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Synthesis of Biomass-Derived Methylcyclopentane as a Gasoline Additive via Aldol Condensation/Hydrodeoxygenation of 2,5-hexanedione

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Supporting Information

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1. Experimental Methods and Materials

1.1. Reactants and Catalysts

All chemicals were used as received without further purification. Starting materials, including 2,5-hexanedione (HD, $\geq$98%) and 3-methyl-2-cyclopentenone (97%), were obtained from Sigma Aldrich, USA. Analytical standards which were used to verify the products observed by GC include 3-methylcyclopentanone (Alfa Aesar, 99%), 3-methylcyclopentanol (Acros, mixture of isomers, 99%), methylcyclopentane (Aldrich, 97%), and dodecane (Aldrich, $\geq$ 99%). Solvents were purchased as HPLC grade solvents from Fisher Scientific, while nanopure water was used for aqueous-phase experiments.

The following basic catalysts were obtained from commercial sources: K_3PO_4 (Acros, 97%), TiO_2 (Aldrich, anatase, 99.7%), and basic Al_2O_3 (Fisher, Brockman Activity I). MgO[1] and Mg-Zr-O[2] were synthesized according to previously reported methods. Mg-Al-O was synthesized by calcination of synthetic hydrotalcite (Sigma Aldrich) in static air in a muffle furnace. The temperature of the furnace was ramped at 2°C/min to 700°C, held for two hours, and cooled to 250°C before removal from the oven and storage.

Amberlyst 70 was obtained as a sample from the Dow Chemical Company. It was dried *in vacuo* at 105°C before grinding into a fine powder and sieving to ensure all particles were less than 63 μm in diameter. The $NbOPO_4$ support was obtained as a sample from CBMM, Brazil and calcined in flowing air at 300°C (2°C/min) prior to use. Supported Pt/$NbOPO_4$ and Pd/$NbOPO_4$ were synthesized by incipient wetness impregnation of calcined $NbOPO_4$. The respective precursors, H_2PtCl_6, hexahydrate (Aldrich) and $Pd(NO_3)_2$, dihydrate (Aldrich), were dissolved in water and slowly added to the catalyst with thorough mixing. The catalysts were then reduced in flowing H_2 (9% in He) for 2 hours at 300°C (2°C/min) to obtain 2 wt% metal loading.

1.2. Product and Catalyst Characterization

Reaction products were characterized by gas chromatography (GC) using a Varian CP-3800 GC equipped with a flame ionization detector (FID) and Varian 320-triple quadrupole mass spectrometer (MS). Product components were identified by GC/MS. Separation by GC was performed with a FactorFour VF-5 capillary column. Product mixtures were diluted such that components of interest were present in concentrations of 0.01-1.0 mg/mL using ethyl acetate, ethanol, or dicholoromethane as a GC solvent.

Quantification was performed using dodecane as an internal standard during reaction. Identity of major intermediates and products were determined from commercially available chemicals. The FID response factors of these components were determined by calibration of the peak area of a known quantity of the analyte compared to a known quantity of dodecane at several concentrations. Quantification of minor components, for which commercial sources were not available, was done by the effective carbon number method using the predicted response factor based on the structure of the molecule determined by GC/MS.[3]

Catalyst surface area was measured using a Micromeritics TriStar system. Approximately 100 mg of the catalyst was added to a tube and degassed for six hours in flowing argon at 180°C. The surface area was then assessed using the BET isotherm. Mean metal particle size on supported metal catalysts was measured using a Micromeritics AutoChem II Chemisorption

Analyzer to perform CO pulse chemisorption. Approximately 125 mg of catalyst was added to the sample tube, and the samples were reduced at 250°C in flowing H_2 (10% in Ar). After 30 minutes at 250°C, the sample was cooled to 40°C and subjected to pulses of CO in He. CO uptake was measured by a TCD. Structure of solid catalysts was assessed using x-ray diffraction patterns on a Bruker D8 instrument. Measurements were taken over a 2θ range of 10-80 degrees with a 0.02 degree step size.

1.3. Experimental Conditions

In a typical base-catalyzed experiment, the catalyst (40-50 mg) was weighed out and added to a 12 mL Q-tube reactor from Q Labtech. The starting materials were then introduced as mixture of toluene (2 mL), HD (1.2 mmol), and dodecane (136 mg). Water or additional toluene was added as required. A Teflon-coated magnetic stir bar was then added and the reactor was sealed with a PTFE seal. The sealed reactor was introduced to a preheated silicone oil bath on an IKA stir plate equipped with an ETS-D5 thermocontroller and stirred at 500 RPM for the prescribed reaction time, after which the reactor was removed and cooled. The product mixture was then diluted as described previously and analyzed by GC.

Hydrogenation testing was performed using an HEL ChemSCAN system that contained eight parallel autoclave reactors with independent temperature and pressure control. The catalyst (0.1 mol% exposed metal with respect to MCP) was added to the autoclave along with the reaction solution (2 mL toluene, 1.2 mmol MCP, 1.14 mg dodecane). The autoclave was then sealed, flushed with N_2 and H_2 (2.0 MPa × 2), and reacted for five hours with 500 RPM stirring and 3.0 MPa H_2 Pressure. After cooling in an ice bath, the reactors were opened, and the material was transferred to a 15 mL centrifuge tube. Transfer of the material was completed with 5 washes of 2 mL of dichloromethane. The product mixture was then diluted as described previously and analyzed by GC.

2. Supplemental Reaction Information

2.1. Measurement of Partition Coefficient

Procedure: Approximately 20.0 mg of MCP, HD, and dodecane were added to a bi-phasic system containing 2.0 mL of nanopure water and 2.0 mL of organic. A stirbar was added and the mixture was allowed to stir and equilibrate for a period of 30 minutes at 25.0°C on the surface of an IKA stir plate. The temperature was controlled via an IKA ETS-D5 thermocontroller. After 30 minutes, 50 μL of sample was removed from the organic phase. The organic layer was then analyzed by GC in 1.0 mL of ethyl acetate as a GC solvent. The total mass balance was assured by also taking a sample of both phases, combining and diluting them with ethanol, and analyzing the total amount of materials by GC.

Measurement of the partition coefficient using toluene as a bi-phasic extractant was also completed at 180°C by creating a mixture at the same concentrations to those listed above, but with 12 mL of each phase instead of 2.0 mL. The 24 mL mixture was loaded into a 50 mL Parr reactor and heated to 180°C with constant stirring. The toluene phase was sampled at 180°C using a dip tube. The combined mass balance was assured after cooling the mixture and sampling both phases, as described previously.

Table S1: Partition Coefficient of HD and MCP in the Organic Phase

Solvent	**Temp (°C)**	**Percent HD in Organic (%)**	**Percent MCP in Organic (%)**	**HD Part. Coeff. (P_{HD})**	**MCP Part. Coeff. (P_{MCP})**	**P_{MCP}/P_{HD}**
Butanol	25	56.4	74.5	1.29	2.92	2.26
$CHCl_3$	25	96.2	99.5	25.10	>50	≥2
Ethyl Acetate	25	64.9	71.8	1.85	2.54	1.38
Hexanes	25	3.3	8.7	0.03	0.10	2.80
Trimethyl Acetonitrile	25	58.7	67.3	1.42	2.06	1.45
Toluene	25	37.3	55.4	0.59	1.24	2.09
Toluene	180	44.0	66.0	0.79	1.94	2.47

2.2. Catalyst Recyclability Data

Procedure: The reaction was performed as described in the manuscript. At the end of reaction, the Q-Tube reactor was centrifuged at 2000 RPM for ten minutes, and the supernatant was decanted and analyzed as normal. The remaining catalyst was resuspended and washed with toluene (4 mL) for mono-phasic reactions or water (4 mL) for bi-phasic reactions. The mixture was then recentrifuged and decanted again. This washing procedure was repeated one additional time. The starting material was then loaded again for the following cycle. After five cycles, the catalyst was separated and re-calcined for two hours at 700°C (2°C/min ramp rate). The material was then subjected to an additional cycle, as shown in Figure S1.

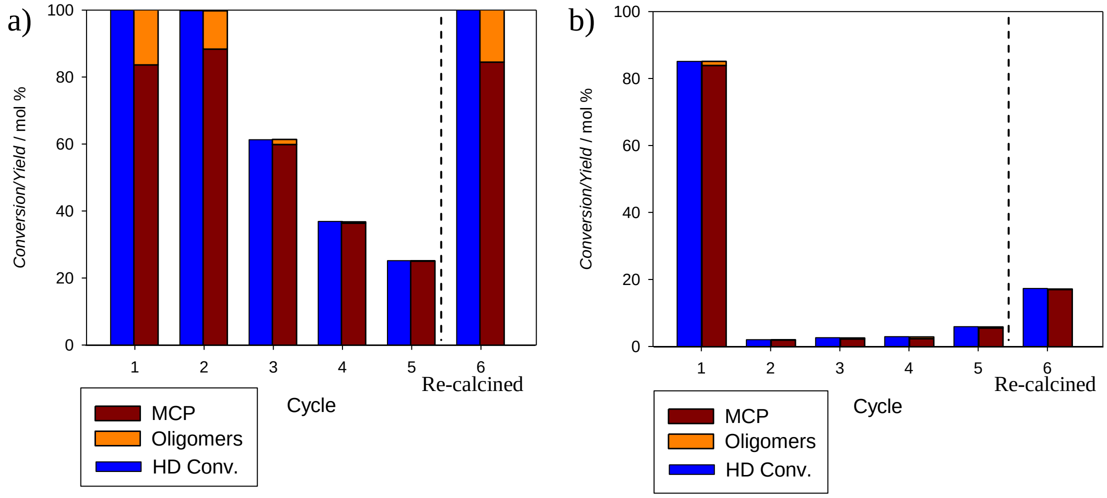


Figure S1: Recyclability of HD cyclization reaction to MCP (a) in toluene and (b) H_2O/toluene using Mg-Al-O. ***Reaction Conditions:*** 4 mL solvent (toluene or 2 mL H_2O/2 mL toluene), 1.2 mmol HD, 40 mg Mg-Al-O, 180°C, 1.5 h. Mg-Al-O was removed and re-calcined after 5 cycles. A 6th cycle was then run on this re-calcined material.

The stability of the hydrogenation catalyst, Pt/$NbOPO_4$ (2 wt%) was also tested under hydrogenation conditions. After three reaction cycles, the catalyst remained stable, achieving a methylcyclopentane yield of 98% and a yield of C_{12} products of 2%. This is nearly identical to the results observed in entry 6 of Table 2 in the main manuscript, indicating the catalyst does not deactivate rapidly.

2.3. Reactions in varied solvent systems

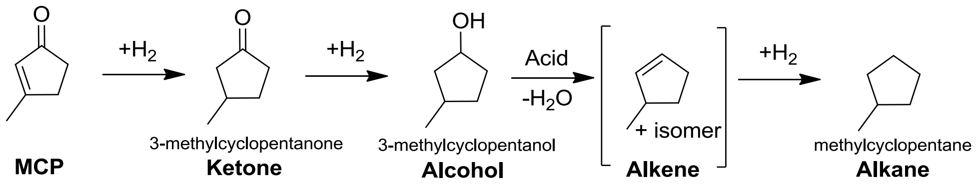
Table S2: Reaction of HD to MCP in various solvents catalyzed by K_3PO_4

Entry	Solvent	Temp (°C)	Time (hr)	K_3PO_4 Loading (mol%)	HD Conv. (%)	MCP Yield (mol%)
1	Toluene	100	4	97%	39.8	11.8
2	Trimethyl Acetonitrile	100	4	97%	27.6	10.8
3	Dimethyl Formamide	100	2	97%	98.3	33.5
4	Propyl Acetate	100	4	97%	37.1	5.4
5	Dioxane	100	4	97%	61.8	25.2
6	Water	100	2	97%	99.9	64.4
7	Water	180	2	2.0%	91.4	82.5
8	Water/Toluene	180	2	6.0%	98.4	95.2

Reaction Conditions: 3.4 mmol HD, 5.8 mL solvent, temperature: 100-180 °C. Catalyst loading is total K_3PO_4 with respect to HD.

2.4. Hydrogenation Screening

Table S3: Hydrodeoxygenation Screening with Pt/$NbOPO_4$



Entry	Pt Loading (mol%)	Temp (°C)	MCP Conv. (%)	Ketone Yield (mol%)	Alcohol Yield (%)	Methylcyclopentane Yield (mol%)	C12 Products (mol%)
1	0.1 mol%	170	100	0	0	96	4
2	0.1 mol%	150	100	0	0	98	2
3	0.05 mol%	110	100	0	68	20	11
4	0.1 mol%	110	100	0	54	32	14
5	0.2 mol%	110	100	0	41	44	15
6	0.1 mol%	90	100	0	64	28	7

Reaction Conditions: 1.2 mmol MCP, 2.0 mL toluene, 0.05-0.2 mol% exposed metal loading, 3.0 MPa H_2 pressure, 5h. Majority of C_{12} products are ether products at $\leq$ 110°C and are C-C bonded dimers at $\geq$ 150°C.

3. Characterization of Minor Products

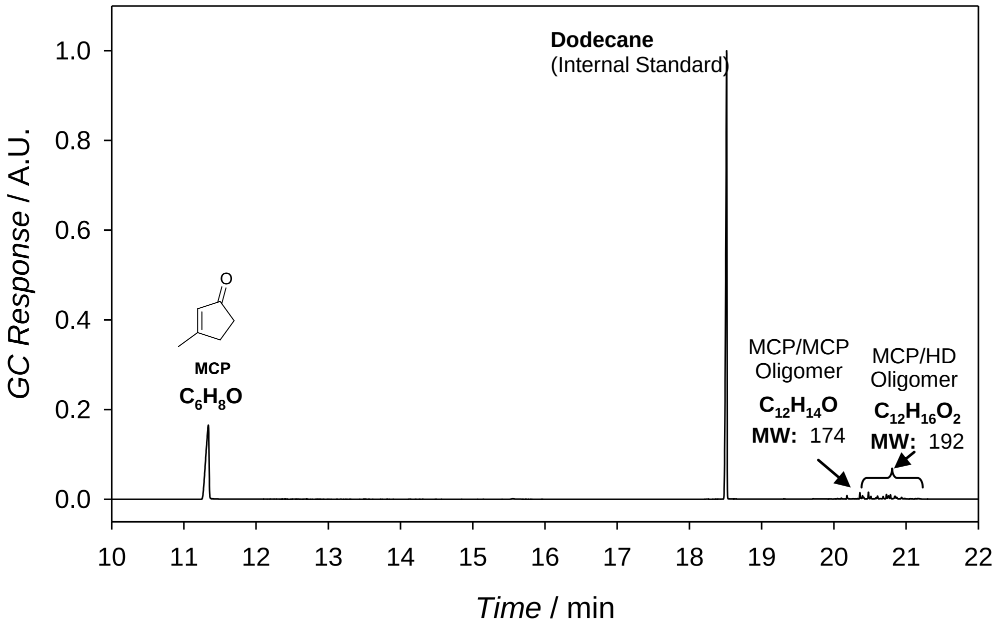


Figure S2: Products of mono-phasic HD cyclization to MCP.

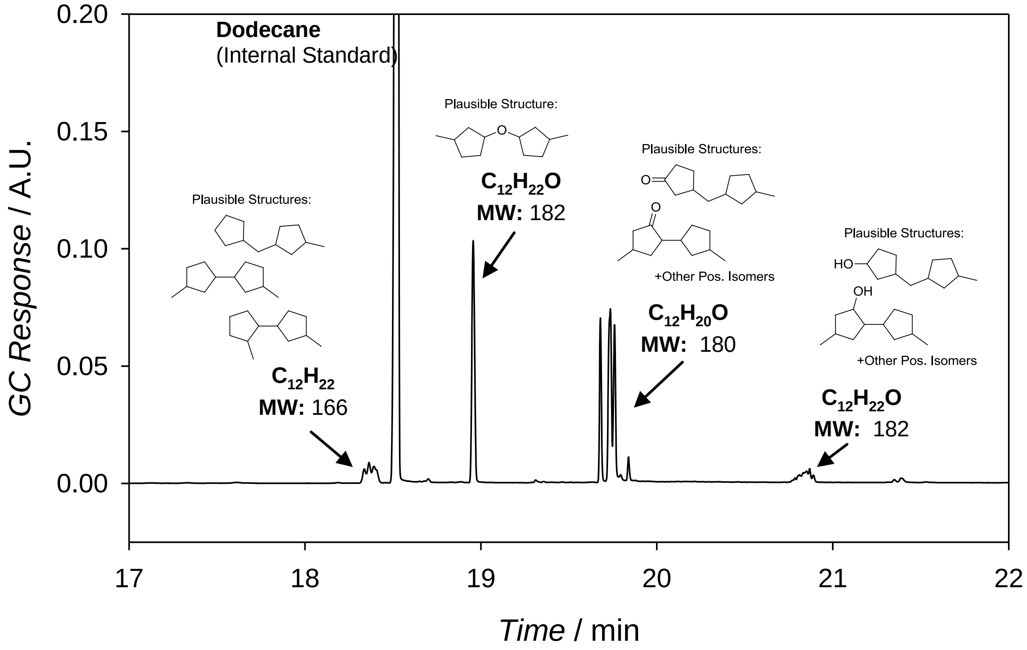


Figure S3: Products of MCP hydrodeoxygenation using ***Pd/NbOPO*** $_4$ (showing oligomer condensates). Plausible structures of hydrogenated oligomers are shown based on mass spectra signatures.

Note: All significant product peaks using Pt/C, Pd/C, or Pt/$NbOPO_4$ were verified with commercially available reference samples and MS.

4. Characterization of Catalysts

4.1. Characterization of Catalyst Surface Area

Table S4: Characterization of catalyst surface area via BET analysis.

Entry	**Catalyst**	**Catalyst Cycle**	**BET Surface Area** [m^2 g^{-1}]
1	K_3PO_4	0	0.15
2	TiO_2	0	118
3	Basic Al_2O_3	0	148
4	MgO	0	182
5	Mg-Zr-O	0	77.2
6	Mg-Al-O	0	178
7	Mg-Al-O	5 (bi-phasic)	67.6
8	Mg-Al-O	5 (mono-phasic)	27.5
9	Mg-Al-O	5 (bi-phasic) – Re-calcined	70.0
10	Mg-Al-O	5 (mono-phasic) – Re-calcined	148

4.2. Characterization of Metal Dispersion and Particle Size

Table S5: Metal dispersion and particle size determined by CO pulse chemisorption.

Sample	**Dispersion [%]**	**Particle Size** [nm]
Pt/C	25	4.6
Pd/C	21	5.4
Ru/C	20	5.0
Rh/C	24	4.5
Pt/$NbOPO_4$	13	8.4
Pd/$NbOPO_4$	35	3.2

4.3. XRD of Optimal Catalyst Materials

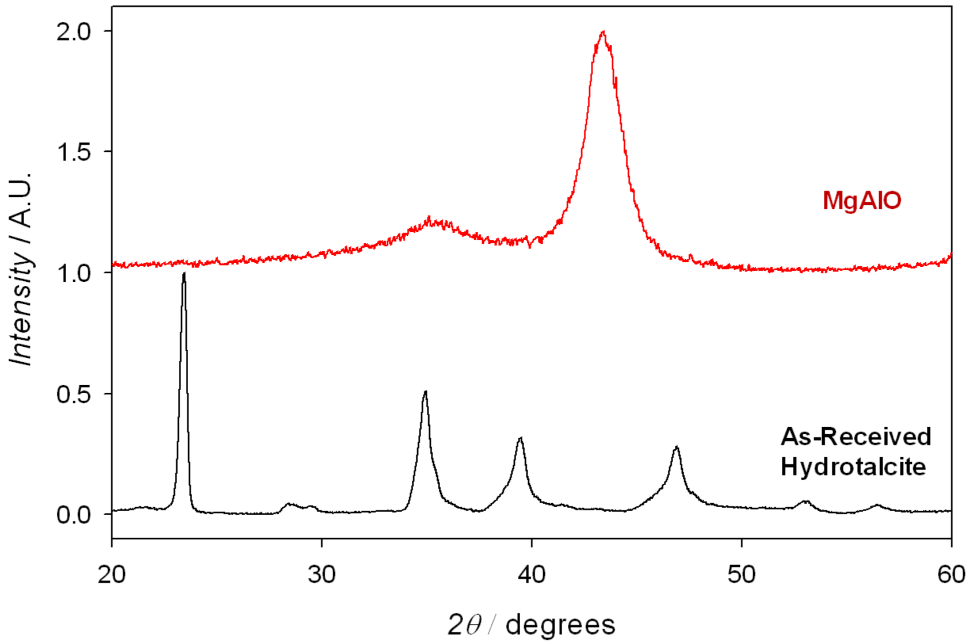


Figure S4: XRD powder patterns of Sigma Aldrich hydrotalcite and Mg-Al-O (calcined hydrotalcite), showing the transition from the brucite-like hydrotalcite to the periclase Mg-Al-O.

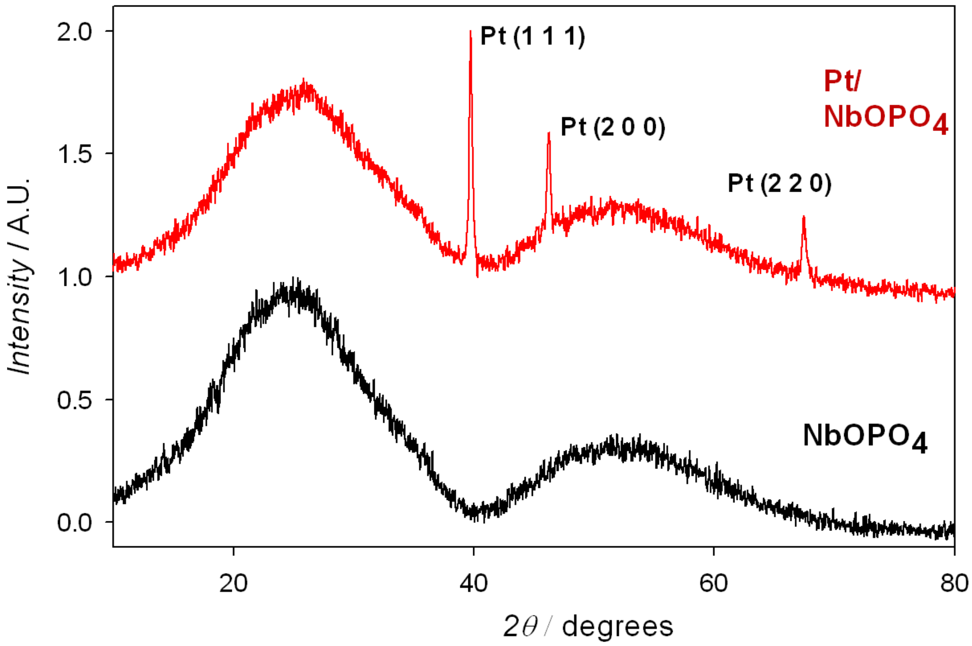


Figure S5: XRD powder patterns of calcined $NbOPO_4$ before and after impregnation of Pt (post-reduction).

5. Catalyst Activity in Water with Varied Calcination Conditions

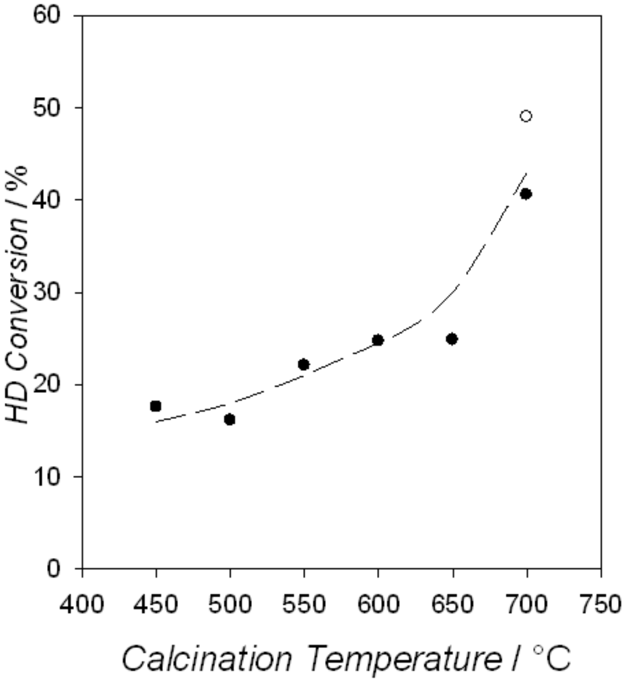


Figure S6: HD conversion (● and ○) in a water/toluene bi-phasic system as a function of Mg-Al-O calcination temperature using a 1 hour holding period (●) and 2 hour holding period (○) ***Reaction Conditions:*** 2 mL toluene, 2 mL H_2O, 1.2 mmol HD, 20 mg Mg-Al-O, 180°C, 1.5 h.

Table S6: Characterization of Mg-Al-O surface area vs. calcination severity.

Entry	**Catalyst**	**Calcination Temp (°C)**	**Holding Period (h)**	**BET Surface Area** [m^2 g^{-1}]
1	Mg-Al-O	450	1	190
2	Mg-Al-O	500	1	236
3	Mg-Al-O	550	1	237
4	Mg-Al-O	600	1	224
5	Mg-Al-O	650	1	218
6	Mg-Al-O	700	1	205
7	Mg-Al-O	700	2	182

6. Additional References

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