From Furfural to Fuel: Synthesis of Furoins by Organocatalysis and their Hydrodeoxygenation by Cascade Catalysis

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The synthesis of furoins from biomass-derived furfural and 2-methylfurfural is demonstrated in high yields in green and renewable solvents using N-heterocyclic carbene organocatalysts. The resulting furoin molecules are used as precursors for fuels using cascade catalysis, first by using Pd/C with acidic co-catalysts under very mild conditions to yield oxygenated C_{12} molecules. Two main products were formed, which we identified as 1,2-bis(5-methyltetrahydrofuran-2-yl)ethane and 1-(5-methyltetrahydrofuran-2-yl)heptanol. The use of a Pd/Zeolite-β catalyst under more extreme conditions resulted in the complete hydrodeoxygenation of 5,5′-dimethylfuroin to dodecanes in high yields (76%) and exceptional selectivity (94%) for n-dodecane.

Introduction

The utilization of biomass in both fuels and chemicals has gained worldwide attention as concerns grow over diminishing fossil fuel sources, global warming, and environmental pollution.[1] Additionally, the building of a biomass-based chemical/fuel infrastructure would decrease dependence on imported petroleum and develop local agricultural economies.[2] A major obstacle to achieve this goal is the high oxygen content of biomass.

To date, many processes have been described to transform biomass into chemical feedstock and fuels. Gasification of biomass followed by Fischer–Tropsch (F–T) synthesis provides fuel-range hydrocarbons. However, F–T is an energy- and capital-intensive process. Alternatively, the pyrolysis of biomass removes ~80% of the oxygen content to yield a liquid bio-oil that is acidic and unstable, which requires further processing to obtain fuels and chemicals.[3]

Solution-phase processing remains one of the most promising routes to biomass utilization. The acid hydrolysis of cellulosic biomass yields a mixture of C_5 and C_6 sugars, which in turn may be dehydrated to yield furanic aldehydes, furfural (FF), and hydroxymethyl furfural (HMF); 5-methylfurfural (MF) may
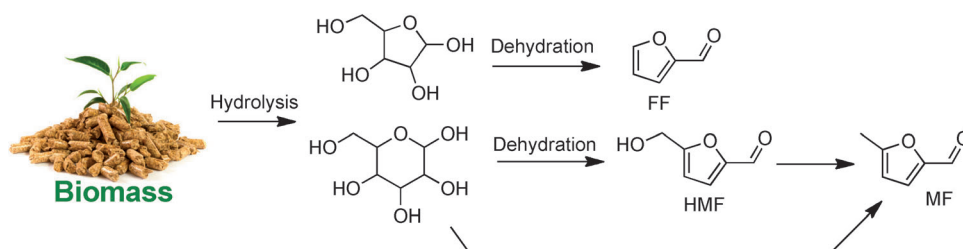
Scheme 1. Acid-catalyzed hydrolysis of biomass and dehydration of sugars to furanic aldehydes.

be prepared from HMF or directly from glucose (Scheme 1).[4] An appealing approach is the use of biphasic reaction media, in which the hydrolysis of biomass and the subsequent dehydration of the resulting sugars occur in the aqueous phase and the furanic aldehydes (HMF and FF) are extracted into the organic phase. As furanic aldehydes are easily susceptible to resinification under acidic conditions,[5] extraction into the organic phase improves their yields by removing them from the reactive acidic aqueous phase. Additionally, the product-containing organic phase can be isolated easily and subjected to additional reactions, and the aqueous phase can be recycled.

The hydrogenation of FF or HMF gives derivatives with similar boiling points and research octane numbers (RONs) to ethanol, which makes them suitable candidates as alternative fuels or additives.[6] However, these are not appropriate as direct drop-in fuels because the carbon chain length is too short. An 'upgrading' step that involves a C–C forming reaction is necessary. The aldol condensation of FF or HMF with acetone gives a C_8 or C_9 product, respectively. Another equivalent of aldehyde may then be added to give either C_{13} or C_{15}. The aldol products can be subjected to sequential hydrogenation and dehydration/hydrogenation reactions to give alkanes.[7] Another approach utilizes 2-methylfuran, which is prepared from FF. Here, a hydroxyalkylation/alkylation reaction is used to couple 2-methylfuran with an aldehyde to result in a branched carbon

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chain. The hydrodeoxygenation (HDO) of the products affords alkanes.[8]

The drawback of the methods described above is that the furan ring is often hydrogenated prior to the HDO reactions. This competing hydrogenation results in a THF ring, which requires harsh conditions to ring-open and leads to the fragmentation of the carbon backbone. Comparatively, the hydrolytic ring-opening of the furan ring can be accomplished under mild conditions followed by HDO, which leads to a better preservation of the carbon backbone. This approach has been described recently for aldol products. Two trends have been noted for which the hydrolytic ring-opening of furan does not proceed: 1) if there is exocyclic unsaturation and 2) if there is no functional group in the 5-position of the furan ring.[9] The same group found a one-pot procedure to convert the aldol products of furfural to alkanes using Pd/C in glacial acetic acid with La(OTf)$_3$.[9b] A recent report has described the application of this procedure to furoin substrates.[10]

One appealing C—C forming reaction that has not been given much attention for the generation of fuel precursors from furanic aldehydes is benzoin coupling. This homocoupling reaction is catalyzed by N-heterocyclic carbenes (NHC) and results in α-hydroxyketone, which precipitates as a solid and can be isolated conveniently by filtration. A recent report has described the investigation of the benzoin coupling of HMF in ionic liquid.[11] Although these results are promising, ionic liquid is not an ideal reaction medium for large-scale biorefinery applications. Herein, we report on the benzoin coupling of FF and MF using NHC organocatalysts to give furoin and 5,5′-dimethylfuroin (Me$_2$-furoin) (Scheme 2), respectively,
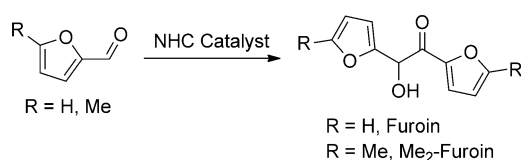
Scheme 2. NHC-catalyzed benzoin condensation of biomass-derived furanic aldehydes (FF and MF).

and their subsequent HDO through cascade catalysis. Inspired by the biphasic production of FF and HMF, we targeted the use of green solvents that are immiscible with water in the initial benzoin coupling reaction, specifically 2-methyltetrahydrofuran (MeTHF).

Results and Discussion

NHC-organocatalyzed synthesis of furoins

To begin our investigation we chose thiamine hydrochloride, which has been heavily studied since the mechanism for benzoin condensation was first established by Breslow in 1958.[12] The challenge for us became the choice of solvent. Thiamine in ethanol with triethylamine (TEA) as the base gave >80% yield of furoin readily. However, ethanol is not a suitable sol-

vent for the integration of this NHC-catalyzed coupling of biomass-derived furanic aldehydes if we consider our goal to use a hydrophobic solvent that may be used in their biphasic production, such as THF or MeTHF. In both these solvents, the yields of furoin were low (35% after 3 h of heating under reflux) because of the poor solubility of thiamine. To maintain the inclusion of a nonpolar solvent, a 1:1 (by volume) mixture of MeTHF and ethanol was investigated. This mixed solvent system gave comparable yields of furoin (78%) to those in ethanol. The reaction is sensitive to the base used. TEA works best with thiamine; 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) gives no furoin under identical conditions, although the conjugate acid has a similar pK_a (protonated TEA pK_a = 10.75, protonated DBU pK_a ≈ 12). The scope of the reaction was limited if we used thiamine as a catalyst (see Supporting Information for examples with other substrates).

Therefore, we prepared and screened a representative library of 10 NHC catalysts (see Supporting Information for structures). This included a mixture of imidazole and benzimidazole catalysts with different substituents on the 1- and 3-positions, along with a couple of triazoles. Our initial investigations with a bridged bisbenzimidazole bromide (BisBIMeHBr) showed that the choice of base affects the yields, and the reaction can be accelerated significantly by microwave heating (from hours at room temperature to seconds in the microwave; see Supporting Information). Under microwave conditions, results from the catalyst library were widespread (the yields of furoin ranged from 0–88%). A general observation is that the benzimidazole catalysts are most efficient. The imidazole catalysts gave mixed results with no clear trend with regard to the catalyst structure. Finally, the triazoles were reasonably effective catalysts. Full descriptions of all the NHC catalysts used in this study and their yields are available in the Supporting Information. A screening of NHC catalysts aimed at the production of furoins from biomass-derived furfurals has not been demonstrated before. Additionally, there have been no reports on the development of a process that utilizes renewable solvents and as-prepared furfurals without a purification step.

The best three catalysts from our library screening with furfural using microwave heating (BIBnHBr, BIMeHI, and TazPyPhHBF$_4$; Table 1) were selected and investigated with benzaldehyde and 5-methylfurfural (MF). Interestingly, the best catalyst with furfural, BIBnHBr, did not perform as well with benzaldehyde. The yield of benzoin decreased to 55% compared to 88% yield for furoin (Table 1). In contrast, the other two catalysts did not show reduced yields. We observed that the choice of base has a significant impact on the yield and that no singular set of reaction conditions can be applied to a wide range of substrates; however, in the absence of NHC, no furoin product is formed.

Control reactions with the best catalyst identified with furfural (BIBnHBr) gave surprising results. The yields for all the microwave reactions were obtained by collecting furoin by filtration, which we accomplished by immediately diluting with ethanol and cooling to −20 °C. If we mimicked this workup with a reaction under ambient conditions, not subjected to microwave heating, we obtained identical yields: 86% compared to

Table 1. Selected NHC catalysts for the synthesis of furoin, Me$_2$-furoin, and benzoin.[a]

NHC catalyst		Yield [%]		
		furoin	Me$_2$-furoin	benzoin
	BIMeHI	82	59	75
	BIBnHBr	88	66	55
	TazPyPhHBF$_4$	79	65	69

[a] Reaction conditions: 10 mmol substrate, 0.5 mmol NHC, 0.5 mmol DBU, 3 mL solvent (1:1 MeTHF/EtOH). Heated by microwave radiation for 20 s at 300 W, followed by extraction with CH$_2$Cl$_2$ and recrystallization from EtOH.

88 % with microwave heating. We wanted to see if other catalysts behaved similarly to BIBnHBr and did not require microwave heating. BIMeHI gave 52 % yield of furoin from furfural under ambient conditions versus 82 % yield under microwave heating. In comparison, benzaldehyde showed a markedly reduced activity with BIBnHBr in the absence of microwave heating, and only 14 % yield of benzoin was obtained. This indicates that the fast reaction we observe for BIBnHBr is indeed unique to furfural.

Transformations of furoins with tandem catalysis

With high yields in hand and an easy way to separate the furoin and Me$_2$-furoin products by simple filtration, we examined a number of possible routes for their conversion to hydrocarbon fuels under mild conditions by employing solution-phase HDO. Two potential pathways to generate alkanes from furoin starting materials can be envisaged as shown in Scheme 3. Path A first uses selective hydrogenation to generate a substrate more susceptible to acid-catalyzed hydrolytic ring-opening followed by HDO to produce alkanes. Path B first
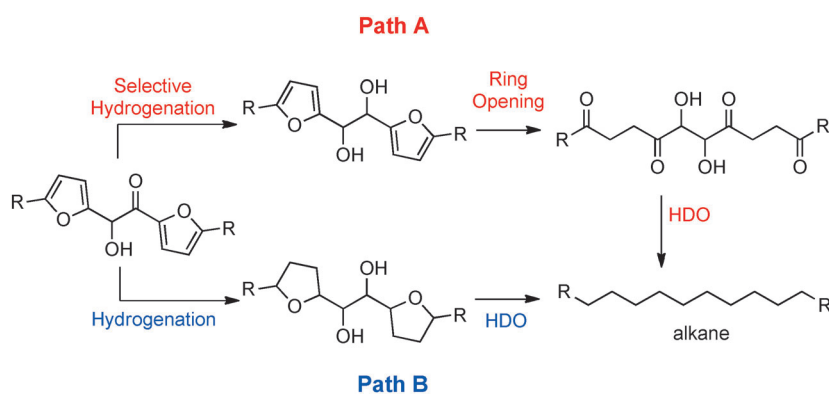
uses nonselective hydrogenation followed by HDO. As discussed earlier, Path B is more energy intensive because the opening of a THF ring is difficult and such a route has been explored previously for furoin, which resulted in only 34 % of C$_{10}$ alkane.[7e] Therefore, we sought to pursue and develop the cascade reactions in Path A.

The hydrogenation of furoin using commercial Pd/C (5 wt %) under mild conditions (20 bar H$_2$ at 80 °C) leads to undesirable and nonselective hydrogenation of the aromatic furan rings (Scheme 4). The addition of a Lewis acid Zn^{II} salt to the reac-
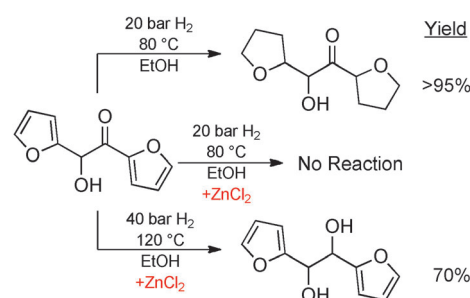
**Scheme 4.** Hydrogenative treatment of furoin with Pd/C with and without ZnCl$_2$ additive.

tion mixture has been shown to have a synergistic effect with Pd/C catalyst, either by improving the selectivity of phenol hydrogenation to cyclohexanone in nonpolar solvents (such as dichloromethane, chloroform) or by suppressing the hydrogenation of aromatics in polar solvents (such as ethanol, methanol, THF).[13] Indeed, if ZnCl$_2$ was added to the reaction mixture, no reaction was observed at 80 °C. However, at 120 °C and 40 bar of H$_2$, the selective hydrogenation of the ketone to alcohol was observed, and the furan ring was left unchanged. Interestingly, the application of the same reaction conditions to Me$_2$-furoin showed no conversion to the diol.

The next step was to study a cascade of reactions in one-pot aimed at the hydrogenation, ring-opening, and HDO of furoin substrates (Path A in Scheme 3). To accomplish this, we added a Brønsted acid cocatalyst to our hydrogenation reactions. A challenge in this endeavor is that the rate of the hydrolytic ring-opening must be faster than the rate of hydrogenation, as once hydrogenated, the furan ring does not open. Initial trials in aqueous solution of oxalic acid at pH 2 in combination with 5 wt % Ru/C were not successful as the main products were from the hydrogenation of the furan rings (see Supporting Information for detailed results). These conditions had been reported to ring-open and hydrogenate HMF.[14] The use of 5 wt % Pd/C promoted by ZnCl$_2$ and with the addition of a homogeneous Brønsted

Scheme 3. Two possible paths for the conversion of furoins, which lead to hydrocarbon liquid fuel.

acid (p-toluenesulfonic acid) at 20 bar H_2 and 120 °C in ethanol gave promising results. GC and NMR spectroscopic analysis of the product mixture showed no starting material left for both furoin and Me_2-furoin substrates. In the ^1H NMR spectrum, we observed the presence of THF-type peaks in the range of $\delta =$ 3.5–4.0 ppm along with a multitude of peaks in the $\delta = 1$– 2 ppm range characteristic of aliphatic protons. The ^{13}C NMR spectrum showed similar evidence for a THF ring along with an aliphatic chain. Control experiments without $ZnCl_2$ proved that in the presence of a Brønsted acid, $ZnCl_2$ had no impact on the reaction. To move towards a completely recyclable system, we tested the use of a solid Brønsted acid. Amberlyst-15 resin, which can be considered as the heterogeneous equivalent of p-touluenesulfonic acid, gave identical results to those observed with the homogeneous acid cocatalyst. Nearly identical results were obtained whether the reaction was performed in a mixture of water/ethanol or in water alone. However, the reaction with furoin was not as clean, and a multitude of products was observed (> 15 peaks in GC), some of which corresponded to products that resulted from HDO.

In an attempt to identify the oxygenate products that resulted from this reaction, further analysis of the reactions with Me_2-furoin was performed using GC–MS and MS^n. The GC trace showed a good conversion to two main products with mass of 198 ($C_{12}H_{22}O_2$) and 200 g mol^{-1} ($C_{12}H_{24}O_2$). The mass spectra indicate clearly that both products contain at least one MeTHF ring. If we take the MS and NMR spectroscopic data into account with comparisons to model compounds, we propose that the 200 g mol^{-1} product results from the hydrogenation of the furan rings followed by HDO, whereas the 198 g mol^{-1} product arises from the ring-opening of one ring followed by partial HDO (Scheme 5). From MS^n analysis, the 200 mass prod-
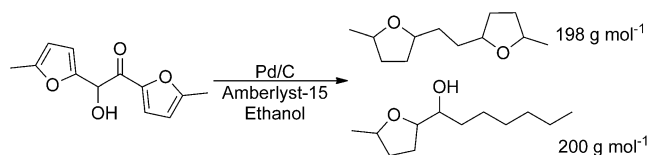
Scheme 5. One-pot HDO treatment of Me_2-furoin at 120 °C under 20 bar H_2.

uct fragments similarly to model compounds with a hydroxyl group along the alkane chain, which leads us to propose the structure shown in Scheme 5; additionally, we believe this product to be present as a mixture of stereo- and regioisomers. The other main product with 198 g mol^{-1} mass, has two possible structures, the carbonyl compound analogous to the alcohol proposed with 200 g mol^{-1} mass or a product with both furan rings left intact and both backbone oxygen atoms removed. From MS^n analysis, this product fragments similarly to a model compound with two THF-type rings, which leads us to believe that the furan rings were hydrogenated without opening. Furthermore, we do not observe any carbonyl carbon atoms in the ^{13}C NMR spectrum, and although this cannot entirely rule out the presence of a carbonyl group, it does add support to our proposed structure.

HDO with a dual-function Pd/Hβ catalyst

The use of more extreme reaction conditions (higher pressures and temperatures) has been shown to allow the conversion of similar biomass-derived compounds to alkanes in a solution-phase reaction.[15] However, amberlyst-15 is limited in the maximum temperature that can be used, so other acidic co-catalysts must be considered. Additionally, careful consideration of catalyst support allows a single dual-function catalyst that will hydrogenate and deoxygenate. Therefore, we decided to examine Pd deposited on zeolite-β (H-form, 360:1 SiO_2/Al_2O_3). Despite a low abundance of acidic sites, studies have shown that the percentage of strong acid sites is higher if the overall number of acid sites is low, which results in a more active catalyst.[15a] After the preparation of a variety of supported metal catalysts, M_x/Support (M = Pd, Ru, Ni; x = wt % metal loading; support = zeolite-β (Hβ), HZSM-5) by standard incipient wetness procedures (TEM and SEM images for Pd_5/Hβ are available in the Supporting Information), we examined their use in solution-phase HDO batch reactions. If we used 20 wt % Pd_5/Hβ (loading of Pd is 1 wt % or 2 mol % relative to substrate) and an initial pressure of 60 bar H_2 in ethanol, Me_2-furoin was deoxygenated successfully to alkane. Analysis of the product mixture shows high yields and selectivity for n-dodecane (66 %, GC yield, Figure 1) after 8 h at 230 °C. The only other product pres-
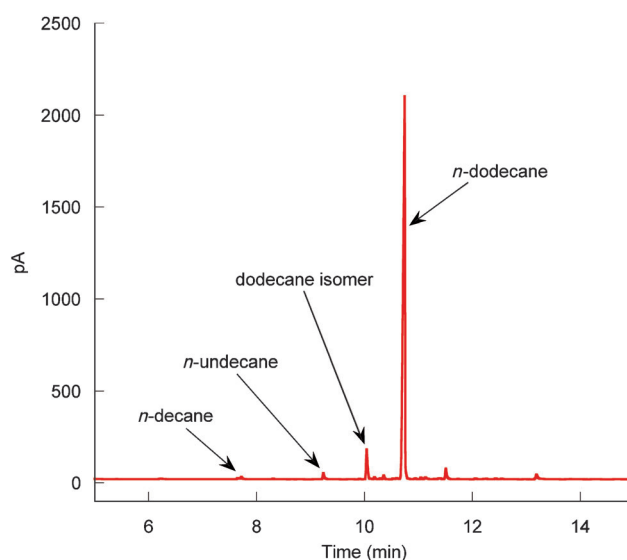
Figure 1. GC chromatogram of the product mixture following the treatment of Me_2-furoin with Pd/Hβ (20 wt %) at 230 °C for 8 h and an initial H_2 pressure of 60 bar.

ent in an appreciable amount is an isomer of dodecane (confirmed by GC–MS), which brings the overall yield of C_{12} alkane for this reaction to 70 % with 94 % selectivity for n-dodecane. As the conversion of starting material is 100 % in all cases and no other major products are observed in the GC trace, the loss in mass balance is attributed to charring. An increase of the catalyst loading or reaction temperature gave minor increases in the yield of dodecane, and our best result was 76 % yield of C_{12} alkane, however, this came at the cost of using 100 wt %

$Pd_5/H\beta$ catalyst loading. Throughout these variations in reaction conditions, the selectivity to *n*-dodecane does not change. NMR spectroscopy of the product gave further confirmation that the product is dodecane. Additionally, we see no evidence for fractionation of the carbon backbone of furoin. C_{10}, C_{11}, or any other shorter chain length alkanes are not present in the product mixture in any appreciable amount (Figure 1). If other catalyst variations using different metals or supports were examined, in each case the results were poorer than that achieved with the $Pd_5/H\beta$ catalyst. Finally, we demonstrated that 230 °C is the necessary temperature to yield alkane product successfully, as very low alkane yields were observed at 220 °C (Table 2, entry 8). Interestingly, we found that no alkane was produced if the HDO batch reaction is run in water or if Pd_5/C is used in conjunction with zeolite-β.

Table 2. Selected results for the conversion of Me₂-furoin to dodecane.				
Entry[a]	Catalyst	Catalyst loading [wt %]	Alkane yield [%]	*n*-Dodecane selectivity [%]
1	$Pd_5/H\beta$	10	27	87
2[b]	$Pd_5/H\beta$	10	66	93
3	$Pd_5/H\beta$	20	70	94
4[c]	$Pd_5/H\beta$	20	76	94
5[d]	$Pd_5/H\beta$	20	60	83
6	$Pd_5/H\beta$	100	76	95
7	$Pd_5/C+H\beta$	20[e]	0	–
8[f]	$Pd_5/H\beta$	20	6	95
9	$Pd_5/HZSM$-5	20	8	95
10	$Ru_5/H\beta$	20	27[g]	67
11	$Ni_5/H\beta$	20	37	98
12	Pd_5/Al_2O_3	20	0	–

[a] All entries have an initial H_2 pressure of 60 bar and are run at 230 °C for 8 h in ethanol solvent with 200 mg of substrate unless otherwise indicated. In all cases, GC analysis shows 100 % conversion of starting material. [b] The reaction time is 16 h. [c] Large-scale reaction with 500 mg substrate to facilitate easier reactivation of catalyst. [d] Catalyst recovered and reactivated from entry 4. [e] The loading for each catalyst was 20 wt %. [f] The reaction temperature was 220 °C. [g] Dodecane yield: 19 %, undecane yield: 4 %, decane yield: 4 %.

Our results here are unique and in contrast to similar reactions in which the yield of diesel-range alkanes might be high but the selectivity toward the theoretical product is low.[15] Furthermore, our system is one of a handful of dual-function catalysts for the HDO of furfural derivatives and only the second one applied to furoins.[15] Other studies on the HDO of furoin have used either $Pt/CsH_2PW_{12}O_{40}$, which gave low yields of alkane, or a hydrogenation catalyst with an added acid cocatalyst.[10, 15b]

As a result of the high catalyst loading used in this HDO reaction, we wanted to investigate both lower loadings and recycling of the recovered catalyst using our $Pd_5/H\beta$ catalyst. The use of 5 wt % catalyst gave significantly reduced activity, which resulted in only 3 % dodecane yield after 8 h at 230 °C and 60 bar H_2. Going up to 10 wt % loading gave a moderate 27 % yield of dodecane under the same conditions. If we extended the reaction time to 16 h with the 10 wt % loading, we obtained 66 % total C_{12} yield with 93 % selectivity to *n*-dodecane.

This result is comparable to that obtained with the 20 wt % catalyst loading after 8 h, which demonstrates the possibility to decrease the catalyst loading. An interesting result of this experiment is that we were able to observe oxygenates that may be intermediates on the way to alkane formation. In the 8 h, 10 wt % loading experiment, we observed dodecane as the main component of the reaction but also saw large amounts of an oxygenate in the GC trace. Analysis by GC–MS gave a molecular weight of 184 g mol⁻¹ for this component with a base peak of $m/z = 85$ characteristic of the MeTHF fragment. Therefore, the only feasible structure for this is 2-heptyl-5-methyltetrahydrofuran. This is somewhat surprising if it is truly an intermediate if we consider our proposed reaction pathway in which a THF-type ring is unlikely to undergo a ring-opening reaction.

The catalyst material, which is a very fine powder, may be recovered from the reaction mixture by centrifugation. Direct recycling of the catalyst in this manner is not successful in the generation of alkane products. However, some catalytic activity is retained, and the predominant product is the 198 g mol⁻¹ product, which we identified previously as 1,2-bis(5-methyltetrahydrofuran-2-yl)ethane. The catalyst retains this reactivity for more recycles. It is a little peculiar that the catalyst retains some activity, yet does not yield alkane. We believe that this partial loss in reactivity is because of the observed charring, which results in coke formation on the catalyst and thus blocks facile access to acidic sites. As mentioned earlier, the acid-catalyzed ring-opening should be the first step in our catalytic process (Path A, Scheme 3); we have accomplished this with the fresh catalyst. However, in the case of the recycled catalyst, it appears as though hydrogenation of the furan rings has become the favored first step (Path B, Scheme 3), thus we become stuck with the THF rings and are unable to complete the HDO.

The issue now becomes whether or not the catalyst can be reactivated. After the catalyst was recovered by centrifugation, it was loaded into a U-shaped drying tube, dried under flowing air, calcined at 450 °C, and reduced under flowing H_2 at 450 °C. This 'reactivated' catalyst was successful to transform Me₂-furoin to alkane, albeit in a lower yield and selectivity compared to the fresh catalyst (Table 2, entries 4 and 5) Unfortunately, after a second recovery followed by the same reactivation process, the catalyst material did not have activity toward alkane production but it did produce various oxygenates, similar to that observed for the recovered catalyst without the reactivation step. Work is ongoing in this area to improve the reusability of the catalyst material.

Conclusions

We have presented herein new approaches for the synthesis of furoins from biomass-derived furfurals using N-heterocyclic carbene organocatalysis. Our methods are green, use renewable solvents, and allow the direct utilization of furanic aldehydes synthesized from biomass with yields that approach 90 % for furfural as a substrate. We have explored a number of routes for the conversion of furoins to hydrocarbon fuels through

ring-opening and hydrodeoxygenation cascade catalysis in a single-pot reaction. Most importantly, we demonstrate success in the conversion of 5,5′-dimethylfuroin to dodecane using a Pd catalyst deposited on zeolite-β (H-form) in high yields (70%) and exceptional selectivity (94%) toward *n*-dodecane. This provides a viable pathway to use biomass resources as precursors to diesel fuels. Additionally, we were able to use a commercial 5 wt% Pd/C in conjunction with a heterogeneous Brønsted acid cocatalyst (amberlyst-15) under mild conditions to effect the conversion of 5,5′-dimethylfuroin to two oxygenated hydrocarbon products, two oxygen atoms away from C_{12} alkane, which could be candidates for oxygenate additives in fuels.

Experimental Section

NHC-catalyzed benzoin condensation

In a typical experiment, aldehyde (10 mmol), NHC precursor (0.5 mmol), and base (0.5 mmol) were combined in solvent (3 mL). Microwave-assisted reactions were performed by using a CEM Discovery SP System. The workup of reactions was accomplished by either direct filtration of products or by extraction with dichloromethane followed by recrystallization. Yields were determined by the mass of collected (isolated) product.

Treatment of furoin

In a typical hydrogenation/HDO experiment, furoin (200 mg) was added to a stainless-steel autoclave reactor (Parr Instruments). Following addition of catalyst, any additives, and solvent, the reactor was assembled and flushed three times with H_2 before it was charged with the desired pressure. After heating for the set time, the reactor was cooled to RT, the reaction mixture was filtered and washed, and the solvent was removed under reduced pressure. Products were characterized by NMR spectroscopy and GC–MS.

Alkane yields were determined by GC by dilution of the reaction mixture to 50 mL and using the peak area and a standard curve prepared from authentic alkane samples to determine the concentration of alkane products. The yield of alkane is defined as shown in Equation (1):

$$Yield = (mol\ alkane/mol\ Me_2\text{-}furoin) \times 100\% \qquad (1)$$

The selectivity of *n*-dodecane is defined as shown in Equation (2):

$$Selectivity = (mol\ n\text{-}dodecane/mol\ observed\ alkane) \times 100\% \qquad (2)$$

Preparation of Pd/Hβ catalyst

The 5 wt% Pd catalyst was prepared by incipient wetness impregnation on a zeolite-β (H-form, 360:1 SiO_2/Al_2O_3, obtained from Alfa Aesar). Briefly, the precursor compound, palladium dichloride, was dissolved in aqueous HCl solution. This was added to the zeolite substrate and stirred for several hours. The mixture was then placed in an oven and allowed to dry overnight. The dried material was then transferred to a Schwartz-type drying tube and calcined under flowing air for 2 h at 450 °C. The gas feed was then switched to H_2, and the catalyst was reduced for 2 h at the same temperature. The material was then cooled to RT under flowing N_2. Ni and Ru catalysts were prepared in a similar manner.

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