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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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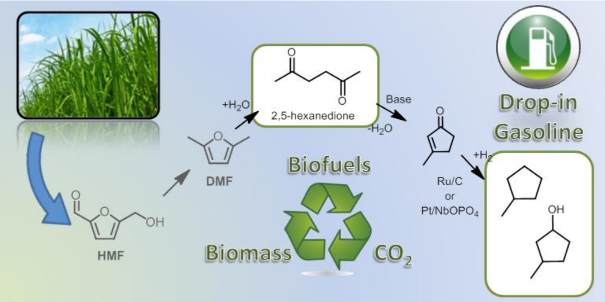

Highlights: We demonstrate that 2,5-hexanedione, a biomass-derived molecule, can be converted selectively in two steps to methylcyclopentane, an exceptional gasoline additive.

Abstract

A novel approach to produce biomass-derived gasoline is the hydrolysis of 2,5-dimethylfuran (DMF) to produce 2,5-hexanedione followed by base-catalyzed intramolecular aldol condensation of this product to form 3-methylcyclopent-2-enone (MCP). By proper choice of catalysts and conditions, MCP yields of 98% can be achieved. We show further that hydrogenation of MCP over Pt/$NbOPO_4$ gives methylcyclopentane with virtually quantitative yields. Methylcyclopentane is an attractive gasoline substitute for ethanol, since its octane number is comparable to ethanol and its gravimetric energy density is 58% higher.

Increasing concern with the environmental effects of greenhouse gases emissions resulting from the combustion of fossil fuels has motivated the search for strategies by which biomass could be converted to transportation fuels in a sustainable manner.[1-3] First generation biofuels produced from sugars, starches and triglycerides offer a temporary solution but face significant limitations because they use a limited portion of the total biomass,[4] produce oxygenated fuels that are not fully compatible with the current infrastructure,[5] and can result in the use of land that would otherwise be used to produce food.[6] Ethanol derived from corn or sugarcane has been used to provide a biomass-derived component that can be blended into gasoline. However, the low energy density of this fuel, together with its limited blending level (<10%) motivate the search for alternative biomass-based fuels. Lignocellulosic biomass derived from non-edible sources of biomass offers an attractive alternative to using starch or sucrose. The carbohydrate portion of lignocellulosic biomass can be converted to sugars[7] that, in turn, can be transformed into a variety of platform molecules for the production of fuels or chemicals.[2, 8-12]

A prominent example of a platform molecule is 5-hydroxymethylfurfural (HMF), which can be produced via dehydration of glucose, fructose or sucrose.[2, 12-13] HMF can be reduced to 2,5-bis(hydroxymethyl)furan, which, following hydrogenolysis (76-79% yield)[14] or formic acid-assisted deoxygenation (>95% yield),[15] produces 2,5-dimethylfuran (DMF). DMF has been suggested as a fuel additive due to its high octane number; however, recent work indicates that its use may be limited by its moderate toxicity.[16] While DMF could be converted to n-hexane by complete hydrodeoxygenation (Figure 1), this product is not attractive because of its low blending octane number, 21.[17] On the other hand, DMF will readily undergo quantitative hydrothermal hydrolysis to 2,5-hexanedione (HD),[18] as shown in Figure 1.

We describe here a previously unreported pathway for producing a gasoline additive from HD that involves base-catalyzed, intramolecular aldol condensation of HD to produce 3-methylcyclopent-2-enone (MCP) as an intermediate. Partial hydrogenation of MCP to 3-methylcylopentanol produces a material with volatility well within the range of gasoline. Additionally, complete hydrodeoxygenation of MCP produces methylcyclopentane, which has a blending octane number of 103[17] and an energy density of 46.8 MJ/kg[19] (vs. 29.7 MJ/kg for ethanol).[20] Therefore, the goal of this work is to develop a method to use HD as a biomass-derived platform molecule for the production of gasoline-range products with high selectivity using heterogeneous catalysts. Previous studies have shown that moderate yields of MCP can be achieved using soluble bases (e.g., NaOH and KOH);[21-25] however, these materials are corrosive and difficult to recover. Therefore, it is desirable to identify solid bases suitable for catalyzing the production of MCP from HD.

The aldol condensation of HD in toluene was investigated using a variety of solid bases; a summary of these efforts is shown in Table 1. The source of the catalysts and their methods of activation are discussed in the Supporting Information. K_3PO_4 (entry 1), a mild base with high selectivity for aldol condensation reactions,[26] exhibited high selectivity to MCP but low activity, most likely due to its low surface area (Supporting Information). Anatase TiO_2 (entry 2) was more active in catalyzing the cyclization of HD, but was less selective than any of the other catalysts screened. Basic Al_2O_3 (entry 3) produced a higher yield of MCP than TiO_2 but also a moderate amount of oligomers. Magnesium oxide and MgO doped with modifiers such as Al and Zr were examined based on previous reports of the activity of such materials for base-catalyzed condensations.[27-28] As noted in Table 1, entries 4-6, these materials enabled attainment of HD conversions of 89-99% and MCP selectivities of 78-93%. Additional products observed in all cases were higher oligomers formed by the reaction of MCP with either another equivalent of MCP or HD. Additional base-catalyzed condensations conducted in other solvents are presented in the Supporting Information with limited success.

To suppress the oligomerization of MCP, we investigated the possibility of using a bi-phasic system, as shown in Figure 2. In this case, HD is preferentially dissolved in water and the less polar MCP is preferentially extracted into an organic solvent. From here, MCP can either be separated and sold directly for specialty chemicals applications,[29-31] or further hydrogenated to produce fuels. Toluene was employed as the extracting solvent because the partition coefficient of MCP in toluene is significantly higher than that in alkanes. Morevoer, HD also has a lower solubility in toluene compared to MCP (see Supporting Information). Entries 7-15 of Table 1 report our findings for MCP condensation in the biphasic system. NaOH (0.2 M) was also investigated in addition to the catalysts considered previously.

While NaOH and K_3PO_4 (Table 1, entries 7 and 8) resulted in 100% conversion of HD in 0.75 h and high yields of MCP, these catalysts were not considered further because they fully dissolve in the aqueous phase. In contrast to what was observed in toluene alone, TiO_2, basic Al_2O_3, MgO, and Mg-Zr-O showed very low activity when the catalysts were exposed to water at 180°C, indicative of inhibition of these catalyst by water. While Mg-Zr-O has been reported to be active and water stable at mild conditions in other reactions,[32-33] it did not prove to be suitable for the present work because of its low activity in forming 3-methylcyclopent-2-enone in the bi-phasic system. For identical reaction conditions, the conversion of HD over Mg-Al-O in the biphasic system was roughly half of that observed for the reaction carried out in the monophasic system (compare entries 13 and 6). Here again, the lower activity of Mg-Al-O in water compared to toluene is attributed to the inhibiting effect of adsorbed water and associated structural changes. This effect, though, can be overcome by increasing the time of reaction from 0.75 h to 2 h and further increased by raising the amount of catalyst used to 50 mg (see Table 1, entries 14 and 15). It is particularly notable that, in the bi-phasic system, virtually all of the converted HD goes to MCP.

The temporal changes in the compositions of HD and MCP are shown in Figure 3 for the reaction of HD in toluene and in a water-toluene mixture with Mg-Al-O as the catalyst. When the reaction was carried out in toluene, 99% of HD was converted within the first 20 min of reaction, whereas the yield of MCP rose to a maximum value of 85%. For longer reaction times, the yield of MCP slowly declined. This loss in MCP is predominantly attributable to the reaction of HD and MCP with MCP to form oligomers (see Figure 1 and Supporting Information). In the biphasic system, the conversion of HD is over eight times slower than in the monophasic system but results in higher yield of MCP, e.g., after 2 h of reaction, the conversion of HD is 99% and the yield of MCP is 98%. The very high yield of MCP in the bi-phasic system is a direct consequence of the extraction of MCP from the aqueous phase, thereby reducing the possibility of its reaction with itself or with unreacted HD.

The stability of Mg-Al-O, calcined at 700°C for 2 h, was evaluated for both the mono-phasic and bi-phasic systems (Supporting Information). For reaction in toluene, after five reaction cycles the conversion of HD decreased from 99% to 25% due to a decrease in the catalyst surface area from 182 to 27 m^2/g. After completion of the fifth cycle, ~2 mg of water had formed per mg of catalyst, facilitating this structural change and inhibiting the activity of the catalyst. However, after re-calcination for 2 h at 700^{o}C, the initial activity was restored and the surface area returned to 149 m^2/g. Based on this knowledge, intermediate drying steps to remove water between cycles or a Dean-Stark apparatus for continuous water removal could also be used to limit deactivation. De-activation occurred much more rapidly in the bi-phasic system; much of the initial activity was lost by the second cycle, and the surface area decreased to 69 m^2/g after the first cycle, at which point it remained stable. While some activity could be regained by re-calcination, the initial catalyst activity and surface area could not be fully restored in the bi-phasic system (see Supporting Information). These results indicated that while conducting MCP condensation in a bi-phasic system results in a high MCP yield, it leads to a loss in catalyst recyclability. By contrast, operation in the monophasic system allows for catalyst regeneration but results in lower MCP yields. Systematic study of the effects of water exposure to hydrotalcite-derived Mg-Al-O materials is in progress using multiple reaction systems and will be reported separately.

To serve as a fuel, the alkene and ketone functionalities in MCP must be removed in order to achieve long storage stability. This can be achieved by hydrogenation. Table 2 demonstrates that the conversion of MCP and the distribution of products are strong functions of the catalyst composition. All carbon-supported catalysts result in 100% conversion of MCP after 5 h of reaction. Pd/C produced principally 3-methylcyclopentanone (87%), whereas Pt/C, Rh/C, and Ru/C produced over 92% 3-methylcyclopentanol. Only very small yields of methylcyclopentane were obtained using any of the carbon-supported catalysts.

Previous studies have demonstrated that hydrodeoxygenation of biomass-derived furanics and their derivatives is enabled by supporting noble metals on acidic supports.[34-35] In Table 2, we show the results of MCP hydrogenation using Pt/C together with Amberlyst 70 (A70) or $NbOPO_4$-supported Pt or Pd. Nearly quantitative yields of methylcyclopentane were obtained using Pt/C+A70 or Pt/$NbOPO_4$ at reaction temperatures of 150°C. These results suggest that the 3-methylcyclopentanol produced by the hydrogenation of MCP over Pt undergoes dehydration over the acidic sites of A70 or $NbOPO_4$ and that the resulting alkene then undergoes hydrogenation over Pt to form methylcyclopentane, as shown in Table 2. Additional screening of $Pt/NbOPO_4$ is reported in the Supporting Information. The $Pt/NbOPO_4$ sample used in this work was also tested for stability, as shown in Table 2, entry 7. After three cycles, the catalyst retained its original activity, showing that it can be recycled without a significant loss in activity. These findings are consistent with those of earlier work, which show that niobium supports are water stable[34] and that $Pt/NbOPO_4$ does not show apparent signs of deactivation after 38 h of time on stream for the hydrodeoxygenation of C_8 diols to octane in a THF solvent.[35]

Hydrodeoxygenation of MCP over $Pd/NbOPO_4$ resulted in production of only 33% methylcyclopentane and formed C_{12} products in significant yields (46%). While some etherification of 3-methylcyclopentanol was observed (14%), most of the observed C_{12} products (32%) were a direct consequence of accumulation of 3-methylcyclopentanone over $Pd/NbOPO_4$. It is proposed that 3-methylcyclopentanone undergoes acid-catalyzed aldol condensation on $NbOPO_4$ to form C_{12} dimer condensates, which in turn undergo various degrees of hydrogenation over Pd (see Supporting Information).

Conclusion

Base-catalyzed condensation of HD to MCP can be performed with exceptional selectivity. While Mg-Zr-O provides the highest selectivity for transformation of HD to MCP in a mono-phasic toluene solution, Mg-Al-O provides higher activity. The formation of water as a byproduct of HD condensation contributes to a loss of catalyst activity, but the original activity can be regained by recalcination of the catalyst. Alternatively, continual removal of water could also be applied to prevent water-associated catalyst deactivation. Higher MCP selectivity could be achieved by conducting HD condensation in an aqueous phase and extracting the product, MCP, into toluene. However, in this case, a significant part of the original activity of Mg-Al-O was lost after one reaction cycle due to structural changes of the catalyst and an associated loss in catalyst surface area which could not be regained by recalcination.

Hydrogenation of MCP to useful products could be achieved by a variety of supported metals. Pt/C and Ru/C provide high selectivity to 3-methylcyclopentanol, a potential octane booster for gasoline, while Pt/$NbOPO_4$ was active and selective for formation of methylcyclopentane, an alkane already found in gasoline. Using the two-step strategy of base-catalyzed condensation followed by hydrogenation, high-quality gasoline additives could be produced from biomass-derived 2,5-hexanedione in exceptional yields. The high blending octane number, energy density, and gasoline miscibility of methylcyclopentane suggest that it would be an excellent biomass-based gasoline blending agent.

Acknowledgements

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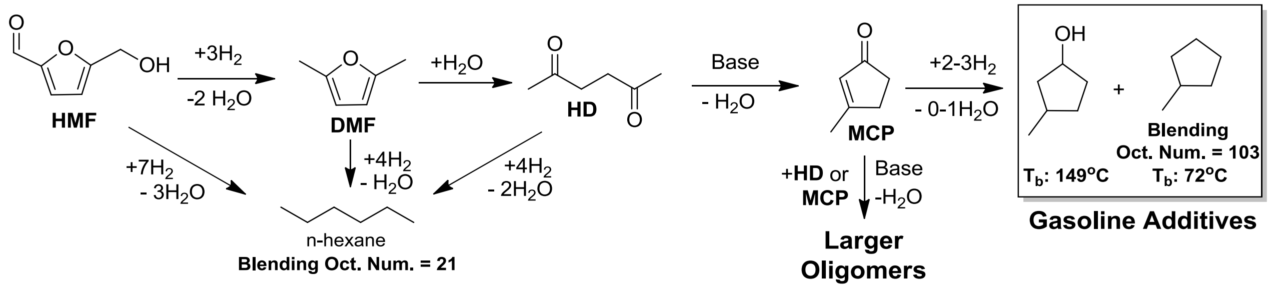


Figure 1: Pathways of HMF and HD Utilization for Gasoline Products

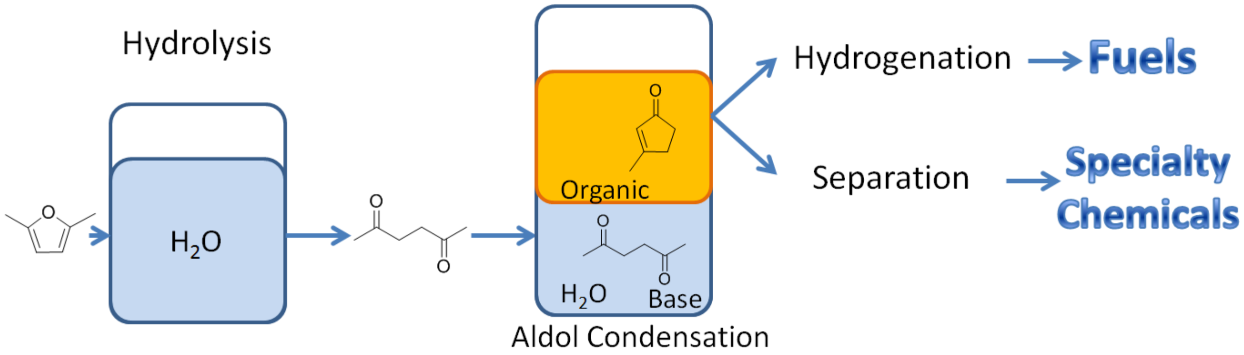


Figure 2: Bi-Phasic Reactor Scheme for HD Cyclization

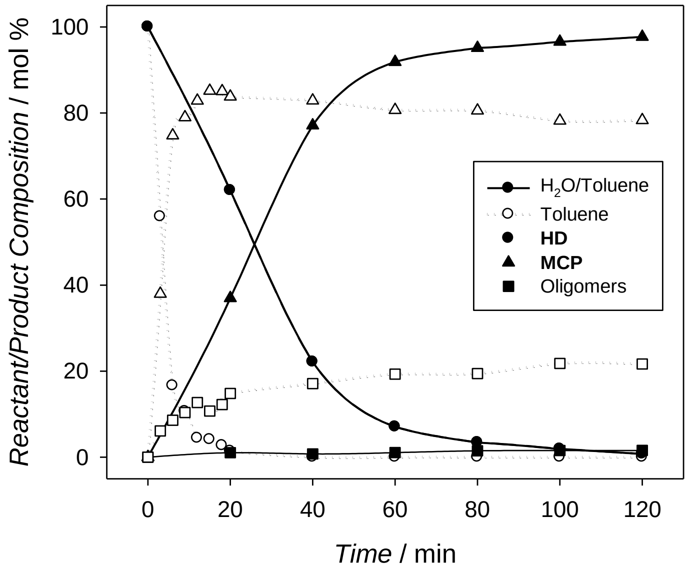


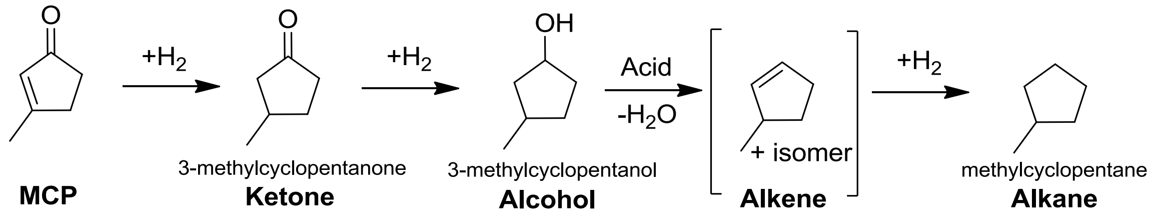
Figure 3: HD cyclization reaction to MCP in toluene (hollow symbols/dashed lines) and H_2O/toluene (solid symbols/lines). *Reaction Conditions:* 4 mL solvent (toluene or 2 mL H_2O/2 mL toluene), 1.2 mmol HD, 50 mg Mg-Al-O as catalyst, 180°C, 2 h.

Table 1: Screening of Basic Catalysts for Aldol Condensation of HD to MCP

Entry	Catalyst	Cat. Amt. [mg]	Solvent	Time [h]	Conv. HD [%]	Yield MCP [mol %]	Yield Oligomers [mol %]	MCP Sel. [mol %]
1	K_3PO_4	40	Toluene	0.75	35	31	3	89
2	TiO_2	40	Toluene	0.75	74	53	16	71
3	Basic Al_2O_3	40	Toluene	0.75	94	78	13	84
4	MgO	40	Toluene	0.75	99	78	17	78
5	Mg-Zr-O	40	Toluene	0.75	89	82	7	93
6	Mg-Al-O	40	Toluene	0.75	94	75	15	80
7	NaOH	0.2 M	H_2O/Toluene	0.75	100	85	15	85
8	K_3PO_4	40	H_2O/Toluene	0.75	100	94	6	94
9	TiO_2	40	H_2O/Toluene	0.75	2	1	0	-
10	Basic Al_2O_3	40	H_2O/Toluene	0.75	2	1	0	-
11	MgO	40	H_2O/Toluene	0.75	3	2	0	-
12	Mg-Zr-O	40	H_2O/Toluene	0.75	4	3	0	-
13	Mg-Al-O	40	H_2O/Toluene	0.75	52	51	0	99
14	Mg-Al-O	40	H_2O/Toluene	2.0	85	84	1	99
15	Mg-Al-O	50	H_2O/Toluene	2.0	99	98	2	98

Reaction Conditions: 1.2 mmol HD, 4.0 mL toluene or 2.0 mL toluene/2.0 mL water, temperature: 180 °C. Catalyst synthesis procedures and sources available in Supporting Information. Mg-Al-O – Mg/Al mixed metal oxide from calcined hydrotalcite (Mg/Al = 3), Mg-Zr-O – Mg/Zr mixed metal oxide (synthesis in Supporting Information).

Table 2: Screening of Catalysts for Hydrogenation of MCP



Entry	Catalyst	Conversion of MCP [%]	Yield of Ketone [mol %]	Yield of Alcohol [mol %]	Yield of Alkane [mol %]	Yield of Coupled C_{12} Products [mol %]
1	Pt/C	100	5	92	2	1
2	Pd/C	100	87	13	0	0
3	Rh/C	100	1	92	2	5
4	Ru/C	100	0	99	1	0
5	Pt/C + A70[a]	100	1	0	98	1
6	Pt/$NbOPO_4$	100	0	0	99	1
7	Pt/$NbOPO_4$ (3rd cycle)	100	0	0	98	2
8	Pd/$NbOPO_4$	100	6	13	33	46

Reaction Conditions: 1.2 mmol MCP, 2.0 mL toluene, 0.1 mol% exposed metal loading, 3.0 MPa H_2 pressure, 150 °C, 5h. [a] 5 mol% acid sites on A70. Catalyst synthesis procedures and sources available in Supporting Information.

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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

Contents

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.

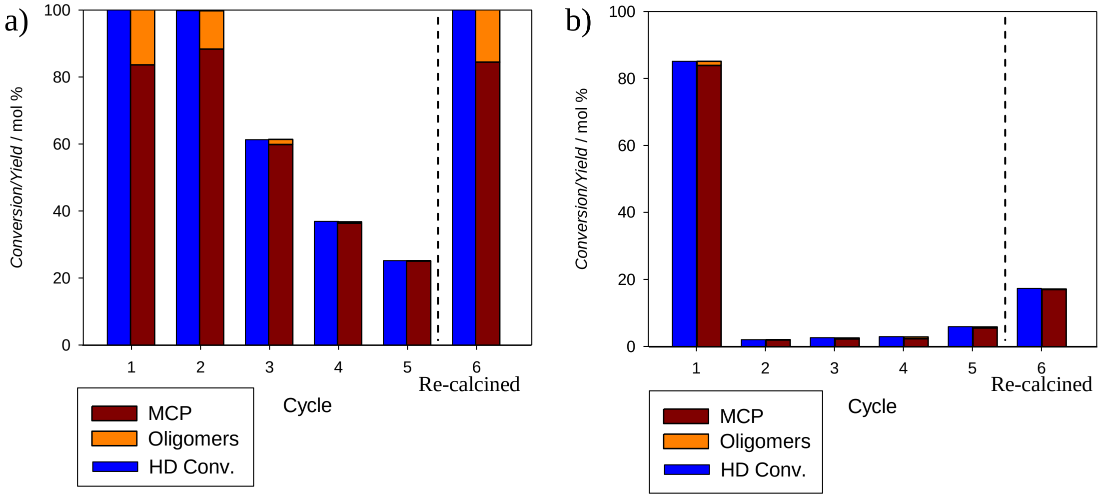


Figure S1: Recyclability of HD cyclization reaction to MCP (a) in toluene and (b) H_2O/toluene using Mg-Al-O. ***Reaction Conditions:*** 4 mL solvent (toluene or 2 mL H_2O/2 mL toluene), 1.2 mmol HD, 40 mg Mg-Al-O, 180°C, 1.5 h. Mg-Al-O was removed and re-calcined after 5 cycles. A 6th cycle was then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

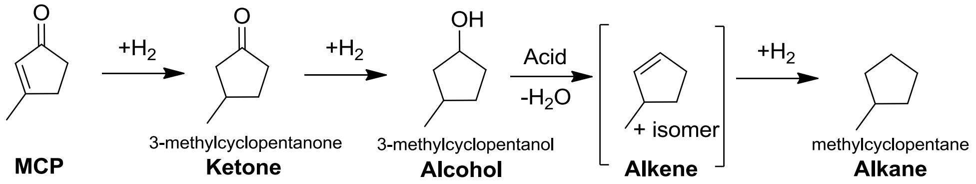
Table S2: Reaction of HD to MCP in various solvents catalyzed by K_3PO_4

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

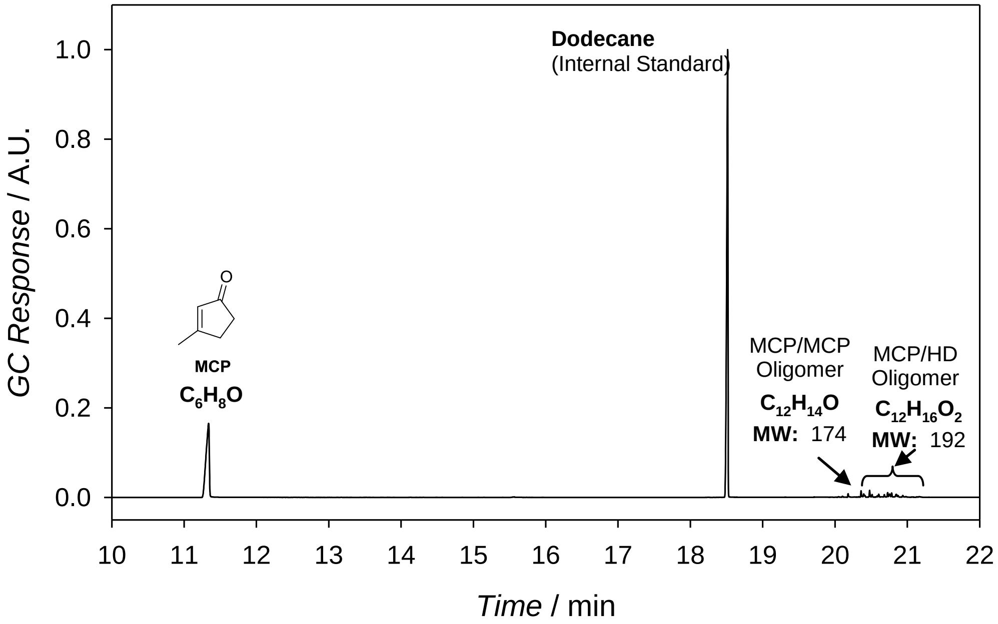


Figure S2: Products of mono-phasic HD cyclization to MCP.

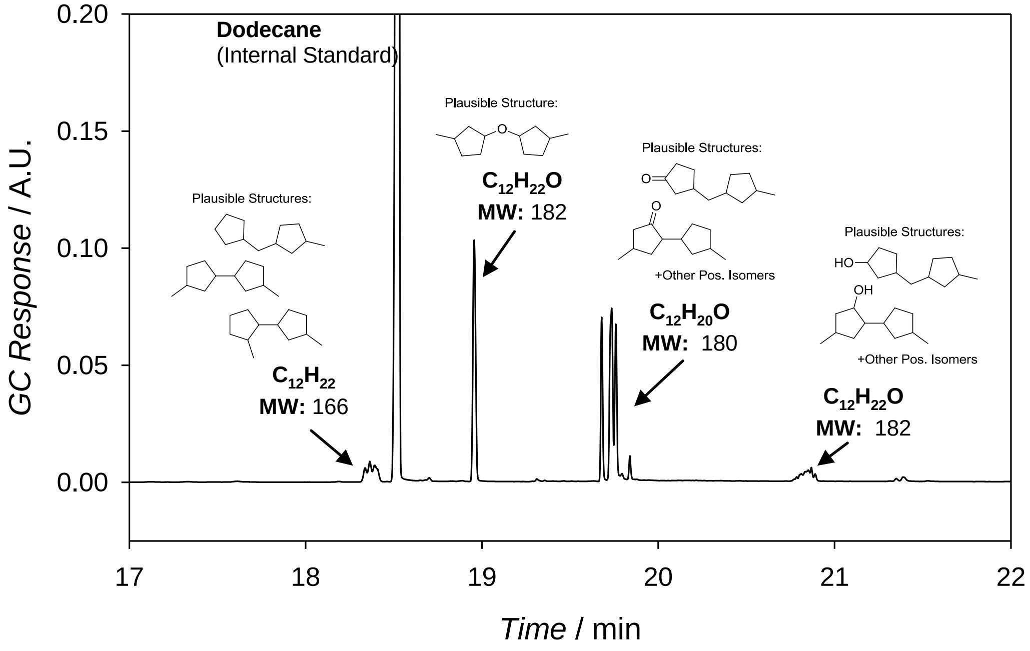


Figure S3: Products of MCP hydrodeoxygenation using ***Pd/NbOPO$_4$*** (showing oligomer condensates). Plausible structures of hydrogenated oligomers are shown based on mass spectra signatures.

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

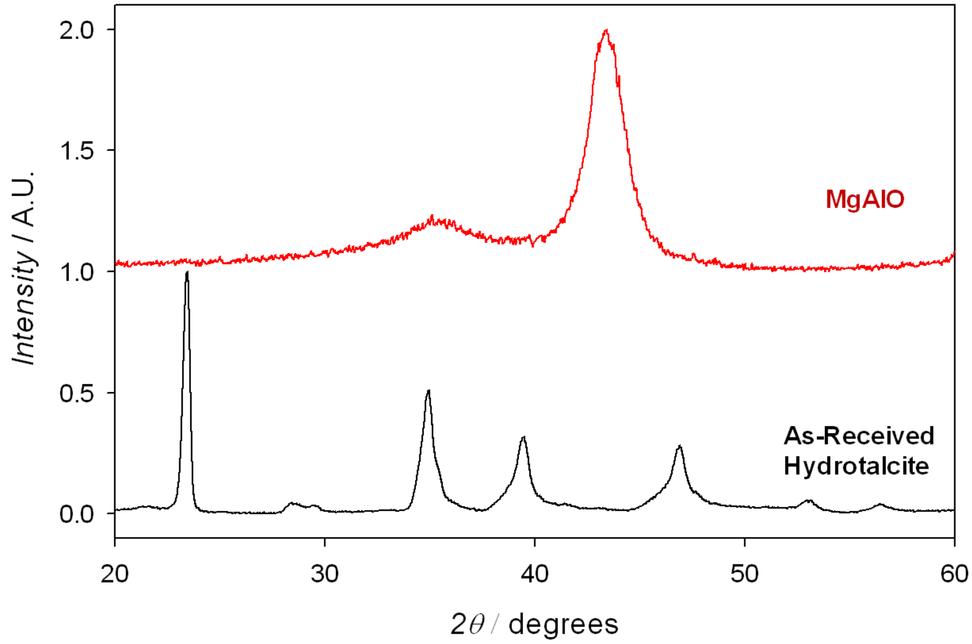


Figure S4: XRD powder patterns of Sigma Aldrich hydrotalcite and Mg-Al-O (calcined hydrotalcite), showing the transition from the brucite-like hydrotalcite to the periclase Mg-Al-O.

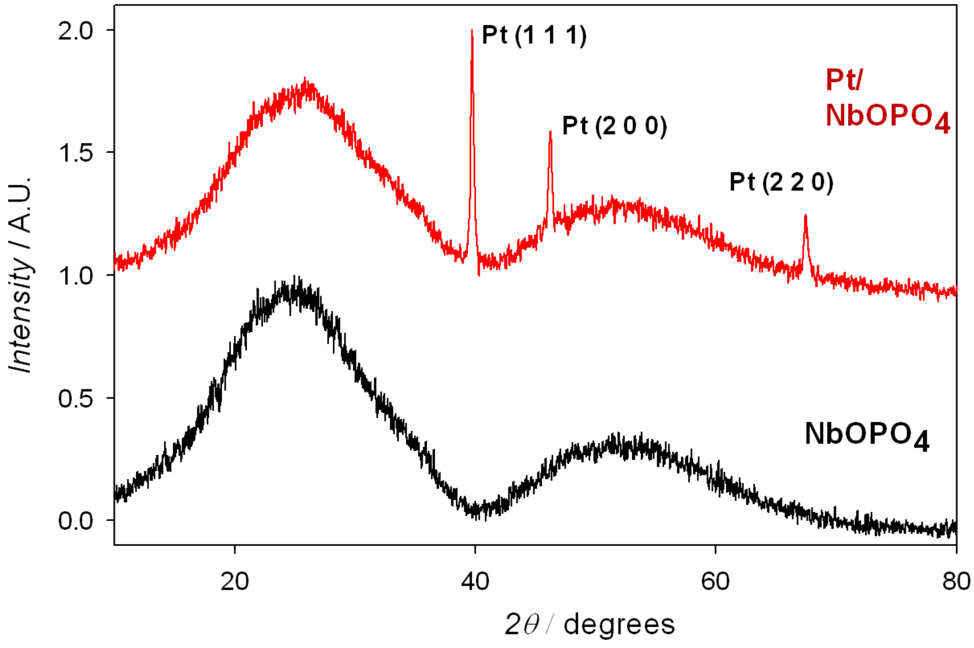


Figure S5: XRD powder patterns of calcined $NbOPO_4$ before and after impregnation of Pt (post-reduction).

5. Catalyst Activity in Water with Varied Calcination Conditions

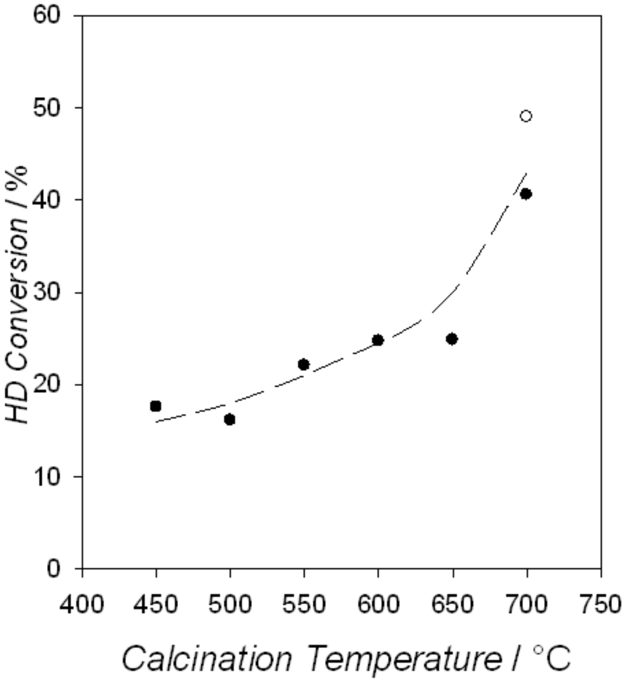


Figure S6: HD conversion (● and ○) in a water/toluene bi-phasic system as a function of Mg-Al-O calcination temperature using a 1 hour holding period (●) and 2 hour holding period (○) ***Reaction Conditions:*** 2 mL toluene, 2 mL H_2O, 1.2 mmol HD, 20 mg Mg-Al-O, 180°C, 1.5 h.

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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