

Supporting information

Of

Lewis Acid Zeolites for Tandem Diels–Alder Cycloaddition and
Dehydration of Biomass-Derivable Dimethylfuran and Ethylene to
Renewable *p*-Xylene

Chun-Chih Chang^{a,d}, Hong Je Cho^{a,d}, Jingye Yu^{b,d}, Ray J. Gorte^{b,d}, Jason Gulbinski^{e,d}, Paul
Dauenhauer^{c,d} and Wei Fan^{*a,d}

^aDepartment of Chemical Engineering, University of Massachusetts Amherst

159 Goessmann Lab, 686 N. Pleasant St., Amherst, MA 01002;

^bDepartment of Chemical and Biomolecular Engineering, University of Pennsylvania, 220 S.
33rd St., Philadelphia, PA 19104;

^cDepartment of Chemical Engineering and Materials Science, University of Minnesota, 421
Washington Ave. SE, Minneapolis, MN, 55455;

^dCatalysis Center for Energy Innovation, a U.S. Department of Energy – Energy Frontier
Research Center. <http://www.efrc.udel.edu/>.

^eDepartment of Chemical Engineering, University of Delaware, 150 Academy Street, Newark,
Delaware 19716;

Corresponding author: wfan@ecs.umass.edu

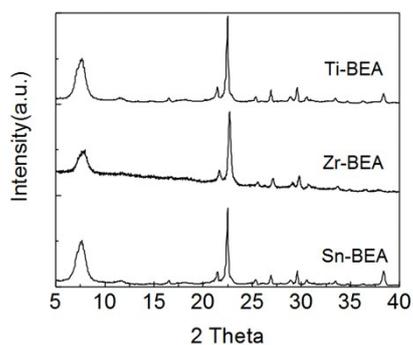


Figure S1. XRD patterns for Sn-, Zr-, and Ti-BEA. Typical reflections for zeolite BEA were observed for all samples, and no impurity phase (i.e., metal oxides) was detected, indicating high-quality crystals were obtained.

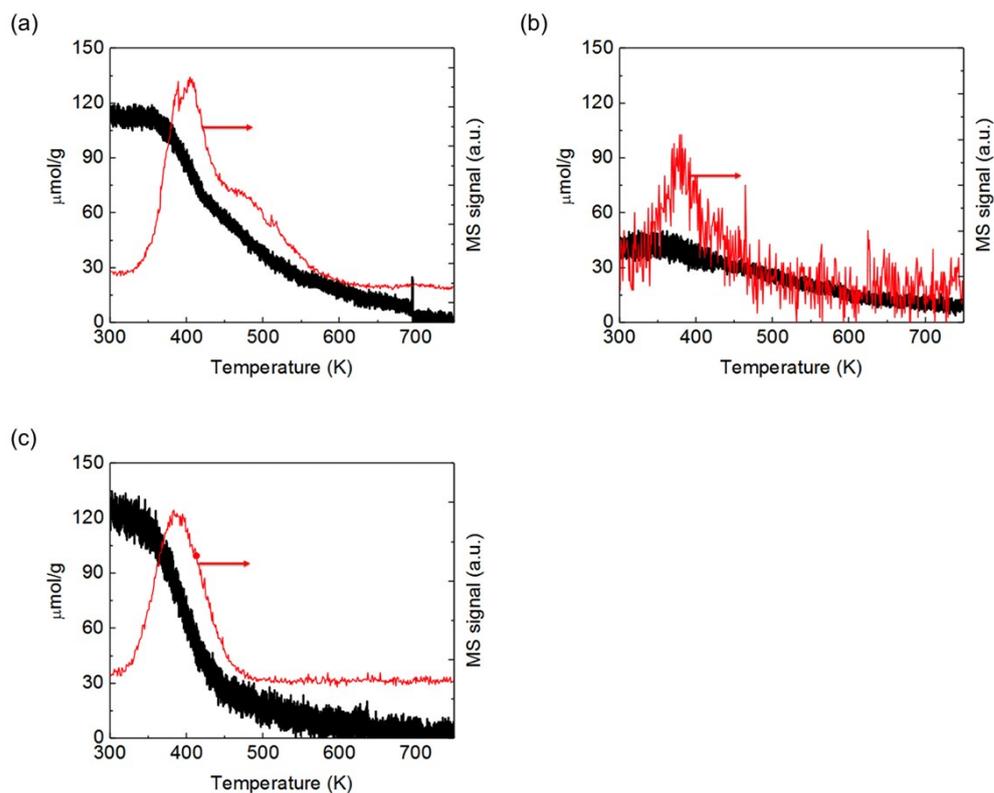


Figure S2. Diethylether TPD-TGA data for (a) Zr-, (b) Ti-, and (c) Sn-BEA. The MS signal represents the signal of $m/e=31$, which is the most abundant species for diethyl ether in a mass spectrum from electron ionization.

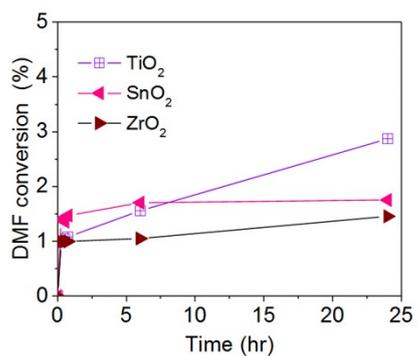


Figure S3. DMF conversion versus time for SnO₂, TiO₂, and ZrO₂. Reaction conditions are the same with the Lewis acid zeolites except for the amount of catalyst used (0.8 g for metal oxides).

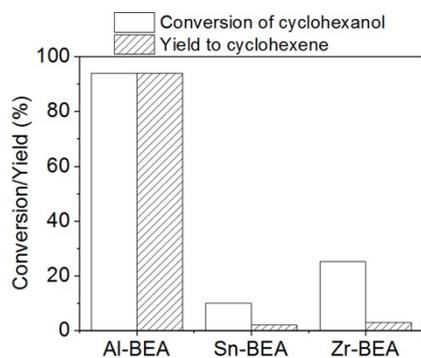


Figure S4 Production rate of cyclohexene from cyclohexanol over Al- and Zr-BEA. Conditions: 0.1 M cyclohexanol in 1,4-dioxane, 0.02 g catalyst, 200 °C for 30 min.

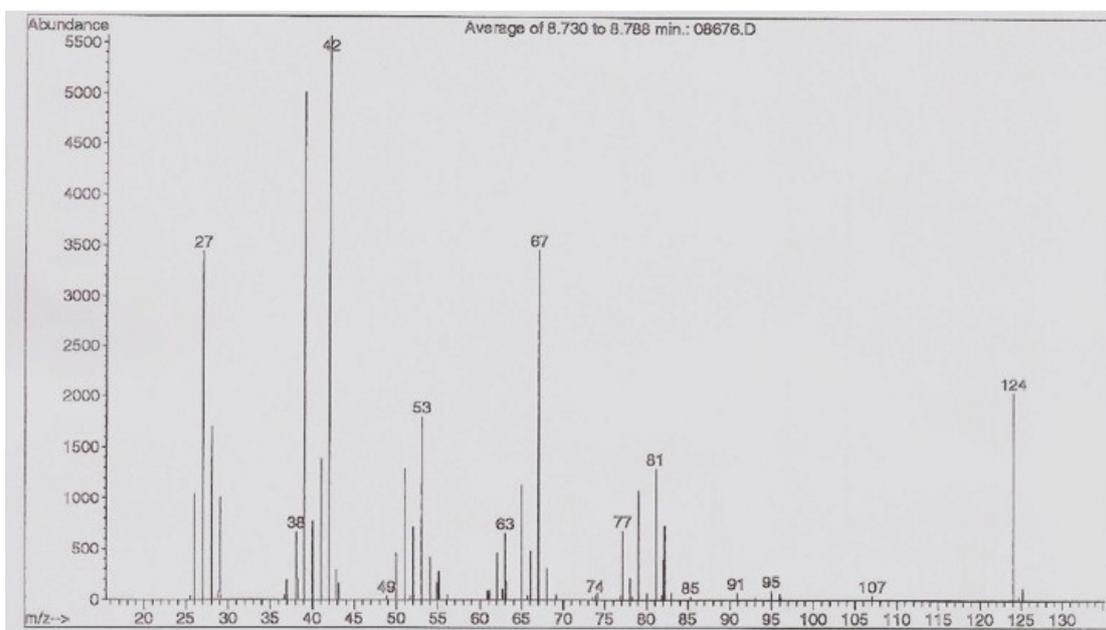
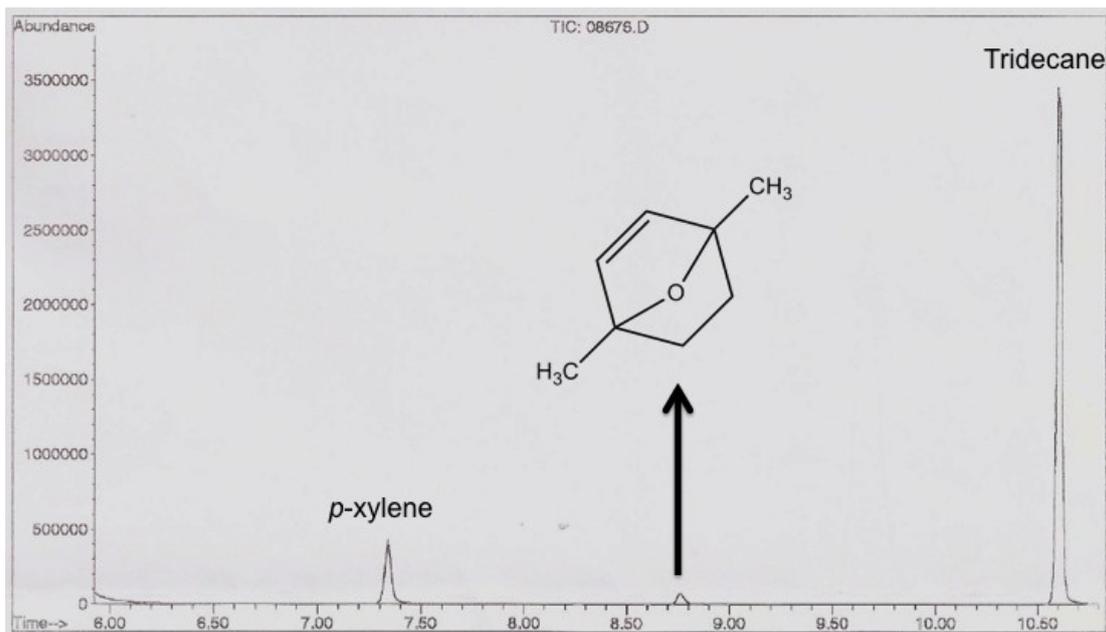


Figure S5. GC chromatogram and electron ionization (EI) spectrum of cycloadduct. The reaction mixture was taken at 30 min reaction time for Zr-BEA at 1 mM acid loading under usual reaction conditions. The EI spectrum is consistent with previous report.¹

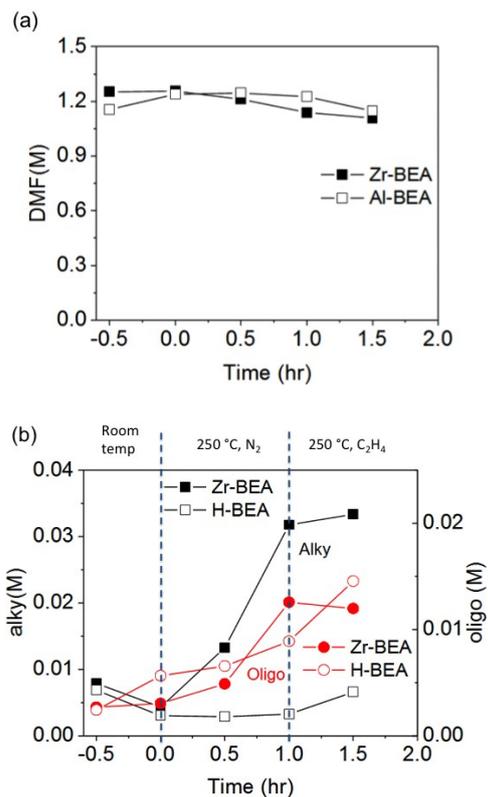


Figure S6. (a) DMF, (b) alkylated products and oligomers concentration evolution with intentional addition of 2, 5-hexanedione into initial reactant solution. The concentration of DMF for Al-BEA and Zr-BEA during the time holding at 250 °C is invariant or slightly decreasing, which suggesting the decrease of diketone is not due to dehydration reaction to form DMF.

References:

1. P. T. M. Do, J. R. McAtee, D. A. Watson and R. F. Lobo, *ACS Catal.*, 2013, **3**, 41-46.