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Solvent-Free Synthesis of C_{10} and C_{11} Branched Alkanes from Furfural and Methyl Isobutyl Ketone

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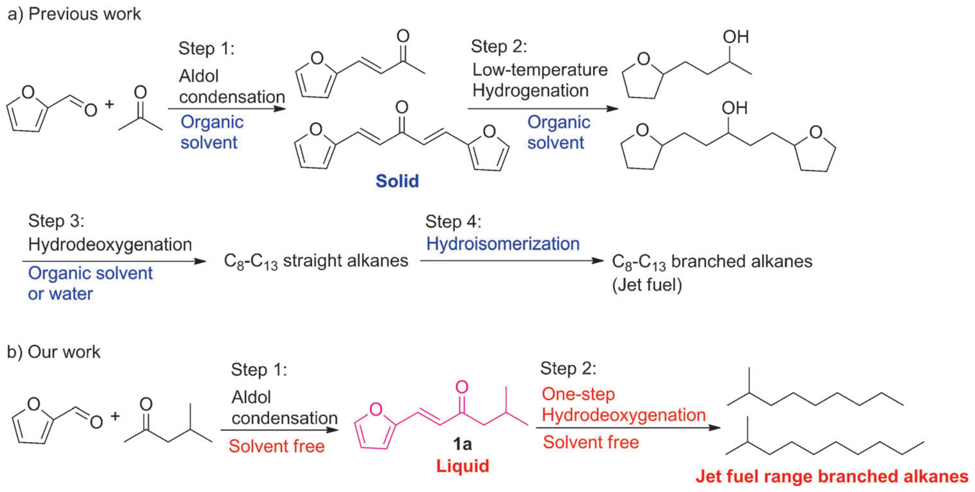
With the decline of fossil energy sources and the increasing social concern about the associated environmental problems, the conversion of biomass to fuel and chemicals has drawn a lot of attention.[1] Jet fuel is one of the most demanding liquid fuels. Lignocellulose is the main component of agricultural wastes and forest residues. Pioneered by the works of the Dumesic group,[2] the synthesis of jet-fuel-range alkanes with the platform chemicals from lignocellulose has attracted intensive interests in recent years.[3]

Furfural is an important chemical that has been produced on an industrial scale through the hydrolysis–dehydration of hemicellulose obtained from agricultural wastes and forest residues.[4] In the recent work of the Dumesic group[5] and Huber et al.,[6] C_8 and C_{13} oxygenates were produced through the aldol condensation of furfural and acetone, which can be produced by the acetone–*n*-butanol–ethanol (ABE) fermentation of lignocellulose.[7] The as-prepared C_8 and/or C_{13} oxygenates were hydrogenated at low temperatures before undergoing hydrodeoxygenation (HDO) to C_8–C_{13} straight alkanes over a Pt-loaded solid acid catalyst (Scheme 1 a). The aldol condensation can be catalyzed by mineral base,[2a, 5] organic base,[8] or solid base catalysts.[2a, 6b, 9] Recently, it was demonstrated that the aldol condensation and low-temperature hydrogenation (Step 1 and Step 2 in Scheme 1a) could be performed in one reactor over Pd-loaded solid base catalysts.[10] However, there are still two limitations for the acetone–furfural route: 1) the aldol condensation products are solid; to obtain better mass transfer, organic solvents are necessary in the aldol condensation and low-temperature hydrogenation. Even in the HDO process, water or organic solvent is still needed; however, this will lead to higher costs and lower energy efficiencies. 2) Straight alkanes are obtained during the HDO process; these alkanes have lower octane numbers and higher freezing points (e.g., the freezing point of *n*-tridecane is about 268 K), and cannot be directly used as jet fuel without hydroisomerization.



Scheme 1. a) Previous route versus b) the new protocol for the synthesis of jet-fuel-range branched alkanes.

Methyl isobutyl ketone (MIBK) is the product of the self-aldol condensation and selective hydrogenation of acetone.[11] It has been used as an extracting solvent to increase the selectivity towards furfural in the dehydration of xylose or its oligomers.[12] From a process integration point of view, it is preferable if MIBK can be directly used as the carbonyl compound in the aldol condensation with furfural. Furthermore, the branched structure of MIBK also renders it a potential feedstock for the direct synthesis of branched alkanes. However, to the best of our knowledge, there is no report on the synthesis of jet-fuel-range alkanes that uses MIBK as a platform chemical. Herein, we report the first highly efficient synthesis of C_{10} and C_{11} branched alkanes from the aldol condensation of MIBK and furfural, followed by the one-step HDO process under solvent-free conditions (Scheme 1 b). These branched alkanes have low freezing points and can be blended into jet fuel without hydroisomerization.

The solvent-free aldol condensation of MIBK and furfural was performed over a series of solid base catalysts. From the

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analysis of HPLC and NMR spectroscopy (see Figures S1 and S2 in the Supporting Information), 1-(furan-2-yl)-5-methylhex-1-en-3-one (i.e., **1 a** in Scheme 1) was identified as the main product. No C_{16} oxygenate (generated through the aldol condensation of one MIBK molecule with two furfural molecules) was detected in the liquid product. This result was different to what has been observed in the aldol condensation of furfural and acetone, and could be explained by the different reactivity of two α-carbon atoms in a MIBK molecule.

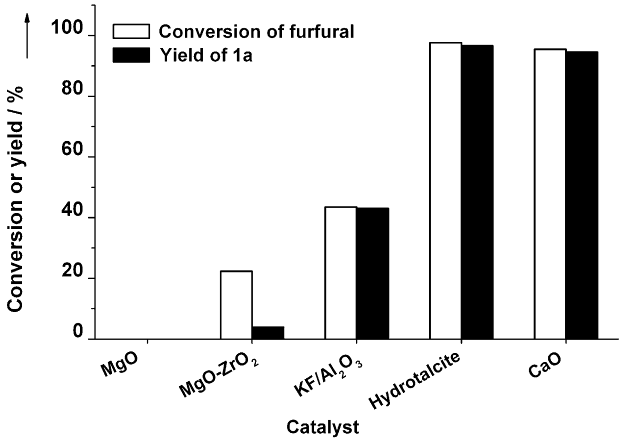


Figure 1. Conversion of furfural (white bar) and the carbon yield of **1 a** (black bar) over different solid base catalysts. The reaction was performed with 2.0 g furfural, 4.17 g MIBK (furfural/MIBK molar ratio = 1:2), and 0.4 g catalyst at 403 K for 8 h in a batch reactor.

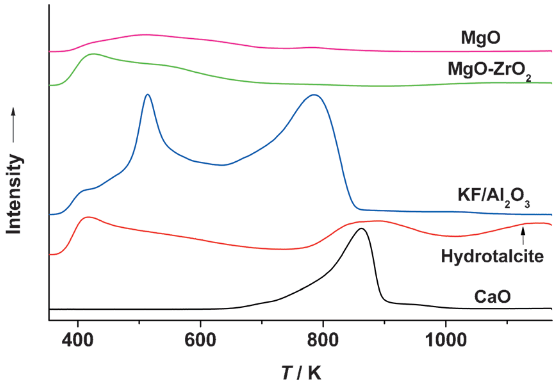
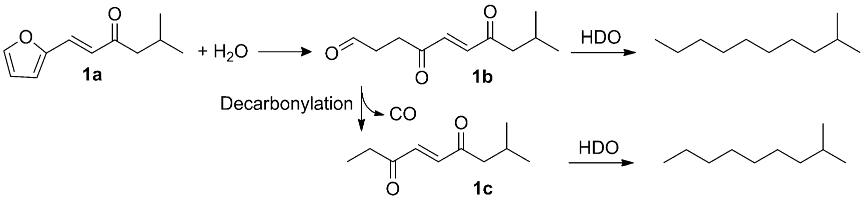


Figure 2. CO_2-TPD of the different solid base catalysts (the experimental detail for the CO_2-TPD tests is provided in the Supporting Information).

Conversion of the furfural and the yield of **1 a** over different solid base catalysts are shown in Figure 1. The hydrotalcite, with a Mg/Al atom ratio of 5:1, and CaO exhibited the best catalytic performances. For example, by using CaO as the catalyst, a **1 a** yield of up to 95 % could be achieved at 403 K after 8 h reaction time. The sequence of the activities of the different catalysts followed the order hydrotalcite ≈ CaO > KF/Al_2O_3 > $MgO–ZrO_2$ > MgO. Under the same reaction conditions, a high furfural conversion (89 %) and a high **1 a** yield (86 %) could also be obtained over the CaO catalyst when the molar ratio of MIBK/furfural was equal to one. This result further proved that the reaction could be performed under solvent-free conditions. To investigate the intrinsic reason for the different catalytic performances, we characterized the catalysts by using CO_2-temperature-programmed desorption (CO_2-TPD). According to Figure 2, the CO_2-TPD curves of both MgO and MgO-ZrO_2 exhibited broad peaks from 363 to 723 K, which could be assigned as the weak base sites. For KF/Al_2O_3, a peak at 786 K was be observed; this peak could be attributed to the CO_2 desorbed from the medium base sites. Over the hydrotalcite and CaO, CO_2 desorption peaks at higher temperatures (> 865 K) were observed, indicating that these materials contain stronger basicity. Combining the results from the activity tests and CO_2-TPD, we believe that the aldol condensation of furfural and MIBK occurred on the strong base sites, which could have been the reason for the improved catalytic performance of hydrotalcite and CaO.

According to our tests, as-prepared **1 a** existed as a red-brown liquid, even at 253 K; this rendered it suitable for the direct HDO process. The liquid state of **1 a** could be explained by the branched structure of MIBK, which could lead to a lower freezing point of the aldol condensation product by incorporating the branched structure. This is very advantageous in practical applications because: 1) the cost of organic solvents and the energy consumption from the evaporation of solvents can both be reduced, 2) the low-temperature hydrogenation and HDO can be integrated into one-step process, which will also improve the energy efficiency.

The direct HDO of **1 a** was performed under solvent-free conditions. According to the analysis of the gas-phase and liquid-phase products by using GC-MS, **1 a** was fully converted into hydrocarbons and CO_2 over carbon-loaded Pt, Pd, and Ir catalysts at 643 K and 6 MPa H_2. According to Figure 3, the carbon yields for jet-fuel-range alkanes over the Pt, Pd, and Ir catalysts were around 90 %. The jet-fuel-range alkanes obtained in this work were composed of 2-methyl-decane and 2-methyl-nonane. Both of which are branched alkanes and have low freezing points (223.5 and 198.3 K, respectively). Therefore, they could be directly blended with conventional jet fuels without hydroisomerization. The obtained molar ratio of 2-methyl-decane/2-methyl-nonane decreased for the cata-



Scheme 2. Reaction pathway for decarbonylation during the HDO of **1 a**.

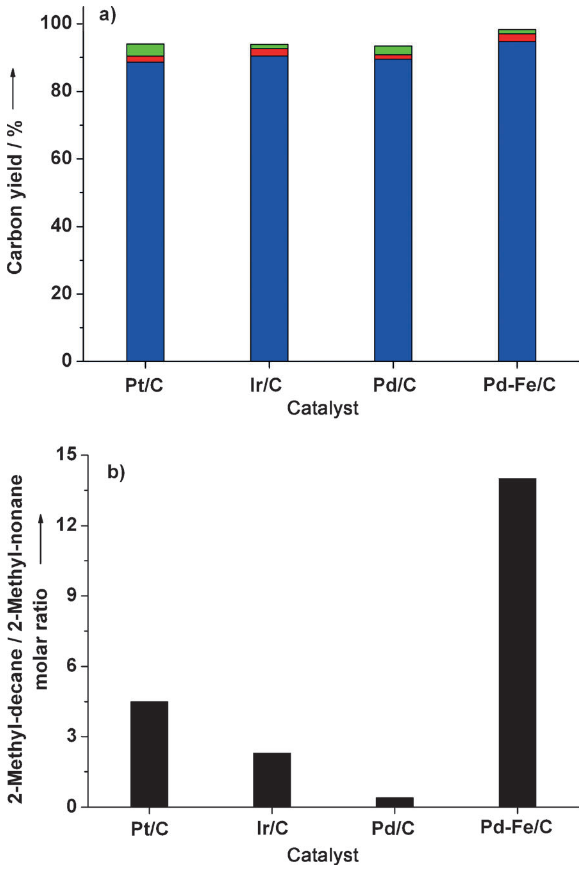


Figure 3. a) Carbon yields for C_1–C_4 light alkanes (green bar), C_5–C_7 gasoline (red bar), and C_8–C_{11} jet-fuel-range alkanes (blue bar). b) 2-methyl-decane/2-methyl-nonane molar ratios (black bar) over the different catalysts. Reaction conditions: 643 K, 6 MPa, 1.8 g catalyst; liquid feedstock **1a** flow rate 0.04 mL min^{-1}, hydrogen flow rate 120 mL min^{-1}.

lysts in the order Pt/C > Ir/C > Pd/C. The higher selectivity of Pd/C for 2-methyl-nonane could be explained by its higher activity in the decarbonylation reaction. According to Scheme 2, the aldehyde group could be generated through the hydrolysis of the furan group in **1a** (catalyzed by the high temperature water generated during HDO process).[3c,13] This aldehyde group could be removed through decarbonylation. It was interesting that, after modification of the Pd/C catalyst with Fe, there was an evident increase in the molar ratio of 2-methyl-decane/2-methyl-nonane (from 0.4 to 14), and a slight increase in the carbon yield to diesel (from 90% to 95%) was observed. This result could be explained by the suppression of decarbonylation. In the recent work of Sitthisa et al.,[14] a similar effect upon addition of Fe was observed for the hydrogenolysis of furfural to 2-methylfuran over a Ni catalyst. As suggested by Sitthisa et al., the presence of Fe increased the stability of the η^2-(C,O) surface species and prevented it from converting into a surface acyl species, which could have been decomposed to CO.

In summary, the solvent-free aldol condensation of furfural and MIBK followed by hydrodeoxygenation (HDO) is shown to be a promising method for the direct production of jet-fuel-range branched alkanes from lignocellulose. Compared with the routes proposed in previous reports, this new protocol has many advantages because it is solvent free, involves fewer steps, and directly produces branched alkanes without hydroisomerization. This work opens a new general strategy for the direct synthesis of jet-fuel-range branched alkanes with MIBK as a platform chemical. Further work regarding the utilization of MIBK in the synthesis of renewable jet-fuel-range branched alkanes with lower freezing points and higher molecular weights are ongoing in our laboratory.

Acknowledgements

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Keywords: aldol reaction · alkanes · hydrodeoxygenation · jet fuel · lignocellulose

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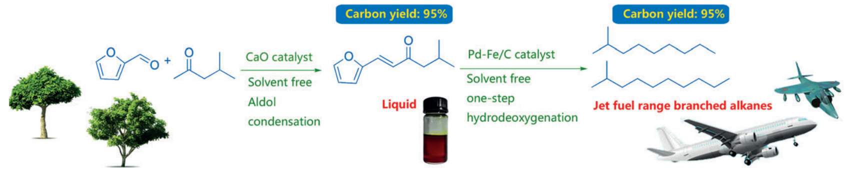

Our best results jet: C_{10} and C_{11} branched alkanes, with low freezing points, are synthesized through the aldol condensation of furfural and methyl isobutyl ketone from lingocellulose, which is then followed by hydrodeoxygenation. These jet-fuel-range alkanes are obtained in high overall yields (≈90%) under solvent-free conditions.

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