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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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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 further show that hydrogenation of MCP over Pt/NbOPO₄ gives methylcyclopentane with virtually quantitative yields. Methylcyclopentane is an attractive gasoline substitute for ethanol, since its octane number is similar to ethanol and its gravimetric energy density is 58% higher.

Increasing concern with the environmental effects of greenhouse gas 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 (Fig. 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 Fig. 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-methylcyclopentanol 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⁻¹ (ref. 19) (*vs.* 29.7 MJ kg⁻¹ 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 ESI.† K₃PO₄ (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 (ESI†). Anatase TiO₂ (entry 2) was more active in catalyzing the cyclization of HD,

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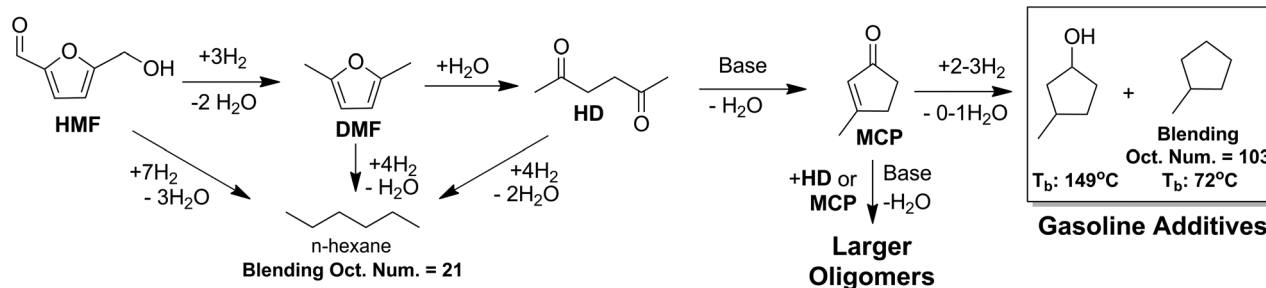
Fig. 1 Pathways of HMF and HD utilization for gasoline products.

Table 1 Screening of basic catalysts for aldol condensation of HD to MCP[a]

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

[a] 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 ESI. Mg–Al–O – Mg/Al mixed metal oxide from calcined hydrotalcite (Mg/Al = 3), Mg–Zr–O – Mg/Zr mixed metal oxide (synthesis in ESI).

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 ESI† with limited success.

To suppress the oligomerization of MCP, we investigated the possibility of using a biphasic system, as shown in Fig. 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. Moreover, HD also has a lower solubility in toluene compared to MCP
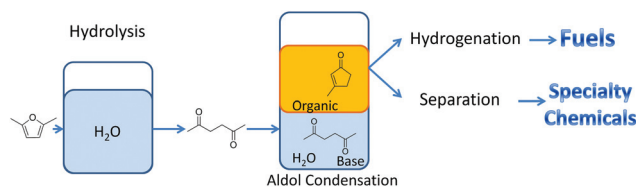

Fig. 2 Bi-phasic reactor scheme for HD cyclization.

(see ESI†). Entries 7–15 of Table 1 report our findings for HD 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, making processing and catalyst recycle more complex. 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 biphasic 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 to the catalyst. 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 Fig. 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 Fig. 1 and ESI†). 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 biphasic 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 monophasic and biphasic systems (ESI†). 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^{-1}. 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 °C, the initial activity was restored and the surface area returned to 149 m^2 g^{-1}. 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 biphasic system; much of the initial activity was lost by the second cycle, and the surface area decreased to 69 m^2 g^{-1} 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 biphasic system (see ESI†). These results indicated that while conducting MCP condensation in a biphasic 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 ESI.† 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]

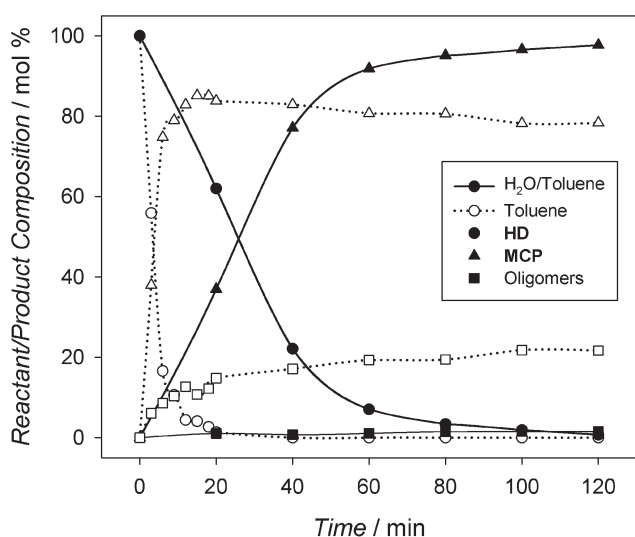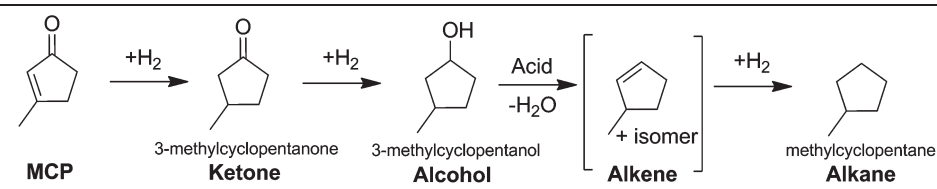Hydrodeoxygenation of MCP over Pd/NbOPO$_4$ resulted in production of only 33% methylcyclopentane and formed C$_{12}$

Fig. 3 HD cyclization reaction to MCP in toluene (hollow symbols/dashed lines) and H$_2$O–toluene (solid symbols/lines). *Reaction conditions*: 4 mL solvent (toluene or 2 mL H$_2$O–2 mL toluene), 1.2 mmol HD, 50 mg Mg–Al–O as catalyst, 180 °C, 2 h.

Table 2 Screening of catalysts for hydrogenation of MCP[a]

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[b]	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

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

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 ESI†).

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 monophasic 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.

Notes and references

1 International Energy Outlook 2014, U.S. Energy Information Administration Report DOE/EIA-0484(2014), U.S. E.I.A., Washington, D.C., 2014.
2 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098.
3 A. Corma, S. Iborra and A. Velty, *Chem. Rev.*, 2007, **107**, 2411–2502.
4 D. M. Alonso, J. Q. Bond and J. A. Dumesic, *Green Chem.*, 2010, **12**, 1493–1513.
5 J. C. Serrano-Ruiz and J. A. Dumesic, *Energy Environ. Sci.*, 2011, **4**, 83–99.
6 J. Hill, E. Nelson, D. Tilman, S. Polasky and D. Tiffany, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 11206–11210.
7 S. Dee and A. T. Bell, *Green Chem.*, 2011, **13**, 1467–1475.
8 M. Balakrishnan, E. R. Sacia and A. T. Bell, *Green Chem.*, 2012, **14**, 1626–1634.
9 M. Balakrishnan, E. R. Sacia and A. T. Bell, *ChemSusChem*, 2014, **7**, 1078–1085.

10 M. Balakrishnan, E. R. Sacia and A. T. Bell, *ChemSusChem*, 2014, **7**, 2796–2800.

11 E. R. Sacia, M. Balakrishnan and A. T. Bell, *J. Catal.*, 2014, **313**, 70–79.

12 M. J. Climent, A. Corma and S. Iborra, *Green Chem.*, 2014, **16**, 516–547.

13 R.-J. van Putten, J. C. van der Waal, E. de Jong, C. B. Rasrendra, H. J. Heeres and J. G. de Vries, *Chem. Rev.*, 2013, **113**, 1499–1597.

14 Y. Roman-Leshkov, C. J. Barrett, Z. Y. Liu and J. A. Dumesic, *Nature*, 2007, **447**, 982–U985.

15 T. Thananatthanachon and T. B. Rauchfuss, *Angew. Chem., Int. Ed.*, 2010, **49**, 6616–6618.

16 J. Phuong, S. Kim, R. Thomas and L. Zhang, *Environ. Mol. Mutagen*, 2012, **53**, 478–487.

17 American Petroleum Institute, in *Knocking Characteristics of Pure Hydrocarbons*, ed. J. M. Derfer, ASTM, Cincinnati, 1958.

18 B. Kuhlmann, E. M. Arnett and M. Siskin, *J. Org. Chem.*, 1994, **59**, 3098–3101.

19 W. D. Good and N. K. Smith, *J. Chem. Eng. Data*, 1969, **14**, 102–106.

20 J. Chao and F. D. Rossini, *J. Chem. Eng. Data*, 1965, **10**, 374–379.

21 J. An, L. Bagnell, T. Cablewski, C. R. Strauss and R. W. Trainor, *J. Org. Chem.*, 1997, **62**, 2505–2511.

22 L. Bagnell, M. Bliese, T. Cablewski, C. R. Strauss and J. Tsanaktsidis, *Aust. J. Chem.*, 1997, **50**, 921–926.

23 R. Acheson and R. Robinson, *J. Chem. Soc.*, 1952, 1127–1133.

24 G. Rosini, R. Ballini and P. Sorrenti, *Tetrahedron*, 1983, **39**, 4127–4132.

25 M. L. Karpinski, D. Nicholas and J. C. Gilbert, *Org. Prep. Proced. Int.*, 1995, **27**, 569–570.

26 P. Anbarasan, Z. C. Baer, S. Sreekumar, E. Gross, J. B. Binder, H. W. Blanch, D. S. Clark and F. D. Toste, *Nature*, 2012, **491**, 235–239.

27 M. a. A. Aramendía, V. Boráu, C. Jiménez, A. Marinas, J. M. Marinas, J. A. Navío, J. R. Ruiz and F. J. Urbano, *Colloids Surf., A*, 2004, **234**, 17–25.

28 J. T. Kozlowski and R. J. Davis, *ACS Catal.*, 2013, **3**, 1588–1600.

29 M. D. Guillen, M. J. Manzanos and L. Zabala, *J. Agric. Food Chem.*, 1995, **43**, 463–468.

30 F. De Vincentiis, G. Bencivenni, F. Pesciaioli, A. Mazzanti, G. Bartoli, P. Galzerano and P. Melchiorre, *Chem. – Asian J.*, 2010, **5**, 1652–1656.

31 J. Buter, R. Moezelaar and A. J. Minnaard, *Org. Biomol. Chem.*, 2014, **12**, 5883–5890.

32 J. N. Chheda and J. A. Dumesic, *Catal. Today*, 2007, **123**, 59–70.

33 C. J. Barrett, J. N. Chheda, G. W. Huber and J. A. Dumesic, *Appl. Catal., B*, 2006, **66**, 111–118.

34 R. M. West, M. H. Tucker, D. J. Braden and J. A. Dumesic, *Catal. Commun.*, 2009, **10**, 1743–1746.

35 W. Xu, Q. Xia, Y. Zhang, Y. Guo, Y. Wang and G. Lu, *ChemSusChem*, 2011, **4**, 1758–1761.