Electronic Supplementary Information for:

cis,cis-Muconic acid: Separation and catalysis to bio-adipic acid for nylon-6,6 polymerization†

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Mass Transfer Considerations

For the batch reactor catalyst screening efforts, reaction conditions were based on those previously examined by the Koros-Nowak criterion to support surface reaction control.[16,94] For the flow reactor time-on-stream stability efforts, the Mears' and Weisz-Prater criterion were calculated to evaluate the influence of external and intraparticle mass transfer on the observed rate of muconic acid hydrogenation, as shown in **Equation S1** and **S2**. For the Mears' criterion, values less than 0.15 indicate that surface reaction kinetics control the observed rate of reaction, as opposed to external mass transfer (e.g., transport of reactants from the bulk liquid to the catalyst surface).[53] For the Weisz-Prater criterion, values less than 0.3 strongly indicate that surface reaction kinetics control the observed rate of reaction, as opposed to intraparticle mass transfer (e.g., diffusion of reactants from the catalyst surface into the pores).[53] In addition, Weisz-Prater values between 1.0-6.0 indicate a transition region that is reaction order dependent, while values greater than 6.0 indicate a strong influence of intraparticle diffusion on the observed rate.[95]

$$\textbf{Eqn. S1.}\quad \text{Mears' Criterion}\left[\text{unitless}\right] = \frac{r_{obs}\left[\frac{\text{mol}}{\text{sec } ml_{catalyst}}\right] R_{particle}\left[\text{cm}\right]}{C_A\left[\frac{\text{mol}}{\text{ml}}\right] k_c\left[\frac{\text{cm}}{\text{sec}}\right]} \; < \; 0.15$$

$$\textbf{Eqn. S2.}\quad \text{Weisz - Prater Criterion}\left[\text{unitless}\right] = \frac{r_{obs}\left[\frac{\text{mol}}{\text{sec } ml_{catalyst}}\right] R_{particle}^2\left[\text{cm}^2\right]}{C_A\left[\frac{\text{mol}}{\text{ml}}\right] D_{eff}\left[\frac{\text{cm}^2}{\text{sec}}\right]} \; < \; 0.30$$

For the trickle bed reactor experiments, the concentration of hydrogen in the bulk liquid phase was assumed to be at equilibrium with the concentration of hydrogen in the bulk gas phase, with values at 24 bar estimated from experimental values reported for hydrogen dissolution in ethanol at 55°C.[96] The radius for the granular catalyst was conservatively assumed to be 90 μm (sieve size 80-100 mesh, 150-180 μm diameter) with a porosity of 0.12 and assumed tortuosity of 1.5. For hydrogen mass transport, the diffusivity in ethanol was estimated using the Wilke-Chang correlation[97], the Sherwood number was estimated using the Thoenes-Kramers correlation,[98] and the hydrogen bulk liquid-to-solid mass transfer coefficient was calculated assuming a completely wetted particle surface. For muconic acid mass transport, the diffusivity in ethanol was approximated using values reported for citral.[95] Even though estimating transport parameters introduces uncertainty, calculation of the Mears' and Weisz-Prater criterion for the trickle bed reactor supports surface reaction controlling conditions for both hydrogen and muconic acid (Mears' < 0.15, Weisz-Prater < 0.30), with relevant calculation parameters and results summarized in **Table S4** and **Table S5**.

Supplementary Figures & Tables

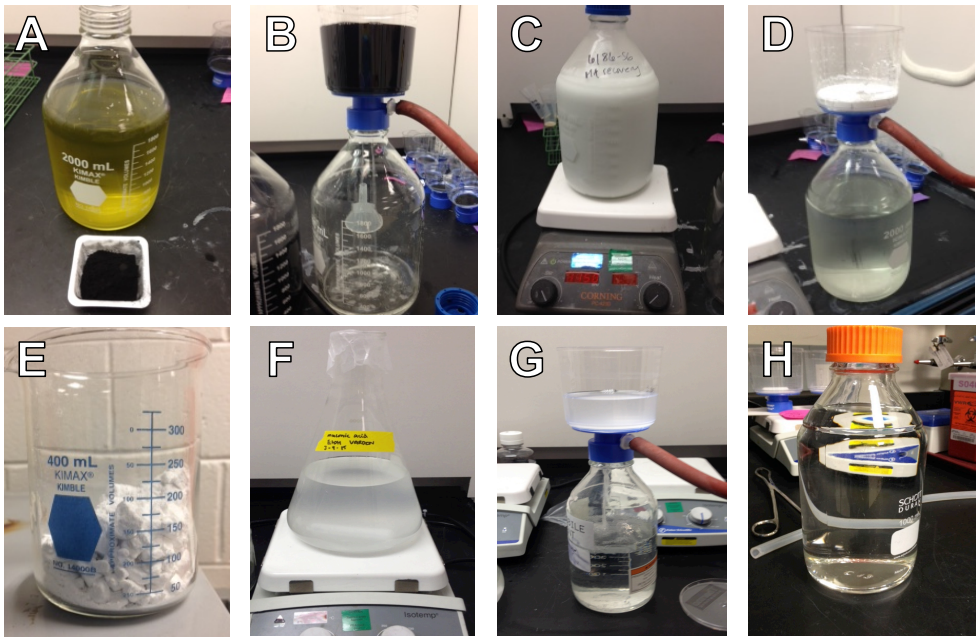

Figure S1. Purification of protein-removed muconic acid culture broth by activated carbon treatment, pH/temperature shift crystallization, and ethanol dissolution with microfiltration. The initial muconic acid culture broth appeared bright yellow colored (A). Activated carbon treatment of the broth significantly removed color compounds (B), while adjustment to pH 2 initiated crystal formation (C). Filtration (D) and drying of the purified broth produced a white crystal solid (E), with a purity of 97.71 ± 0.07% by DSC melting point analysis. Muconic acid crystals dissolved in ethanol resulted in a cloudy solution (F), that upon 0.2-µm microfiltration (G) resulted in a clear solution (H), with a final muconic acid purity of 99.82 ± 0.04% upon drying.

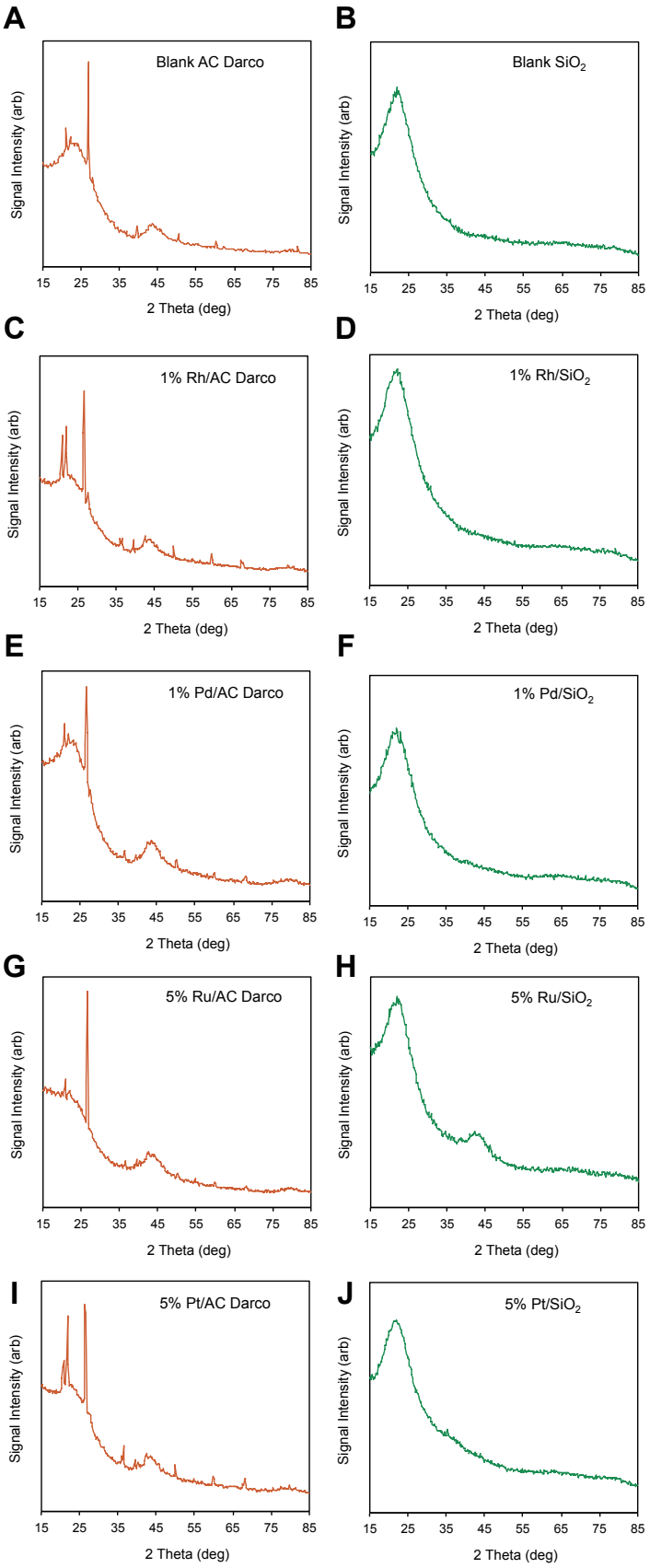

Figure S2. XRD spectra of blank supports and virgin catalysts used for batch reactor screening experiments. Spectra were provided for blank powdered AC (A) and silica (B) supports, as well as Rh, Pd, Ru, and Pt supported on AC (C, E, G, I) and silica (D, F, H, J). Catalyst XRD spectra were collected after metal loading and catalyst reduction.

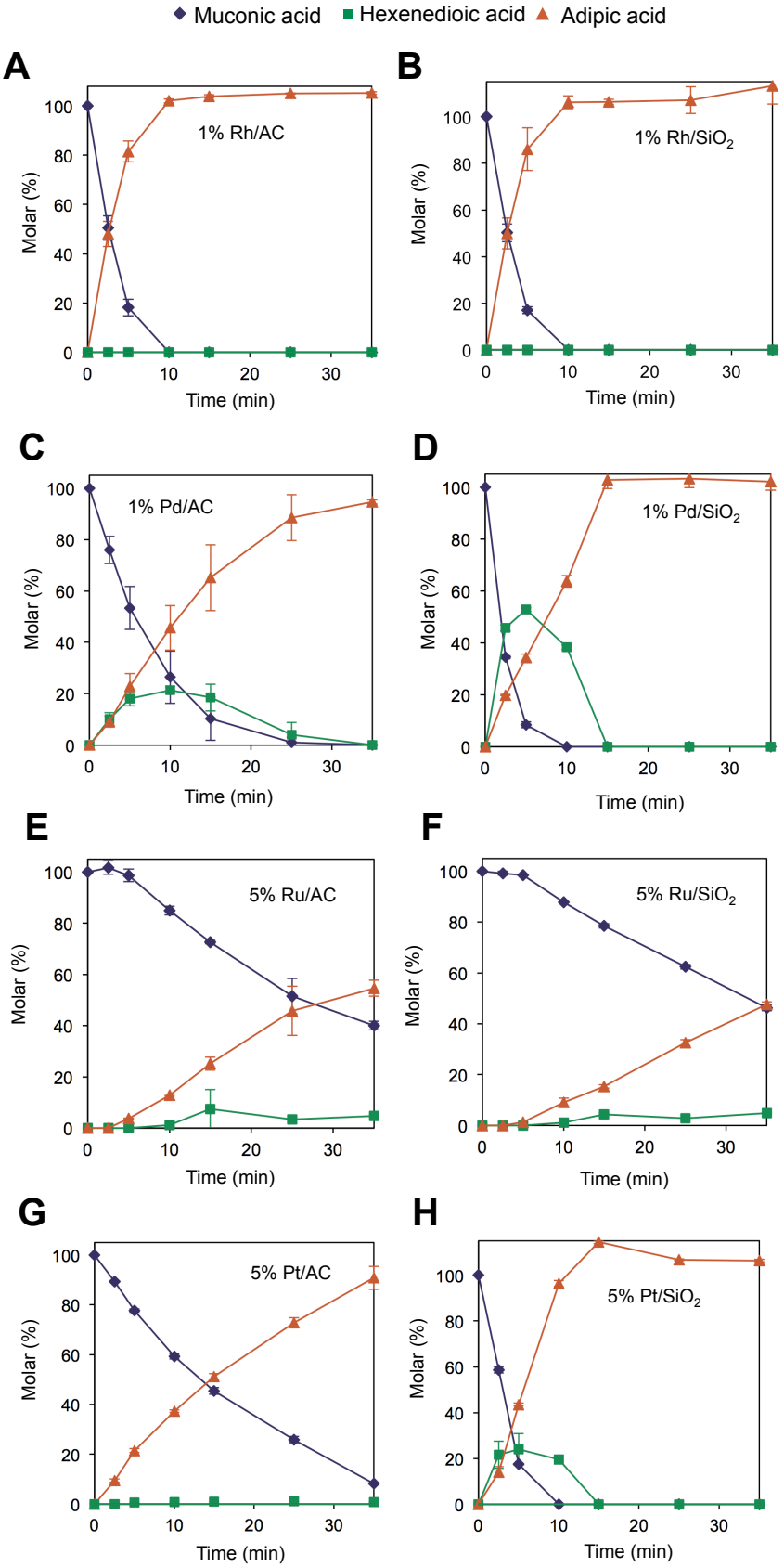

Figure S3. Batch reactor catalyst activity screening for muconic acid hydrogenation. Catalysts included Rh, Pd, Ru, and Pt supported on AC (A, C, E, G) and silica (B, D, F, H). Reactions were performed in a minimum of duplicate batch reactors, with error bars indicating standard deviations. Typical mass closure was ± 10%. Reaction conditions were as follows: temperature 24°C, muconic acid 200 mg, catalyst loading 15 mg, H_2 pressure 24 bar, EtOH solvent 19.8 g.

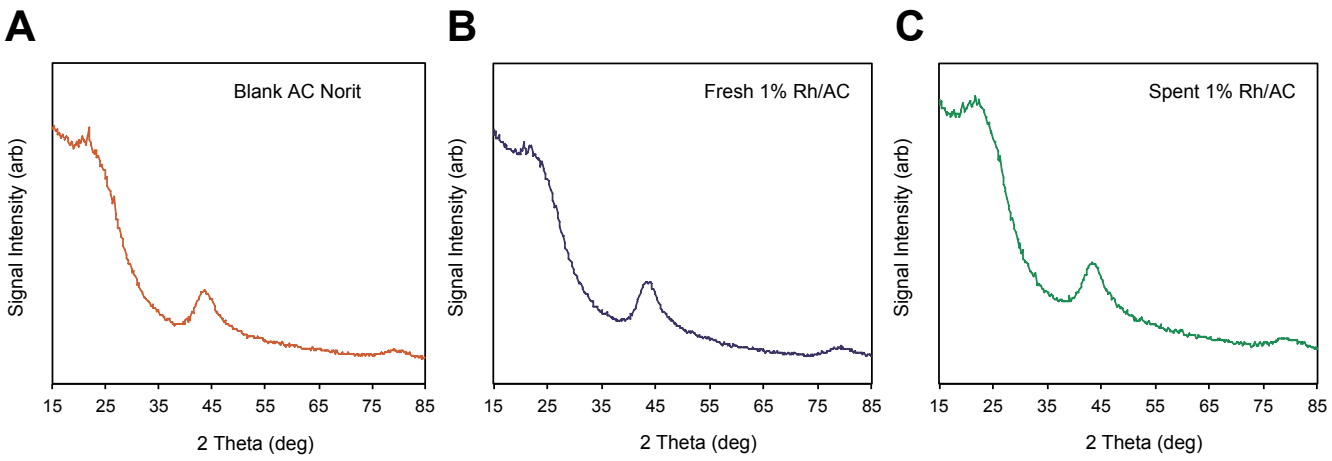

Figure S4. XRD spectra of blank AC support and 1% Rh/AC catalyst granules used for the trickle bed hydrogenation of muconic acid. Major XRD peaks for rhodium occur at 2θ values of 40.99°, 47.83°, 69.58°, and 84.10°. Spectra of the blank Norit activated carbon granule support provided for comparison (A). The virgin catalyst spectra was collected after metal loading and reduction (B), while the post reaction catalyst was collected after > 100 h of time-on-stream testing (C).

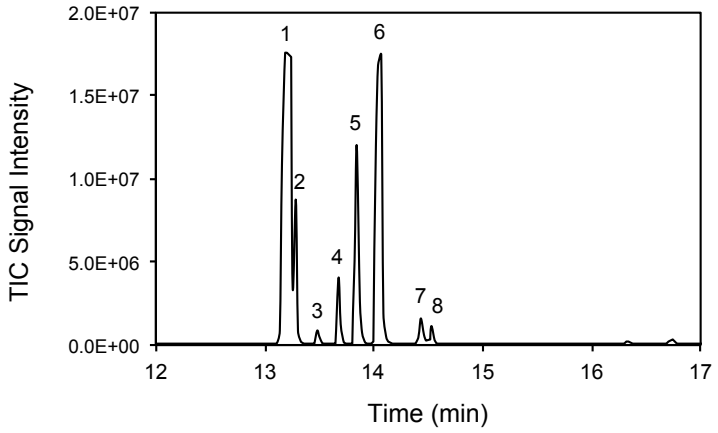

Figure S5. GC-MS TIC of methylated acids produced during the trickle bed hydrogenation of muconic acid at partial conversion conditions. Identified compounds are listed in Table S1.

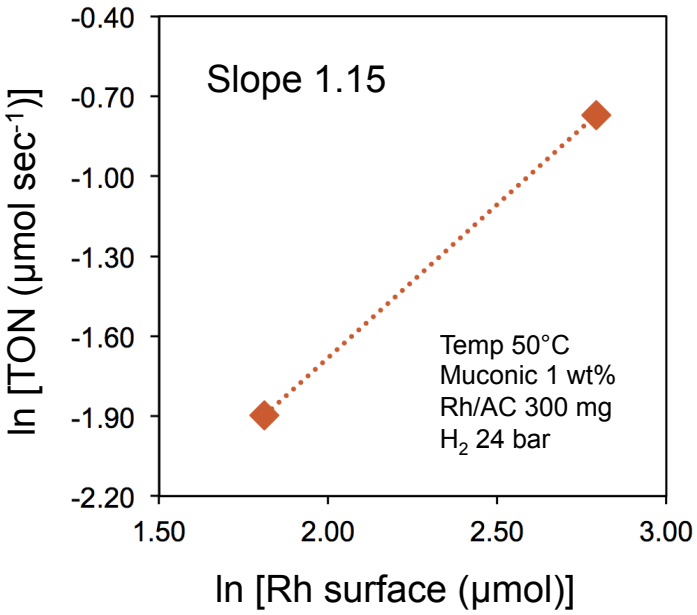

Fig S6. Koros-Nowak criterion to evaluate the influence of mass transfer on the trickle bed hydrogenation of muconic acid with Rh/AC. A slope of unity supports surface reaction-controlling conditions, with a measured slope of 1.15 in this work. Tests were conducted using 1 wt% and 2 wt% Rh/AC granules. Reaction conditions were as follows: muconic acid 1 wt% in ethanol, liquid flow rate 0.5 mL min^{-1}, temperature 50°C, H_2 200 sccm at 24 bar, catalyst loading 300 mg.

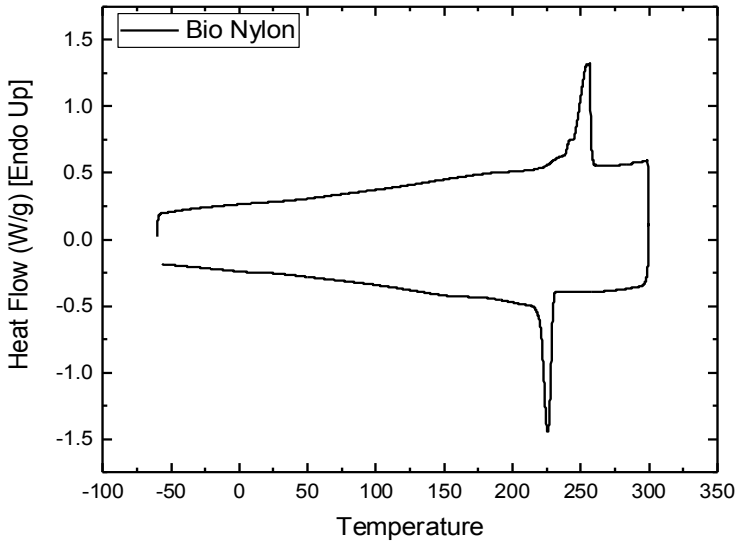

Fig S7. DSC thermal analysis of nylon-6,6 produced from biologically derived adipic acid. The polymer was scanned from -60°C to 200°C at a rate of 10°C/minute.

Table S1. Elemental impurities screened in muconic acid of chemical and biological origin, as well as adipic acid produced from the catalytic hydrogenation of muconic acid.

Elemental Impurity *(ppm)*	Commercial Muconic Acid *(chemical origin)*	Muconate Broth *(biological origin*	Crystallized Muconic Acid *(biological origin)*	EtOH Purified Muconic Acid *(biological origin)*	Bio-Adipic Acid *(muconic derived)*
Al	11	0.6	0.8	0.5	2.5
Ca	42	3.6	3.6	<1.0	1.2
Cl*	<10	497	318	217	18
Cu	0.2	<0.1	<0.1	0.1	<0.1
Fe	141	<0.2	0.4	0.4	1.4
K	3	1,320	1,120	261	6
Mg	7	28	22	0.2	0.3
Mn	0.1	<0.1	<0.1	<0.1	<0.1
Na	16	15,600	13,400	470	391
N	10	301	147	90	60
P	108	3,680	3,150	1,790	1,520
S	21	1,220	8,950	<10	23
Si	10	30	24	3	17

*Total halogens (Cl + Br + I) reported as equivalent chlorine.

Table S2. Volatile components identified by GC-MS for the trickle bed hydrogenation of muconic acid under partial conversion conditions. Compounds were methylated prior to analysis.

Peak No.	Ret. Time (min)	Compound Identified
1	13.22	Dimethyl Adipate
2	13.31	Dimethyl 2-Hexenedioate (Z)
3	13.51	Dimethyl Muconate
4	13.70	Dimethyl 3-Hexenedioate (Z)
5	13.87	Dimethyl 3-Hexenedioate (E)
6	14.09	Dimethyl 2-Hexenedioate (E)
7	14.46	Dimethyl Hexanedioate, 3-Methoxy
8	14.56	Dimethyl Muconate

Table S3. Time-on-stream results for the trickle bed hydrogenation of muconic acid.[a] Compounds were monitored by HPLC-RID.

Time (h)	Muconic (g/L)	2-HDA (g/L)	3-HDA (g/L)	Adipic (g/L)	Sum (g/L)
2	0.00	0.00	0.61	2.76	3.37
4	0.00	0.00	0.64	5.04	5.68
6	0.00	0.00	0.63	5.54	6.17
8	0.00	0.00	0.61	5.81	6.42
24	0.00	1.24	0.35	4.69	6.28
26	0.00	2.20	0.87	4.02	7.09
28	0.00	2.42	1.00	3.95	7.37
30	0.00	2.56	1.08	3.98	7.62
32	0.00	2.62	1.15	3.92	7.69
48	0.00	2.67	1.34	3.91	7.92
50	0.00	2.90	1.50	3.86	8.26
52	0.00	2.81	1.58	3.74	8.13
54	0.00	2.79	1.58	3.73	8.10
56	0.00	2.76	1.63	3.67	8.06
72	0.00	2.53	1.51	3.59	7.63
74	0.00	2.57	1.51	4.04	8.12
76	0.00	2.46	1.44	4.12	8.02
78	0.00	2.47	1.44	4.17	8.08
80	0.00	2.51	1.45	4.16	8.12
96	0.00	2.56	1.47	4.10	8.13
98	0.00	2.61	1.50	3.94	8.05
100	0.00	2.60	1.48	4.07	8.15
102	0.00	2.56	1.46	4.02	8.04
104	0.00	2.59	1.49	4.04	8.12

[a]Reaction conditions were as follows: Muconic acid 1 wt% in ethanol, liquid flow rate 0.5 mL/min, H_2 flow 200 sccm, system pressure 24 bar, 1100 mg 1% Rh/AC granules.

Table S4. Reaction and mass transport parameters evaluated for the trickle bed reactor hydrogenation of muconic acid after 24 h of time-on-stream.

Parameters	Values
Temperature	50°C
H_2 Pressure	24 bar
Solvent	Ethanol
Solvent vol. flow rate at ambient	8.33 E-3 ml sec^{-1}
Flow cross sectional area	0.317 cm^2
Ethanol density at 50°C	0.758 g cm^{-3}
Dissolved H_2 conc.[a]	1.00 E-4 mol cm^3
Dissolved muconic acid conc.	5.63 E-5 mol cm^3
Catalyst particle radius	9.00 E-3 cm
Catalyst bulk packing density	0.33 g cm^{-3}
Catalyst porosity[b]	0.4 unitless
Catalyst tortuosity[b]	1.5 unitless
Hydrogen D_{eff}[c]	3.89 E-5 cm^2 sec^{-1}
Muconic D_{eff}[c]	1.33 E-5 cm^2 sec^{-1}
Volumetric rate for H_2 consumption	5.13 E-7 mol sec^{-1} cm_{cat}^3
Volumetric rate for muconic acid conversion	2.57 E-7 mol sec^{-1} cm_{cat}^3
Reynolds number	0.09 unitless
Schmidt number for H_2	232 unitless
Schmidt number for muconic acid	677 unitless
Sherwood number for H_2[d]	3.1 unitless
Sherwood number for muconic acid[d]	3.6 unitless
Liquid-solid mass transfer coeff. for H_2	6.69 E-3 cm sec^{-1}
Liquid-solid mass transfer coeff. for muconic acid	2.63 E-3 cm sec^{-1}

[a]Values based on ref.[96] [b]Assumed value for tortuosity and porostiy.[53] [c] Calculated using the Wilke-Chang correlation, with diffusivity parameters of muconic acid based on citral.[95] [d]Calculated using the Frössling correlation.[53]

Table S5. Results for the Mears' and Weisz-Prater criterion for the trickle bed hydrogenation of muconic acid after 24 h of time-on-stream.

Parameter	Mears' criterion	Weisz-Prater criterion
Surface reaction control	< 0.15	< 0.30
Hydrogen consumption	0.033	0.002
Muconic acid conversion	0.086	0.005

Table S6. XPS peak-fitting parameters for the Rh 3d spectra.

Peak Label	Rh^0		Rh^{1+}		Rh^{3+}	
Orbital	Rh $3d_{5/2}$	Rh $3d_{3/2}$	Rh $3d_{5/2}$	Rh $3d_{3/2}$	Rh $3d_{5/2}$	Rh $3d_{3/2}$
Gauss-Lorentzian	80	80	80	80	80	80
Binding energy	307.5	312.2	308.4	313.1	310.2	314.9
FWHM	0.8	1.05	1.63	1.88	2.57	2.82
Separation	4.72		4.74		4.74	
Fresh catalyst Rh $3d_{5/2}$ relative area	33%		46%		21%	
Spent catalyst Rh $3d_{5/2}$ relative area	41%		39%		20%	