Supplementary Information

Alkylation of poly-substituted aromatics to probe effects of mesopores in hierarchical zeolites with differing frameworks and crystal sizes

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¹Department of Chemical and Biological Engineering, Princeton University, New Jersey, USA *msarazen@princeton.edu **S.1 Detailed catalyst synthesis methods.** In methods employing a PTFE-lined, stainless steel autoclave, the autoclave was filled to 1/3 capacity.

BEA was synthesized as nanocrystals (*n*BEA, $d_{crystal} < 0.5 \mu m$) and microcrystals (μ BEA, $d_{crvstal} > 0.5 \ \mu m$) from molar gel compositions of 10 SiO₂: 0.050 Al₂O₃: 2.5 (TEA)₂O: 0.39 Na₂O: 0.20 K₂O: 0.58 HCl: 150 H₂O and 10 SiO₂: 0.050 Al₂O₃: 2.5 (TEA)₂O: 0.22 Na₂O: 0.38 K₂O: 0.58 HCl: 300 H₂O, respectively, where TEA⁺ (tetraethylammonium) served as the organic structuredirecting agent.^{1–5} First, KCl (> 99.0 %, Sigma-Aldrich) and NaCl (> 99.0 %, EMD Chemicals) were dissolved in TEAOH (35 wt. % in H₂O, Beantown Chemical) and 75 % of the total deionized H₂O by mass in a high-density polyethylene (HDPE) bottle. Fumed silica (99.8 %, Beantown Chemical) was then added under vigorous magnetic stirring, for ≥ 10 min, until the resulting translucent gel was homogenous. Separately, NaAlO₂ (50-56 wt. % Al₂O₃, 37-45 % Na₂O, Sigma-Aldrich) was dissolved in 10 wt. % solution NaOH (98.7 %, Fisher Scientific) in H₂O and the remaining deionized H₂O to yield a transparent, colorless solution, which was then added dropwise to the homogenized gel under vigorous stirring. The mixture was stirred for an additional 10 min, then transferred to a PTFE-lined, stainless steel autoclave for static crystallization at 423 K for 72 h (nBEA) or 144 h (µBEA). Solid BEA was then collected and washed repeatedly via centrifugation in fresh deionized H₂O until supernatant pH \leq 9 and dried overnight at 343 K. The dried BEA was then calcined overnight at 823 K under 150 sccm Air Zero (Airgas) to yield Na*n*BEA or Na-*µ*BEA by first ramping to 653 K at 7.5 K/min, then to 823 K at 0.8 K/min.

MFI was synthesized as *n*MFI from a molar gel composition of 10 TEOS: 0.17 Al₂O₃: 3.6 TPAOH: 190 H₂O, where TEOS (tetraethylorthosilane) served as the Si source and TPA⁺ (tetrapropylammonium) served as the organic structure-directing agent.^{6,7} First, TEOS (> 99.0 %, Alfa Aesar) and 56 % of the TPAOH (20 wt. % in H₂O, Sigma-Aldrich) by mass were mixed at 298 K for 13 h under magnetic stirring in a sealed HDPE bottle. NaAlO₂ was separately dissolved in deionized H₂O and the remaining TPAOH to yield a transparent, colorless solution, which was added dropwise to the previous TEOS-TPAOH mixture while stirring. The combined solution was vigorously stirred at 298 K in the sealed HDPE bottle for 5 min, then heated to 371 K and held for 2 h while stirring in an oil bath. The resulting gel was transferred to a PTFE-lined, stainless steel autoclave for static crystallization at 393 K for 15 h. MFI was then collected and washed repeatedly via centrifugation in fresh deionized H₂O until supernatant pH ≤ 9 and dried overnight at 343 K. The dried MFI was then calcined overnight at 823 K under 150 sccm Air Zero to yield Na-*n*MFI

by first ramping to 653 K at 7.5 K/min, then to 823 K at 0.8 K/min.

MOR was synthesized as μ MOR from a molar gel composition of 10 SiO₂: 0.33 Al₂O₃: 2 Na₂O: 260 H₂O.^{8,9} First, silica gel (Davisil Grade 12, 28-200 mesh, Sigma-Aldrich) was stirred in 50 % of the deionized H₂O and 50 % of the aqueous NaOH (10 wt. %) by mass at 298 K for 16 h in a sealed HDPE bottle. Separately, NaAlO₂ was dissolved in the remaining aqueous NaOH and deionized H₂O to yield a transparent solution, which was then added dropwise to the previous SiO₂ mixture while stirring. The combined gel was stirred vigorously for 2 h, and then transferred to a PTFE-lined, stainless steel autoclave for static crystallization at 443 K for 168 h. MOR was then collected and washed with deionized H₂O via vacuum filtration until the filtrate pH ≤ 9, and then dried overnight at 373 K to yield Na- μ MOR.

Al-MCM-41 was synthesized from a molar gel composition of 10 SiO₂: 0.39 Al₂O₃: 0.43 Na₂O: 1.27 $(TEA)_2O$: 0.83 $(HDTMA)_2O$: 471 H_2O , where HDTMA⁺ (hexadecyltrimethylammonium) served as the organic structure-directing agent.¹⁰ First, NaAlO₂ was dissolved in TEAOH (35 wt. % in H₂O) and added dropwise to silica sol (40 wt. % in H₂O, Alfa Aesar) under vigorous magnetic stirring in an HDPE bottle. The gel was stirred vigorously for an additional 30 min. HDTMAOH (10 wt. % in H₂O, Tokyo Chemical Industry) was then added to the gel, which was subsequently stirred for an additional 30 min. The final gel was crystallized inside the lightly capped HDPE bottle at 373 K for 168 h. The resulting solid was then collected and washed with deionized H₂O via vacuum filtration until the filtrate pH \leq 9, and then dried overnight under vacuum. The dried catalyst was then calcined overnight at 823 K under 150 sccm Air Zero to yield Na-Al-MCM-41 by first ramping to 653 K at 7.5 K/min, then to 823 K at 0.8 K/min.

S.2 SEM images of lab-synthesized zeolites



Fig. S1 SEM images of lab-synthesized microporous (nBEA, µBEA, µMOR, nMFI) and hierarchical (nBEA-h, µBEA-h, µMOR-h, nMFI-h1) zeolites on carbon tape at 5-20 kV.



Fig. S2 Size distributions of (a) nBEA (n = 83, $x = 0.20 \pm 0.04 \mu m$), (b) μ BEA (n = 85, $x = 0.90 \pm 0.16 \mu m$), (c) nMFI (n = 45, $x = 0.20 \pm 0.03 \mu m$), (d) nBEA-h (n = 54, $x = 0.20 \pm 0.04 \mu m$), (e) μ BEA-h (n = 49, $x = 0.90 \pm 0.19 \mu m$), and (f) nMFI-h1 (n = 43, $x = 0.20 \pm 0.19 \mu m$) obtained from SEM images.



S.3 DFT-optimized structures and vdW surfaces

Fig. S3 DFT-optimized (RPBE, PAW) CPK structures for (a) BA, (b) TMB, (c) DBE, and (d) TM2B with measured limiting lengths (green), longest lengths (blue), and angles (yellow); respective (e)-(h) van der Waals surfaces of molecules.



Fig. S4 DFT-optimized (PBE, PAW) for DBE adsorbed in BEA, viewed (a) down the length of 12-MR channel, and (b) top view of 12-MR channel.



S.4 Statistical analysis of deactivation reaction model (Eqn. 5-7)

Fig. S5 Parity plots for (a)-(c) X_{BA} and (d)-(f) S_{TM2B} for Al-MCM-41 (\bullet), nMOR (\bullet), μ MOR (\bullet), nMOR-h (\bullet), μ MOR-h (\bullet), nBEA (\bullet), nBEA (\bullet), nBEA-h (\bullet), μ BEA-h (\bullet), nBFI (\blacktriangle), nMFI-h1 (\bigstar), and nMFI-h2 (\bigstar) for ODE reaction model accounting for second-order deactivation and vacant protons as abundant surface intermediates (Eqn. 5-7).



Fig. S6 Parity plots for temporal [TM2B] and [DBE] for Al-MCM-41 (\bullet), nMOR (\bullet), μ MOR (\bullet), nMOR-h (\bullet), nBEA (\bullet), nBEA-h (\bullet), nBEA-h (\bullet), nMFI (\blacktriangle), nMFI-h1 (\bigstar), and nMFI-h2 (\bigstar) for reaction model according for second-order deactivation model accounting for vacant protons as abundant surface intermediates (Eqn. 5-7).

Catalyst	X _{BA}		[DBE]		[TM2B]		S _{TM2B}	
	RMSE	р	RMSE	р	RMSE	р	RMSE	р
Al-MCM-41	0.0511	1.31E-06	3.40E-06	0.00184	1.29E-05	2.47E-06	0.0265	7.36E-05
nMOR-h	0.0964	5.15E-05	7.78E-06	0.0139	2.51E-05	0.000151	0.0197	1.27E-05
nMOR	0.0302	5.86E-07	1.43E-06	1.62E-07	1.07E-05	1.08E-04	0.0208	0.42
μMOR	0.0139	0.0607	8.60E-07	7.65E-02	2.39E-06	7.99E-02	0.00189	0.637
µMOR-h	0.0179	5.33E-05	9.16E-07	0.000308	6.43E-06	0.00547	0.0056	0.0838
nBEA	0.0868	0.000198	6.80E-06	0.00137	1.17E-05	0.000107	0.0126	0.0109
μBEA	0.0832	0.157	9.62E-06	0.197	5.92E-06	0.073	0.00466	0.28
µBEA-h	0.0421	1.01E-05	3.57E-06	0.000249	1.63E-05	0.00242	0.0214	0.0669
nBEA-h	0.0789	2.91E-05	4.67E-06	0.000125	1.43E-05	5.88E-05	0.0221	0.029
nMFI	0.0111	1.77E-06	7.32E-07	1.09E-05	3.20E-06	6.65E-05	0.00424	0.235
<i>n</i> MFI-h1	0.0216	4.24E-08	2.09E-06	7.20E-08	5.62E-06	4.66E-06	0.0124	0.000457
nMFI-h2	0.0252	2.43E-07	2.58E-06	7.60E-08	5.83E-06	0.000116	0.0208	0.0688

Table S1 Root mean squared error (RMSE) and p-values for ANOVA analysis of experimental and fitted X_{BA} , [DBE], [TM2B] and S_{TM2B} for nanocrystalline, microporous zeolites and Al-MCM-41 according to reaction model of Eqn. 5-7.

S.5 Alternative reaction network model. An alternative reaction network model was tested assuming both BA and vacant protons were surface intermediates, and no second-order deactivation term was included:



Fig. S7 (a) Temporal X_{BA} (b) and S_{TM2B} data for Al-MCM-41 (\bullet), nMOR (\bullet), nBEA (\blacksquare), and nMFI (\blacktriangle) fitted to alternative model (neat, [TMB]₀:[BA]₀ = 35:1, 373 K).



Fig. S8 Parity plots for temporal (a) X_{BA} , (b) S_{TM2B} , (c) [TM2B], and (d)[DBE] for Al-MCM-41 (\bullet), nMOR (\bullet), nBEA (\blacksquare), and nMFI (\blacktriangle) according to ODE reaction model alternative model accounting for both BA and vacant protons as abundant surface intermediates, with no deactivation term (Eqn. S1-S3).

Table S2 Root mean squared error (RMSE) and p-values for ANOVA analysis of experimental and fitted X_{BA} ,	[DBE],	[TM2B]
and S _{TM2B} for nanocrystalline, microporous zeolites and Al-MCM-41 according to reaction model of Eqn. S1-	S3.	

Catalyst	X _{BA}		[DBE]		[TM2B]		S _{TM2B}	
	RMSE	р	RMSE	р	RMSE	р	RMSE	р
Al-MCM-41	0.0462	8.96E-07	2.57E-06	0.000656	7.99E-06	1.81E-07	0.0178	1.17E-05
nMOR	0.0168	8.42E-09	2.08E-06	7.38E-07	1.19E-05	1.09E-04	0.0265	0.545
nBEA	0.147	0.00118	2.53E-05	0.00728	1.19E-05	0.00142	0.0204	0.0603
<i>n</i> MFI	0.0362	2.14E-04	1.38E-06	1.03E-04	7.97E-06	0.00131	0.00723	0.366

S.6 Effectiveness factor plot for BEA catalysts



Fig. S9 Effectiveness factor plot for nBEA (•), μ BEA (\blacktriangle), nBEA-h (\Box) and μ BEA-h (+) showing shift to $\phi = 1.0$ at threshold of kinetic control.

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