Electronic Supplementary Information (ESI)

Synthesis of high Si hierarchical Beta zeolites without mesoporogen and their catalytic application in the methanol to propene reaction

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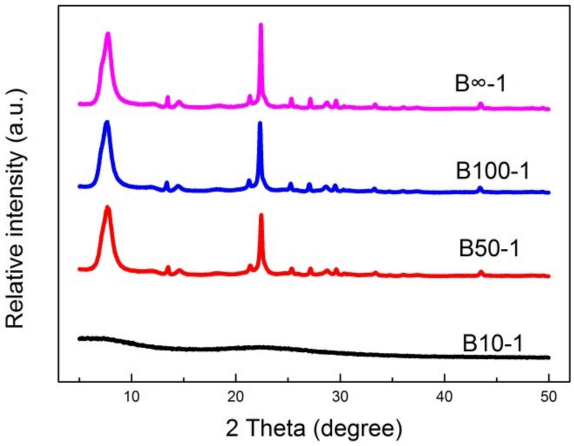

Figure S1 XRD patterns of the samples synthesized with different Si/Al ratios.

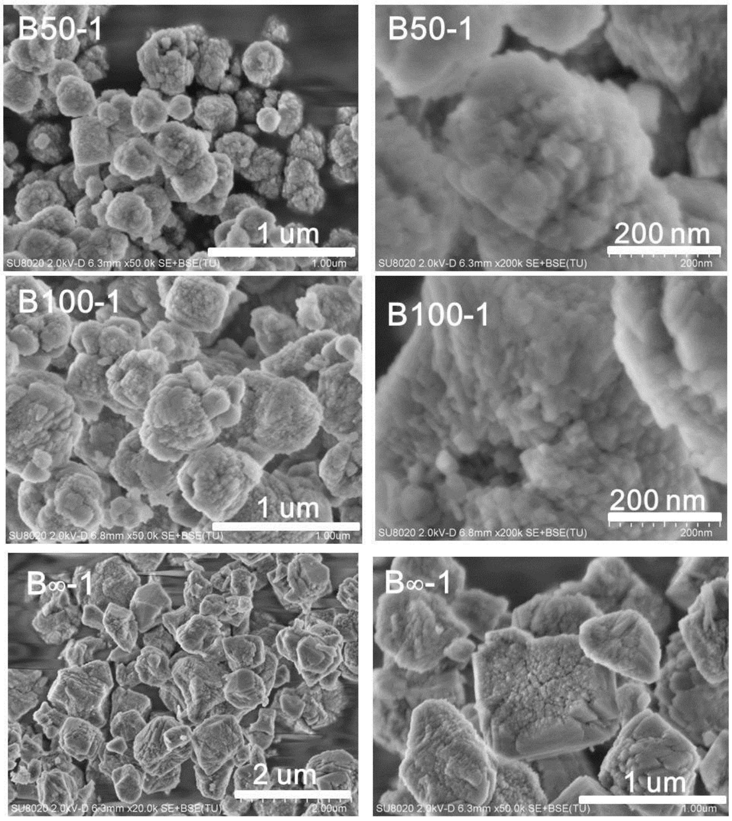

Figure S2 SEM images of the samples synthesized with different Si/Al ratios.

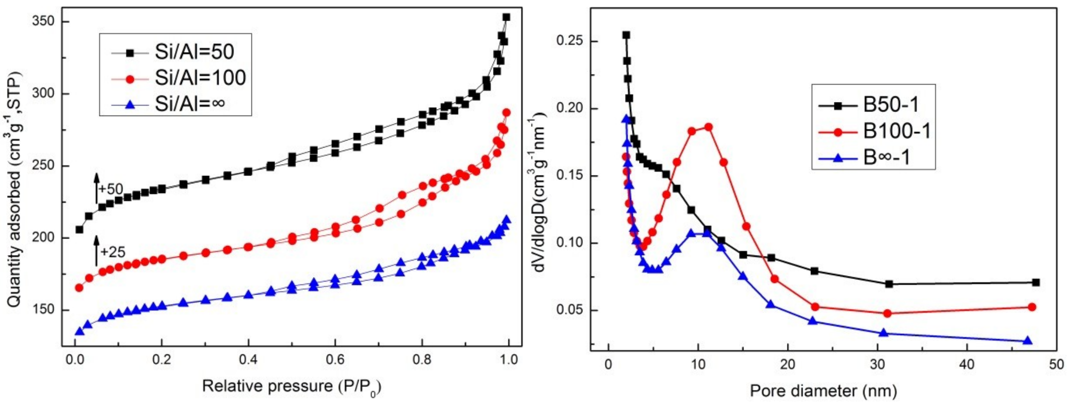

Figure S3 N_2 adsorption-desorption isotherms of the samples synthesized with different Si/Al ratios and the corresponding pore size distribution curves from the adsorption branches.

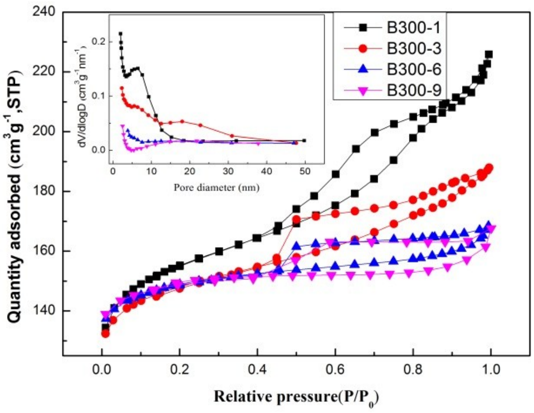

Figure S4 N_2 adsorption-desorption isotherms of the samples synthesized with different H_2O/SiO_2 ratios and the corresponding pore size distribution curves from the adsorption branches.

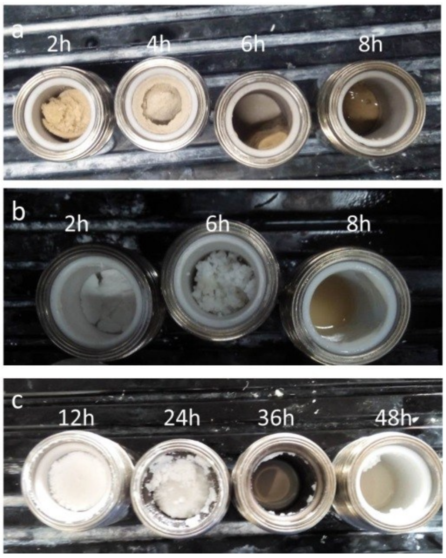

Figure S5 The photos of the crystallization products before separation and washing (a) H_2O/SiO_2=1; (b) H_2O/SiO_2=3; (c) H_2O/SiO_2=6.

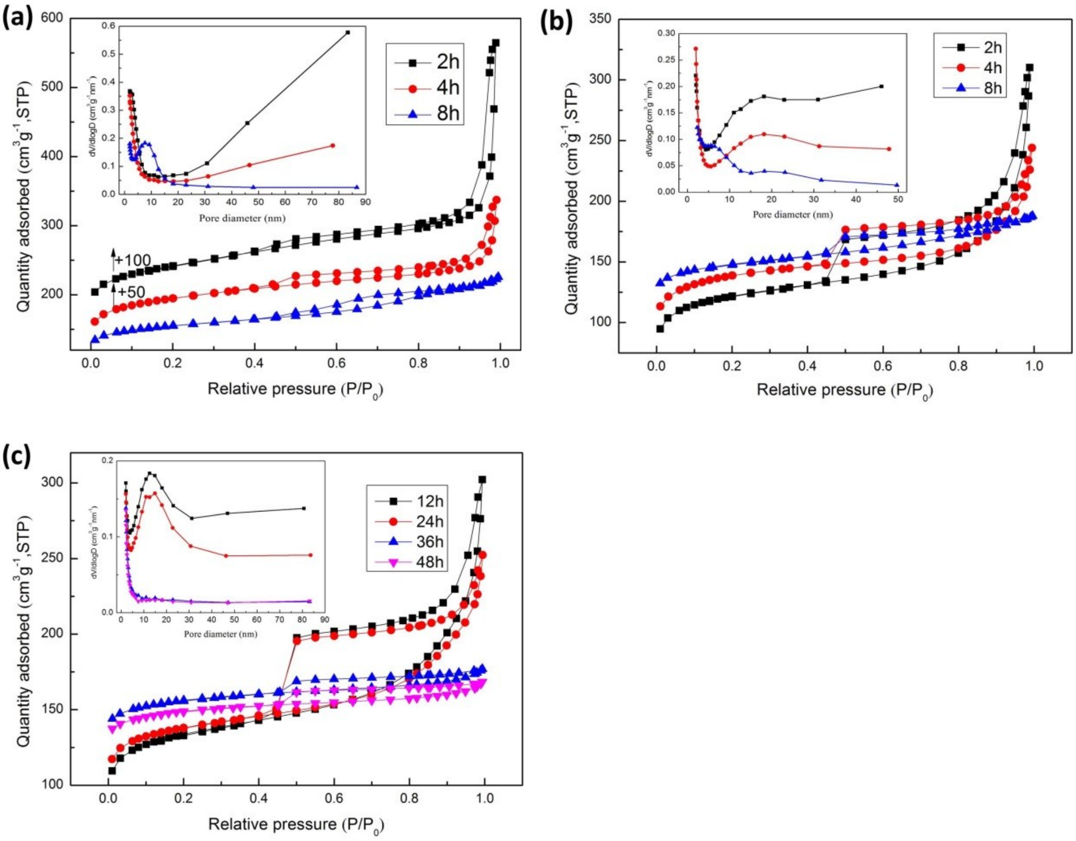

Figure S6 The N_2 adsorption-desorption isotherms and pore size distribution curves from the adsorption branches of the samples synthesized with different crystallization time and H_2O/SiO_2 ratio. (a): H_2O/SiO_2=1, (b): H_2O/SiO_2=3, (c): H_2O/SiO_2=6.

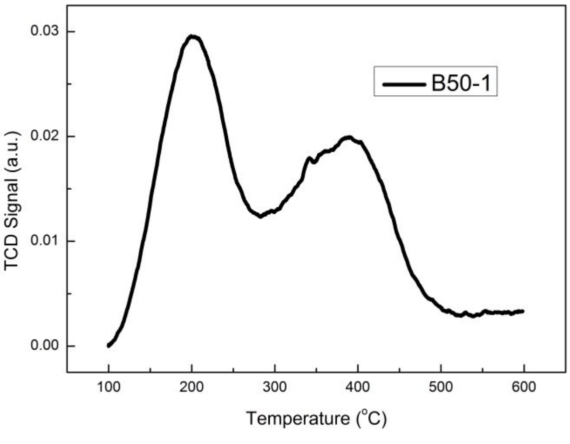

Figure S7 NH_3-TPD curve of sample B50-1.

Table S1 Texture properties of the samples synthesized with different H2O/SiO2 ratios and crystallization times.[a]

H_2O/SiO_2	t [b]/h	R [c] /%	Solid yields/%	Si/Al [d]	Surface area [e] (m^2/g)			Pore volume [f] (cm^3/g)	
					S_{BET}	S_{micro}	S_{ext}	V_{micro}	V_{ext}
1	2	0	92.6	280	480	209	271	0.10	0.32
	4	19.1	89.3	269	481	260	221	0.13	0.20
	8	89.9	90.0	257	539	392	147	0.19	0.14
3	2	0	94.3	270	402	244	158	0.12	0.25
	4	63.7	92.1	263	455	299	156	0.15	0.17
	8	96.8	93.7	284	474	371	102	0.18	0.11
6	12	0	95.3	240	438	292	146	0.14	0.23
	24	48.3	90.8	231	448	324	124	0.16	0.18
	36	106.4	87.6	237	501	419	82	0.21	0.06
	48	111.2	89.6	228	447	399	78	0.25	0.05

[a]: The molar ratio of the initial gel: $1SiO_2$:1/$600Al_2O_3$:0.5TEAOH:0.45HF:xH_2O; [b]: Crystallization time; [c]: Relative crystallinity calculated based on the intensity of the characteristic peaks at 7.8° and 22.4°; [d]: Determined by XRF; [e]: S_{BET}: BET surface area, S_{micro}: t-plot external surface area, S_{ext}=S_{BET}-S_{micro}; [f]: V_{micro}: t-plot microporous volume, V_{ext}=V_{total}-V_{micro} (V_{total} is evaluated at P/P_0 = 0.98)

Table S2 Methanol conversion and product selectivities on sample B50-1. [a]

TOS (min)	Conversion (%)	Selectivity/%						$C_3^=/C_2^=$	HTI[b]
		C_{1-4}^0	$C_2^=$	$C_3^=$	$C_4^=$	C_{5+}^N	Aro		
5	100.0	31.3	14.4	18.8	8.3	2.5	24.8	1.3	0.89
54	98.2	7.0	1.2	2.5	1.3	1.1	86.9	2.1	0.19
103	66.0	18.3	1.1	0.6	0.3	1.6	78.1	0.5	0.26

[a] reaction condition: 550 °C, methanol WHSV=4.0 h^{-1}. [b] HTI represents hydrogen transfer index ($C_4^0/C_4^=$)

Part 1 Operating conditions and fitting process for the ^{27}Al MAS NMR spectra of samples B300-1 and B300-6

^{27}Al MQ MAS NMR experiments were performed at a spinning speed of 12 kHz. An rf field of 200 kHz was used for the creation (0Q→±3Q) and the first conversion (±3Q→0Q) pulses. An rf field of 10 kHz was used for the last conversion step (0Q→±1Q), which was the central transition selective soft 90° pulse. A two-dimensional (2D) Fourier transformation followed by a shearing transformation gave a pure absorption mode 2D contour plot.[1-3]

The ^{27}Al MQ MAS NMR spectrum of sample B300-1 was first determined and displayed in Figure S8. According to the literature[4], the representative four slices parallel to the F2 dimension of MQ MAS NMR spectra at selected F1 chemical shift positions were extracted and then fitted to obtain the isotropic chemical shifts (δ_{iso}) and quadrupole interaction constants. The parameters are listed in Table S3. Based on these parameters, the ^{27}Al MAS NMR spectra were fitted by Q mass 1/2 method (Figure 11), in which the different T sites were determined by the isotropic chemical shifts according to the DFT calculations reported by Lercher et al[5].

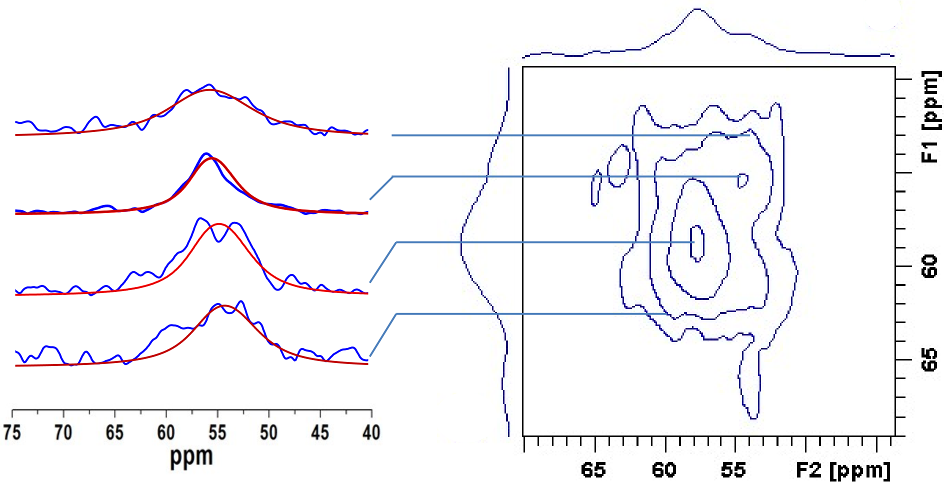

Figure S8. The ^{27}Al MQ MAS NMR spectrum of the calcined sample B300-1 on the right and the representative four slices (blue) parallel to the F2 dimension at selected F1 chemical shift positions with the fitted lines (red) on the left.

Table S3 The ^{27}Al isotropic chemical shift (δ_{iso}) and related parameters of the framework Al species deduced from ^{27}Al MQ MAS NMR spectrum of samples B300-1.

δ_{iso} (ppm)	lb(ppm)[a]	C_Q(kHz)[b]	η_Q[c]
61.5	8.6	3597	0.60
59.0	4.6	2884	0.21
55.6	5.2	3410	0.41
53.7	6.0	3451	0.38

[a]: Line broadening applied on top of the ideal quadrupolar line shapes obtained from the fitting;[b]: C_Q is second order quadrupolar interaction constants; [c]: η_Q is asymmetry parameters.

References

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