Electronic Supplementary Information (ESI)

For

One-pot Ethanol-Mediated Synthesis of Surface Si-Zoned ZSM-5 Zeolites

Jiayu Yu,[a] Di Pan,[a] Ke Du,[a] Wei Chen,[a] Jian Zhou,*[b] Yi Tang[a] and Yahong Zhang*[a]

[a.] Department of Chemistry, Laboratory of Advanced Materials, College of Smart Materials and Future Energy, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, State Key Laboratory of Porous Materials for Separation and Conversion, Fudan University, Shanghai 200433, P. R. China.

E-mail: zhangyh@fudan.edu.cn

[b.] State Key Laboratory of Green Chemical Engineering and Industrial Catalysis, Sinopec Shanghai Research Institute of Petrochemical Technology Co., Ltd., Shanghai, 201208, China.

E-mail: zhouj.sshy@sinopec.com

Derivation of the Final Particle Diameter and Shell Thickness

The detailed derivation of the equation describing the dependence of the final particle diameter on the added amount is provided below.

The yield of Z5-200 zeolite is conventionally determined based on the total silica content in the solid product, i.e., the solid silica yield. It is defined as:

$$Yield_{Z5-200} = \frac{Mass\ of\ SiO_2\ in\ the\ calcined\ solid\ product}{Total\ mass\ of\ SiO_2\ in\ the\ initial\ reaction\ mixture} \times 100\% \quad (1)$$

m_1 represents the mass of SiO_2 in the calcined solid product. The total mass of SiO_2 in the initial mixture can be expressed as $n_0 M_{SiO_2}$, where n_0 is the total molar amount of SiO_2 in the initial system and M is molar mass of SiO_2, Therefore, the above equation can be simplified as:

$$Yield_{Z5-200} = \frac{m_1}{n_0 \times M_{SiO_2}} \times 100\% \quad (2)$$

Theoretically, the mass of a Z5-200 zeolite particle can be expressed by approximating the Z5-200 particles as spheres. In this case, the total mass of Z5-200 solid is:

$$m_1 = \frac{4}{3} \times \pi \times \left(\frac{d}{2}\right)^3 \times \rho_{S-1} \times N \quad (3)$$

$$\therefore Yield_{Z5-200} = \frac{\frac{4}{3} \times \pi \times \left(\frac{d}{2}\right)^3 \times \rho_{S-1} \times N}{n_0 \times M_{sio_2}} \times 100\% \quad (4)$$

where N is the number of Z5-200 particles, ρ is the density of the zeolite framework (approximated by that of silicalite-1 (S-1)), d is the average diameter of Z5-200. Assuming the total number of particles remains constant during incorporation of additional silicate species (i.e., no secondary particles or new nuclei are formed), the mass of the product after shell growth can be written as follows:

$$m_2 = \frac{4}{3} \times \pi \times \left(\frac{D}{2}\right)^3 \times \rho_{S-1} \times N \quad (5)$$

where D is the average diameter of the final Z5-200-*k*Si particles. At this stage, the total molar amount of silica *n* in the system is:

$$n = n_0(1 + k) \quad (6)$$

where *k* is the fraction of SiO_2 molar amount added in the secondary step relative to the initial SiO_2 molar amount.

If utilization of SiO_2 during the secondary shell-growth step is 100%, then the total mass of SiO_2 in the final product satisfies:

$$m_2 = nM_{sio_2} \tag{7}$$

Thus, combining equation (5)-(7), the following relation between particle size and silica content can be derived:

$$\frac{4}{3} \times \pi \times \left(\frac{D}{2}\right)^3 \times \rho_{S-1} \times N = n_0 \times (1+k) \times M_{sio_2} \tag{8}$$

$$\therefore \frac{\frac{4}{3} \times \pi \times \left(\frac{D}{2}\right)^3 \times \rho_{S-1} \times N}{n_0 \times M_{sio_2}} = 1 + k \tag{9}$$

Taking the ratio of equation (9) to equation (4) yields:

$$\frac{D^3}{d^3} = \frac{(1+k) \times 100\%}{Yield_{Z5-200}} \tag{10}$$

$$\therefore D = d \times \sqrt[3]{\frac{(1+k) \times 100\%}{Yield_{Z5-200}}} \tag{11}$$

Furthermore, if the yield of Z5-200 is taken to be 100%, i.e., the initial silica is assumed to be fully utilized, equation (11) can be further simplified:

$$D = d \times \sqrt[3]{1+k} \tag{12}$$

Experimentally, the yield of Z5-200 reaches 98.4% on average over four independent syntheses, which justifies this approximation and supports the use of the simplified relation in the main text. In addition, to directly illustrate the variation in shell thickness, the shell-thickness parameter *T* is introduced:

$$D = d + 2T \tag{13}$$

By combining equation (12) and (13), *T can be described by equation (14)*:

$$T = d \times \frac{\sqrt[3]{1+k} - 1}{2} \tag{14}$$

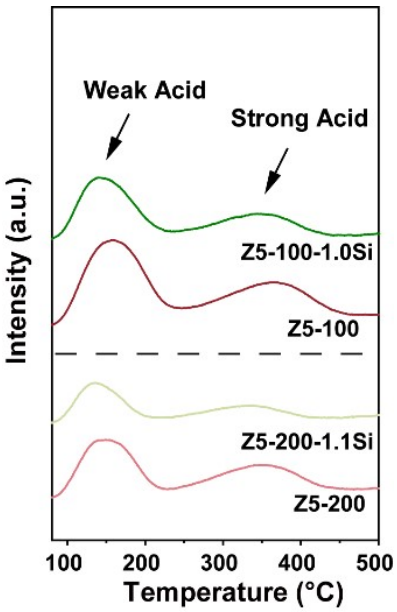

Figure S1. NH_3-TPD profiles of core ZSM-5 and the corresponding Si-zoned ZSM-5 samples.

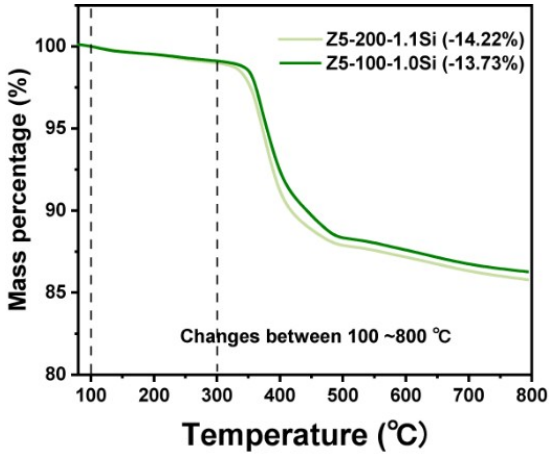

Figure S2. TGA curves of Si-zoned ZSM-5 zeolites.

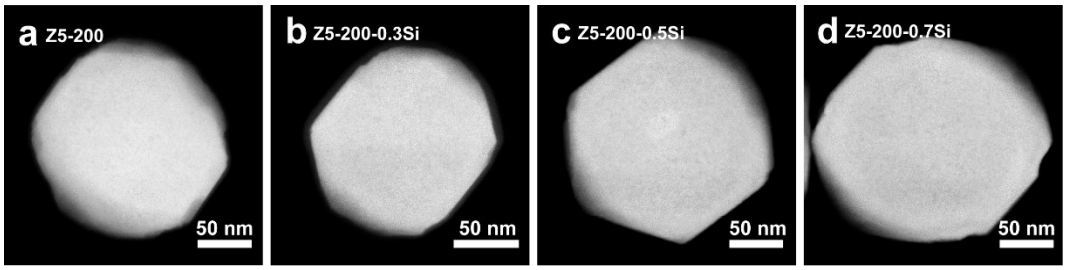

Figure S3. HAADF-STEM images of (a) Z5-200, (b) Z5-200-0.3Si, (c) Z5-200-0.5Si, and (d) Z5-200-0.7Si.

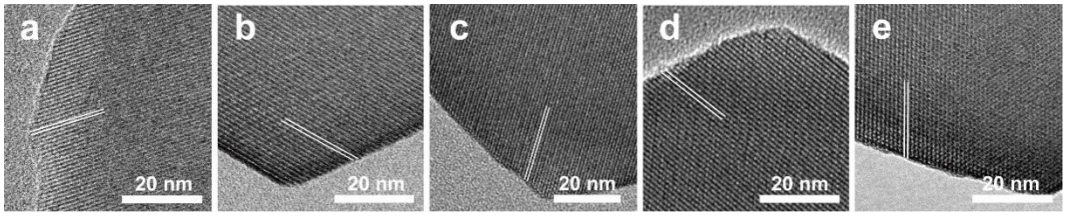

Figure S4. HRTEM images of (a) Z5-200-0.3Si, (b) Z5-200-0.5Si, (c) Z5-200-0.7Si, (d) Z5-200-0.9Si, and (e) Z5-200-1.1Si.

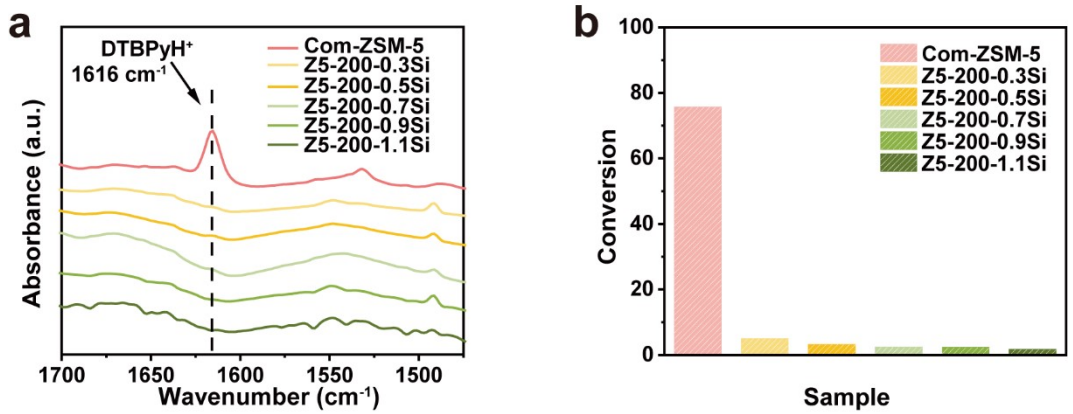

Figure S5. (a) In situ FT-IR spectra of 2,6-DTBPy adsorption at 200 °C and (b) Catalytic TIPB cracking over ZSM-5 samples at 450 °C.

Figure S6. Optical photograph of Z5-200 mother liquid subjected to different heating times.

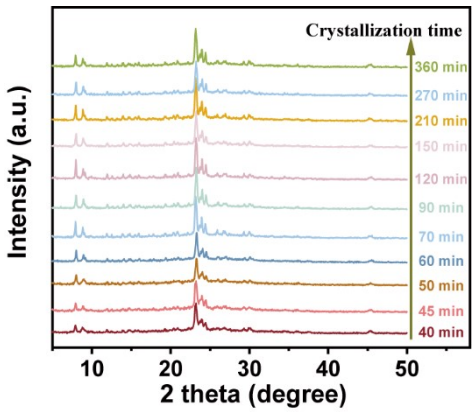

Figure S7. XRD patterns of Z5-200_x samples collected at different times (x in min).

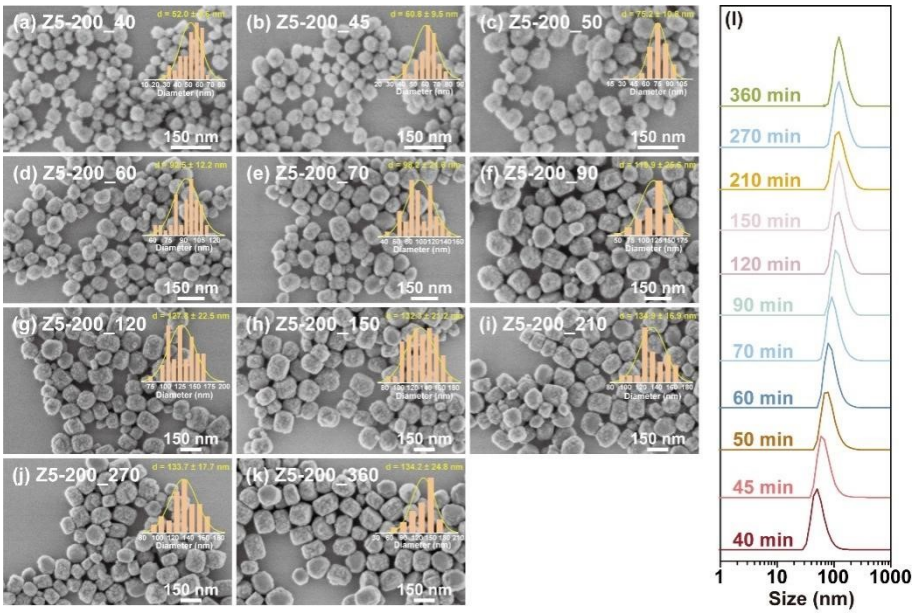

Figure S8. (a-k) SEM images of Z5-200_x samples collected at different times (x in min) (Insets: size distribution of samples in the visual field) and (l) the DLS particle size distribution at different time points during Z5-200 crystallization.

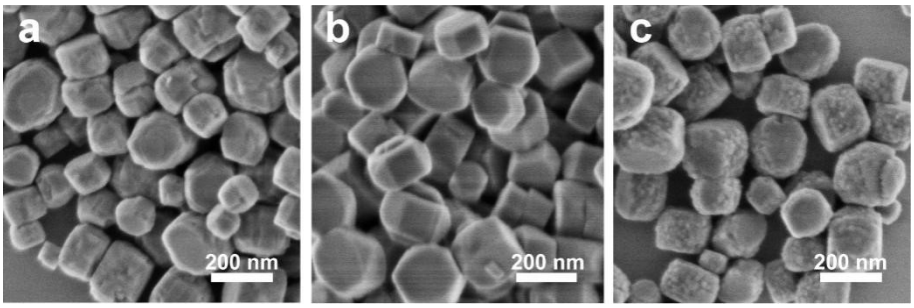

Figure S9. SEM images of (a) Z5-200; (b) ZS-200-0.35Si (adding ethanol-rich silicate solution) and (c) ZS-200-0.35Si (adding solution with a reduced OH^-/Si molar ratio).

SEM images show that the zeolite particles obtained by subsequent one-pot addition of the ethanol-rich silicate solution (Figure S9b) exhibit smoother surfaces and more regular outlines than the core ZSM-5 (Figure S9a), consistent with a layer-by-layer shell growth mode rather than particle attachment. In contrast, zeolite particles obtained by subsequent one-pot addition of the solution with a reduced OH^-/Si molar ratio (Figure S9c) show significantly rougher surfaces with evident particle attachment and irregular morphologies, indicative of a particle-aggregation growth mode that disrupts the formation of a smooth, conformal shell.

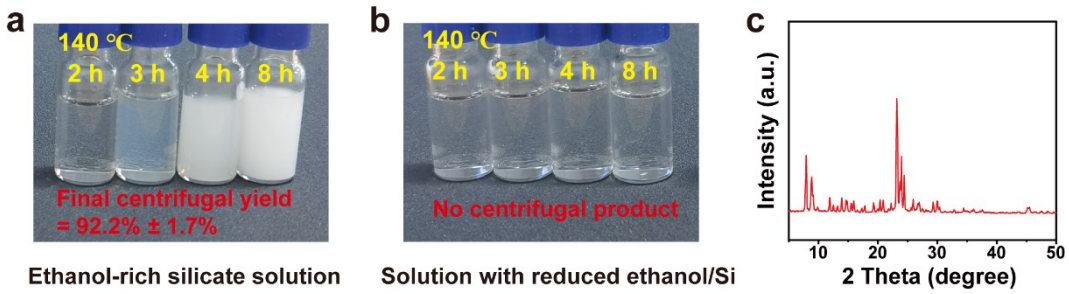

Figure S10. (a, b) Optical photographs of secondary silicate solutions with different initial compositions subjected to heating at 140 °C for varying durations: (a) ethanol-rich silicate solution; (b) solution with a reduced ethanol/Si ratio. The final centrifugal yield was determined after removal of the structure-directing agent by calcination at 550 °C. (c) XRD pattern of the final product obtained from the ethanol-rich silicate solution.

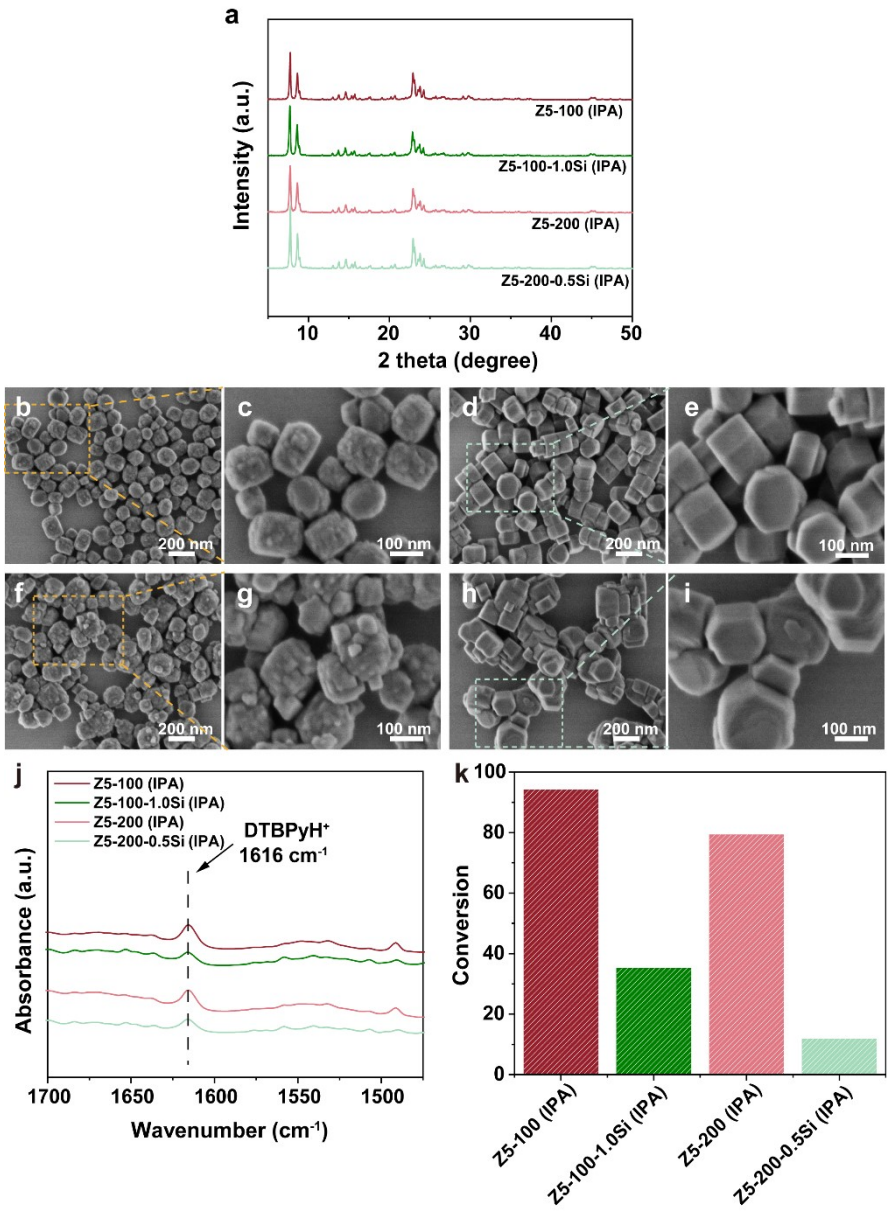

Figure S11. Characterization results of core ZSM-5 and the corresponding Z5-x-kSi samples synthesized in the presence of IPA: (a) XRD patterns; SEM images of (b, c) Z5-200 (IPA), (d, e) Z5-200-0.5Si (IPA), (f, g) Z5-100 (IPA), and (h, i) Z5-100-1.0Si (IPA); (j) In situ FT-IR spectra of DTBPy adsorption at 200 °C and (k) Catalytic TIPB cracking over ZSM-5 samples at 450 °C.

Table S1. Acid properties obtained by NH_3-TPD [a].

Sample name	Total acidity (μmol g^{-1})	Weak acidity (μmol g^{-1})	Strong acidity (μmol g^{-1})
Z5-200	162	94	68
Z5-200-1.1Si	86	54	32
Z5-100	243	152	91
Z5-100-1.0Si	152	100	52

[a] The weak and strong acid amounts were determined by the amounts of NH_3 desorbed at 100-250 °C and 250-450 °C, respectively.

Table S2. Particle diameters of samples determined by different methods.

Sample name	Diameter [a] (calculated)	Diameter [b]	Diameter [c]	Shell thickness [d] (calculated)	Shell thickness [e]
Z5-200	/	149.5 ± 2.9 nm	144.4 ± 21.2 nm	/	/
Z5-200-0.3Si	163.2 nm	162.0 ± 6.6 nm	161.5 ± 23.1 nm	6.8 nm	6.3 ± 3.3 nm
Z5-200-0.5Si	171.1 nm	170.2 ± 4.0 nm	169.3 ± 23.9 nm	10.8 nm	10.4 ± 2.0 nm
Z5-200-0.7Si	178.4 nm	176.5 ± 4.8 nm	175.9 ± 21.4 nm	14.5 nm	13.5 ± 2.4 nm
Z5-200-0.9Si	185.2 nm	183.5 ± 5.3 nm	182.2 ± 26.7 nm	17.8 nm	17.0 ± 2.7 nm
Z5-200-1.1Si	191.4 nm	189.7 ± 2.3 nm	191.7 ± 27.2 nm	21.0 nm	20.1 ± 1.2 nm

[a] Obtained according to the equation (12) in supporting information, where the diameter of Z5-200 from DLS i.e., 149.5 nm; [b] Particle diameter determined by DLS and present as mean ± standard deviation (n = 6); [c]Average particle diameter obtained from SEM image analysis and presented as mean $\pm$ standard deviation ($n \geq 50$); [d] Obtained according to the equation (14) in supporting information, where the diameter of Z5-200 from DLS i.e., 149.5 nm; [e] Estimated as half of the difference between the particle diameter [b] and the ZS-200 core average diameter from DLS (149.5 nm).

Table S3. Yield of Z5-x synthesized with different initial Si/Al ratios after ethanol addition.

Sample name	Centrifugal yield [a]
Z5-100	99.7% ± 0.2%
Z5-200	98.4% ± 0.7%

[a] Centrifugal yields were calculated after removing the structure-directing agent by calcination at 550 °C and presented as mean ± standard deviation (n = 4).

Table S4. Yield of Z5-200_360 sample before and after ethanol addition (without further heating) [a].

Sample		Dialysis yield	Centrifugal yield
Z5-200_360	before ethanol addition	74.5% ± 0.7%	74.4% ± 1.7%
	after ethanol addition	73.9% ± 0.3%	74.2% ± 0.3%

[a] All yields were calculated after removing the structure-directing agent by calcination at 550 °C and presented as mean ± standard deviation (n = 4). In detail, the liquid was transferred into a dialysis tube with a molecular weight cutoff of 3.5 kDa and then the sealed dialysis tube was immersed in 6 mmol/L TPAOH aqueous solution for 24 h. Subsequently, the dialysis tube was transferred and immersed into deionized water for 48 h, with replacing deionized water every 12 h. Consequently, it was freeze-dried in vacuum at -50 °C, and solid yields were calculated after removing the structure direct agent by calcination at 550 °C.

Table S5. Dialysis yields of secondary silicate aging solutions with varying initial compositions.

Entry	Solution composition	Dialysis yield [a]
1 [b]	$0.5SiO_2$: 0.39TPAOH: $13.21H_2O$: 10 ethanol	< 1%
2 [c]	$1.0SiO_2$: 0.39TPAOH: $13.21H_2O$: 10 ethanol	39.7% ± 1.6%
3 [d]	$0.5SiO_2$: 0.39TPAOH: $13.21H_2O$: 2 ethanol	< 1%

[a] Secondary silicate aging solutions aged at room temperature for 12 h without heating were directly dialyzed, and dialysis yields were calculated after calcination at 550 °C to remove the structure-directing agent; [b] Ethanol-rich silicate solution; [c] Solution with a reduced OH^-/Si molar ratio and [d] Solution with a reduced ethanol/Si molar ratio.