Zinc-Assisted Hydrodeoxygenation of Biomass-Derived 5-Hydroxymethylfurfural to 2,5-Dimethylfuran

Basudeb Saha,*[a] Christine M. Bohn,[a] and Mahdi M. Abu-Omar*[a, b]

2,5-Dimethylfuran (DMF), a promising cellulosic biofuel candidate from biomass derived intermediates, has received significant attention because of its low oxygen content, high energy density, and high octane value. A bimetallic catalyst combination containing a Lewis-acidic Zn^{II} and Pd/C components is effective for 5-hydroxymethylfurfural (HMF) hydrodeoxygenation (HDO) to DMF with high conversion (99%) and selectivity (85% DMF). Control experiments for evaluating the roles of zinc and palladium revealed that $ZnCl_2$ alone did not catalyze the reaction, whereas Pd/C produced 60% less DMF than the combination of both metals. The presence of Lewis acidic component (Zn) was also found to be beneficial for HMF HDO with Ru/C catalyst, but the synergistic effect between the two metal components is more pronounced for the Pd/Zn system than the Ru/Zn. A comparative analysis of the Pd/Zn/C catalyst to previously reported catalytic systems show that the Pd/Zn system containing at least four times less precious metal than the reported catalysts gives comparable or better DMF yields. The catalyst shows excellent recyclability up to 4 cycles, followed by a deactivation, which could be due to coke formation on the catalyst surface. The effectiveness of this combined bimetallic catalyst has also been tested for one-pot conversion of fructose to DMF.

Introduction

Rapid depletion of nonrenewable petroleum reserves, the high volatility of the crude oil price, and global warming due to increased carbon dioxide emissions have directed current research efforts towards the development of renewable alternatives to meet the growing energy demand for the future generation.[1] Therefore, innovation of new synthetic routes and related technologies for generating fuels from biorenewable resources is a cutting-edge research area. Currently, ethanol is the only renewable liquid fuel produced on a commercial scale, primarily from food crops such as grains, sugar beet, and oil seeds. Due to competition with other land requirements and its adverse effect on food production, it is realized that 1st-generation bioethanol will not achieve targets for oil-product substitution, climate change mitigation, and economic growth.[2] Therefore, the production of 2nd-generation biofuels from lignocellulose, such as low-cost crop and forest residues, wood chips, and municipal waste, has been targeted in recent years to meet a significant portion of the 36 billion gallons (1 gallon = 3.785 L) of cellulosic biofuels target to be produced by 2022.

Although ethanol production from 2nd-generation lignocellulose is gaining momentum to meet the production target, its high oxygen content (O/C = 0.5) and low energy density (23.4 $MJ L^{-1}$ vs. 31 $MJ L^{-1}$ for gasoline) are seen as disadvantages. While the lower energy density of ethanol is largely offset by its higher octane number (RON = 110) as compared to gasoline (RON = 87–93), the average fuel economy of E15 fuel is still about 5% lower than regular gasoline. Therefore, researchers in both industry and academia are developing technologies for the next-generation advanced liquid fuels based on biorenewable platform chemicals, 5 hydroxymethylfurfural (HMF) and furfural (Ff).[3–4] In this context, the development of economically and environmentally viable routes for producing 2,5-dimethylfuran (DMF), 5-ethoxymethylfurtutal (EMF), ethyl levulinate (EL), γ-valerolactone (VL), and long-chain hydrocarbons of diesel fractions has received significant attention.[5–9] It has been reported that DMF is a superior liquid fuel compared to ethanol because of its higher energy density (30 $MJ L^{-1}$), higher octane number (RON = 119), and lower oxygen content (O/C = 0.17).[10, 11] Additionally, DMF is immiscible with water and is easier to blend with gasoline than ethanol. Recently, DMF has been tested as a biofuel on a single-cylinder gasoline direct-injection (GDI) research engine.[11] Test results of DMF were satisfactory against gasoline in terms of combustion, ignition, and emission characteristics.

The chemical transformation of lignocellulose into DMF is a multistep process, involving (i) pretreatment of lignocellulose into glucose, (ii) acid-catalyzed dehydration of fructose to HMF, and (iii) catalytic hydrodeoxygenation (HDO) of HMF to DMF.[12] Dumesic et al. reported a two-step process for the conversion of fructose to DMF (71% yield) involving Cu–Ru/C-catalyzed

[a] Dr. B. Saha, C. M. Bohn, Prof. Dr. M. M. Abu-Omar
Department of Chemistry and the
Center for Catalytic Conversion of Biomass to Biofuels (C3Bio)
Purdue University
560 Oval Drive, West Lafayette, IN 47907 (USA)
E-mail: sahab@purdue.edu
        mabuomar@purdue.edu
[b] Prof. Dr. M. M. Abu-Omar
School of Chemical Engineering
Purdue University
560 Oval Drive, West Lafayette, IN 47907 (USA)

HDO of HMF under 6.8 bar H_2.[5] Raines et al. reported the production of DMF from untreated corn stover, giving 9% DMF yield based on the cellulose content of the corn stover.[6] Raines's two-step process of DMF preparation involved the $CrCl_3$–HCl catalyzed transformation of corn stover into HMF, followed by HDO of HMF to DMF using Cu–Ru/C catalyst in the presence of H_2. In this process, toxic chromium salt along with mineral acid was used as a catalyst for the degradation of corn stover into HMF. Sen et al. reported the conversion of carbohydrates to 2,5-dimethyltetrahydrofuran (DMTHF)[13] in 81% yield using homogeneous $RhCl_3$/HI catalyst. In the same year, Bell et al. attempted HMF HDO with activated carbon (AC) supported palladium, ruthenium, and rhodium catalysts in 1-ethyl-3-methylimidazolium chloride ([EMIM]Cl) solvent under 62 bar H_2 pressure.[14] Among several reactions, the Pd/C-catalyzed HDO reported maximum 19% HMF conversion with 13% DMF selectivity. Although both HMF conversion and DMF selectivity improved to 47% and 32%, respectively, when acetonitrile was mixed with [EMIM]Cl solvent, total DMF yield (15%) was not high enough. An additional drawback of this method was that ionic liquid decreased the solubility of H_2. Hence, high pressures of H_2 (62 bar) were required, making the process energy-intensive. Under similar reaction conditions, the authors showed that Ru/C catalyst failed to produce DMF from HMF. Most recently, Ru/Co_3O_4 has been reported as an effective catalyst for HMF HDO in THF.[15] The only disadvantage of this process is that the reaction requires high catalyst loading (40 wt% based on substrate loading).

Recently, we have demonstrated that Pd/C is very effective catalyst in the presence of a small amount of Lewis-acidic $ZnCl_2$ for HDO of monomeric lignin surrogate molecules.[16] Herein, we demonstrate the benefit of a Pd/Zn/C catalytic system for the conversion of HMF to DMF under mild reaction conditions and low H_2 pressures. From the two solvent systems studied, tetrahydrofuran (THF) is a more effective solvent than methanol. The synergistic effect of $ZnCl_2$ with Ru/C and Ni/C catalysts has also been investigated for HMF HDO under comparable reaction conditions. The results show that the Pd/Zn/C catalyst is most effective for quantitative conversion of HMF to DMF with very high selectivity. The effectiveness of the later catalyst is also examined for one-pot conversion of fructose to DMF.

Results and Discussion

AC-supported palladium, rhodium, and ruthenium catalysts are effective for hydrogenation of organic substrates at low temperature and pressure. However, these catalysts have proved ineffective for hydrogenation of HMF even at high pressures of H_2 (62 bar).[14] A recent study has demonstrated a synergistic effect between zinc and palladium, and reported a significant improvement in yields and selectivity of the corresponding hydrodeoxygenation products from their respective phenolic alcohol and aldehyde precursors.[16] Mechanistic studies have suggested Zn^{2+} adsorption onto AC, and the resulting bimetallic catalyst activated phenolic substrates via binding to —OH groups and inducing reactivity with Pd—H sites on the surface via hydrogen spillover. To examine the catalytic effectiveness of the combined $ZnCl_2$–Pd/C catalyst for a simple reaction system, we investigated HMF HDO under mild reaction conditions.

Catalyst screening

A preliminary reaction for HMF HDO with combined Pd/C and $ZnCl_2$ catalytic species was carried out in MeOH solvent at 150°C and 20 bar H_2 pressure by using 0.04 g Pd/C, 0.04 g $ZnCl_2$, and 0.2 g HMF (1.58 mmol). The yield of DMF was 39% after 2 h with about 75% conversion of HMF. The yield of DMF remained unchanged when the same reaction was repeated for 4 and 8 h. Based on previous reports,[18] it is hypothesized that etherification of HMF with MeOH in the presence of the Lewis acid $ZnCl_2$ results in the formation of 5-methoxymethyl-furfural (MMF), and hence blocks the hydroxymethyl group of HMF from the desired HDO reaction. Therefore, we used THF as a solvent for HMF conversion by adopting the following experimental conditions: HMF = 3.96 mmol (0.50 g), Pd/C = 0.05 g, $ZnCl_2$ = 0.05 g, and THF = 15 mL at 150°C and 22 bar of H_2. The later reaction achieved 85% DMF yield with complete HMF conversion in 8 h (Supporting Information, Figure S3). This DMF yield is about 82% higher than that observed by Bell and co-workers[14] using Pd/C catalyst alone at 62 bar H_2 pressure. The GC–MS analysis of the product solution showed the peaks for MTHFA and HD, accounting for their respective yields of 2.6% and 1.6%. Other products (OP) accounting for 9–10% of total carbon mass balance corresponds to the unidentified peaks between retention times 9.6 to 12 min as shown in the GC chromatogram (Figure S3). Another reaction at lower H_2 pressure (8 bar) gave similar DMF yield (84%). A control experiment without $ZnCl_2$ produced only 27% DMF under comparable reaction conditions between HMF and Pd/C catalyst (Supporting Information, Figure S4). As evident by the comparison in Figure 1, a small amount of $ZnCl_2$ improved DMF yield as much as 60%. $ZnCl_2$ alone did not catalyze the reaction as HMF remained unconverted without Pd/C.

Assuming that the acidity of $ZnCl_2$ could be the reason for the enhanced activity of the Pd/Zn system, we tested the activity of the Pd/C catalyst in the presence of a small amount of Amberlyst-15 as co-catalyst. Under comparable conditions, a reaction using 0.025 g Amberlyst-15 in place of $ZnCl_2$ resulted in the formation of the furan ring-hydrogenation product of DMF, 2,5-dimethyl tetrahydrofuran (DMTHF), as a major product (13%), along with small amount of DMF (6%) and other ring-hydrogenation intermediate products such as 2-hexanone (1.6%), tetrahydrofurfuryl alcohol (THFA) (3%), MTHFA (6%), 2-methyl-tetrahydrofuran-5-aldehyde (4.5%), 2,5-bis(dihydroxy) tetrahydromethyfuran (13%), and some unidentified peaks (Supporting Information, Figure S5). The formation of multiple ring-hydrogenation products has also been observed for HMF HDO using HI/RhI$_3$[19] and ruthenium–porous metal oxide (Ru–PMO)[20] catalysts. This result demonstrates that the acidity of $ZnCl_2$ is not the only reason for the enhanced activity of the catalyst, resulting in high DMF yield, as the reaction in the presence of Amberlyst-15 favored furan ring hydrogenation with the formation of multiple products.
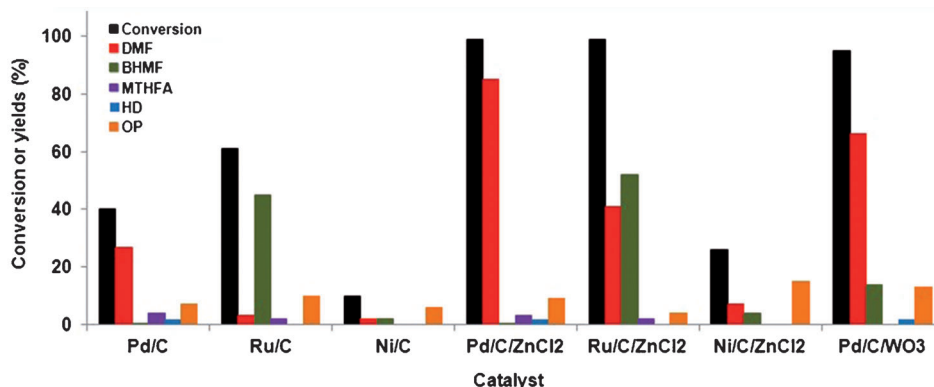
These are not the final page numbers! ↗↗

Figure 1. The results of HMF hydrodeoxygenation using different catalysts. DMF = 2,5-dimethylfuran; BHMF = 2,5-bis(hydroxymethyl)furan; MTHFA = 5-methyltetrahydrofurfural alcohol; HD = 2,5-hexane dione; OP = other products.

The beneficial effect of ZnCl$_2$ has been further extended to Ru/C- and Ni/C-catalyzed HDO of HMF. Bell et al. have shown that Ru/C catalyst was ineffective for HMF HDO at high pressures of H$_2$.[14] Although Ru/C facilitates DMF production using formic acid as a source of hydrogen in THF,[8] the present work shows that a combined catalytic system comprising ZnCl$_2$ and Ru/C is more effective than the earlier report. Under comparable reaction conditions, the combined ZnCl$_2$-Ru/C catalyst enables 41% DMF yield along with 52% yield of BHMF intermediate product and quantitative conversion of HMF. In the absence of ZnCl$_2$, HMF HDO with Ru/C catalyst alone produces only 3% DMF, which is significantly lower than the yield obtained with Pd/C catalyst (27%). While the percentage of HMF conversion with the Ru/C catalyst is moderately higher than the Pd/C, the former catalyst predominantly facilitates hydrogenation of HMF, resulting in the formation of a significant amount of BHMF (45%) intermediate and poor DMF selectivity.

When Lewis-acidic ZnCl$_2$ was added along with Ru/C, the yield of DMF distinctly improved (41%), which is presumably due to enhanced deoxygenation of BHMF in the presence of Zn^{2+}. Noteworthy, the conversion of HMF has also increased in the presence of Zn^{2+}, suggesting that synergism of Zn^{2+} with ruthenium plays a role in enhancing hydrogenation of HMF as well. The latter reaction with the ZnCl$_2$–Ru/C catalyst also showed a significant amount of unconverted BHMF intermediate (52%) for 8 h reaction. Assuming that continuing this reaction for a longer time could deoxygenate unconverted BHMF to DMF, we repeated this reaction for 20 h, which revealed a further conversion of BHMF and hence lowered the concentration of BHMF intermediate from 52% to 31%, but the overall DMF yield (45%) did not improve to the same extent due to the formation of other products (11% MTHFA and 7% 2,5-bis(dihydroxy) tetrahydromethyfuran). This result suggests that BHMF deoxygenation with the Ru/Zn/C catalyst is slower than the Pd/Zn/C catalyst. The latter catalyst resulted in complete conversion of BHMF in 8 h with the formation of 88% DMF.

When comparing the activity of the Ru/C system with that of Pd/C, the latter catalyst provided a higher DMF yield than the former (Figure 1). Therefore, it can be inferred that the palladium catalyst alone can catalyze both hydrogenation of HMF to BHMF

and deoxygenation of BHMF to DMF. In the presence of ZnCl$_2$, the activity of the palladium catalyst for both hydrogenation of HMF and deoxygenation of BHMF improved to achieve significantly higher DMF yield (85%). Although total HMF conversions for both ZnCl$_2$-Ru/C and ZnCl$_2$-Pd/C catalyzed reactions were similar, the higher DMF yield in the reaction catalyzed by the latter is attributed to a more pronounced synergistic effect for the Pd–Zn system than the Ru–Zn one.

To further understand the role of the hydrogenation metal component of the bifunctional catalyst in determining the overall HMF HDO, we studied HMF conversion with Ni/C catalyst in the absence and presence of ZnCl$_2$. Under comparable conditions, of 8 bar H$_2$ and 150 °C, a reaction between 3.96 mmol HMF and 0.05 g Ni/C showed only 10% HMF conversion with the formation of a trace amount of DMF. In the presence of ZnCl$_2$ (0.05 g), HMF conversion increased to 26%, although the yield of DMF remained poor (7%). This comparison indicates that the bifunctional catalyst containing a poor hydrogenation metal component, which is the case for Ni/C, shows poor synergism between the hydrogenation and Lewis acidic metal sites of the bifunctional catalyst. Based on a previous report showing the synergy between tungsten oxide (WO$_3$) and hydrogenation metals,[21] we tested the activity of Pd/C catalyst in the presence of a small amount of WO$_3$ for HDO of HMF in THF. A reaction of 3.96 mmol HMF with a mixture of 0.1 g WO$_3$ and 0.05 g Pd/C at 150 °C and 19 bar H$_2$ for 8 h achieved 66 mol% DMF, 2% HD, 14% BHMF and 1.4% 2-MF. Notably, the WO$_3$ component mostly remained undissolved in the solution, as was confirmed by performing a parallel experiment without using Pd/C. The latter reaction confirmed that WO$_3$ did not catalyze the reaction by itself, but partially dissolved W^{VI} species enhanced the activity of the Pd/C component. A comparison of HMF conversions and product distributions using different catalytic systems is summarized in Figure 1.

The effect of reaction temperature

The effectiveness of the ZnCl$_2$-Pd/C catalyst was evaluated by performing HMF HDO at varying reaction parameters such as H$_2$ pressure and reaction temperature. The reaction temperature was varied in the range of 120 to 200 °C. As shown in Figure 2, the DMF yield increased from 69 to 84% upon increasing the reaction temperature from 120 to 150 °C, but the yield decreased to 58% when the temperature was further increased to 200 °C. Overhydrogenation of the aromatic furan ring of DMF and other intermediate furanic species was the reason for the lower DMF yield at higher temperature. This interpretation was supported by the fact that a GC chromatogram of the product solution showed a new peak with a significant peak area close
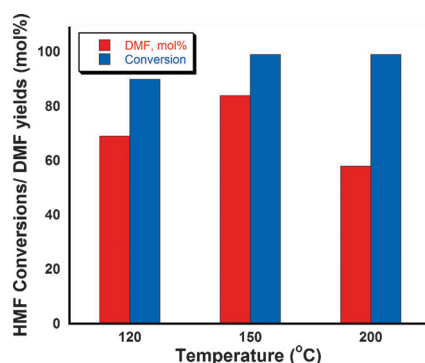
These are not the final page numbers! ↗↗

Figure 2. The effect of reaction temperature on HMF hydrodeoxygenation to DMF.

to the peak for DMF, along with other small peaks in the retention time region 9–12 min. GC–MS revealed the mass number of the new peak as 100, which could be either due to 2-methyl tetrahydro-5-furanone or dihydrofurfural alcohol. The formation of similar dihydro species has been noted previously in the literature.[13, 14] However, further analysis of the reaction product by ^{1}H NMR spectroscopy did not provide sufficient information about the identity of the new species because of overcrowded proton signals from multiple products.

The effect of H$_2$ pressure

More experiments were designed for optimizing the reaction conditions, by varying the H$_2$ pressure in the range of 2–40 bar at a fixed reaction temperature (150 °C). The percentage of HMF conversion and the corresponding DMF yields are shown in Figure 3. The yield of DMF increased from 29 to 84 % upon increasing H$_2$ pressure from 2 to 8 bar, and remained unchanged up to 20 bar. A further increase of H$_2$ pressure to 40 bar did not significantly influence the overall DMF yield.

The effect of reaction time

To elucidate the reaction sequence, we conducted a reaction between 3.96 mmol HMF and ZnCl$_2$ (0.05 g)–Pd/C (0.05 g) catalyst at 150 °C for multiple times by varying the reaction time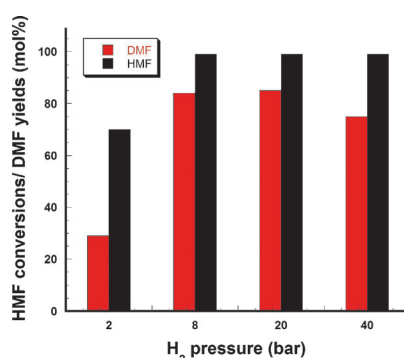 from 1 h to 20 h. As shown in Figure 4, HMF HDO for 1 h produced 35 % BHMF as intermediate along with 55 % DMF. The yield of BHMF intermediate decreased from 35 % to 12 % upon increasing the reaction time from 1 h to 2.5 h, during which the yield of DMF also increased from 55 % to 71 %. A further increase in reaction time from 2.5 h to 8 h resulted in complete conversion of BHMF to DMF. The yield of DMF and the concentration of MTHFA and HD by-products remained unchanged
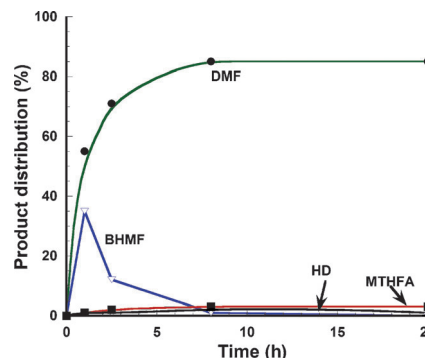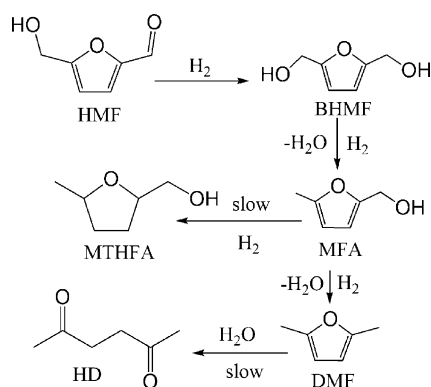

Figure 4. Reaction profile of HMF hydrodeoxygenation with ZnCl$_2$–Pd/C as catalyst.

up to 20 h. To validate the formation of BHMF as intermediate in HMF HDO pathway, we performed a separate experiment using BHMF as a starting substrate. Under comparable reaction conditions, BHMF deoxygenation with the ZnCl$_2$-Pd//C catalyst achieved 88 % conversion in 8 h and produced 82 % DMF (Supporting Information, Figure S6). This observation of HMF HDO sequence partly agrees with previous findings by Bell et al.,[14] in which the −CHO group of HMF is hydrogenated first to form BHMF as an intermediate (Scheme 1). Subsequent deoxygenation of hydroxymethyl groups of BHMF results in the formation of DMF via 5-methylfurfural alcohol (MFA) as intermediate. As MFA was not detected in the GC–MS spectra of product solutions, it is believed that MFA was rapidly deoxygenated to DMF under the reaction conditions, as evidenced in earlier reports.[21b] The formation of small amounts of MTHFA and HD attributes to the fact that hydrogenation of furan ring of MFA and hydration of DMF took place during the reaction.[22–24] The yields of MTHFA and HD were, however, below 3 % even after 20 h, which suggests that these side reactions occur at much slower rates. Mechanistically, we postulate that the zinc component facilitates hydrogenolysis of BHMF to DMF by cleavage of C−O bonds, as discussed in our earlier report involving HDO of phenolic alcohols and aldehydes.[16] A similar observation was made in the HDO of HMF with Ru/Co$_3$O$_4$ as catalyst, in which the ruthenium component hydrogenated HMF to BHMF and CoO$_x$ facilitated hydrogenolysis of BHMF to DMF.[15]

Comparison of catalyst activity

To explore the commercial potential of this process for DMF production, we prepared the Pd/Zn/C catalyst by impregnating Zn^{2+} on commercially purchased Pd/C by the incipient wetness method, as discussed in the Experimental section. Instead of adding the Pd/C and ZnCl$_2$ components separately, we examined the effectiveness of as-synthesized Pd/Zn/C catalyst by

Figure 3. HMF hydrodeoxygenation as a function of H$_2$ pressure.

These are not the final page numbers! ↗↗

Scheme 1. Proposed reaction pathway for HMF hydrodeoxygenation with the $ZnCl_2$-Pd/C catalyst.

performing an experiment in which 3.96 mmol HMF was reacted with 0.05 g catalyst at 150 °C and 8 bar H_2 for 8 h. The activity of the Pd/Zn/C catalyst was comparable to the $ZnCl_2$-Pd/C catalytic system, giving 85 % DMF. Additionally, the inherent fuel properties of small amounts of overhydrogenation products, accounting for the carbon mass balance, eliminate the necessity of an expensive separation step of DMF from the product stream.

The effectiveness of the Pd/Zn/C catalyst was also compared to previously reported catalytic systems (Table 1). Among other effective catalytic systems reported in the literature, Pd/C and Ru/C catalysts (entries 7 and 8) using alternate hydrogen sources, generated in situ from isopropanol and formic acid, gave 70 and 81 % DMF, respectively. However, in both cases the concentrations of active metals in the catalysts were at least 4 times higher than the present catalyst. Similarly, the dosage of both ruthenium and copper metals in the Cu-Ru/C catalyst was at least 50 times higher than the metal loadings in the Pd/Zn/C catalyst. This comparison suggests that our Pd/Zn/C catalyst, containing the least amount of palladium (0.013 mmol Pd) but giving comparable or higher DMF yields, is certainly superior to the other reported systems.

Recyclability studies

As catalytic effectiveness of Zn^{2+}-preloaded Pd/Zn/C material is similar to that of combined $ZnCl_2$-Pd/C catalyst, we used as-synthesized Pd/Zn/C catalyst for recyclability studies. In this experiment, 3.96 mmol (0.5 g) of HMF was reacted with 0.05 g Pd/Zn/C catalyst in 15 mL THF at 150 °C and 8 bar H_2 for 8 h. After the 1st reaction cycle, the solid catalyst was recovered by simple filtration, washed with about 10–15 mL THF, dried in air, and reused for the next cycle. The next cycle was started by adding 3.96 mmol of HMF and 15 mL THF. Some amount of fresh catalyst (10–15 wt % of total catalyst) was also added to replenish the loss of mass in recycled catalyst during recovery. The aliquot from each cycle was analyzed by GC to quantify DMF yields. The results, as shown in Figure 5, reveal a deactivation of the catalyst, in terms of DMF yield, after the 4th cycle.

To examine the catalyst deactivation, we analyzed the fresh Pd/Zn/C catalyst and the recovered catalyst after the 3rd and 5th cycles by ICP–AES to measure palladium and zinc contents. There was a loss of zinc metal in the recovered catalyst obtained after the 3rd cycle. While this loss of zinc did not significantly influence activity in the 4th cycle, we found a noticeable deactivation in catalyst activity in the 5th cycle. ICP–AES analysis of the recovered catalyst after the 5th cycle showed that the zinc content in the catalyst was almost the same as after the 3rd cycle, but the amount of palladium was decreased by about 0.54 %.

While catalyst deactivation in the 5th cycle can be interpreted either by (i) loss of palladium metal in the solution, or by (ii) dilution of palladium concentration in the catalyst due to coke formation on the catalyst surface, we performed a separate experiment to examine the possibility of palladium loss and involvement of homogeneous palladium metal in HMF HDO. In this experiment, 0.05 g Pd/Zn/C catalyst was heated in 15 mL THF at 150 °C and 8 bar H_2 for 22 h, which is almost the time needed for recycling the catalyst for 4 cycles. Upon cooling the reactor, the catalyst was separated by filtration and 3.96 mmol HMF was added into the filtrate, and the reaction was continued at 150 °C and 8 bar H_2 without any solid catalyst. A GC chromatogram of the aliquot showed no peaks for DMF or other hydrogenated intermediates. The peak area of HMF accounted for 95 % of unconverted HMF. This result precludes the hypothesis of palladium metal leaching from the catalyst during 22 h heating with the solvent. Additionally, ICP analysis of the filtrate after five cycles showed that palladium loss in the filtrate was very negligible (0.0065 mg or 0.34 % based on 1.9 mg palladium metal present in the synthesized Pd/Zn/C catalyst). These results indirectly support the hypothesis of coke formation on the catalyst surface as cause of deactivation and dilution of the palladium concentra-

Table 1. Results of HMF HDO with different catalysts as a function of temperature and H_2 pressure.

Entry	Catalyst	T [°C]	t [h]	Solvent	P_{H_2} [bar]	Conv. [%]	DMF yield [%]	Ref.
1	Pd/C/Zn	150	8	THF	8	> 99	85	this work[a]
2	Rh/C	120	1	[EMIM]Cl	62	16	1	[14]
3	Pd/C	120	1	[EMIM]Cl	62	19	2	[14]
4	Pt/C	120	1	[EMIM]Cl	62	11	< 1	[14]
5	Ru/C	120	1	[EMIM]Cl	62	23	0	[14]
6	Cu-Ru/C	220	10	2-butanol	6.8	–	71	[5][b]
7	Pd/C	150	15	THF	generated in situ	–	70	[9][c]
8	Ru/C	190	6	isopropanol	generated in situ	> 99	81	[25][d]

[a] HMF = 0.5 g, Pd/Zn/C = 0.05 g (0.018 mmol Pd). [b] 30 wt % catalyst loading based on HMF (Cu = 1.78 mmol; Ru = 0.74 mmol). [c] 160 wt % catalyst loading based on HMF (Pd = 0.188 mmol). [d] 35 wt % catalyst loading based on HMF (Ru = 0.049 mmol).
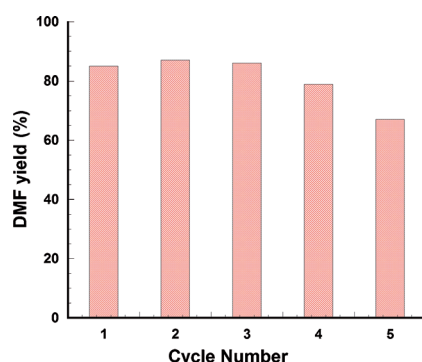
These are not the final page numbers! ↗↗

Figure 5. Recyclability of the Pd/Zn/C catalyst for HMF hydrodeoxygenation to DMF.

tion in the recycled catalyst. Transmission electron microscopy (TEM) images of the as-synthesized and the recovered catalysts, showing their nanostructure and lattice fringes, are shown in Figure S7 (Supporting Information).

Substrate scope

The scope of the present investigation was further extended to the direct conversion of fructose to DMF in one pot. The two-step conversion of fructose to DMF involves dehydration of fructose to HMF in the first step, followed by HDO of HMF to DMF in the 2nd step. As the present catalytic system contains both a Lewis-acidic ($ZnCl_2$) and hydrogenation component (Pd/C), we investigated the effectiveness of the $ZnCl_2$-Pd/C catalyst for the conversion of fructose in THF at 150 °C under 8 bar H_2. A reaction between 1.8 mmol (0.324 g) of fructose and $ZnCl_2$ (0.2 g)-Pd/C (0.05 g) for 8 h produced 22% DMF, 2% HMF, and 3% 5-methylfurfural. Some unidentified GC peaks, accounting in total for half the peak area relative to that of DMF, were also observed. Under comparable reaction conditions, a control experiment using only $ZnCl_2$ as a dehydration catalyst produced only 13 mol% HMF. This result suggests that fructose conversion to HMF and its subsequent HDO to DMF increased in the presence of Pd/C. Assuming high pressure of H_2 is a limitation for HMF production in the beginning of experiment, we designed an experiment in which 1.8 mmol fructose was reacted with $ZnCl_2$ (0.2 g)-Pd/C (0.05 g) in 15 mL THF at 150 °C for 1.5 h and then the reactor was pressurized at 8 bar H_2 to continue the reaction for another 8 h. The latter reaction showed no improvement in DMF yield. Considering the solvent to be a barrier for effective dehydration of fructose to HMF, we conducted a similar experiment in a water/THF mixture (1 mL water + 14 mL THF). However, total yields of DMF (19%) and HMF (6.5%) in the later experiment were similar.

Conclusions

2,5-Dimethylfuran (DMF) is a promising biofuel candidate, with features that are more desirable when compared to ethanol. Although several research articles demonstrating different catalytic technologies for DMF production have been published in recent years, selective production of DMF in high yields remains

a challenge. We demonstrate a bimetallic palladium and zinc catalyst that achieves a DMF yield as high as 85% under mild reaction conditions (150 °C and 8 bar H_2). Under comparable reaction conditions, Pd/C alone produces only 27% DMF. $ZnCl_2$ alone does not catalyze deoxygenation or hydrogenation of 5-hydroxymethylfurfural (HMF), suggesting a strong synergistic effect between the two metals. Separate experiments using as-synthesized Pd/Zn/C catalyst give similar yields of DMF as the $ZnCl_2$-Pd/C combination. A reaction catalyzed by Ru/C produces 2,5-bis(hydroxymethyl)furan (BHMF) as its major product. The effectiveness of the Ru/C catalyst improves in the presence of $ZnCl_2$, but the overall DMF yield is much lower (41%) than when using the Pd/Zn/C system. The less-effective hydrogenation catalyst Ni/C shows little improvement with $ZnCl_2$, giving only 7% DMF. The Pd/C-catalyzed reaction in the presence of Brønsted-acidic Amberlyst 15 produces multiple products containing overhydrogenated tetrahydrofuran rings. The as-synthesized Pd/Zn/C catalyst shows excellent recyclability up to 4 cycles, followed by some deactivation. Control experiments suggest that coke deposition on the catalyst surface is the reason for catalyst deactivation. The effectiveness of the Pd/Zn/C catalyst for the one-pot conversion of fructose to DMF is also investigated. The zinc component facilitates hydrogenolysis of BHMF to DMF. Further experiments to understand the exact role of the zinc component in the bifunctional catalysts are underway.

Experimental Section

Materials

HMF, DMF, methanol, and fructose were purchased from Sigma–Aldrich and used as-received. Pd/C and Ru/C catalysts containing 5 wt% of the respective metal loading, supported on activated carbon (AC) with a Brunauer–Emmett–Teller (BET) surface area of 1200 m^2 g^{-1}, were purchased from Strem Chemicals. However, inductively coupled plasma–atomic emission spectroscopic (ICP-AES) analysis by Galbraith Laboratory showed the palladium loading in the purchased catalyst was 3.9%. THF containing butylated hydroxyl toluene (BHT) as stabilizer was purchased from Fisher Chemicals. $ZnCl_2$ was purchased from Acros Organics and used without further purification. Ni/C catalyst was prepared by following a literature method.[17] According to this method, nickel(II) nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 1.3 g) was dissolved in 6 mL water in a beaker. About 2 g AC support of 100 mesh particle size was added into the Ni^{II} solution and the mixture was stirred for 24 h. The sample was dried overnight at 120 °C. The dried sample was then reduced in a U-shaped quartz dried tube (Schwartz).[17] The resultant powder was washed with water to remove any free nickel, filtered, and dried overnight at 120 °C. 2,5-Bis(hydroxymethyl)furan (BHMF) was prepared by NaBH$_4$ reduction of HMF in ethanol. In this method, 0.17 g NaBH$_4$ was dissolved in 10 mL ethanol and the solution was cooled in an ice bath for 15 min. To this solution, 1 g HMF was slowly added while the solution was continuously stirred. Upon stirring at 0 °C for 1 h, the solution was warmed to room temperature and stirred overnight. The pH of the solution was adjusted to approximately 7 by dropwise addition of dilute HCl and the solution was decanted to another round-bottom flask. BHMF was isolated (90% yield) after rotary evaporation of solvent and its purity was determined by ^{1}H NMR spectroscopy (Supporting Information, Figure S1). As-synthesized Pd/Zn/C catalyst was prepared by incipient

These are not the final page numbers! ↗↗

wetness method. In this method, Pd/C and ZnCl$_2$ in 1:3 ratio (w/w) were mixed in water and the mixture was stirred overnight at room temperature. The resultant solid was filtered and washed several times with water to remove any free zinc salt and dried under vacuum. ICP–AES analysis of as-synthesized Pd/Zn/C catalyst showed the presence of palladium and zinc metals. Further analysis of this catalyst using SEM elemental mapping (NOVA nanoSEM FEI) confirmed that both metals are uniformly distributed throughout the sample (Supporting Information, Figure S2).

Catalysis

Catalytic HDO of HMF was carried out in a stainless steel Parr reactor equipped with a stirring impeller, gas line, and programmable control device for setting reaction time and temperature. In a typical experiment, the reactor was loaded with 0.5 g HMF (3.96 mmol), 0.05 g Pd/C, 0.05 g ZnCl$_2$, and 15 mL solvent, and then properly sealed with the reactor head. After purging the mixture with UHP-grade H$_2$ for a couple of minutes with continuous stirring, the reactor was pressurized with H$_2$ in the pressure range of 2–40 bar and heated at 150 °C for the desired time (1–20 h). Upon completion of reaction for the set time, the reactor was cooled to room temperature and the pressure released. The reactor vessel was removed and the solution was filtered. The collected filtrate was analyzed by GC and GC–MS.

Recyclability study

Catalyst reusability studies were performed by using as-synthesized Pd/Zn/C material by following the aforementioned procedure. After the 1st cycle of reaction between 3.96 mmol of HMF and 0.05 g Pd/Zn/C catalyst at 150 °C and 8 bar H$_2$ for 8 h, the aliquot was filtered. The recovered catalyst was washed several times with THF, dried in air, and loaded in the reactor for the next cycle. The aliquot of each cycle was analyzed by GC for quantification of products.

Determination of DMF yield

The yield of DMF and other products were measured by analyzing the product solutions on a GC instrument (Agilent 6890N) equipped with a FID detector and DB-5 capillary column of dimension 0.25 mm ID×0.25 µm×30 m. Essential parameters of GC analysis are as follows: injection volume 1.0 µL, inlet temperature 250 °C, detector temperature 250 °C, and a split ratio 1:5. Initial column temperature was 50 °C (2 min) with a temperature rise of 10 °C min^{-1} and final temperature was 300 °C. DMF was identified by its retention time in comparison with an authentic sample and by GC–MS analysis. 5-methyltetrahydrofurfural alcohol (MTHFA) and 2,5-hexane dione (HD) peaks were characterized by GC–MS analysis. Each peak of the GC chromatogram was properly integrated and the actual concentration of DMF was obtained from a pre-calibrated plot of peak area against concentrations. Unless otherwise mentioned, all yields are reported in mol %. GC–MS spectrometry analyses were carried out using an Agilent 5975C (Agilent Labs, Santa Clara, CA) mass spectrometer system. Typical electron energy was 70 eV with the ion source temperature maintained at 250 °C. The individual components were separated using a 30 meter DB-5 capillary column (250 µm i.d. × 0.25 µm film thickness).The initial column temperature was set at 35 °C (for 3 min) and programmed to 280 °C at 10.0 °C min^{-1}. The flow rate was typically set at 1 mL min^{-1}. The injector temperature was set at 250 °C.

[1] J. Goldemberg, Science 2007, 315, 808–810.
[2] R. Sims, M. Taylor, J. Saddler, W. Mabee, From 1st to 2nd Generation Biofuel Technologies, in An Overview of Current Industry and R&D Activities, International Energy Agency, November 2008. See http://www.iea.org/publications/freepublications/publication/2nd_Biofuel_Gen.pdf (accessed August 2014).
[3] G. W. Huber, S. Iborra, A. Corma, Chem. Rev. 2006, 106, 4044–4098.
[4] J. O. Metzger, Angew. Chem. Int. Ed. 2006, 45, 696–698; Angew. Chem. 2006, 118, 710–713.
[5] Y. Román-Leshkov, C. J. Barrett, Z. Y. Liu, J. A. Dumesic, Nature 2007, 447, 982–985.
[6] J. B. Binder, R. T. Raines, J. Am. Chem. Soc. 2009, 131, 1979–1985.
[7] S. Dutta, S. De, I. Alam, B. Saha, M. M. Abu-Omar, J. Catal. 2012, 288, 8–15.
[8] S. De, S. Dutta, B. Saha, ChemSusChem 2012, 5, 1826–1833.
[9] T. Thananatthanachon, T. B. Rauchfuss, Angew. Chem. Int. Ed. 2010, 49, 6616–6618; Angew. Chem. 2010, 122, 6766–6768.
[10] M. T. Barlow, D. J. Smith, D. G. Steward, Eur. Pat. EP0082689, 1983.
[11] S. Song, R. Daniel, H. Xu, J. Zhang, D. Turner, M. L. Wyszynski, P. Richards, Energy Fuels 2010, 24, 2891–2899.
[12] R. Rinaldi, F. Schüth, ChemSusChem 2009, 2, 1096–1107.
[13] W. Yang, A. Sen, ChemSusChem 2010, 3, 597–603.
[14] M. Chidambaram, A. T. Bell, Green Chem. 2010, 12, 1253–1262.
[15] Y. Zu, P. Yang, J. Wang, X. Liu, J. Ren, G. Lu, Y. Wang, Appl. Catal. B 2014, 146, 244–248.
[16] T. H. Parsell, B. C. Owen, I. Klein, T. Jerrell, M. Marcum, L. J. Haupert, L. M. Amundson, H. I. Kenttamaa, F. Ribeiro, J. T. Miller, M. M. Abu-Omar, Chem. Sci. 2013, 4, 806–813.
[17] Q. Song, F. Wang, J. Cai, Y. Wang, J. Zhang, W. Yua, J. Xu, Energy Environ. Sci. 2013, 6, 994–1007.
[18] Z. Hong, C. Quan, L. Chunhu, M. Xindong, Carbohydr. Res. 2011, 346, 2016–2018.
[19] M. G. Grochowski, W. Yang, A. Sen, Chem. Eur. J. 2012, 18, 12363–12371.
[20] H. S. Thomas, B. Katalin, P. T. Anastas, P. C. Ford, A. Riisager, Green Chem. 2012, 14, 2457–2461.
[21] a) A. Wang, R. Zhang, Acc. Chem. Res. 2013, 46, 1377–1386; b) Y. K. Kwon, E. D. Jong, S. Raoufmoghaddam, M. T. M. Koper, ChemSusChem 2013, 6, 1659–1667.
[22] Y. Zhang, S. Wei, Chinese Patent, CN101423467, 2009.
[23] T. Noguchi, K. Takayama, M. Nakano, Biochem. Biophys. Res. Commun. 1977, 78, 418–423.
[24] G. Wang, Z. Guan, R. Tang, Y. He, Synth. Commun. 2010, 40, 370–377.
[25] J. Jae, W. Zheng, R. F. D. G. Vlachos, ChemSusChem 2013, 6, 1158–1161.

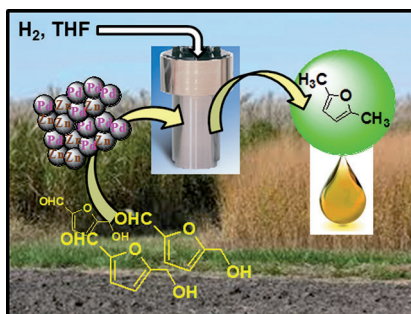## These are not the final page numbers! ⌐⌐

FULL PAPERS

B. Saha,* C. M. Bohn, M. M. Abu-Omar*

■■ – ■■

🖥 **Zinc-Assisted Hydrodeoxygenation of Biomass-Derived 5-Hydroxymethylfurfural to 2,5-Dimethylfuran**

Are you thinking what I'm zincing? The addition of zinc salt enhances the catalytic effectiveness of a palladium–carbon (Pd/C) catalyst in the hydrodeoxygenation (HDO) of 5-hydroxymethylfurfural (HMF) into 2,5-dimethylfuran (DMF) by a factor of more than 3. The finding allows to use catalysts with less palladium. The synergistic effect of the zinc salt with different hydrodeoxygenation catalysts is compared to elucidate the role of the zinc component.

These are not the final page numbers! ↗↗