Supporting information for

A versatile mono-quaternary ammonium salt as mesoporogen 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 | $V_{\text{tot}}$ (cm$^3$ g$^{-1}$) | $V_{\text{micro}}$ (cm$^3$ g$^{-1}$) | $V_{\text{meso}}$ (cm$^3$ g$^{-1}$) | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | $S_{\text{ext}}$ (m$^2$ 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                         |

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

$V_{\text{micro}}$, micropore volume calculated by the $t$-plot method

$V_{\text{meso}}$, mesopore volume calculated by the BJH method

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

$S_{\text{ext}}$, 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 C\textsubscript{16}NMP. 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 | $V_{\text{tot}}$ (cm$^3$ g$^{-1}$) | $V_{\text{micro}}$ (cm$^3$ g$^{-1}$) | $V_{\text{meso}}$ (cm$^3$ g$^{-1}$) | $S_{\text{BET}}$ (m$^2$ g$^{-1}$) | $S_{\text{ext}}$ (m$^2$ 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                         |

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

$V_{\text{micro}}$ micropore volume calculated by the $t$-plot method

$V_{\text{meso}}$ mesopore volume calculated by the BJH method

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

$S_{\text{ext}}$ 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-,$^1$H MAS NMR spectroscopy.

| Zeolite  | Si/Al (ICP) | Al distribution<sup>a</sup> (%) | BAS<sup>b</sup> (mmol g<sup>-1</sup>) |
|----------|-------------|----------------------------------|-------------------------------------|
|          |             | tetra Al<sup>IV</sup> | octa Al<sup>VI</sup> |                          |
| 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                   |

<sup>a</sup> 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

<sup>b</sup> density of Brønsted acid sites calculated from $^1$H MAS NMR spectra.

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

| Zeolite  | $t_{50}$<sup>a</sup> (h) | Selectivity (%) |   |   |   |   |
|----------|--------------------------|-----------------|---|---|---|---|
|          |                          | C<sub>2</sub>  | C<sub>2</sub><sup>+</sup> | C<sub>3</sub> | C<sub>3</sub><sup>+</sup> | C<sub>4+</sub> |
| 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 |

<sup>a</sup> 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  | $t_{50}$<sup>a</sup> (h) | Selectivity (%) |   |   |   |   |
|----------|--------------------------|-----------------|---|---|---|---|
|          |                          | C<sub>2</sub>  | C<sub>2</sub><sup>+</sup> | C<sub>3</sub> | C<sub>3</sub><sup>+</sup> | C<sub>4+</sub> | 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 |

<sup>a</sup> lifetime taken as time to reach methanol conversion of 50 %.