SUPPORTING INFORMATION

Altering the Arrangement of Framework Al Atoms in MEL Zeolites Using Mixtures of Tetrabutylammonium and Sodium Structure-Directing Agents

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Figure S1. XRD patterns of MEL samples synthesized with TBA⁺ only a) MEL XRD pattern reproduced from Treacy *et al.*¹, b) MEL(C), c) MEL(15,0.0), d) MEL(28,0.0), e) MEL(50,0.0)-1, f) MEL(50,0.0)-2, g) MEL(98,0.0).



Figure S2. XRD patterns of MEL samples synthesized with different Na⁺/TBA⁺ a) MEL XRD pattern reproduced from Treacy *et al.*¹, b) MEL(50, 0.0)-1, c) MEL(50, 0.0)-2, d) MEL(50, 0.1), e) MEL(50,0.3), f) MEL(50, 0.5), g) MEL(50, 1.0), h) MEL(50, 1.5), i) MEL(50, 2.0), j) MEL(50, 2.5), k) MEL(50, 3.0), l) MEL(50, 5.0). MFI impurities yield additional peaks at $2\theta = 23.2^{\circ}$, 23.4, 24.5, and 45.5².





Figure S3. N₂ adsorption-desorption isotherms (77 K) measured for MEL samples synthesized with TBA⁺ only a) MEL(C), b) MEL(28,0.0), c) MEL(50,0.0)-1, d) MEL(50,0.0)-2, e) MEL(98,0.0). Isotherms vertically offset by 200 cm³ g⁻¹.



Figure S4. N₂ adsorption-desorption isotherms (77 K) measured for MEL samples synthesized with different Na⁺/TBA⁺ a) MEL(50, 0.1), b) MEL(50, 0.3), c) MEL(50, 0.5), d) MEL(50, 1.0), e) MEL(50, 1.5), f) MEL(50, 2.0), g) MEL(50, 2.5), h) MEL(50, 5.0). Isotherms vertically offset by 200 cm³ g⁻¹.

Section S.3. SEM Images of MEL Samples



Figure S5. SEM images of a) MEL(50, 0.0)-2, b) MEL(50, 0.5), c) MEL(50, 1.0), d) MEL(50, 1.5), e) MEL(50, 2.0), f) MEL(50, 2.5).



Section S4. H⁺ Site Quantification by NH₃ TPD on MEL Samples

Figure S6. NH₃ TPD profiles for NH₄-form MEL samples synthesized with TBA⁺ only a) MEL(98,0.0), b) MEL(50,0.0)-1, c) MEL(50,0.0)-2, d) MEL(28,0.0).



Figure S7. NH₃ TPD profiles for NH₄-form MEL samples synthesized with different Na⁺/TBA⁺ a) MEL(50, 0.1), b) MEL(50, 0.3), c) MEL(50, 0.5), d) MEL(50, 1.0), e) MEL(50, 1.5), f) MEL(50, 2.5).

Section S.5. ²⁷Al MAS NMR on MEL Samples



Figure S8. ²⁷Al MAS NMR spectra of MEL samples synthesized with TBA⁺ only a) MEL(98,0.0), b) MEL(50,0.0)-1, c) MEL(50,0.0)-2, d) MEL(28,0.0).



Figure S9. ²⁷Al MAS NMR spectra of MEL samples synthesized with different Na⁺/TBA⁺ a) MEL(50, 0.5), b) MEL(50, 1.0), c) MEL(50, 1.5).

Section S.6. Co²⁺ Ion-Exchange Isotherms for MEL Samples

The conditions for Co²⁺ titration of Al-Al pairs were determined by measuring Co uptake over a range of Co(NO₃)₂ solution molarities (0.25–0.75 M) and temperatures (ambient–353 K). Co uptakes were systematically higher with increasing temperature (Figure 8, main text); however, Co-exchanges performed at 353 K resulted in more Co uptake than could be charge-compensated by the sites removed if all Co were divalent (Figure 8 insets, main text), indicating Co-oxide species were formed at this temperature. In contrast, the higher Co uptake at 333 K cannot be attributed to the formation of Co-oxide because two H⁺ sites are removed per Co present on the sample (e.g., insets in Figure 8a, 8b, main text Figure S10, SI) within the error of Co uptake measurements denoted with error bars in these figures (i.e., ~10%). Therefore, all paired Al are not titrated at temperatures \leq 313 K and a higher temperature (333 K) is required to titrate all Al pairs. Notably, Co-exchange on MEL(C) with a 0.5 M Co(NO₃)₂ solution resulted in Co uptake that was slightly higher (by ~ $0.05 \text{ Co}^{2+}/\text{Al}$) than half the number of H⁺ sites removed, suggesting that some Co-oxide did form on this sample at this molarity (Figure 8a inset, main text). However, Co exchange at 333 K with a higher and lower Co(NO₃)₂ solution molarity (i.e., 0.25, 0.75 M) resulted in similar Co uptakes (~0.2 2× Co/Al (solid)) and subsequent quantification of residual H⁺ sites indicated that two H⁺ sites were removed for each Co exchanged at these molarities. Thus, by considering Co uptake and corroborating this with quantities of residual sites on multiple MEL samples (MEL (C), MEL(50, 0.5)) over a range of Co molarities (0.25–0.75 M), we conclude Coexchange at 333 K saturates Al-Al pairs without the concurrent formation of significant quantities of Co-oxide species.

Differences in Co²⁺ titration conditions were observed for MEL samples synthesized with TBA⁺ only compared to those synthesized with combinations of Na⁺ and TBA⁺. The amount of

Co retained on MEL(50, 0.0)-2 exchanged at different temperatures (313 K and 333 K) and $Co(NO_3)_2$ molarities (0.3-0.5) is shown in Figure S11. The amount of Co^{2+} retained was significantly higher than the number of H⁺ sites removed (0.3 Co/Al vs. 0.2 H⁺/Al removed, Figure S11 inset), suggesting that non-ion-exchanged Co species (e.g., Co-oxides) formed on this sample when using the same exchange conditions that selectively formed Co^{2+} species for MEL(50,0.5) and MEL(C). One difference between MEL samples synthesized with TBA⁺ only compared to those crystallized with Na⁺ and TBA⁺ is the larger amount of extra-framework Al present on samples synthesized with only TBA⁺ (H⁺/Al = 0.48-0.64). Co²⁺ has been proposed to titrate nonframework Al species (e.g., Al in amorphous domains) in other studies². We note, however, that MEL(C) contains high fractions of extra-framework Al but also does not form detectable amounts of non-ion-exchanged Co species under the exchange conditions used, suggesting that extraframework Al alone cannot be responsible for the formation of Co-oxides on MEL samples crystallized with TBA⁺ only. Other differences between samples crystallized with TBA⁺ only and those crystallized with mixtures of Na⁺ and TBA⁺ include different crystallite morphologies (Figure S9) and crystallite sizes. Regardless of the origin of non-ion-exchanged Co species on MEL samples synthesized with TBA⁺ only, the quantity of Co²⁺-titratable framework Al on these samples can be estimated using a cation site balance combined with a Co²⁺ titration isotherm. The number of H⁺ sites (per Al) removed by Co titration using Co(NO₃)₂ solutions of different molarities is shown in Figure S12. For temperatures of 313–333 K, the fraction of H⁺ sites removed remained constant and did not increase with increasing Co(NO₃)₂ molarity, suggesting that all Co²⁺-titratable Al-Al pairs are saturated at 333 K and Co(NO₃)₂ molarities > 0.25 M. The fraction of paired Al can be approximated as one-half the number of H⁺ sites removed after Co titration at conditions that saturate Co²⁺-titratable Al pairs. Thus, we conclude that arrangements of proximal

Al in MEL crystallized with TBA⁺ only can be fully titrated at 333 K using $Co(NO_3)_2$ solutions with concentrations of 0.25-0.75 M, but should be verified with an attendant cation site balance to estimate the fraction of Co^{2+} titratable framework Al.

While conditions for Co²⁺ titration are framework dependent, similar conditions for Co titration between the MEL and MFI framework might be expected due to their similar topological features. MFI and MEL possess similar structures (e.g., 3-D intersecting channels, 10-, 8-, 6-, 5-, 4-MRs); thus, we hypothesize that Co²⁺ titrates similar arrangements of Al-Al pairs in MEL and MFI. In this work, Co²⁺ titrations at 353 K led to the formation of Co-oxides on NH₄-form MEL, while titrations at 333 K resulted in saturation of Co²⁺ binding sites on NH₄-form and Na-form MEL without the concomitant formation of other Co species. In contrast, saturation of Co²⁺ binding sites without the concurrent formation of non-ion-exchanged Co species has been reported on Na-form MFI samples at 353 K³. The higher temperature required for complete Co²⁺ titration of Al-Al site pairs on MFI was rationalized by Nimlos et al. as a being a possible consequence of diffusional constraints on Co cations diffusing through 5- and 6-MRs to reach energetically favorable binding sites in the subunits of MFI³. The difference in saturation temperatures between MFI and MEL may reflect the absence of favorable Co binding sites in the subunits in MEL, or possibly more facile diffusion of Co²⁺ complexes in MEL due to the absence of sinusoidal channels.



Figure S10. Co^{2+} titration isotherm on Na-form MEL(C) exchanged at ambient (O), 313 K (O), and 333 K (O). Inset shows the site balances of divalent Co^{2+} and residual monovalent (H⁺ and Na⁺) cations after Co titration (0.25–0.75 M Co(NO₃)₂). The dashed line corresponds to of the removal of two monovalent cations with each divalent Co^{2+} ion.



Figure S11. Co^{2+} titration isotherm on NH₄-form MEL(50, 0.0)-2 exchanged 313 K (O) and 333 K (\bullet). Inset shows the site balances of divalent Co^{2+} and residual monovalent (H⁺) cations after Co titration (0.25–0.75 M Co(NO₃)₂). The dashed line corresponds to of the removal of two monovalent cations with each divalent Co^{2+} ion.



Figure S12. Quantity of H⁺ sites per Al removed TPD after Co titration on NH₄-form MEL(50, 0.0)-2 exchanged 313 K (\bigcirc) and 333 K (\bigcirc) quantified by NH₃ saturation.

Section S.7. Comparison of Coulombic Prediction with DFT-calculated TBA-form Energies



Figure S13. Parity plot of DFT-calculated relative E_0 (kJ mol⁻¹) and relative E_0 predicted by a coulombic model (described by Eq. 4 in the main text) for TPA-form MFI (orange) and TBA-form MEL (blue) with one OSDA in the unit cell for all 96 Al positions. MEL values include the TBA⁺ in both the A and B intersections.

Section S.8. DFT calculations for Na(H₂O)_x binding in MFI and MEL



Figure S14. Binding energies of the radical $Na \cdot (H_2O)_2$ as a function of the cationic $Na^+(H_2O)_2$ binding energies in MEL with three TBA⁺ (green) and MFI with three TPA⁺ (blue).



Figure S15. Most stable MFI structures with (a-d) three TPA⁺ and (e-h) four TPA⁺ and (a,e) one, (b,f) two, (c,g) three, or (d,h) four Na⁺ occluded with the TPA⁺.



Figure S16. Most stable MEL structures with (a–d) three TBA⁺ and (e–h) four TBA⁺ and (a,e) one, (b,f) two, (c,g) three, or (d,h) four Na⁺ occluded with the TBA⁺.



Figure S17. Most stable MFI structures with (a-d) three TPA⁺ and (e-h) four TPA⁺ and (a,e) one, (b,f) two, (c,g) three, or (d,h) four Na⁺(H₂O)₄ occluded with the TPA⁺.



Figure S18. Most stable MEL structures with three TBA^+ and (a) one, (b) two, and (c) three $Na^+(H_2O)_4$ occluded with the TPA^+ .



Figure S19. Most stable $Na(H_2O)_6$ structures in (a) MFI with three TPA⁺ and (b) MEL with three TBA⁺.

References

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