Supplementary Information for

Direct, single-step synthesis of hierarchical zeolites without secondary templating

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Zero length column chromatography (ZLC) data analysis

The data was analyzed using linear ZLC analysis of desorption curves developed by Eic and Ruthven.[1] Assuming gas-solid equilibrium and neglecting holdup in the gas phase, the transient mass balance for diffusion from three dimensional particles is solved with an infinite series for normalized concentration exiting the chamber,

$$\frac{C}{C_0} = 2L\sum_{n=1}^{\infty}\frac{\exp\left(-\frac{{\beta_n}^2 D_{eff}}{R^2}t\right)}{\left[{\beta_n}^2 + L(L-1)\right]} \tag{1}$$

where C is the gas phase adsorbate concentration and C_0 is the initial gas phase adsorbate concentration in the effluent. β_n is the infinite series satisfying

$$\beta_n cot\beta_n + L - 1 = 0 \tag{2}$$

and L is,

$$L = \frac{1}{3KV_s}\frac{FR^2}{D_{eff}} \tag{3}$$

where F is the purge flow rate, K is the Henry's law constant, V_s is the adsorbent volume. Assuming a linear FID response with concentration, the dimensionless concentration was calculated by following equation

$$\frac{C}{C_0} = \frac{I(t) - I_\infty}{I_0 - I_\infty} \tag{4}$$

where I_∞ is the GC-FID signal at long time (the background signal) and I_0 is the initial signal in the desorption curve. In the long time region, the solution of equation (1) can be further reduced to

$$\frac{C}{C_0} = \frac{2L}{{\beta_1}^2 + L(L-1)}\exp\left(-{\beta_1}^2\frac{D_{eff}}{R^2}t\right) \tag{5}$$

By plotting $\ln(C/C_0)$ vs. time, the long-time slope can be fit to the above relationship. The parameter D_{eff}/R^2 can be extracted from the slope, while L can be determined from the intercept. The obtained D_{eff}/R^2 and L for 200 nm ZSM-5, 3DOm-i ZSM-5 and hierarchical ZSM-5 are shown in Table S4 and plotted in Figure 5. The obtained L is between 80 and 200, indicating the validity of using long-time slope in the desorption curve to analyze the diffusion data.

Calculation of effectiveness factor and Thiele modulus

The catalyst effectiveness factor (η) and Thiele modulus (ϕ) are calculated using the following equations.

$$\eta = \frac{k_{app}}{k_{int}} \tag{6}$$

herein, k_{app} is the apparent reaction rate constant, and k_{int} is the intrinsic reaction rate constant for the self-etherification of benzyl alcohol.

$$\phi = x_p \sqrt{\frac{k_{int} C_{H^+}}{D_A}} \tag{7}$$

herein, x_p, the characteristic length, is defined as the radius of the zeolite particles. In the case of 3DOm-i zeolite, it is the radius of spherical element (i.e. 0.5×35 nm = 17.5 nm). C_{H^+} is the Brønsted acid site concentration inside the catalyst which is determined by IPA TPD and collidine TPD, D_A is the effective diffusion coefficient of benzyl alcohol in the catalyst, and k_{int} is the intrinsic rate constant. Detailed calculation method for k_{app} and k_{int} can be found in our previous report.[2] Effectiveness factors and the Thiele modules of the ZSM-5 samples were plotted in η and ϕ diagram along with a plot of the theoretically expected behavior for effectiveness factor $(\eta = \frac{tanh\phi}{\phi})$ based on the pseudo first order reaction-diffusion model. [3] For the hierarchical ZSM-5 sample, the characteristic length is calculated from the Thiele module value obtained from the point of intersection of measured

effectiveness factor (η) with the theoretical curve. Detailed information can be found in Table S3.

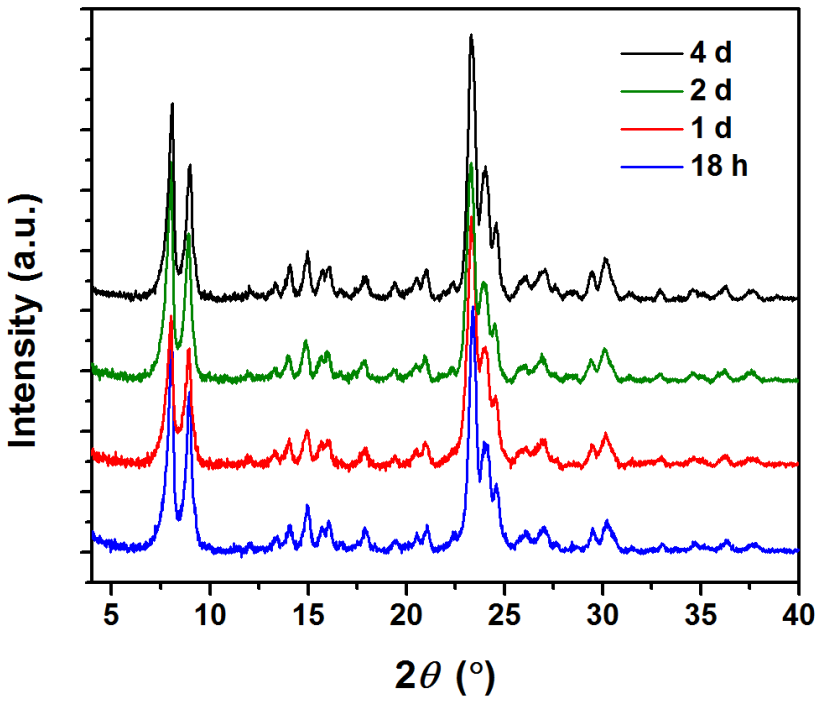

Figure S1. XRD patterns of mesoporous ZSM-5 samples synthesized with 18 h, 1 d, 2 d and 4 d of hydrothermal treatment. (Si/Al = 30).

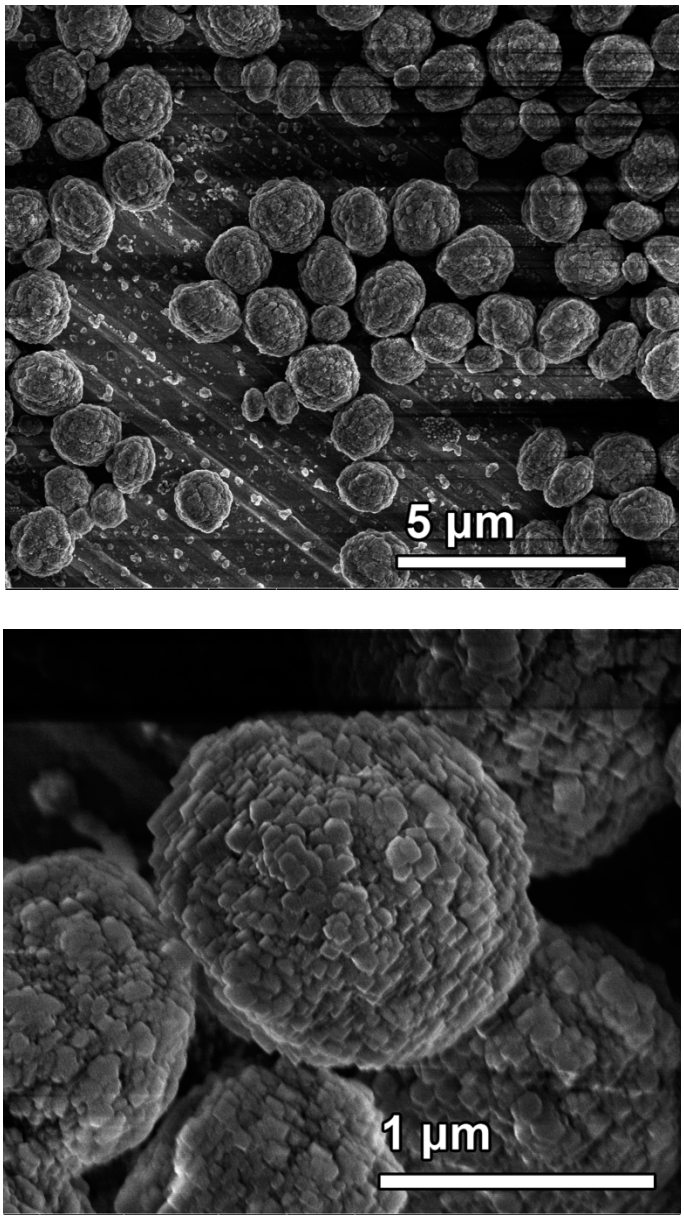

Figure S2. SEM images of mesoporous ZSM-5 samples synthesized with 4 d of hydrothermal treatment (Si/Al = 30) at low magnification (top) and higher magnification (bottom).

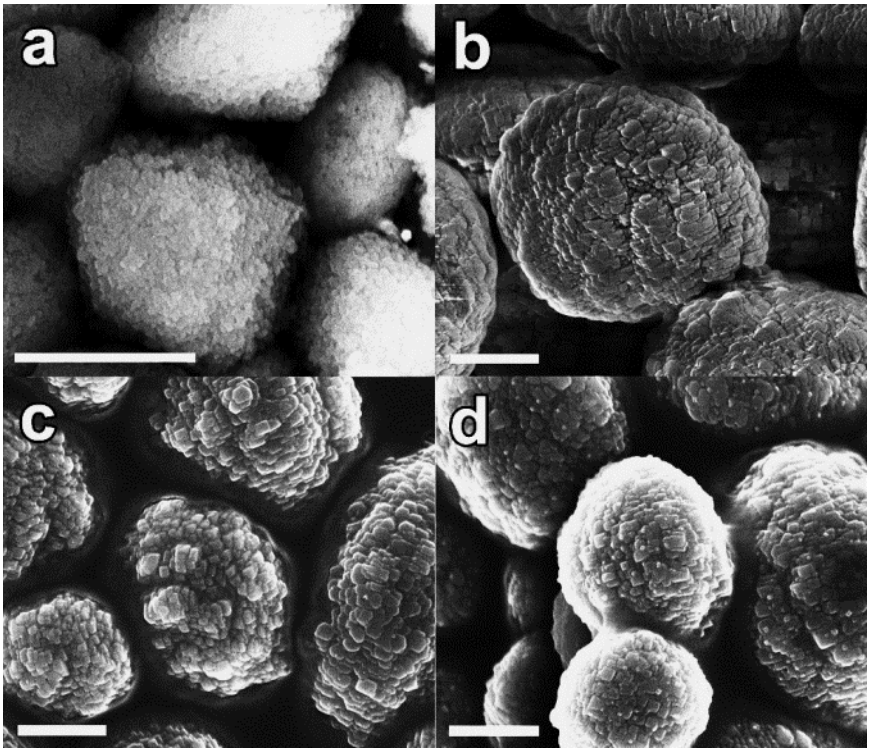

Figure S3. SEM images of mesoporous ZSM-5 samples synthesized with a) 18 h, b) 1 d, c) 2 d and d) 4 d of hydrothermal treatment (Si/Al = 30). Scale bar is 500 nm.

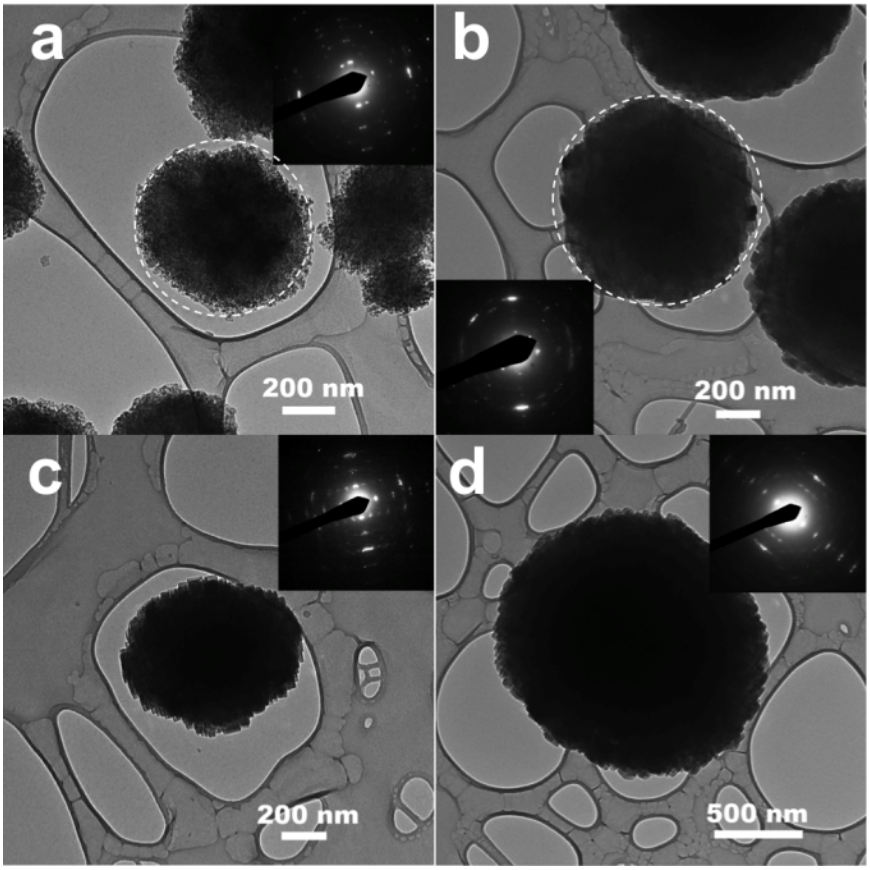

Figure S4. TEM images and SAED patterns (inset) of mesoporous ZSM-5 samples synthesized with a) 18 h, b) 1 d, c) 2 d and d) 4 d of hydrothermal treatment (Si/Al = 30). White dashed circles indicate the actual selected area for the electron diffraction.

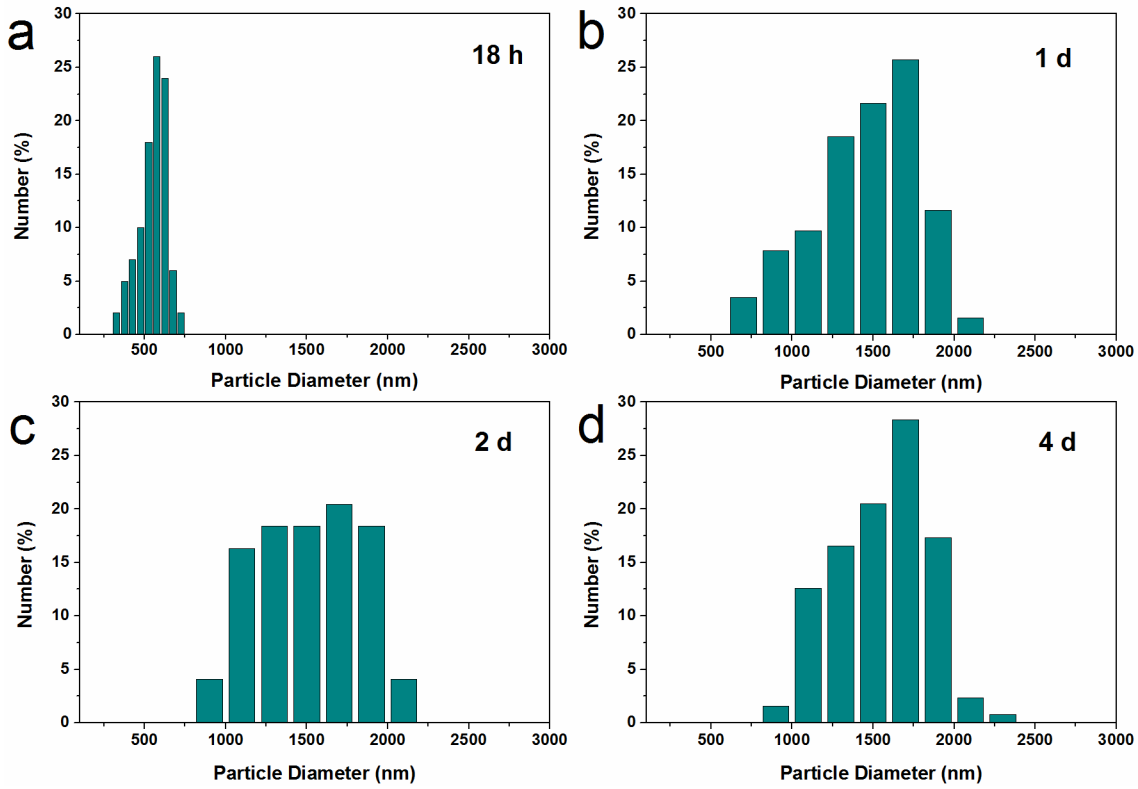

Figure S5. Particle size distribution of mesoporous ZSM-5 samples measured from SEM: a) 18 h, b) 1 d, c) 2 d and d) 4 d of hydrothermal treatment with Si/Al ratio of 30.

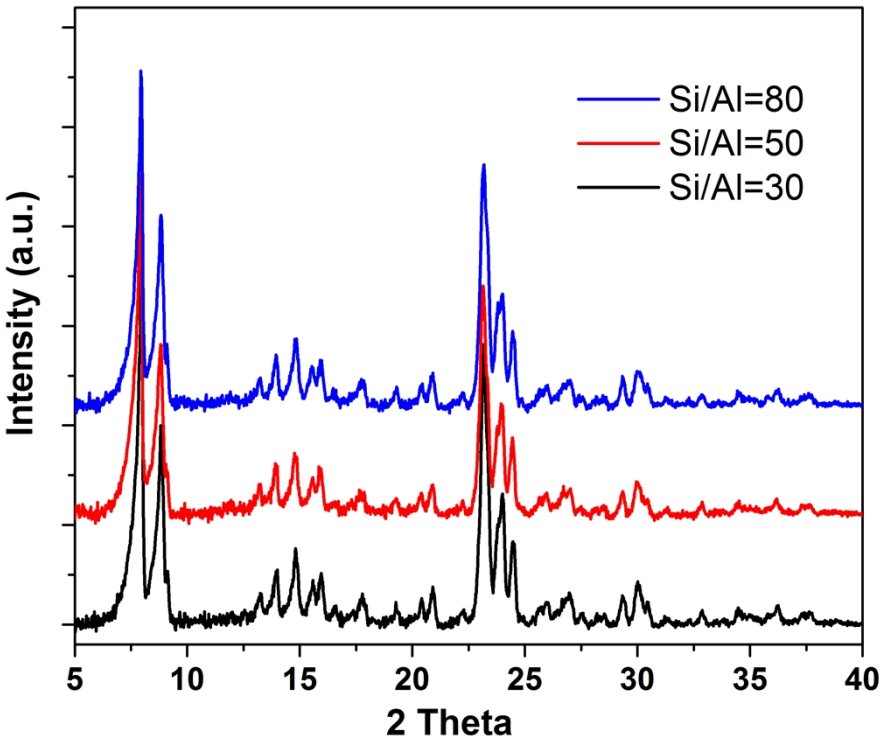

Figure S6. XRD patterns of mesoporous ZSM-5 samples with different Si/Al ratios. The crystallization time is 1d.

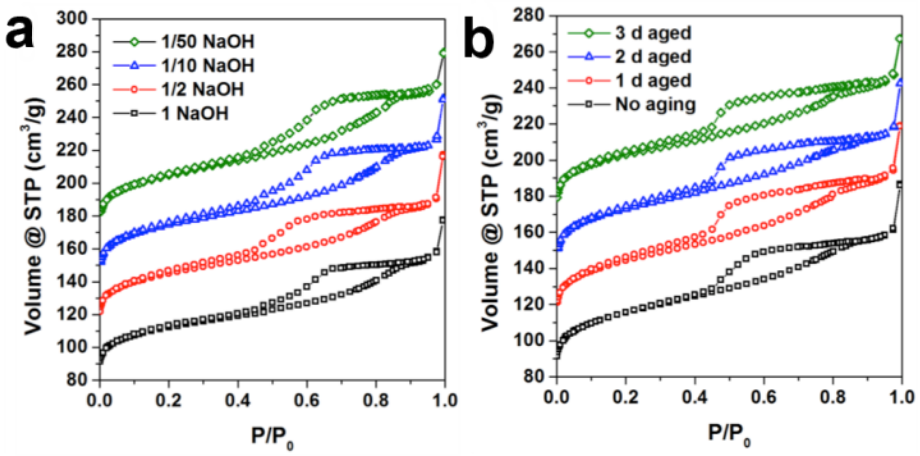

Figure S7. N_2 adsorption/desorption isotherms of mesoporous ZSM-5 samples with different a) NaOH concentration and b) aging time Si/Al = 30. See Table S1 for detailed sample information.

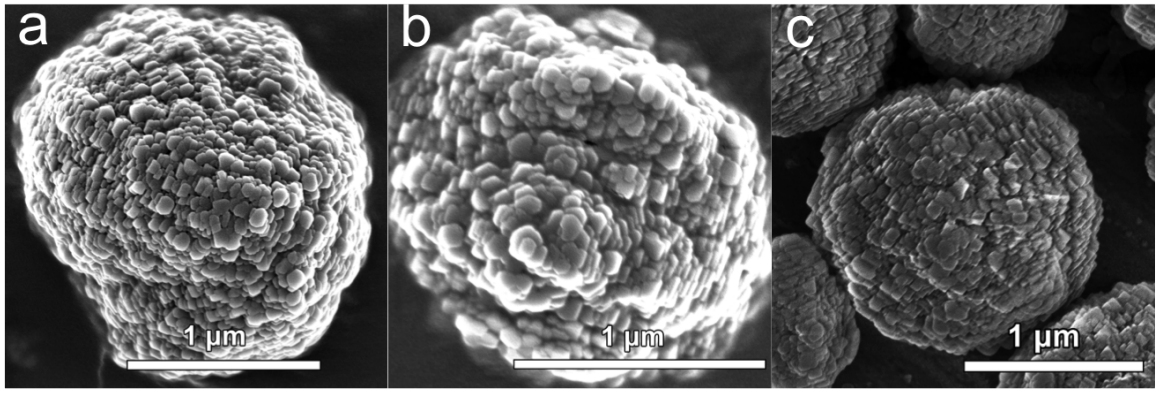

Figure S8. SEM images of mesoporous ZSM-5 samples with less amount of NaOH: a) 1/2 NaOH (a fraction of the amount in a typical run); b) 1/10 NaOH; c) 1/50 NaOH.

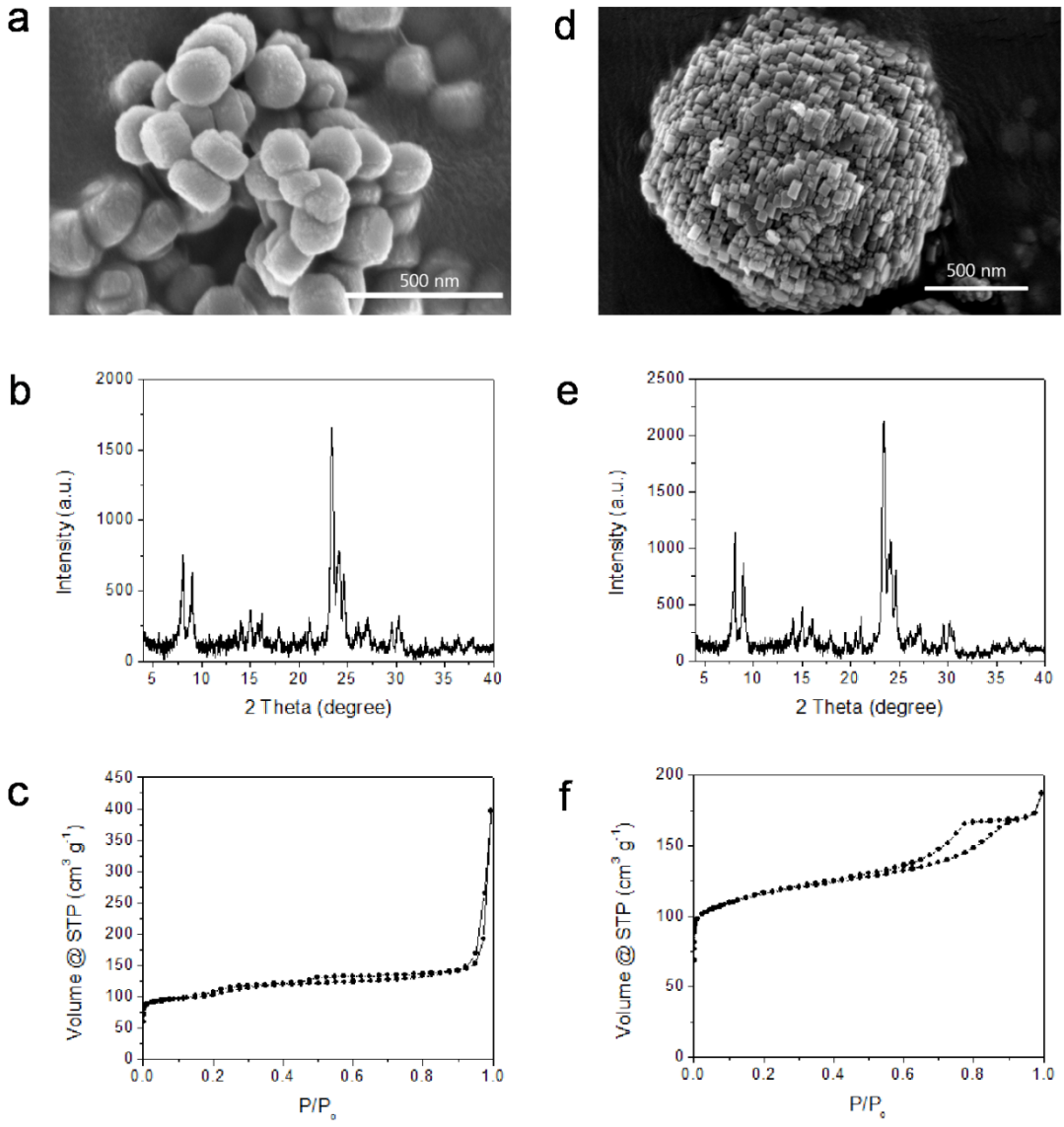

Figure S9. SEM images (a and d), XRD patterns (b and e) and N_2 adsorption/desorption isotherms (c and f) at 77 K of ZSM-5 samples obtained with TEOS and fumed silica as the silicon source, respectively.

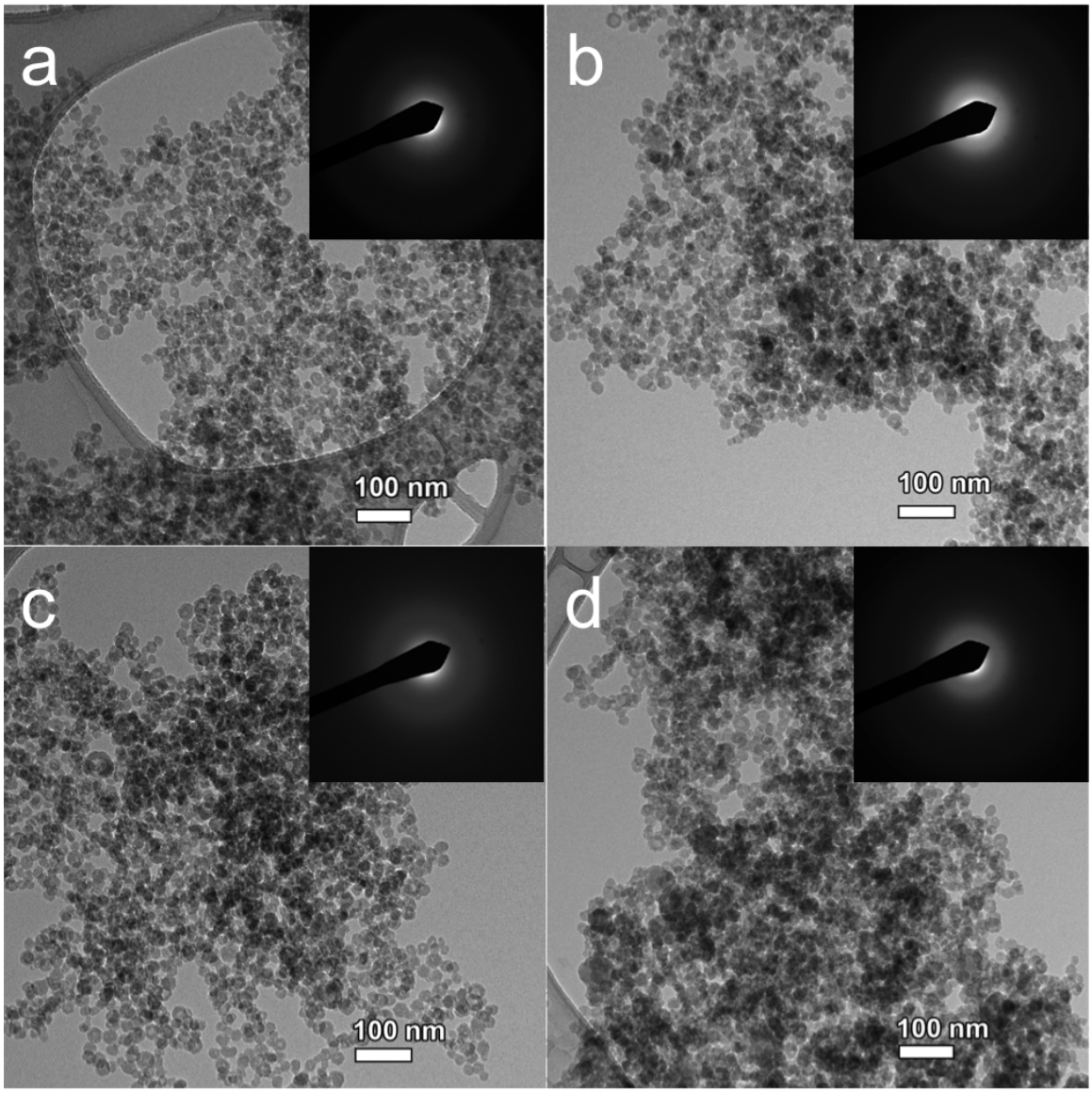

Figure S10. TEM images and SAED patterns (insets) of the precursors extracted from synthetic sol at different time: a) 3 h, b) 6 h, c) 9 h, and d) 13 h.

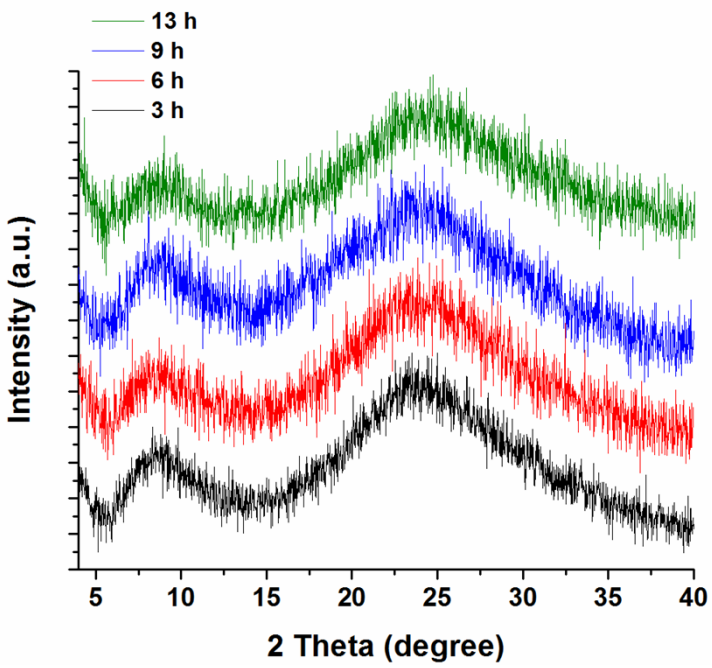

Figure S11. XRD patterns of the precursors extracted from synthetic sol at different time.

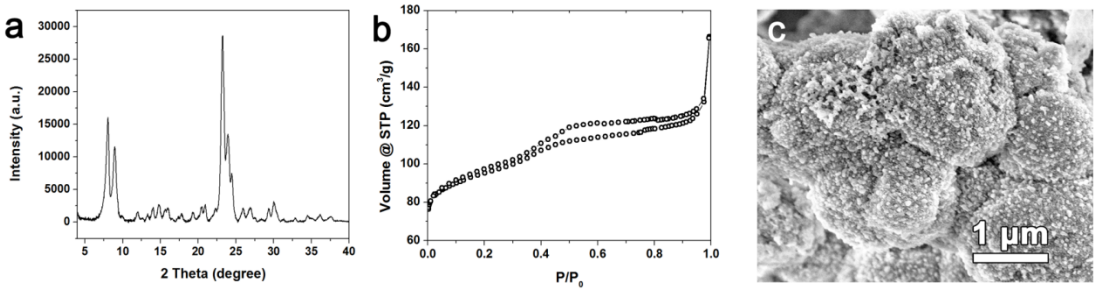

Figure S12. a) XRD pattern, b) N_2 adsorption/desorption isotherm and c) SEM image of the sample obtained from the dry gel conversion for 5 d at 135 °C. The sample for the dry gel conversion was extracted from the synthesis solution after 3 h of synthesis.

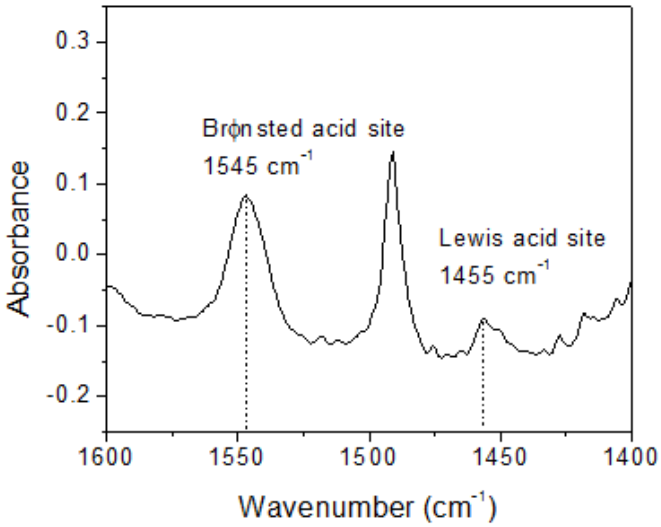

Figure S13. FT-IR spectrum of mesoporous ZSM-5 (Si/Al = 30) after the adsorption of pyridine on the sample. Compared with the bond at 1545 cm^{-1} (Brønsted acid site), the bond associated with Lewis acid site (1455 cm^{-1}) is much lower, indicating most of Al atoms are in the framework.

Table S1. Synthesis conditions and textual properties of the synthesized ZSM-5 samples.

Si/Al	Si source	Crystallization time (h)	Aging time (d)	NaOH	S_{BET} (m^2/g) [a]	$S_{ext.}$ (m^2/g) [b]	$V_{mic.}$ (cm^3/g) [b]	$V_{meso.}$ (cm^3/g) [c]	V_{total} (cm^3/g) [d]
30	Ludox HS40	18	0	1	464.4	224.7	0.099	0.042	0.281
30	Ludox HS40	21	0	1	458.1	234.9	0.093	0.109	0.247
30	Ludox HS40	24	0	1	438.1	187.9	0.102	0.100	0.244
30	Ludox HS40	48	0	1	429.4	166.2	0.106	0.091	0.240
30	Ludox HS40	96	0	1	413.2	169.5	0.099	0.073	0.229
30	Ludox HS40	24	1	1	433.4	190.1	0.099	0.087	0.248
30	Ludox HS40	24	2	1	429.7	184.4	0.100	0.089	0.239
30	Ludox HS40	24	3	1	430.2	182.4	0.101	0.085	0.239
30	Ludox HS40	48	0	1/2	439.6	176.0	0.107	0.095	0.243
30	Ludox HS40	48	0	1/10	436.2	183.8	0.103	0.109	0.252
30	Ludox HS40	48	0	1/50	435.2	182.8	0.103	0.119	0.256
50	Ludox HS40	24	0	1	433.1	145.8	0.115	0.051	0.200
80	Ludox HS40	24	0	1	454.0	148.5	0.122	0.052	0.202
30	TEOS	48	0	1	349.2	131.2	0.101	0.026	0.201
30	Fumed silica	48	0	1	432.5	170.5	0.110	0.090	0.243

[a] Calculated from P/P_0 range of 0.05 - 0.25 using BET equation.

[b] Calculated from *t*-plot method.

[c] Calculated from α_s-plot method.

[d] Calculated from the amount adsorbed at P/P_0= 0.975.

Table S2 Comparison of composition of ZSM-5 syntheses from clear solutions.

No.	H_2O/SiO_2	Na_2O/Al_2O_3	SiO_2/TPAOH	Si/Al	Si source	Product	Ref.
1	19.2	0.4	2.78	50	TEOS	Nano ZSM-5	Zeolites 1995, 15, 611.
2	60	0.4	2.78	50	TEOS	Nano ZSM-5	Zeolites 1995, 15, 611.
3	60	1	8.33	25	TEOS	Meso ZSM-5	Ind. Eng. Chem. Res. 2011, 50, 11872–11878
4	10.8	0	2.80	30	TEOS	Nano ZSM-5	Microporous Mesoporous Mater. 2000, 39, 135.
5	12	0.16	2.78	25	TEOS	Nano ZSM-5	Langmuir 2004, 20, 8301.
6	15	0	5.45	30	TEOS	Nano ZSM-5	Microporous Mesoporous Mater. 2004, 75, 41.
7	16.44	0.017-0.84	4	30	Ludox HS40	Meso-ZSM-5	This work

Table S3. Acid site concentration of the ZSM-5 samples

Catalysts	Si/Al [a] (ICP)	Total Brønsted acid sites [b] ([mmol H^+]·g^{-1})	External Brønsted acid sites [c] ([mmol H^+]·g^{-1})	Internal Brønsted acid sites [d] ([mmol H^+]·g^{-1})	$f_{B,ext}$ [e] (%)
200 nm ZSM-5	32	0.50	0.015	0.482	2.9
Mesoporous ZSM-5	30	0.53	0.039	0.494	7.3
3DOm-i ZSM-5	32	0.50	0.045	0.453	9.1

[a] Determined from the elemental analysis (ICP-OES, Analytical Geochemistry Lab, University of Minnesota).

[b] Determined by IPA-TPD.

[c] Determined by CLD-TPD.

[d] Internal Brønsted acid sites = Total Brønsted acid sites - External Brønsted acid sites.

[e] The fraction of external Brønsted acid sites = Internal Brønsted acid sites/Total Brønsted acid sites.

Table S4. Reaction rate constant and Thiele modules analysis for benzyl alcohol self-etherification with ZSM-5 catalysts.

Catalysts	Si/Al	Reaction rate constant K_{app} (10^{-6} Ls^{-1})[$molH^{+}$]$^{-1}$	Effectiveness factor η	Thiele modules ϕ	Diffusion length x_p (nm)
200 nm ZSM-5 [a]	32	66.2	0.093	12.20	100
Mesoporous ZSM-5	30	697	0.211	/	/
3DOm-i ZSM-5 [a]	32	783.1	0.349	2.00	17
SPP MFI [b]	75	854	0.83	0.06	1.0
SPP MFI [b]	253	820.7	0.80	0.03	1.0
Pillared MFI [b]	69	1398	1.36	0.10	1.6
1.4 μm MFI [b]	30	38.5	0.038	21	200
17 μm MFI [b]	28	1.05	0.001	997	8500

[a] The data was from ref. 7.

[b] The data was from ref. 6.

Table S5. Parameters (D_{eff}/R^2 and L) extracted from ZLC desorption curves of three zeolite samples.

Temperature (K)	200 nm ZSM-5		Mesoporous ZSM-5		3DOm-i ZSM-5	
	D_{eff}/R^2 (s^{-1})	L	D_{eff}/R^2 (s^{-1})	L	D_{eff}/R^2 (s^{-1})	L
323	8.35×10^{-5}	189	4.00×10^{-5}	340	2.28×10^{-6}	378
343	1.92×10^{-4}	115	1.02×10^{-4}	203	3.87×10^{-6}	253
363	4.85×10^{-4}	28	3.45×10^{-4}	69	7.82×10^{-6}	92
383	/	/	8.56×10^{-4}	30	/	/

References:

[1] M. Eic, D. M. Ruthven, *Zeolites* **1988**, *8*, 40-45.

[2] Z. Wang, P. Dornath, C.-C. Chang, H. Chen, W. Fan, *Microporous Mesoporous Mater.* **2013**, *181*, 8-16.

[3] R. Aris, in *Elementary Chemical Reactor Analysis*, Courier Dover, Boston, **1989**.