

Supporting information for

A versatile mono-quaternary ammonium salt as mesoporegen for the synthesis of hierarchical zeolites

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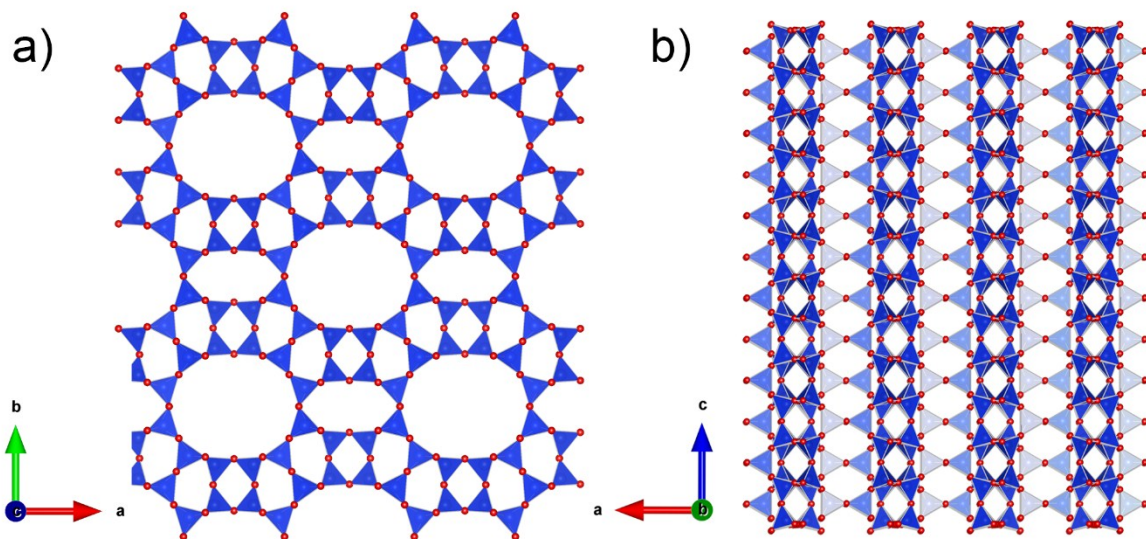


Figure S1. MOR structure and its a) 12 membered ring and b) 8 membered ring side pockets.

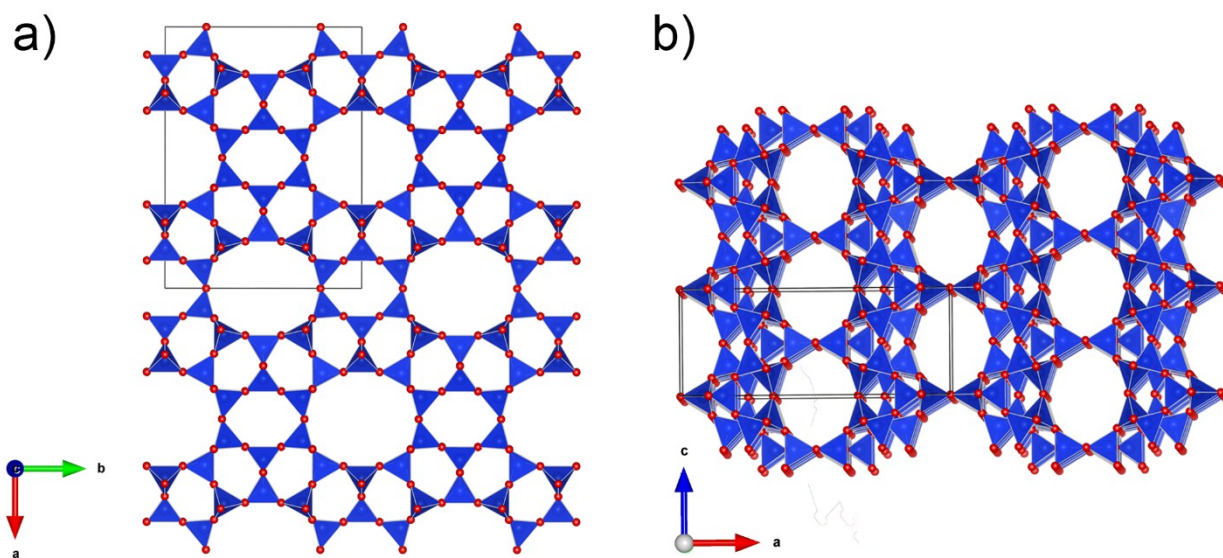


Figure S2. FER structure and its a) 10 membered ring and b) 8 membered ring channels.

Table S1. Textural properties of FER samples synthesized at different SDA concentration.

Zeolite	V_{tot} ($\text{cm}^3 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{ext} ($\text{m}^2 \text{g}^{-1}$)
FER-C	0.16	0.11	0.05	343.1	38.3
FER-0.10	0.30	0.09	0.21	341.2	130.2
FER-0.15	0.33	0.08	0.25	316.3	153.8

V_{tot} total pore volume at $p/p_0 = 0.95$

V_{micro} micropore volume calculated by the *t*-plot method

V_{meso} mesopore volume calculated by the *BJH* method

S_{BET} Brunauer-Emmett-Teller (BET) surface area ($p/p_0 = 0.05-0.25$)

S_{ext} external surface area determined by the *t*-plot method.

Table S2. Properties of synthesized samples determined by ICP-OES analysis and ^{27}Al MAS NMR.

Zeolite	Si/Al (ICP)	Al distribution* (%)	
		tetra Al ^{IV}	octa Al ^{VI}
FER-C	9.9	78.7	21.3
FER-0.10	9.4	72.1	27.9
FER-0.15	10.5	71.6	28.4

* Al tetra determined by integration of NMR signal between 20 and 100 ppm; Al-octa determined by integration of NMR signal between 20 and -50 ppm.

Table S3. Acidic properties of the zeolites determined by IR spectroscopy of adsorbed pyridine and H_2 chemisorption.

Zeolite	BAS (mmol g^{-1})			LAS (mmol g^{-1})		
	150 °C	300 °C	500 °C	150 °C	300 °C	500 °C
FER-C	0.45	0.45	0.33	0.06	0.06	0.09
FER-0.10	0.36	0.32	0.20	0.07	0.06	0.08
FER-0.15	0.31	0.26	0.16	0.07	0.06	0.07

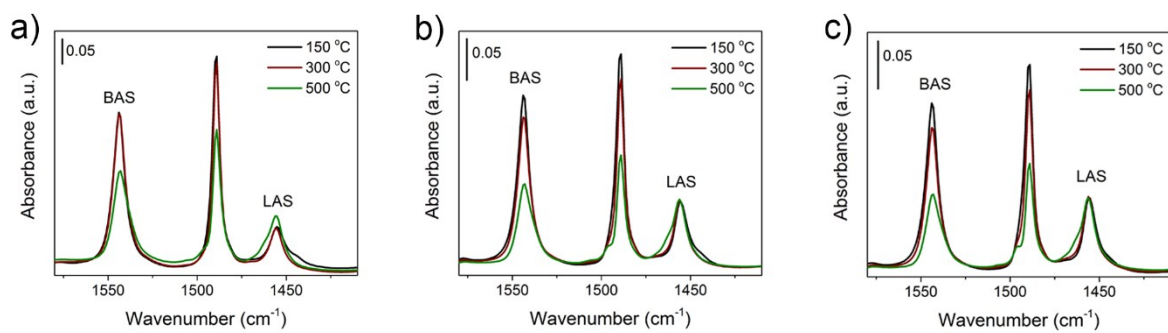


Figure S3. Infrared spectra of pyridine adsorbed on the proton forms of a) FER-C, b) FER-0.10 and c) FER-0.15 sample after evacuation at 150 °C, 300 °C and 500 °C, IR spectra were recorded at 150 °C.

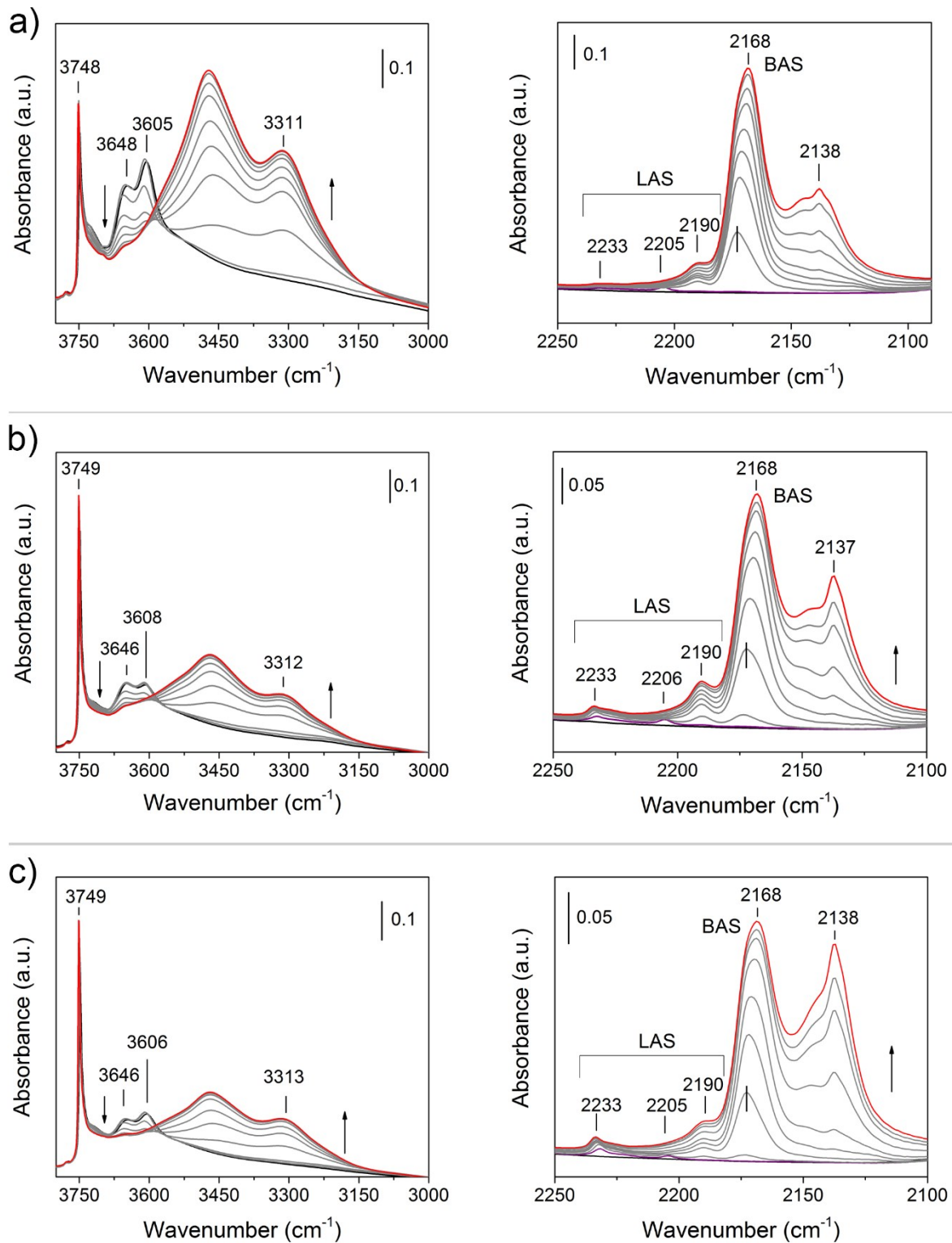


Figure S4. (Left) hydroxyl and (right) CO stretch regions of FTIR spectra of a) FER-C, b) FER-0.10 and c) FER-0.15 as a function of the CO coverage.

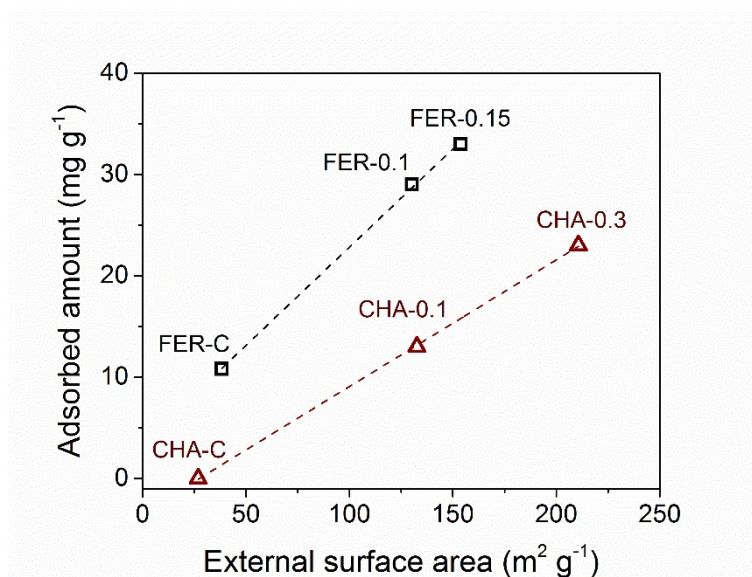


Figure S5. Correlation between the external surface area of FER (black) and CHA (red) samples and initial uptake of benzene after 2 minutes of He/benzene exposure.

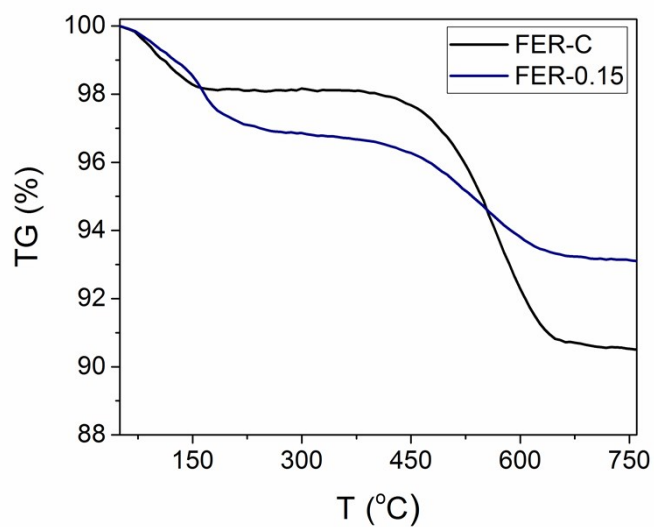


Figure S6. Thermogravimetric analysis (TGA) of the spent FER catalysts after 108 h of Butanol conversion. The weight losses for FER-C and FER-0.15 are 9.5 % and 6.9 %, respectively.

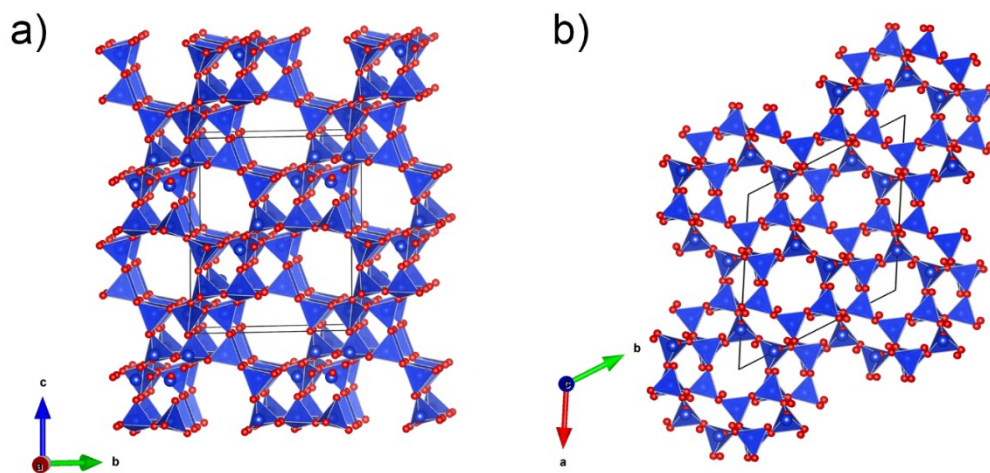


Figure S7. CHA structure a) viewed along a -axis and b) its projection along $[001]$.

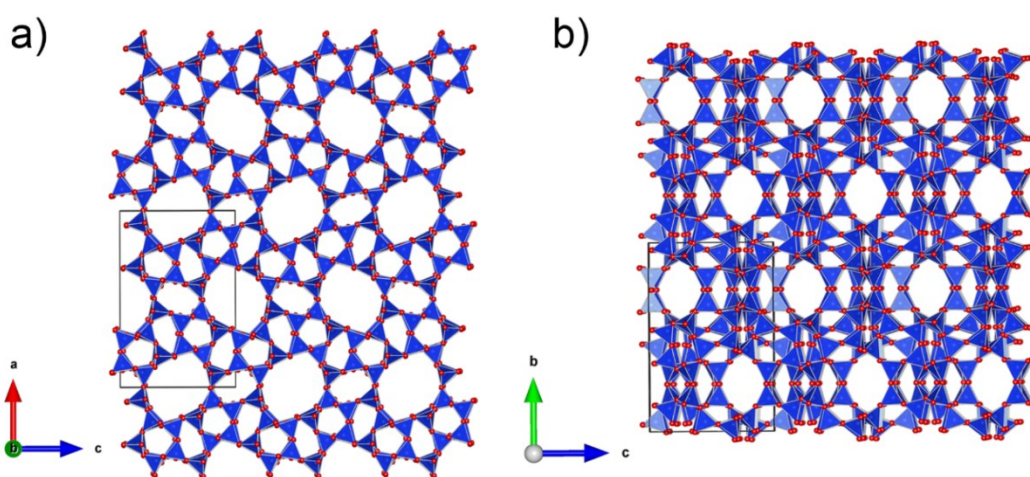


Figure S8. MFI structure a) viewed along b -axis and b) its projection along $[100]$.

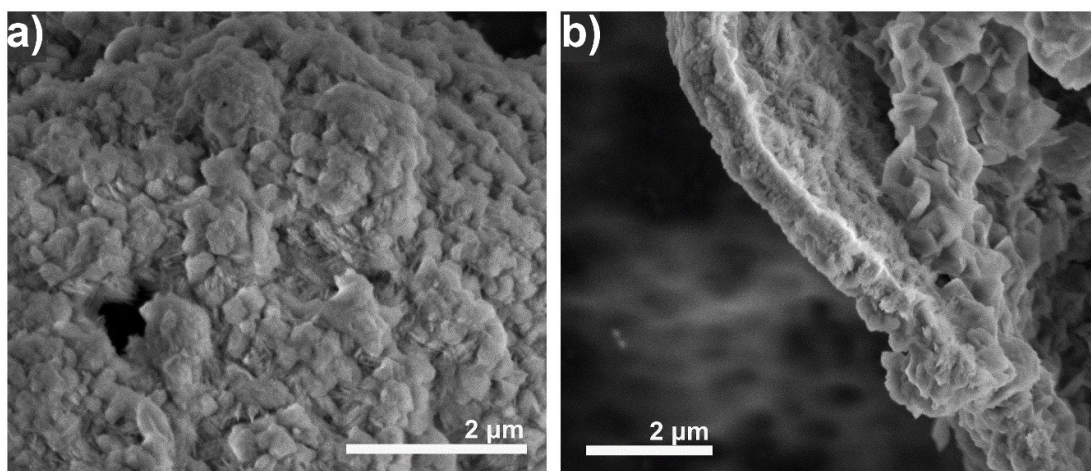


Figure S9. SEM images of calcined MFI zeolites: a) MFI-0.3 and b) MFI-0.4.

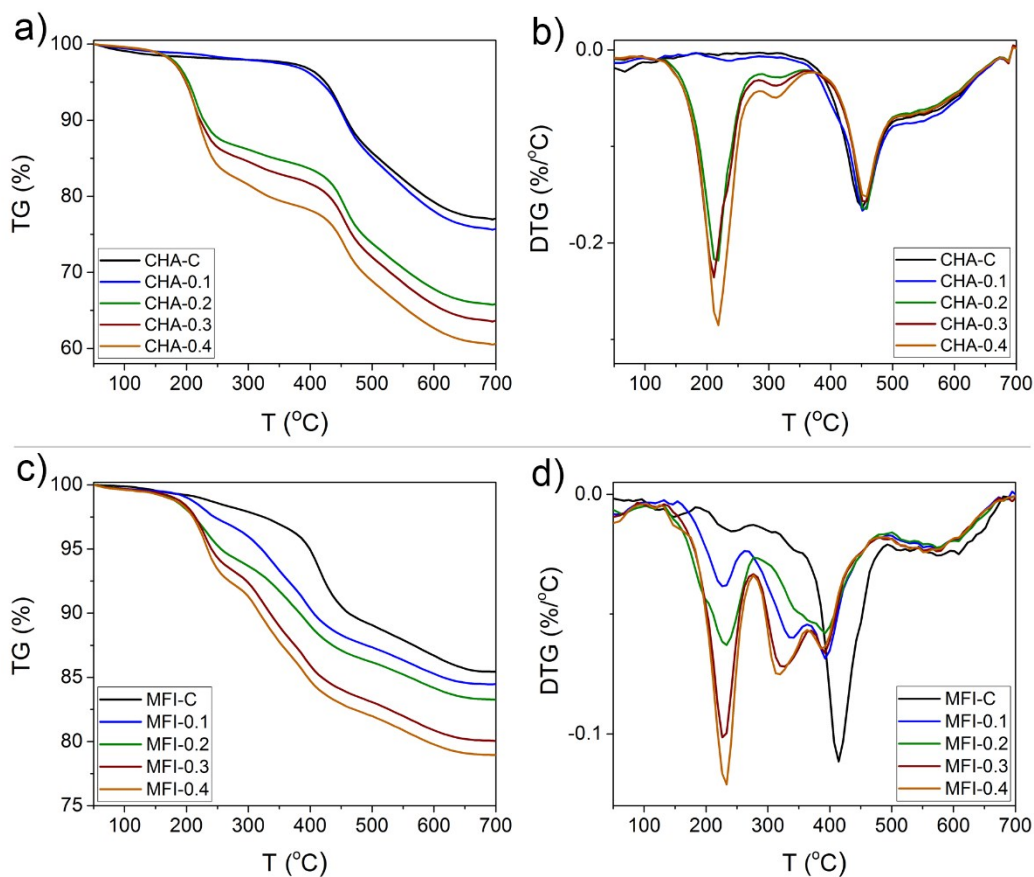


Figure S10. a,c) Thermogravimetric analysis (TGA) and b,d) derivative thermogravimetry (DTG) of the as-synthesized CHA (a,b) and MFI (c,d) samples obtained at different concentration of C₁₆NMP. The weight losses for CHA-C, CHA-0.1, CHA-0.2, CHA-0.3 and CHA-0.4 are 22.9 %, 24.2 %, 34.1 %, 36.3 % and 39.3 %, respectively. The weight losses for MFI-C, MFI-0.1, MFI-0.2, MFI-0.3 and MFI-0.4 are 14.6 %, 15.5 %, 16.7 %, 19.9 % and 21.0 %, respectively.

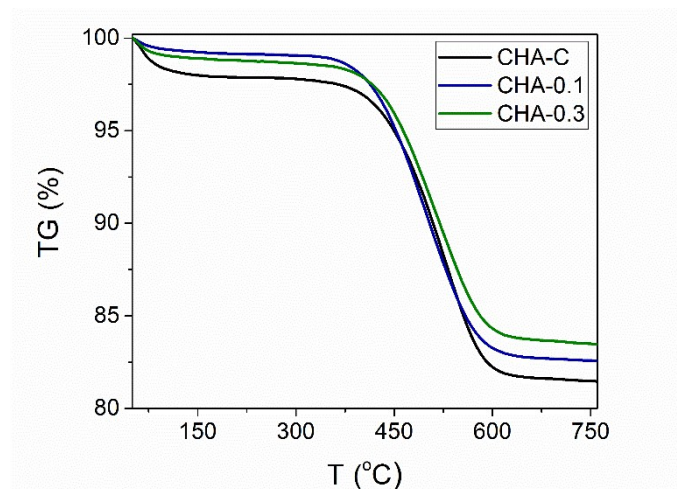


Figure S11. Thermogravimetric analysis (TGA) of the spent CHA catalysts after 16.8 h of methanol conversion. The weight losses for CHA-C, CHA-0.1 and CHA-0.3 are 18.6 %, 17.4 % and 16.5 %, respectively.

Table S4. Textural properties of CHA and MFI samples synthesized at different SDA concentration.

Zeolite	V_{tot} ($\text{cm}^3 \text{g}^{-1}$)	V_{micro} ($\text{cm}^3 \text{g}^{-1}$)	V_{meso} ($\text{cm}^3 \text{g}^{-1}$)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	S_{ext} ($\text{m}^2 \text{g}^{-1}$)
CHA-C	0.28	0.25	0.03	736.6	26.9
CHA-0.1	0.31	0.19	0.11	672.3	132.6
CHA-0.2	0.33	0.19	0.13	689.5	166.9
CHA-0.3	0.36	0.18	0.17	668.1	210.7
CHA-0.4	0.43	0.18	0.24	682.1	180.4
CHA-0.5	0.44	0.18	0.24	679.6	162.4
MFI-C	0.18	0.16	0.02	317.1	6.6
MFI-0.1	0.25	0.13	0.13	315.8	61.0
MFI-0.2	0.28	0.12	0.17	317.4	104.5
MFI-0.3	0.25	0.10	0.15	316.4	118.2

V_{tot} total pore volume at $p/p_0 = 0.95$

V_{micro} micropore volume calculated by the *t*-plot method

V_{meso} mesopore volume calculated by the *BJH* method

S_{BET} Brunauer-Emmett-Teller (BET) surface area ($p/p_0 = 0.05-0.25$)

S_{ext} external surface area determined by the *t*-plot method.

Table S5. Physico-chemical properties of CHA and MFI zeolites determined by ICP-OES elemental analysis and ^{27}Al -, ^1H MAS NMR spectroscopy.

Zeolite	Si/Al (ICP)	Al distribution ^a (%)		BAS ^b (mmol g ⁻¹)
		tetra Al ^{IV}	octa Al ^{VI}	
CHA-C	18.7	88.3	11.7	0.70
CHA-0.1	19.8	81.4	18.6	0.40
CHA-0.3	21.2	86.8	13.2	0.61
CHA-0.4	23.2	83.8	16.2	-
MFI-C	38.6	90.2	9.8	0.37
MFI-0.1	40.7	86.8	13.2	0.30
MFI-0.2	40.9	89.3	10.7	0.27

^a Al tetra determined by integration of NMR signal between 20 and 100 ppm; Al-octa determined by integration of NMR signal between 20 and -50 ppm

^b density of Brønsted acid sites calculated from ^1H MAS NMR spectra.

Table S6. Lifetime, product selectivity of MTH reaction after 2 h time on stream over CHA samples.

Zeolite	t_{50} ^a (h)	Selectivity (%)				
		C ₂	C ₂ ⁼	C ₃	C ₃ ⁼	C ₄ -C ₆
CHA-C	5.2	1.0	42.4	1.9	37.6	17.1
CHA-0.1	12.0	0.9	43.1	0.4	39.4	16.2
CHA-0.3	14.0	1.0	43.7	0.3	39.0	16.0

^a lifetime taken as time to reach methanol conversion of 50 %.

Table S7. Lifetime, product selectivity of MTH reaction after 2 h time on stream over MFI samples.

Zeolite	t_{50} ^a (h)	Selectivity (%)					
		C ₂	C ₂ ⁼	C ₃	C ₃ ⁼	C ₄₊	Aromatics
MFI-C	26.0	0.2	8.6	1.8	35.9	50.3	3.2
MFI-0.1	75.9	0.2	7.6	1.7	33.5	52.7	4.3
MFI-0.2	63.7	0.2	7.8	2.2	31.4	53.9	4.5

^a lifetime taken as time to reach methanol conversion of 50 %.