Electronic Supplementary Information for

Selective Production of Para-Xylene from Biomass-derived 2,5-Dimethylfuran through Tandem Diels–Alder/Dehydration Reactions with a Bifunctional Ga,Al-Zeolite Catalyst

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Supplementary Methods

Materials. The following reagents were purchased from Sigma-Aldrich: tetraethylammonium hydroxide (TEAOH, 35%), Al metal powder (>99.95%), and *n*-tridecane (>99%). Gallium nitrate hydrate (99.999%, metals basis) was purchased from Alfa Aesar. Fumed silica (Cab-O-Sil M5) was bought from Spectrum Chemical. 2,5-DMF (98+%) and *n*-heptane (99%) was obtained from Thermo-Fisher Scientific. Gases for catalyst preparation and reaction testing were nitrogen (99.999%, Matheson Tri-gas Inc.), ethylene (99.999%, Matheson Tri-gas Inc.), and air (O₂: 20-22%, zero grade, Matheson Tri-gas Inc.). All reagents were used as received without further purification. Deionized (DI) water was produced with an Aqua Solutions RODI-C-12A purification system (18.2 M Ω).

Synthesis of Ga-impregnated Al-*BEA. Samples with composition $Ga_x/Al_{1.0}$ -*BEA (x Ga_2O_3 : 1 Al₂O₃: 50 SiO₂ with x = 0.2, 0.4, and 0.6) were prepared by an incipient wetness impregnation method. The starting material for preparation was the H-form Al_{1.0}-*BEA zeolite synthesized according to the protocol described in the manuscript (using a growth mixture with a molar composition of 8 TEAOH: 1 Al₂O₃: 50 SiO₂: 743 H₂O). The zeolite was first converted to proton form. Approximately 1.00 g of Al_{1.0}-*BEA (1 Al₂O₃: 50 SiO₂) zeolite was placed into contact with an aqueous gallium solution prepared by dissolving 0.05, 0.10, or 0.15 g of Ga(NO₃)₃·xH₂O in 0.90 g of DI water. The impregnation solutions were prepared to yield Ga_x/Al_{1.0}-*BEA, with x = 0.2, 0.4, and 0.6 respectively. Each impregnated sample was dried at 50 °C overnight, followed by calcination under flow of dried air (100 ml min⁻¹) at 500 °C for 4 h with a temperature ramp rate of 1 °C min⁻¹.

Synthesis of Al_{1.0}-*BEA zeolites with different sizes. The reference Al_{1.0}-*BEA sample in the manuscript was prepared using a procedure that resulted in ca. 700 nm particles. For the data presented in Fig. 4b of the manuscript, we prepared two additional aluminosilicate samples with different sizes (ca. 200 and 500 nm) using the following procedures. Sample Al_{1.0}-*BEA (200 nm) was prepared from a growth mixture with a molar composition of 15 TEAOH: 1 Al₂O₃: 50 SiO₂: 495 H₂O using tetraethylammonium (TEA) as the organic structure-directing agent. This solution was generated by the combination of two pre-mixed solutions. In the first solution, 6.311 g TEAOH (35 wt% in water) and 0.108 g Al were mixed and stirred for 3 h. The second solution was made with 6.311 g TEAOH (35 wt%), 9.724 g H₂O, and 6.000 g fumed silica. Sample Al_{1.0}-*BEA (500 nm) was prepared from a growth mixture with a molar composition of 10 TEAOH: 1 Al₂O₃: 50 SiO₂: 495 H₂O. This solution was generated by the combination of two pre-mixed solutions. In the first solution, 4.207 g TEAOH (35 wt% in water) and 0.108 g Al were mixed and stirred for 3 h. The second solution was made with 4.207 g TEAOH (35 wt%), 12.458 g H₂O, and 6.000 g fumed silica. The mixture was vigorously stirred until it became a gel phase. The following steps were identical: The growth mixture was aged at room temperature for 24 h under continuous stirring before being transferred to a 23mL Teflon-lined stainless-steel acid digestion bomb (Parr Instruments). Hydrothermal treatment was carried out at 140 °C under rotation (ca. 30 rpm) in a Thermo-Fisher Precision Premium 3050 Series gravity oven. The synthesis times for Al1.0-*BEA with 200 and 500 nm were 5 and 11 days, respectively. Solids were isolated from the supernatant by three cycles of centrifugation and washing with DI water, followed by drying at 50 °C. The dried samples were calcined under the flow of dried air (100 mL min⁻¹) at 550 °C for 8 h with a ramp rate of 1 °C min⁻¹ to generate H-form catalysts for further characterization.

Supplementary Tables

Entry Synthesis Time (#) (day)		TEAOH/SiO ₂ H ₂ O/SiO ₂		Average particle size (nm)		
а	5	0.30	10	200		
b	8	0.20	10	500		
с	11	0.20	10	500		
d	14	0.20	10	500		
e	11	0.16	10	600		
f	11	0.14	10	650		
g	11	0.067	10	Amorphous		
ĥ	11	0.20	15	650		
i	11	0.20	25	Amorphous		
i	42	0.16	15	700		

 Table S1. Systematic parametric analysis of Al-*BEA synthesis conditions.

Table S2. Solids yield of *BEA zeolites.

*BEA zeolite	Solids yield (%) ^b
Al _{1.0} -*BEA (200 nm)	73.8
Al1.0-*BEA (500 nm)	88.2
Al1.0-*BEA (700 nm)	69.0
Ga _{0.6} ,Al _{0.6} -*BEA	81.9
Ga _{0.4} ,Al _{0.6} -*BEA	82.5
Ga _{0.2} ,Al _{0.6} -*BEA	81.9
Ga _{0.6} /Al _{1.0} -*BEA ^a	
Ga _{0.4} /Al _{1.0} -*BEA ^a	
Ga _{0.2} /Al _{1.0} -*BEA ^a	

a. Zeolite *BEA samples prepared by postsynthesis impregnation of $Al_{1.0}$ -*BEA (700 nm); b. calculated using the weight of solids after calcination to remove OSDA.

Table S3. Elemental analysis (ICP) of *BEA zeolites.

*BEA zeolite ^a	Weight percent (%)			Mole (µmol/g)			S:/A1	S:/Ca
	Ga	Al	Si	Ga	Al	Si	51/AI	51/Ga
Al1.0-*BEA (200 nm)		1.69	41.04		627	14613	23.3	
Al _{1.0} -*BEA (500 nm)		1.54	41.62		570	14818	26.0	
Al _{1.0} -*BEA (700 nm)		1.46	41.86		541	14906	27.6	
Ga _{0.6} ,Al _{0.6} -*BEA	2.08	0.84	39.48	298	311	14056	45.2	47.2
Ga _{0.4} ,Al _{0.6} -*BEA	1.49	0.86	40.90	214	318	14564	45.8	68.1
Ga _{0.2} ,Al _{0.6} -*BEA	0.88	0.95	40.94	126	352	14576	41.4	116
Ga _{0.6} /Al _{1.0} -*BEA	2.13	1.40	38.62	305	518	13752	26.5	45.1
Ga _{0.4} /Al _{1.0} -*BEA	1.48	1.47	40.12	212	543	14284	26.3	67.4
Ga _{0.2} /Al _{1.0} -*BEA	0.76	1.49	40.80	108	552	14529	26.3	135

a. Proton-form zeolites without Ga (Al_{1.0}-*BEA), one-pot syntheses with Ga (Ga_x,Al_y-*BEA), and samples prepared with Ga by incipient wetness impregnation (Ga_x/Al_y-*BEA)

*DEA moolito	Al/Ga ratio		$\mathbf{DET}(\mathbf{m}^2/\mathbf{a})$	$\mathbf{S} = (\mathbf{m}^2/\mathbf{r})$	$V = (am^3/a)$	
"DLA Zeonte	ICP	EDS	DET (III /g)	Sext (III /g)	v micro (CIII'/g)	
Al _{1.0} -*BEA (200 nm)			716	75	0.25	
Al1.0-*BEA (500 nm)			638	66	0.23	
Al1.0-*BEA (700 nm)			608	60	0.22	
Ga _{0.6} /Al _{1.0} -*BEA	1.7	1.1	563	45	0.22	
Ga _{0.4} /Al _{1.0} -*BEA	2.6	1.6	578	35	0.22	
Ga _{0.2} /Al _{1.0} -*BEA	5.0	3.4	583	30	0.23	

Table S4. Physicochemical properties of aluminosilicate and Ga-impregnated *BEA zeolites.

Table S5. Relative proportions of framework and extra-framework Ga Species in *BEA zeolites.

*BEA zeolite	Framework (%) ^a	Extra-framework (%) ^a
Ga _{0.6} ,Al _{0.6} -*BEA	82.1	17.9
Ga _{0.4} ,Al _{0.6} -*BEA	85.4	14.6
Ga _{0.2} ,Al _{0.6} -*BEA	96.8	3.2
Ga _{0.6} /Al _{1.0} -*BEA	72.9	27.1
Ga _{0.4} /Al _{1.0} -*BEA	81.3	18.7
Ga _{0.2} /Al _{1.0} -*BEA	91.8	8.2

a. Proportion of framework and extra-framework Ga species are approximated from XPS spectra of Ga 2p_{3/2} (see Figure 2 and S5).

	Si/(Al+Ga) mole ratio		Total acidity ^b	TOF ^c		Carbon
*BEA zeolite *				$(mol_{DMF}mol_{site}^{-1}h^{-1})$		balance
	Gel	ICP	(µmorg)	(ICP)	(Acidity)	(%)
Al1.0-*BEA (200 nm)	25.0	23.3	640	9.95	9.74	87.2
Al _{1.0} -*BEA (500 nm)	25.0	26.0	632	9.81	8.84	92.1
Al _{1.0} -*BEA (700 nm)	25.0	27.6	630	7.28	6.25	91.9
Ga _{0.6} ,Al _{0.6} -*BEA	20.8	23.1	625	8.04	7.83	90.1
Ga _{0.4} ,Al _{0.6} -*BEA	25.0	27.4	558	8.82	8.41	94.5
Ga _{0.2} ,Al _{0.6} -*BEA	31.3	30.5	533	8.72	7.82	81.8
Ga _{0.6} /Al _{1.0} -*BEA	15.6	16.7	514	4.04	6.47	98.5
Ga _{0.4} /Al _{1.0} -*BEA	17.9	18.9	427	4.26	7.53	94.8
Ga _{0.2} /Al _{1.0} -*BEA	20.8	22.0	370	4.94	8.81	87.2

Table S6. Turnover frequency (TOF) of DMF during the first 3 h of reaction.

a. Proton-form aluminosilicate zeolites (Al_{1.0}*BEA) prepared with different sizes, and galloaluminosilicates prepared by direct (one-pot) synthesis (Ga_x,Al_y*BEA) and by incipient wetness impregnation (Ga_x/Al_y*BEA); b. total acidity measured by NH₃-TPD; c. measured as the slope of conversion versus time plots within the first 3 h and scaled by the moles of sites calculated from ICP (total moles of Al and Ga) and from NH₃-TPD (total acidity).

Supplementary Figures



Figure S1. (a) Powder XRD patterns of Al-*BEA (Ga-free), Ga,Al-*BEA (direct (one-pot) synthesis), and Ga/Al-*BEA (Ga-impregnated) samples. (b) Enlarged region of the dashed box in panel (a) for one-pot syntheses showing peak shifts to lower 2-theta with Ga heteroatom exchange.



Figure S2. Scanning electron micrographs of *BEA catalysts: (a) $Ga_{0.6}/Al_{1.0}$ -*BEA, (b) $Ga_{0.4}/Al_{1.0}$ -*BEA, (c) $Ga_{0.2}/Al_{1.0}$ -*BEA, (d) $Ga_{0.6},Al_{0.6}$ -*BEA, (e) $Ga_{0.4},Al_{0.6}$ -*BEA, (f) $Ga_{0.2},Al_{0.6}$ -*BEA, and (g) $Al_{1.0}$ -*BEA. All scale bars equal to 1 μ m.



Figure S3. Scanning electron micrographs of Al-*BEA catalysts. The alphabet on each image indicates the corresponding entry in Table S1. All scale bars equal to $1 \mu m$.



Figure S4. Nitrogen adsorption/desorption isotherms of *BEA zeolites prepared in the proton H-form.



Figure S5. X-ray photoelectron spectroscopy (XPS) spectra of Ga $2p_{3/2}$ for Ga-impregnated Ga/Al-*BEA: (a) Ga_{0.6}/Al_{1.0}-*BEA, (b) Ga_{0.4}/Al_{1.0}-*BEA, and (c) Ga_{0.2}/Al_{1.0}-*BEA samples. Carbon was used as a reference to determine systematic peak shifts. Peak deconvolution was executed using Gaussian fits to obtain relative proportions of framework (blue) and extra-framework (red) Ga species (see Table S5). Green lines indicate composite spectra.



Figure S6. (a) Ammonia temperature programmed desorption (NH₃-TPD) of Ga,Al-*BEA and Al-*BEA zeolites. (b) Pyridine-Fourier transform infrared (Py-FTIR) spectra of Ga,Al-*BEA and Al-*BEA zeolites.



Figure S7. Potential framework (a) and extra-framework (b - e) Ga species as follows: (a) Ga^{3+} , (b) Ga^{+} , (c) $[GaH_2]^+$, (d) $[GaO]^+$, and (e) $[GaH]^{2+}$ (where T=Al or Ga).¹⁻²



Figure S8. Time-resolved evolution of (by-)product selectivity: (a) p-xylene, (b) 2,5-hexanedione, (c) alkylated products, and (d) oligomer selectivity. Comparisons are made for Ga-free zeolite ($Al_{1.0}$ -*BEA) and one-pot syntheses of Ga,Al-zeolites (Ga_x , Al_y -*BEA).



Figure S9. DMF turnover frequency (TOF) calculated from the total moles of Al and Ga from ICP elemental analysis (see Table S6). Values reported here correspond to DMF conversion within the first 3 h of reaction for $Al_{1.0}$ -*BEA catalysts (closed black squares) prepared with different sizes (where the reference 700 nm sample is highlighted with an asterisk), Ga_x, Al_y -*BEA catalysts from one-pot syntheses (open red circles), and Ga-impregnated samples $Ga_x/Al_{1.0}$ -*BEA (open green diamonds).



Figure S10. Statistical analysis of reproducibility where we compare the results of three separate reactions using $Al_{1.0}$ -*BEA (700 nm). Before the reaction, samples were dried at 120 °C overnight to remove accumulated moisture. The weight change of samples after drying was 13.4 ± 0.5%. Reactions were carried out at the following conditions: 0.23 M DMF in n-heptane, 250 °C, 60 bar, and 600 mg of catalyst. Catalyst performance is shown as the average values of (a) DMF conversion and (c) p-xylene selectivity with error bars spanning two standard deviations. Averages were calculated from the three separate experiments, shown in (b) and (d), respectively. Dashed lines are interpolated to guide the eye.

References

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