Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Tailoring the Physicochemical Properties of Zeolite Catalysts

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S1 Experimental Methods

S1.1 Materials

All of the zeolite syntheses listed below were prepared using deionized water (18.2 MΩ) purified with an Aqua Solutions purification system (RODI-C-12A) and all reagents were used as received without further purification.

LTL and MER synthesis. The following chemicals from Sigma-Aldrich (St. Louis, MO) were used as reagents: LUDOX (40 wt% suspension in water), potassium hydroxide (85% pellets), and aluminum sulfate hydrate (98%). The following chemicals from Sigma-Aldrich were used as growth modifiers in LTL syntheses: ethanol (200 proof), 1-propanol (ACS reagent, ≥ 99.5%), 1-butanol (ACS reagent, ≥ 99.4%), 1-pentanol (≥99%), 1-hexanol (≥98%), 1,2-butanediol (98%), 1,2-pentanediol (96%), 1,5-pentanediol (purum, ≥ 97% (GC) Fluka), 1,2-hexanediol (98%), 1,2,3-hexanetriol (BIOXTRA, ≥98.0%), 1,2,6-hexanetriol (96%), ethylene glycol (99%), 1,2-propanediol (99.5%), glycerol (≥99.5%), diethyl ether (anhydrous, ≥99.7%), dimethoxymethane (reagent plus, 99%), 1,2-dimethoxyethane (≥99.5% (GC)), poly(diallyldimethylammonium chloride) (MW 150K, 20%), 1-ethyl-1-methylpyrrolidinium bromide (99%), propylamine (≥99%), butylamine (99.5%), hexamethylenediamine (98%), triethyleneglycol (≥99%), (R/S)-1,3-butanediol (99%), tributylphosphine oxide (95%), and triethylenetetramine (≥97%).

Silicalite-1 synthesis. The following chemicals from Sigma Aldrich were used as reagents: tetraethylorthosilicate (TEOS, 98%), LUDOX (40 wt% suspension in water), sodium hydroxide (>97%), potassium hydroxide (85% pellets), aluminum sulfate hydrate, piperidine (>99.5%), methanol (>99.8%). Tetrapropylammonium hydroxide (TPAOH, 40%) and silicon(IV) oxide (15% in H_2O, colloidal dispersion) were purchased from Alfa Aesar. Aluminum nitrate (9 hydrate crystal) was purchased from J.T. Baker. The following chemicals (Sigma Aldrich) were used as growth modifiers: 2-dimethylaminoethanol purum (≥98.0% (GC)), dipropylamine (99%), polyethylenimine (MW_w 1300), polyethylenimine branched (MW_w 25000), spermine (≥97%), triethylenetetramine hydrate (98%), tris(2-aminoethyl)-amine (96%), ethylenediaminetetraacetic acid (99.4-100.06% ACS reagent), tris (hydroxymethyl) aminomethane (99.8%, A.C.S. reagent), D-arginine (98% (TLC)), poly-L-lysine hydrobromide (0.5 to 2.0 kDa), L-threonine (98% reagent grade), tributylphosphine oxide (95%).

MOR synthesis. The following chemicals from were used as reagents for MOR syntheses: Silica gel 60 (230-400 mesh, Mallinckrodt chemical), sodium hydroxide pellet (98%) (Macron fine chemical) and sodium aluminum oxide (technical, Alfa Aesar). The following chemicals from Sigma-Aldrich were used as growth modifiers: ethanol (200 proof), 1-butanol (ACS reagent, ≥ 99.4%), 1,2-butanediol (98%), (R/S)-1,3-butanediol (99%),1,2-hexanediol (98%), 1,2,6-hexanetriol (96%), glycerol (≥99.5%), Meso-erythritol (≥99%), cyclohexane-1,4-diol(≥99%), penta-erythritol (≥99%), triethyleneglycol (≥99%), Dulcitol (≥99%), diethyl ether (anhydrous, ≥99.7%), butylamine (99.5%), tert-butylamine (≥98%), triethylenetetramine (≥97%), Polyethyleneiminie branched (M_n 10,000), tributylphosphine oxide (95%), poly(diallyldimethylammonium chloride) (MW 150K, 20%), 1-ethyl-1-methylpyrrolidinium bromide (99%).

LTA, FAU, SOD, GIS, CAN, ANA, and JBW syntheses. LUDOX AS-40 colloidal silica (40%) was purchased from Sigma Aldrich. Sodium hydroxide was purchased from either Sigma Aldrich or Macron Fine Chemicals (both providers list the purity at 98%). Sodium aluminate (technical) was purchased from Alfa Aesar.

S1.2 Synthesis of zeolites in the absence of OSDAs

Zeolites were prepared by adding sodium aluminate (for Na^+ syntheses) or aluminum sulfate hydrate (for K^+ syntheses) and sodium or potassium hydroxide to deionized water. After stirring until the solution was homogenous, LUDOX or silica gel, depending on the desired crystal, was added. The solution was stirred for an additional 24 hours, except for MOR syntheses in which the solution was stirred for 4 hours. The homogeneous mixture was transferred to a Teflon liner, which was capped and placed in a stainless steel autoclave. The autoclave was placed in a preheated oven for a desired period of time. Upon removal from the oven, the autoclave was cooled to ca. 25 ˚C in a water bath for 1 hour prior to centrifugation or filtration to recover the solid sample for eventual analysis.

Table S1. Synthesis composition and conditions used to prepare zeolites in Figures 1 – 4.

Molar Composition			Crystallization Temperature (°C)	Crystallization Time (days)	Crystal Phase[a]
SiO_2	Al_2O_3	H_2O			
1.8	1.8	173	65	7	Na-LTA
3.6	0.9	173	65	7	Na-FAU
1.6	1.5	173	100	7	Na-SOD
7.4	2.4	173	100	7	Na-GIS
25.0	0.8	646	175	3	Na-MOR
2.5	0.3	505	180	4	K-MER
9.8	0.3	505	180	3	K-LTL
3.6	1.7	173	180	21	Na-CAN
5.5	1.2	173	180	21	Na-ANA
38.5	0.4	1760	190	1	Na-MFI[b]
7.5	4.8	173	230	7	Na-JBW

(a) Syntheses carried out using either NaOH or KOH as the mineralizing agent, the cation used is noted before the framework type. The molar composition for OSDA-free synthesis is $x\ SiO_2$: $y\ Al_2O_3$: 10 MOH: $z\ H_2O$ where M is either Na^+ or K^+ heated at various temperatures and times.

(b) Synthesis conditions taken from Dai et al.[1]

S1.3 Synthesis of zeolite L (LTL type) and mordenite (MOR type) with ZGMs

Crystals synthesized by the procedure mentioned previously in the absence of growth modifier are referred to as the control. It should be noted that the molar ratio for alumina in the chemical composition of LTL synthesis reported in Lupulescu et al.[2] was found to be incorrect due to a misrepresentation of hydrate content in the aluminum source specifications listed by the supplier. This oversight was corrected in Table S1 above. For studies of different zeolite growth modifiers, the modifier of choice was added in a molar ratio of 1.5 ZGM:1.0 SiO_2 to the growth solution and the crystallization procedure was the same as described in Section S1.2. The product was isolated by vacuum filtration using a 0.4-μm membrane (47 mm Whatman nuclepore polycarbonate track-etched membrane) with repeated deionized water washings.

S1.4 Preparation of silicalite-1 (MFI type) crystals and growth solutions for *in situ* AFM

Crystallization. Silicalite-1 hexagonal platelets were synthesized from clear solutions containing a molar ratio of $40SiO_2$:40TPAOH:$9420H_2O$:160EtOH, with tetrapropylammonium (TPA^+) as the organic structure-directing agent. TPAOH was added to deionized water followed by drop-wise addition of TEOS. The mixture was stirred at room temperature for 2 hours. The growth modifier of choice was added (in various weight percentages) to the growth solution, which was then crystallized according to the procedure listed in Section S1.2. After heating, the solutions were filtered (1-µm Whatman Nuclepore Track-Etch membrane), washed 3 times with deionized water, and dried in air to recover the product.

Preparation of growth solutions for *in situ* AFM. Mixtures of various compositions that mimic realistic growth solutions of silicalite-1 syntheses were used as the growth solutions for *in situ* AFM experiments. These solutions contained a molar ratio of x SiO_2: y TPAOH: $9500H_2O$: $4x$ EtOH. TPAOH was added to de-gassed deionized water followed by drop-wise addition of TEOS. The mixtures were stirred at room temperature overnight, yielding solutions of varying pH depending on the selection of the x SiO_2: y TPAOH molar ratio. Each solution was filtered using a 0.45 µm syringe filter before injection into the AFM closed cell configuration.

S2 Characterization

Zeolite samples were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), and atomic force microscopy (AFM). XRD patterns were collected on a Siemens D5000 X-ray diffractometer using CuKα radiation (40 kV, 30mA, λ = 1.54 Å). SEM was conducted using a FEI-235 Dual-Beam Focused Ion Beam microscope or a Nova NanoSEM 230 instrument with ultra-high-resolution FESEM (operated at 15 kV and a 5 mm working distance). Energy dispersive X-ray (EDX) spectroscopy was conducted with a JEOL JSM 6330F Field Emission SEM instrument. AFM analysis was performed on a MFP- 3D-SA instrument (Asylum Research, Santa Barbara, CA). Tapping mode images were obtained with 256 scans/line at an average scan velocity of 1.2 µm/s using Olympus AC240TS probes (2 N/m spring constant).

S3 Analysis of zeolite MER prepared without OSDAs

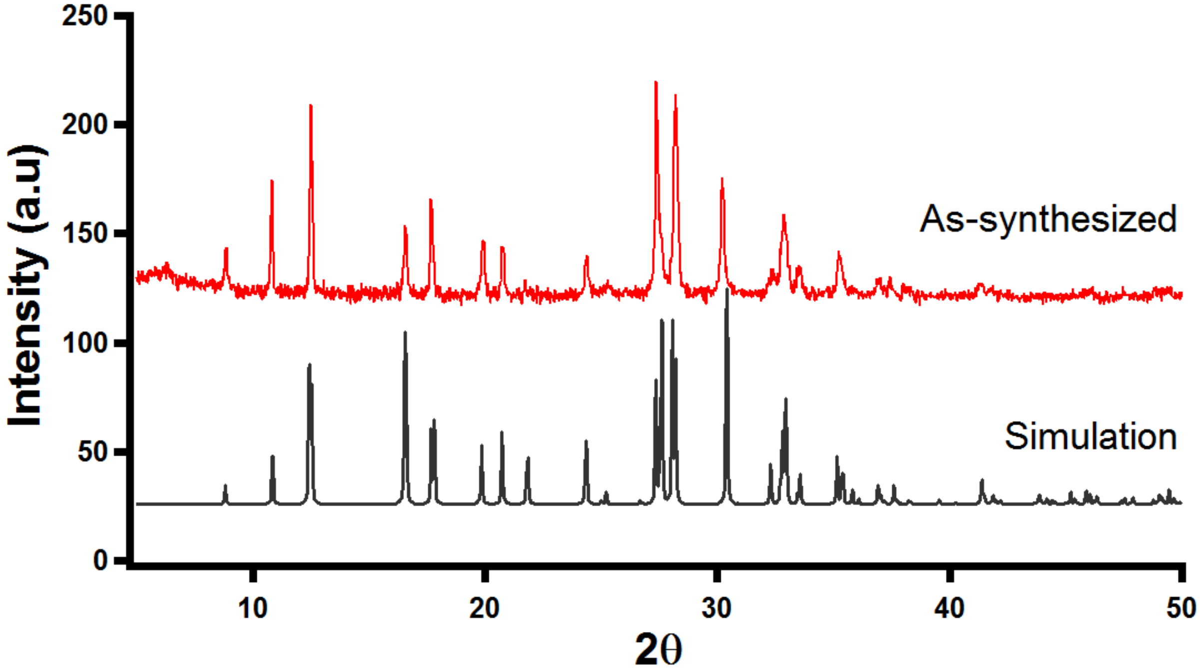
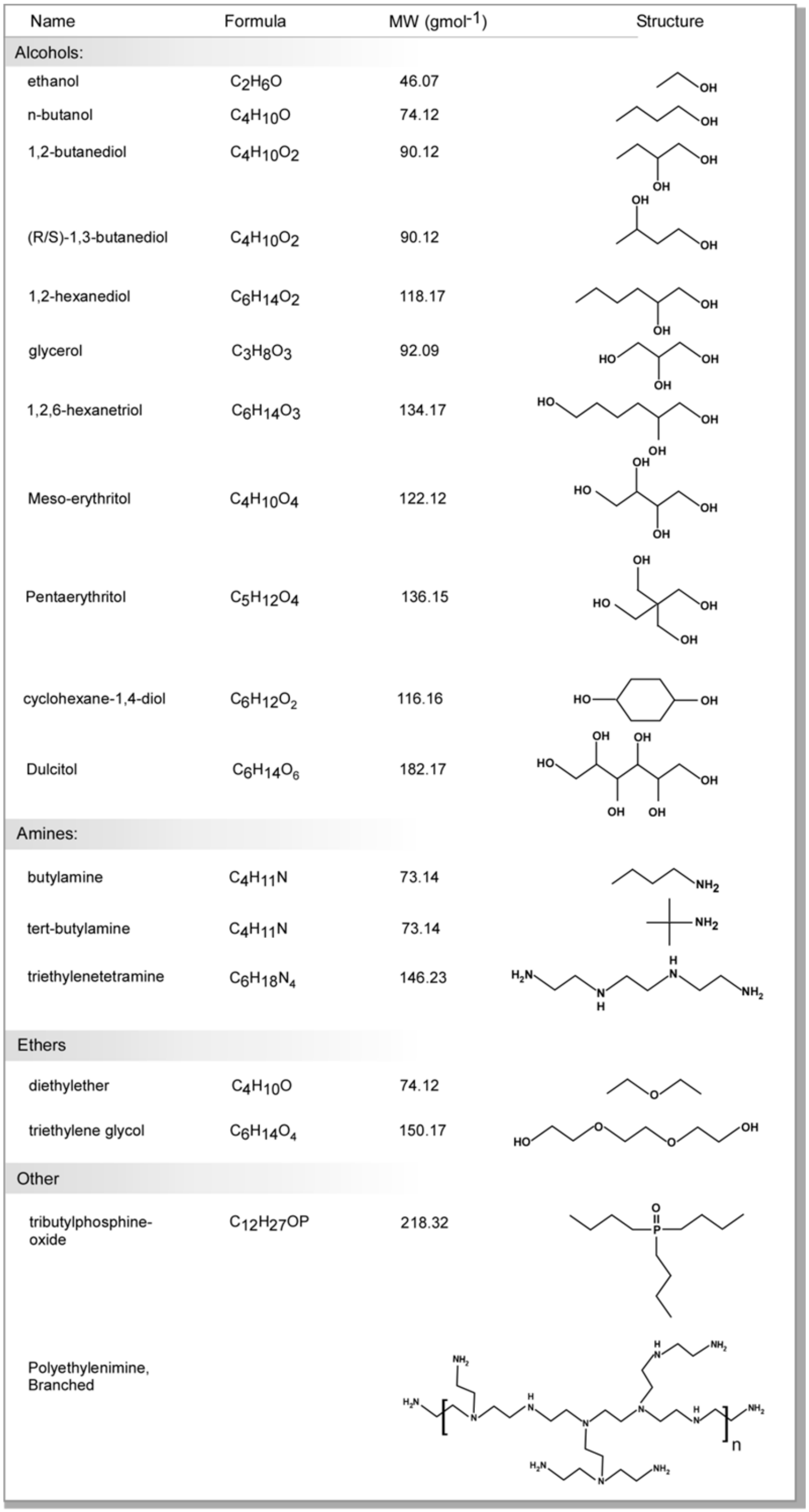


Figure S1. Powder X-ray diffraction pattern of the as-synthesized MER zeolite after heating a growth solution with molar composition 2.5 SiO_2:0.3 Al_2O_3:10 KOH:505 H_2O at 180 °C for 4 days (red line). A spectrum of the empty sample holder was measured and subtracted from the MER sample This pattern is compared to a simulated MER patter (black line) that was obtained from the International Zeolite Association (IZA).[3]

S4 Growth modification of mordenite

Table S2. Organic molecules screened as potential growth modifiers of MOR.



Name	Formula	MW (gmol^{-1})	Structure
Alcohols:			
ethanol	C_2H_6O	46.07	
n-butanol	$C_4H_{10}O$	74.12	
1,2-butanediol	$C_4H_{10}O_2$	90.12	
(R/S)-1,3-butanediol	$C_4H_{10}O_2$	90.12	
1,2-hexanediol	$C_6H_{14}O_2$	118.17	
glycerol	$C_3H_8O_3$	92.09	
1,2,6-hexanetriol	$C_6H_{14}O_3$	134.17	
Meso-erythritol	$C_4H_{10}O_4$	122.12	
Pentaerythritol	$C_5H_{12}O_4$	136.15	
cyclohexane-1,4-diol	$C_6H_{12}O_2$	116.16	
Dulcitol	$C_6H_{14}O_6$	182.17	
Amines:			
butylamine	$C_4H_{11}N$	73.14	
tert-butylamine	$C_4H_{11}N$	73.14	
triethylenetetramine	$C_6H_{18}N_4$	146.23	
Ethers			
diethylether	$C_4H_{10}O$	74.12	
triethylene glycol	$C_6H_{14}O_4$	150.17	
Other			
tributylphosphine-oxide	$C_{12}H_{27}OP$	218.32	
Polyethylenimine, Branched			

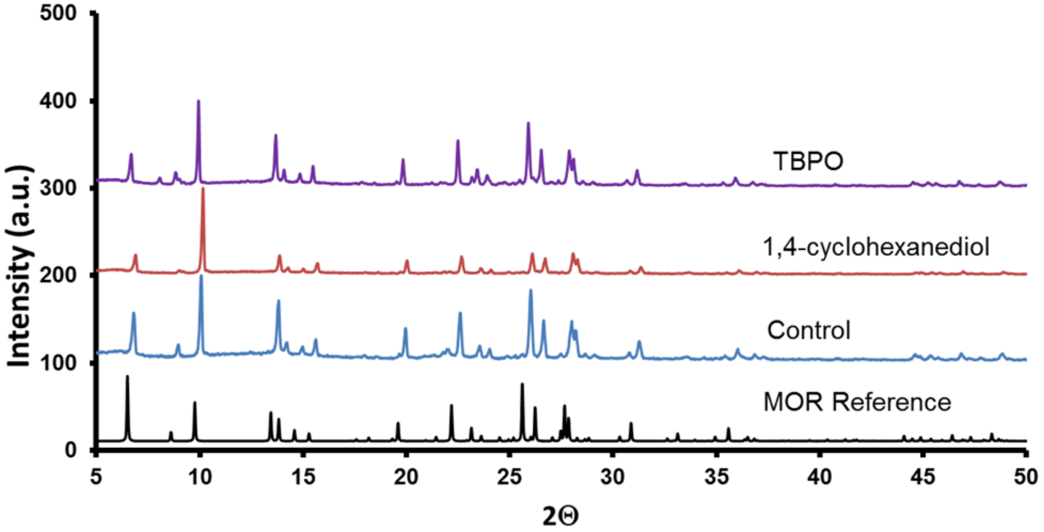


Figure S2. X-ray diffraction patterns of MOR synthesized in the absence of growth modifier (control) and with the addition of cyclohexane-1,4-diol and TBPO as ZGMs. A simulated pattern of MOR from the IZA is provided as a reference.[3]

S5 Supporting references

1. F. Y. Dai, M. Suzuki, H. Takahashi and I. Saito, in *New developments in zeolite science and technology*, eds. Y. Murakami, A. Iijima and J. W. Ward, Elsevier, 1986, vol. 28, pp. 223-230.
2. A. I. Lupulescu, M. Kumar and J. D. Rimer, *J. Am. Chem. Soc.*, 2013, 135, 6608-6617.
3. www.iza-online.org.