Electronic Supplementary Information (ESI)

For

Distinguishing and unraveling classical and non-classical pathways in MFI zeolite crystallization: Insights into their contributions and impact on the final product

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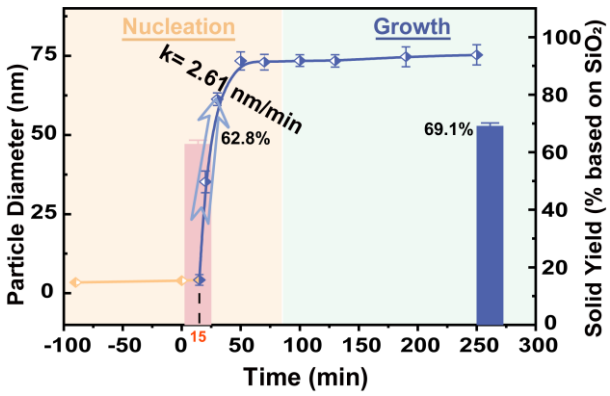

Figure S1. Sizes and solid yields of silicalite-1 zeolite particles synthesized with ethanol/SiO2 ratios of 0 and H2O/SiO2 of 10.16 under different hydrothermal treatment times. The curves represent particle diameters, while the bar charts show the solid yields obtained by dialysis (pink) or centrifugation (blue) after removing the structure direct agent via calcination at 550 °C. Error bars indicate standard deviation (SD) and data for size are presented as the mean ± SD (n = 6) and for yield are presented as the mean + SD (n = 4)

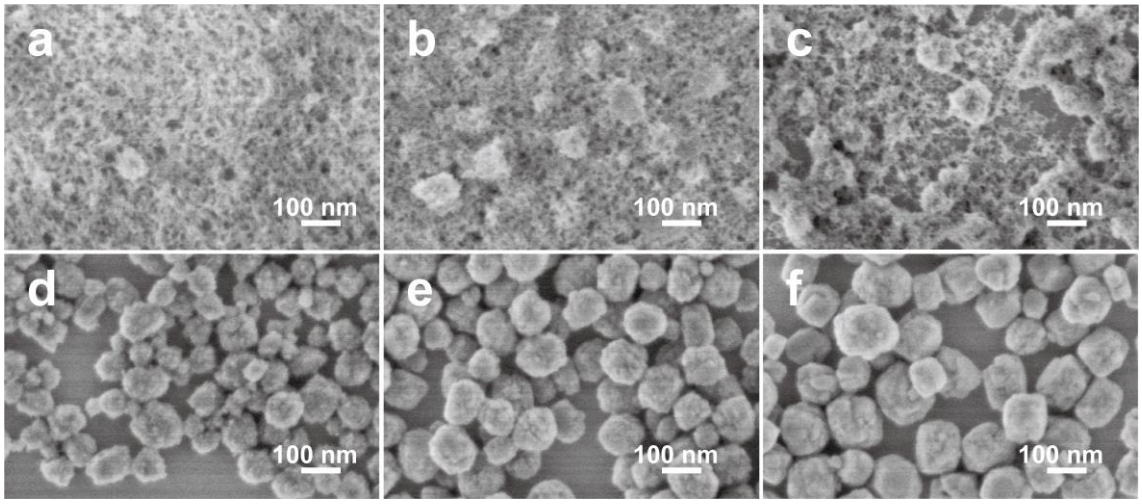

Figure S2. SEM images of silicalite-1 samples obtained by dialysis at the different crystallization time. (a) 135 min; (b) 165 min; (c) 185 min; (d) 215 min (e) 245 min; (f) 305 min.

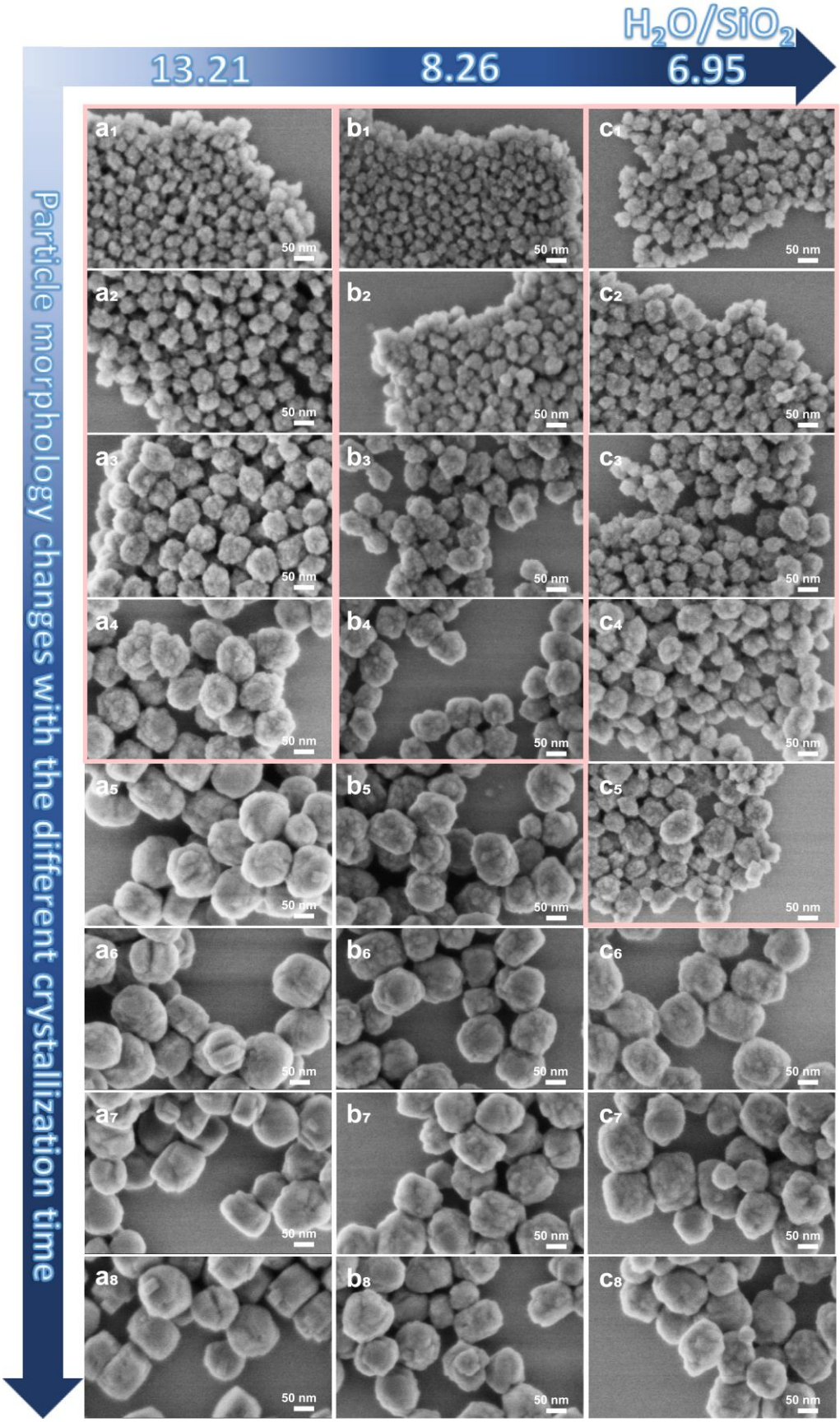

Figure S3. The SEM images of silicalite-1 obtained by centrifugation under different H_2O/SiO_2 molar ratios at the stage of growth with different crystallization time. (a_1-a_8) 13.21; (b_1-b_8) 8.26; (c_1-c_8) 6.95. The pink lines represent the growth occurred during the linear growth stage.

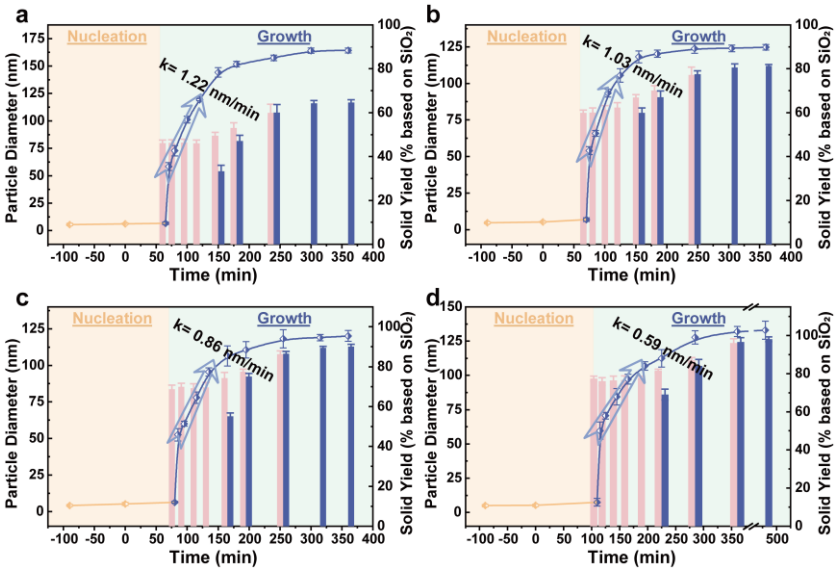

Figure S4. Sizes and solid yields of ZSM-5 zeolite particles synthesized with different H_2O/SiO_2 molar ratios under different hydrothermal treatment times: (a) 13.21; (b) 10.16; (c) 8.26; (d) 6.95. The curves represent particle diameters, while the bar charts show the solid yields obtained by dialysis (pink) or centrifugation (blue) after removing the structure direct agent via calcination at 550 °C. Error bars indicate standard deviation (SD) and data for size are presented as the mean ± SD (n = 6) and for yield are presented as the mean + SD (n = 4).

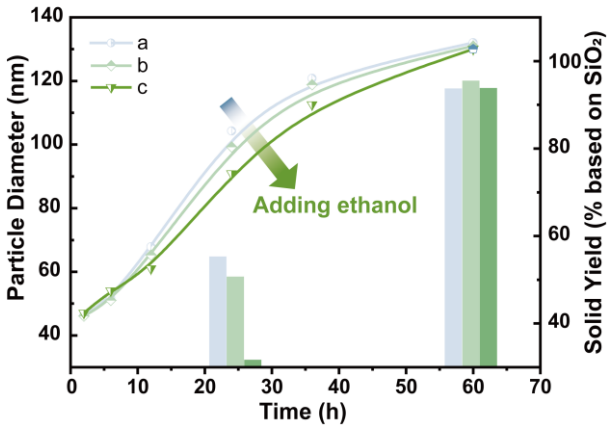

Figure S5. The growth curves and solid yield of the dialysis solution with different ethanol/SiO_2 molar ratios or H_2O/SiO_2 molar ratios at 80 °C. (a) ethanol/SiO_2 = 0; (b) ethanol/SiO_2 = 4; (c) ethanol/SiO_2 = 10. The curves represent particle diameters, while the bar charts show the solid yields obtained by centrifugation after removing the structure direct agent via calcination at 550 °C.

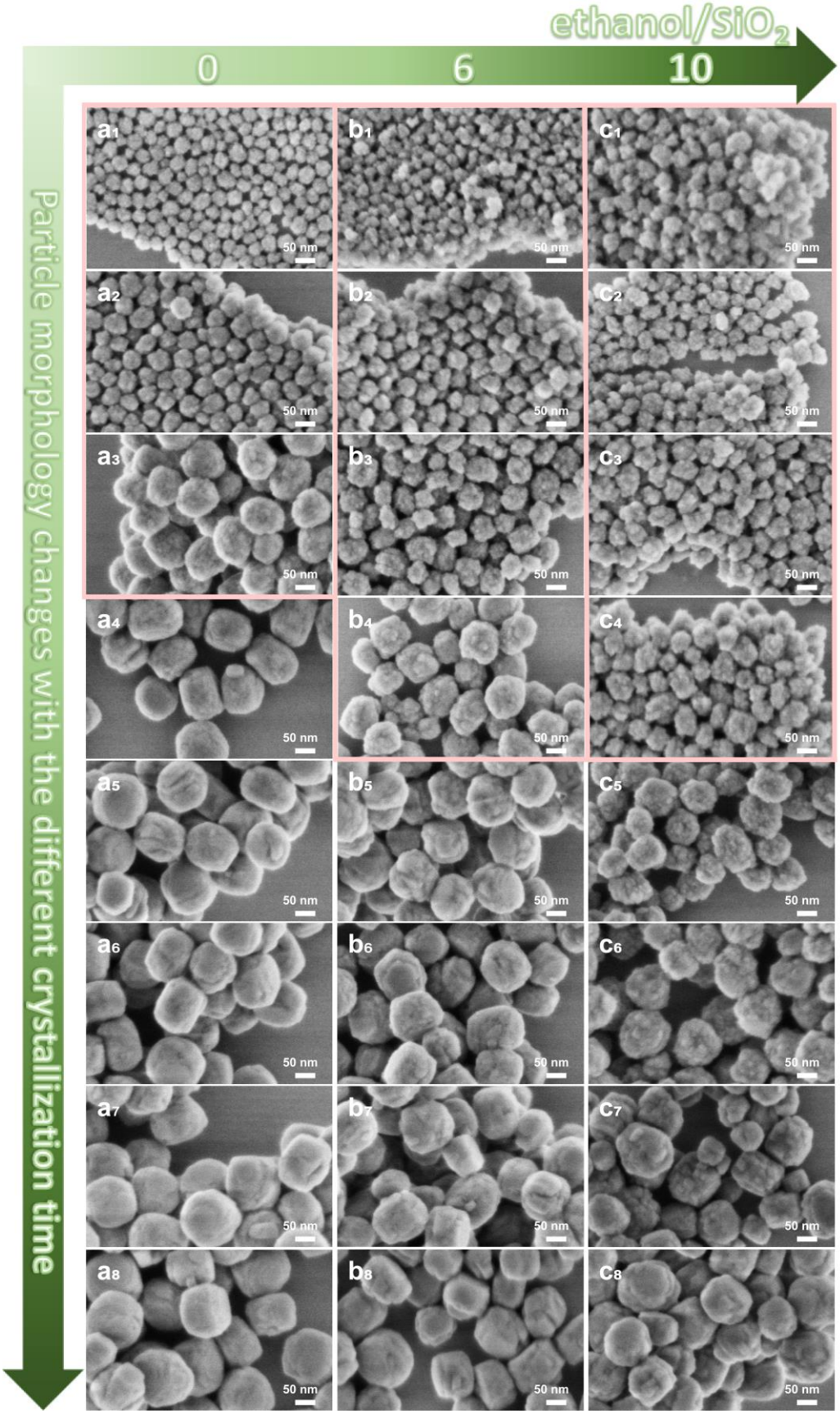

Figure S6. The SEM images of silicalite-1 obtained by centrifugation under different ethanol/SiO_2 molar ratios at the stage of growth with different crystallization time. (a_1-a_8) 0; (b_1-b_8) 6; (c_1-c_8) 10. The pink lines represent the growth occurred during the linear growth stage.

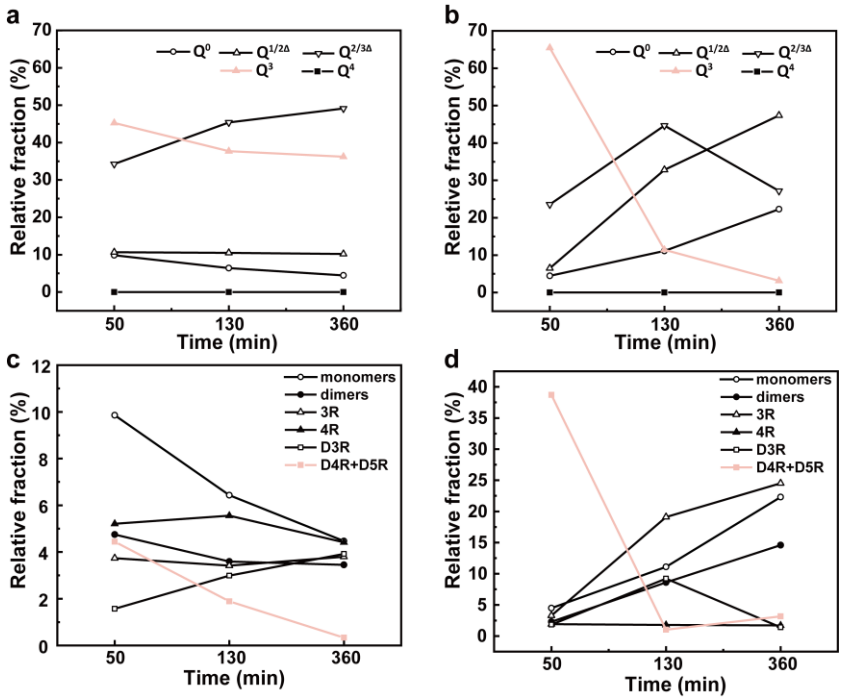

Figure S7. Distribution of Q^n in (a, b) all oligomers and (c, d) some representative selected oligomers (monomer, dimer, cyclic trimer (3R), cyclic tetramer (4R), prismatic hexamer (D3R), cubic octamer (D4R) and double-five-ring (D5R)) in the supernatants obtained by centrifugation at different time before (a, c) and after (b, d) the addition of ethanol determined with liquid-state ^{29}Si NMR spectroscopy. $Q^{n\Delta}$ means Si site with n connectivity present in a 3-membered ring.

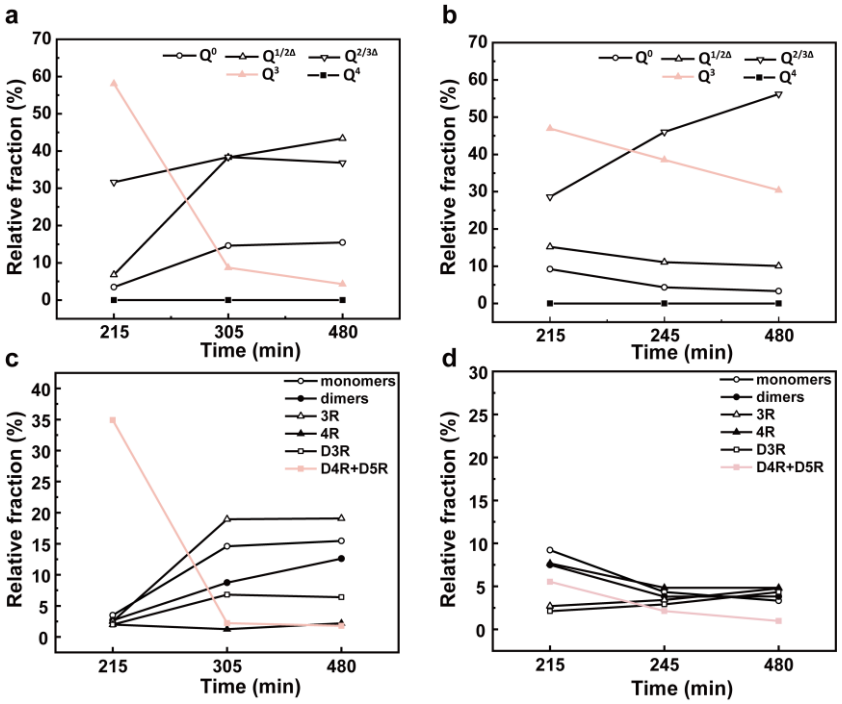

Figure S8. Distribution of Q^n in (a, b) all oligomers and (c, d) some representative selected oligomers (monomer, dimer, cyclic trimer (3R), cyclic tetramer (4R), prismatic hexamer (D3R), cubic octamer (D4R) and double-five-ring (D5R)) in the supernatants obtained by centrifugation at different time before (a, c) and after (b, d) the removal of ethanol determined with liquid-state ^{29}Si NMR spectroscopy. $Q^{n\Delta}$ means Si site with n connectivity present in a 3-membered ring.

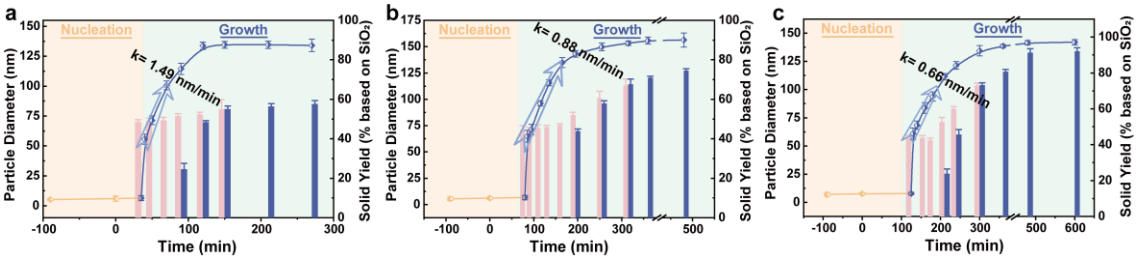

Figure S9. Sizes and solid yields of ZSM-5 zeolite particles synthesized with different ethanol/SiO_2 molar ratios under different hydrothermal treatment times: (a) 0; (b) 6; (c) 10. The curves represent particle diameters, while the bar charts show the solid yields obtained by dialysis (pink) or centrifugation (blue) after removing the structure direct agent via calcination at 550 °C. Error bars indicate standard deviation (SD) and data for size are presented as the mean ± SD (n = 6) and for yield are presented as the mean + SD (n = 4)

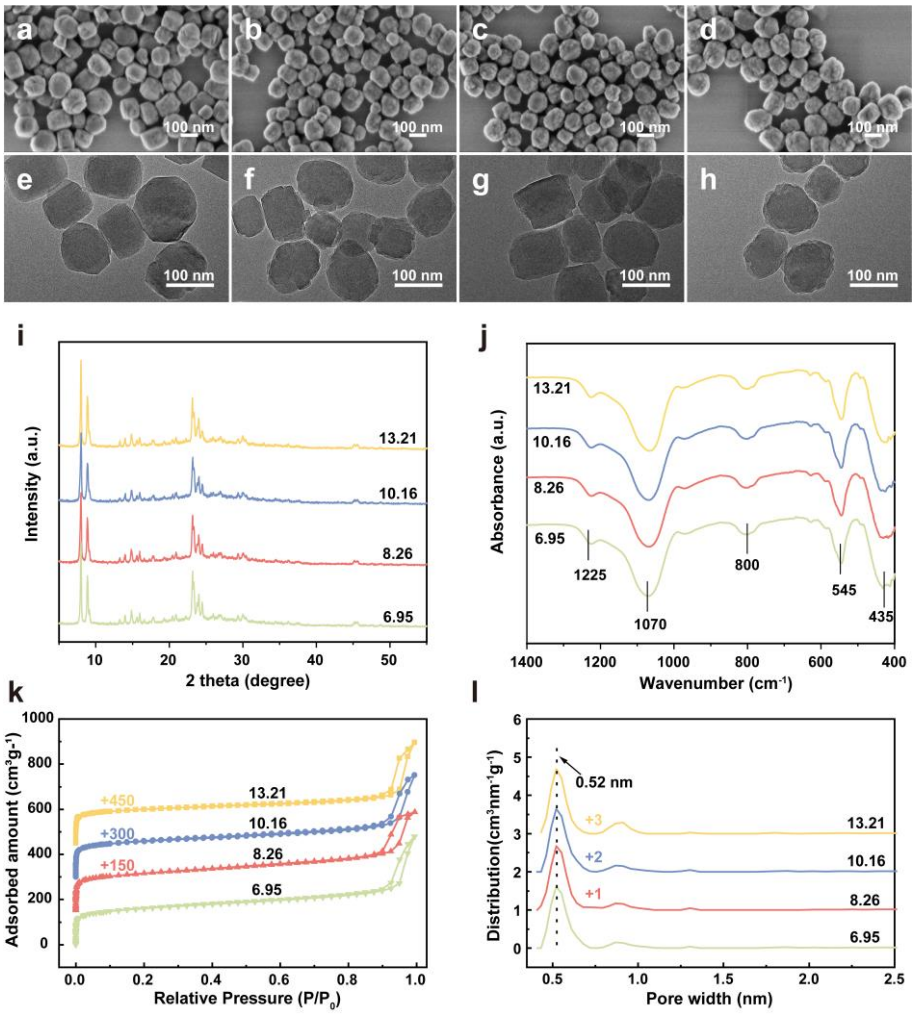

Figure S10. (a-d) SEM images of final silicalite-1 obtained at different H_2O/SiO_2 ratios: (a) 13.21, (b) 10.16, (c) 8.26 and (d) 6.95. (e-h) corresponding TEM images. (i) XRD patterns and (j) FTIR patterns of final silicalite-1 obtained at different H_2O/SiO_2 ratios. (k) Ar adsorption-desorption isotherms at 87 K and (l) pore size distribution of the final silicalite-1.

FTIR spectra show that the peaks at 1225 cm^{-1}, 1070 cm^{-1}, 800 cm^{-1}, 545 cm^{-1}, 435 cm^{-1} (Figure S10j) appearing in all samples, correspond to MFI framework characteristic peaks, which indicate definite MFI framework, consistent with the results of their XRD patterns (Figure S10i).

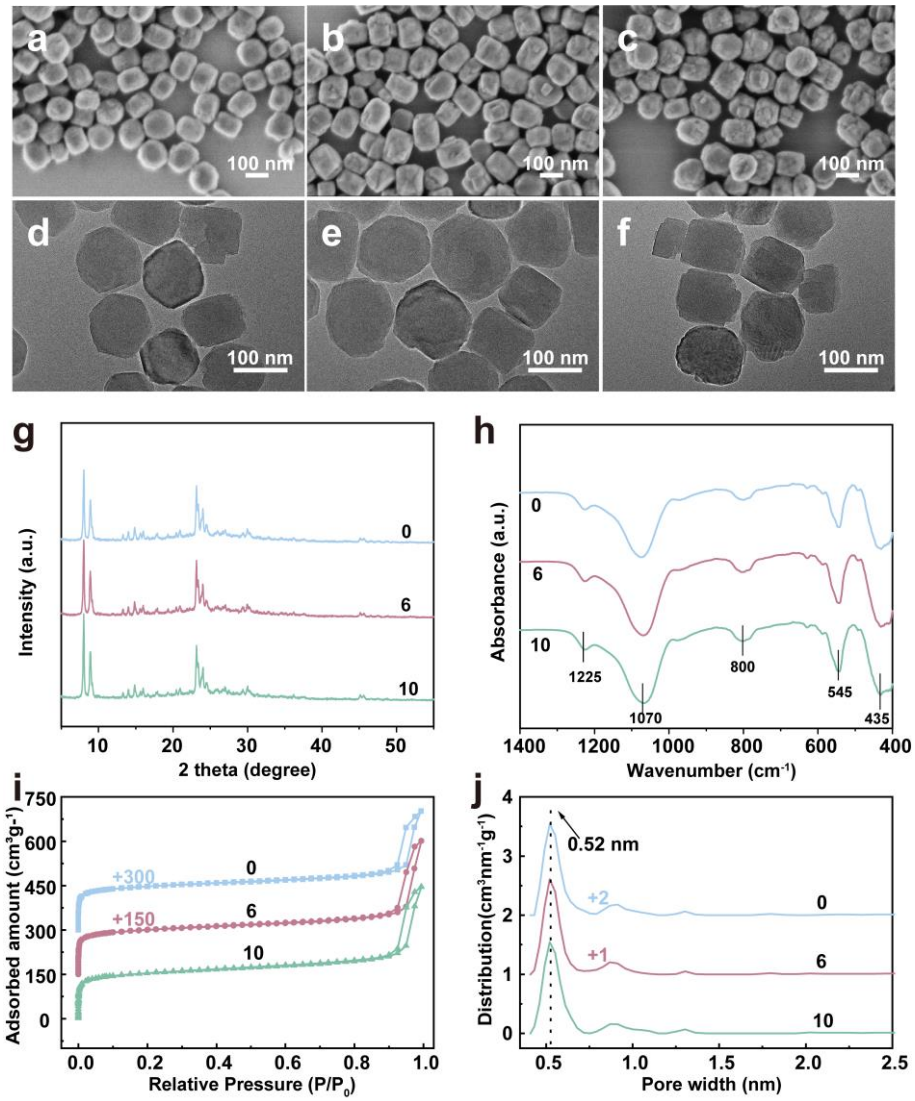

Figure S11. (a-c) SEM images of final silicalite-1 obtained at different ethanol/SiO_2 ratios: (a) 0, (b) 6 and (c) 10. (d-f) corresponding TEM images. (g) XRD patterns and (h) FTIR patterns of final silicalite-1 obtained at different ethanol/SiO_2 ratios. (i) Ar adsorption-desorption isotherms at 87 K and (j) pore size distribution of the final silicalite-1.

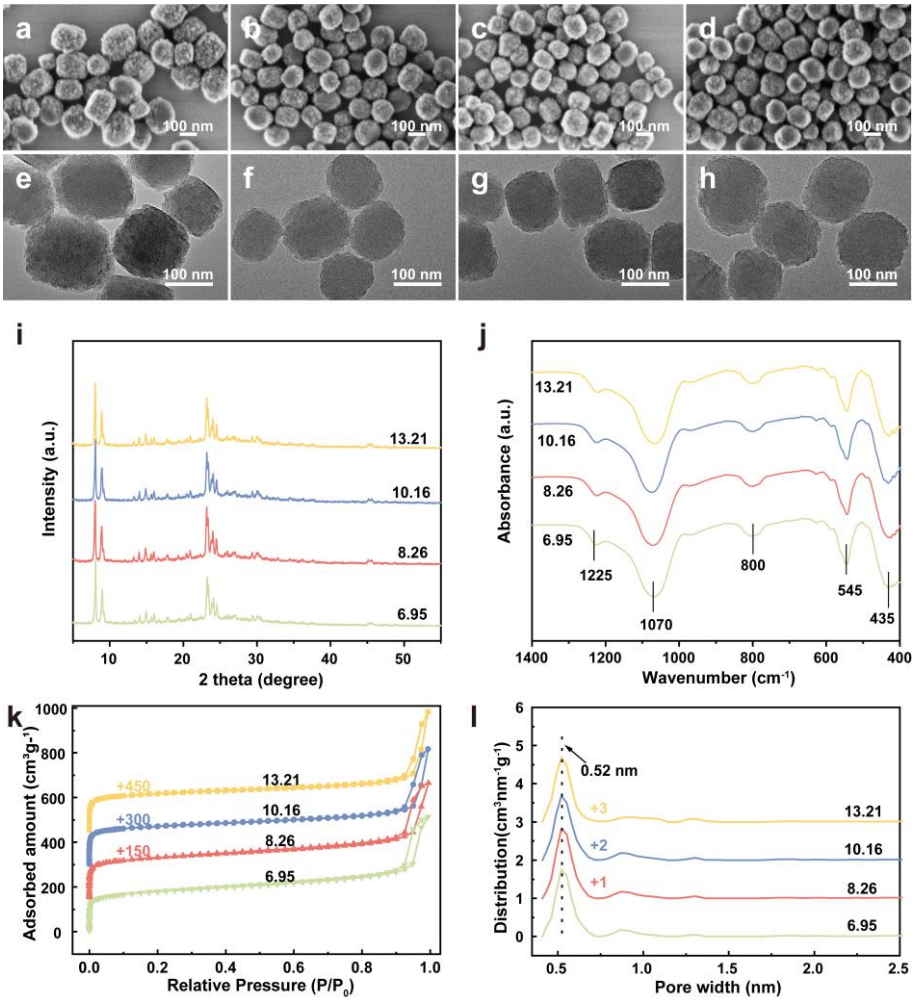

Figure S12. (a-d) SEM images of final ZSM-5 obtained at different H_2O/SiO_2 ratios: (a) 13.21, (b) 10.16, (c) 8.26 and (d) 6.95. (e-h) corresponding TEM images. (i) XRD patterns and (j) FTIR patterns of final ZSM-5 obtained at different H_2O/SiO_2 ratios. (k) Ar adsorption-desorption isotherms at 87 K and (l) pore size distribution of the final ZSM-5.

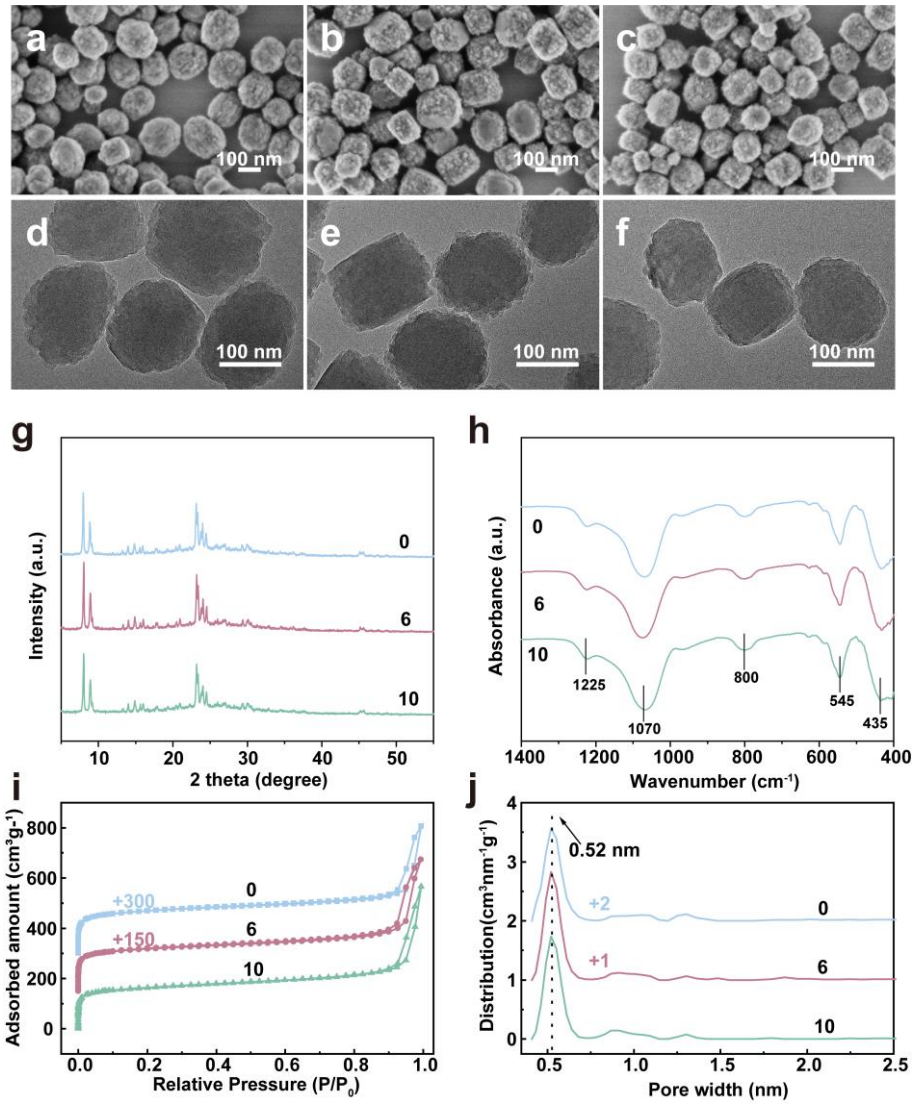

Figure S13. (a-c) SEM images of final ZSM-5 obtained at different ethanol/SiO_2 ratios: (a) 0, (b) 6 and (c) 10. (d-f) corresponding TEM images. (g) XRD patterns and (h) FTIR patterns of final ZSM-5 obtained at different ethanol/SiO_2 ratios. (i) Ar adsorption-desorption isotherms at 87 K and (j) pore size distribution of the final ZSM-5.

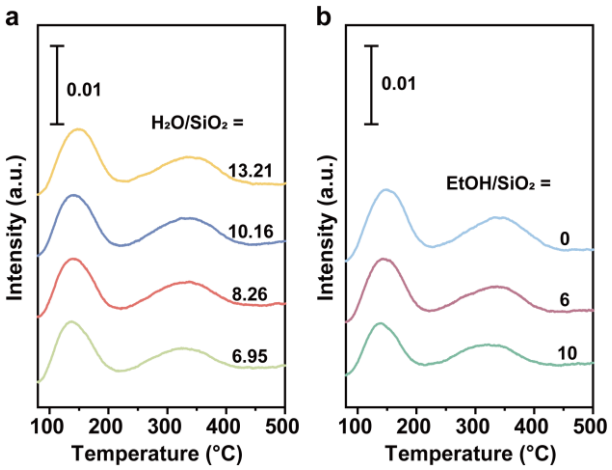

Figure S14. NH_3-TPD profiles of ZSM-5 samples prepared under different H_2O/SiO_2 (a) and ethanol/SiO_2 (b) ratios.

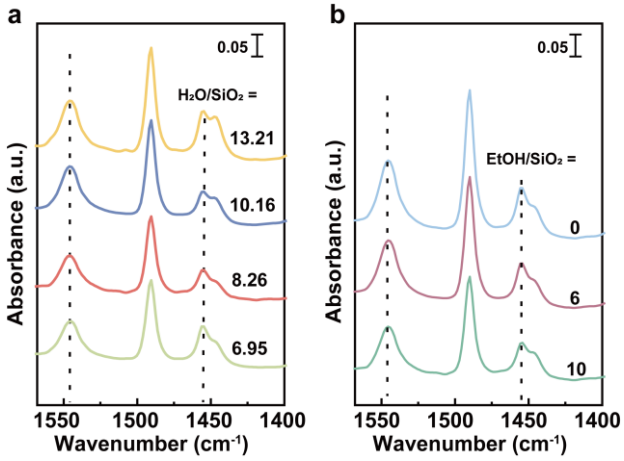

Figure S15. Py-IR spectra at 300 °C of ZSM-5 samples prepared under different H_2O/SiO_2 (a) and ethanol/SiO_2 (b) ratios.

Table S1. silicon and aluminum contents (mg/L) and Si/Al ratios in the supernatant of the final products [a]

Sample	H_2O/SiO_2	Si	Al	Si/Al ratio
1	13.21	2.22×10^4	-	∞
2	10.16	1.42×10^4	1.42	9643
3	8.26	1.13×10^4	2.79	3906
4	6.95	7.78×10^3	2.46	3050

[a] Determined by ICP and then converted by isobaric columns.

Table S2. The textural properties of silicalite-1 obtained at different Initial gel compositions

Entry	Initial gel composition		Surface Area ($m^2\ g^{-1}$)			Pore Volume ($cm^3\ g^{-1}$)	
	H_2O/SiO_2	$EtOH/SiO_2$	S_{BET} [a]	S_{micro} [b]	S_{extra} [b]	V_{total} [c]	V_{micro} [b]
1	13.21	4	496	407	89	0.48	0.16
2	10.16	4	516	411	105	0.48	0.16
3	8.26	4	528	390	138	0.50	0.16
4	6.95	4	517	395	122	0.52	0.16
5	13.21	0	489	411	78	0.44	0.16
6	13.21	6	497	407	90	0.45	0.16
7	13.21	10	509	413	96	0.48	0.16

[a] Determined by the multi-point BET method. [b] Analyzed by t-plot method. [c] Using the adsorption data at $P/P_0 = 0.974$.

Table S3. The textural properties of ZSM-5 obtained at different Initial gel compositions

Entry	Initial gel composition		Surface Area ($m^2 g^{-1}$)			Pore Volume ($cm^3 g^{-1}$)	
	H_2O/SiO_2	$EtOH/SiO_2$	S_{BET} [a]	S_{micro} [b]	S_{extra} [b]	V_{total} [c]	V_{micro} [b]
1	13.21	4	554	464	90	0.46	0.18
2	10.16	4	566	459	107	0.45	0.18
3	8.26	4	589	454	135	0.52	0.18
4	6.95	4	585	442	143	0.59	0.17
5	13.21	0	557	457	100	0.45	0.18
6	13.21	6	555	455	100	0.57	0.18
7	13.21	10	540	433	107	0.52	0.17

[a] Determined by the multi-point BET method. [b] Analyzed by t-plot method. [c] Using the adsorption data at $P/P_0 = 0.974$.