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$^{c,d}$, Paul Dauenhauer$^{c,d}$ and Wei Fan*$^{a,d}$

$^a$Department of Chemical Engineering, University of Massachusetts Amherst
159 Goessmann Lab, 686 N. Pleasant St., Amherst, MA 01002;

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

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


$^e$Department 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 SnO$_2$, TiO$_2$, and ZrO$_2$. 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-hexanediione 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: