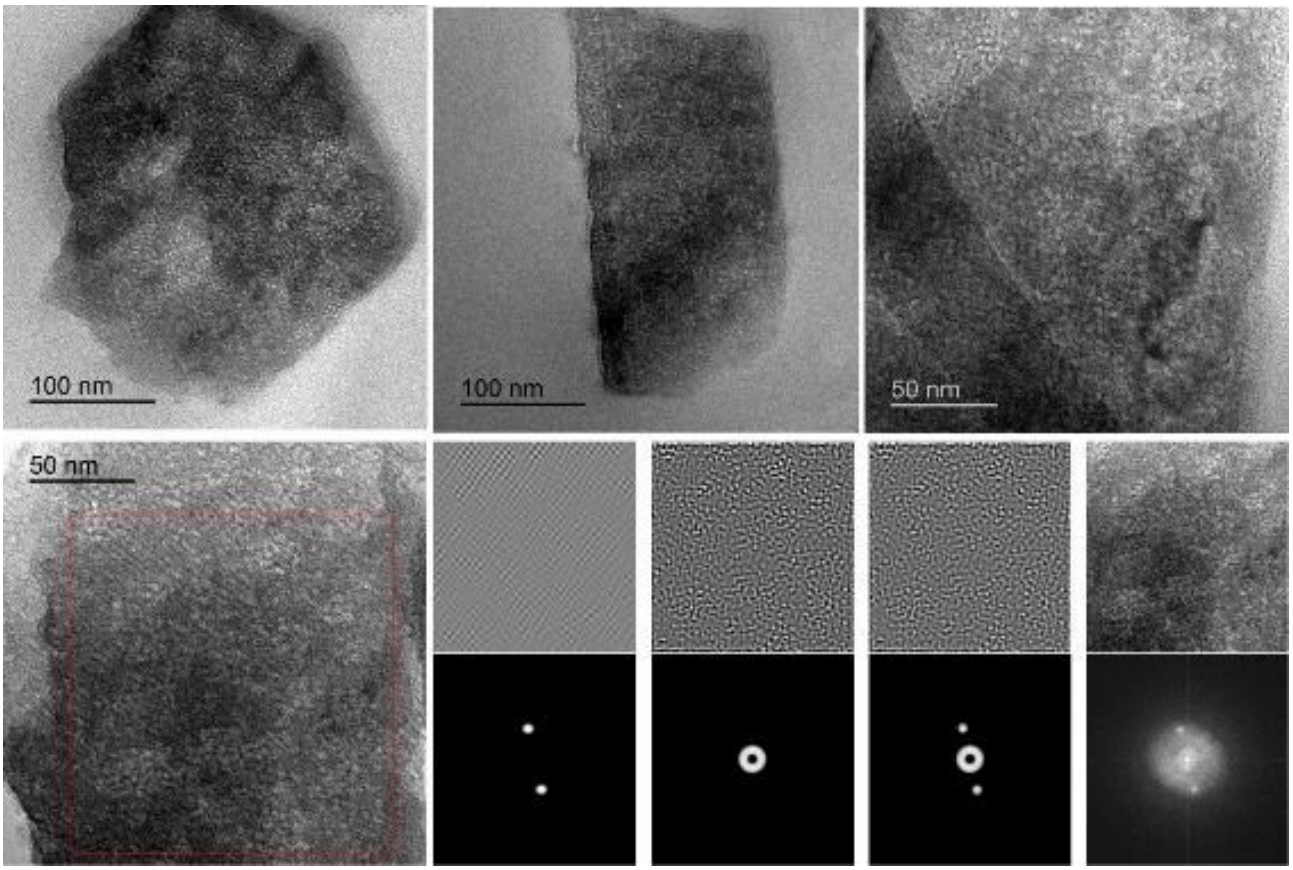

Figure S8. TEM micrographs of ultramicrotomed mesoporous zeolites prepared at 1 min using the flow reactor. The area marked by the red squared was analyzed by Fast Fourier Transform (FFT) analysis. The reconstruction of both the crystalline structure and the mesopore architecture of the sample was successfully achieved by doing the inverse FFT of the spots and the halo, respectively.