One-Pot Deoxygenation of Fructose to Furfuryl Alcohol by Sequential Dehydration and Decarbonylation

Jinhang Dai, Xing Fu, Liangfang Zhu,* Jinqiang Tang, Xiawei Guo, and Changwei Hu^{*[a]}

Fructose was deoxygenated to furfuryl alcohol (FFA) by tandem dehydration and decarbonylation in one pot over the AlCl₃·6H₂O/Pd(OAc)₂ catalyst combination to give a high FFA yield of 40.6%. AlCl₃·6H₂O behaves as an effective Lewis acid to catalyze the dehydration of fructose to 5-hydroxymethylfurfural (HMF), and subsequently, Pd(OAc)₂ catalyzes the removal of a CO moiety from HMF to produce FFA selectively. The hydroxyl group on the HMF intermediate was stabilized by poly(1-vinyl-2-pyrrolidinone) through an intermolecular hydrogen bond, which accelerated the dehydration of fructose and inhibited the hydrogenation of HMF by formic acid. The decarbonylation of HMF was promoted and the unwanted decomposition of fructose was inhibited through the use of 4 Å molecular sieves. This research highlights a "one-pot" catalytic system to transform renewable carbohydrates into fine chemicals by tandem dehydration and decarbonylation reactions without the separation or purification of HMF.

Introduction

The impending shortages of fossil resources combined with increasing environmental concerns have promoted the search for a new source of both bulk chemicals and transportation fuels.^[1] The abundance and structural diversity of biomass-derived sugars make them excellent alternatives for fossil resources. The development of effective methods for the conversion of sugars to value-added chemicals and fuels has become one of the major issues of the 21st century.^[2]

A fundamental challenge for the conversion of sugars is that saccharides are significantly more oxygen rich than the majority of current commodity chemicals and fuels. The selective deoxygenation of sugars is of great significance for the effective utilization of biomass-derived feedstocks.^[3] Dehydration and decarbonylation/decarboxylation are elementary reactions for deoxygenation. Recent efforts have been devoted to the selective dehydration of C₆ sugars to synthesize 5-hydroxymethylfurfural (HMF).^[4] Moreover, the further transformation of HMF to value-added furan derivatives and fuels is investigated frequently because of the reactivity of HMF.^[5] Among these investigations, the decarbonylation of HMF by removing a CO moiety further lowers the oxygen content of the biomass-derived molecule to produce furfuryl alcohol (FFA). For instance, an early example was reported in 1978 on the decarbonylation

 [a] J. Dai, X. Fu, Dr. L. Zhu, J. Tang, X. Guo, Prof. C. Hu Key Laboratory of Green Chemistry and Technology Ministry of Education College of Chemistry Sichuan University Chengdu, Sichuan 610064 (P.R. China) E-mail: zhulf@scu.edu.cn changweihu@scu.edu.cn
 Supporting Information for this article can be found under http:// dx.doi.org/10.1002/cctc.201501292. of HMF with Pd- or Rh-based catalysts in neutral to weakly alkaline media.^[6] Recently, Geilen et al.^[7] demonstrated the highly selective decarbonylation of HMF to FFA with Ir–phosphine catalysts in a CO₂-expanded organic solvent under high temperature (> 220 °C) and pressure (2~5 MPa). Huang et al.^[8] and Mitra et al.^[9] reported the milder decarbonylation of HMF over Pd/SBA-15 and Pd/C catalysts, respectively, at 120~130 °C, which gave satisfactory FFA yields of above 90%. Although the deoxygenation efficiency of HMF decarbonylation is high, the thermally unstable nature of HMF makes it hard to separate it from solvent, which limits the application of pure HMF as the starting material for further utilization.

A promising strategy to lower the oxygen content of biomass-derived sugars is to integrate the elementary reactions of dehydration and decarbonylation in "one pot". The concept of one-pot reactions in which a multifunctional catalyst or catalyst combination is used to synthesize furan derivatives directly from sugars via the HMF intermediate has been investigated frequently.^[10] Such one-pot reactions have unique environmentally friendly benefits, that is, the avoidance of the isolation and purification of the thermally unstable HMF intermediate, which thus lowers energy consumption and production costs. The exploration of the integrated deoxygenation reactions in one pot to produce FFA is of particular significance to increase the deoxygenation efficiency and lower the energy consumption of any separation and purification step. Although the current route for FFA production is through the hydrogenation of furfural that comes from the dehydration of C₅ sugars,^[11] the hydrogenation reaction needs an additional H₂ source. However, C₆ sugars are naturally more available because they make up almost half of lignocellulose. Therefore, the development of methods to transform C₆ sugars to FFA through tandem dehydration and decarbonylation reactions provides an alternative strategy for FFA synthesis because it utilizes the naturally more



available resource. This is important to increase the number of types of biomass transformations available.^[12]

Herein, we report our investigation of the sequential dehydration and decarbonylation from fructose to FFA by a one-pot approach over a combined catalyst of $AlCl_3 \cdot 6H_2O$ and $Pd(OAc)_2$ at 150 °C under autogenous pressure. $AlCl_3 \cdot 6H_2O$ behaves as an effective Lewis acid to catalyze the dehydration of fructose to HMF, and subsequently, $Pd(OAc)_2$ catalyzes the removal of a CO moiety from HMF to produce FFA selectively. The addition of additives such as 4 Å molecular sieves and poly(1-vinyl-2-pyrrolidinone) (PVP) promotes the deoxygenation efficiency. The roles of each component in the catalytic system and the influence of water and byproducts formed in the dehydration step on the yield of FFA are discussed. A possible reaction network for the one-pot conversion of fructose to FFA is proposed.

Results and Discussion

There are several reaction possibilities that exist in a one-pot reaction. In the case of the sequential deoxygenation of fructose, any parallel reactions from fructose or derivations from HMF will inevitably result in a low yield and selectivity to FFA. For example, in addition to dehydration to form HMF, fructose could be converted to furfural and formaldehyde or formic acid (FA) and humins by direct decomposition^[13] or to polyols by decarbonylation under specific reaction conditions. The HMF formed would undergo further transformation to some undesirable products such as insoluble humins.^[14] Therefore, a key issue for the one-pot deoxygenation of fructose to FFA lies mainly in the integration of the tandem reactions of dehydration and decarbonylation, whereas unexpected side-reactions should be inhibited. That is, the catalytic system should be active and highly selective for the dehydration of fructose to HMF firstly and then for the decarbonylation of HMF to FFA secondly. Side-reactions (i.e., the formation of humins) should be limited as far as possible. Additionally, the catalysts should be water tolerant to retain their catalytic activity because the dehydration step produces water to accompany the formation of HMF.

Investigation of the background reactions of dehydration and decarbonylation

We investigated each background reaction in the one-pot deoxygenation of fructose to FFA. As Pd(OAc)₂ was insoluble in water and has been proved recently to be active for the decarbonylation of aldehydes to alkanes without the use of a CO scavenger,^[15] we were initially interested in its activity for the decarbonylation of HMF to FFA. The yield of FFA was $89.6\,\%$ over Pd(OAc)₂ in 1,4-dioxane (Table 1, entry 1), which highlights the high activity of Pd(OAc)₂ for the decarbonylation reaction. Inspired by these results, we replaced HMF tentatively with fructose as the starting material. The results revealed that both HMF (1.4%) and FFA (2.2%) were produced in 1,4-dioxane over Pd(OAc)₂ (Table 1, entry 2). It was possible that Pd(OAc)₂ was active for both the dehydration of fructose to the intermediate HMF and decarbonylation of HMF to FFA. However, its activity was extremely low. A slight increase of the FFA yield (3.1%) was obtained upon the addition of 4 Å molecular sieves (Table 1, entry 3). No polyols were detected, which indicates that Pd(OAc)₂ was not selective for the direct decarbonylation of fructose.

To increase the yield of FFA from fructose in a one-pot reaction, we reconstructed the dehydration reaction by adding a dehydration catalyst. As $AlCl_3 \cdot 6 H_2O$ is an active and low-toxicity catalyst for the dehydration of C_5/C_6 sugars in THF/ water,^[16] we tested its dehydration activity in 1,4-dioxane. An HMF yield of 23.4% was obtained with $AlCl_3 \cdot 6 H_2O$ as the only catalyst (Table 1, entry 4). The yield of HMF was not increased if 4 Å molecular sieves were added (Table 1, entry 5). However, a significant increase of the HMF yield (48.1%) was obtained upon the addition of PVP as an additive (Table 1, entry 6). Notably, the combined use of $AlCl_3 \cdot 6 H_2O$, PVP, $Pd(OAc)_2$, and 4 Å

Table 1. Conversion of HMF and fructose in 1,4-dioxane. ^[a]							
Entry	AICl ₃ ·6H ₂ O [$\times 10^{-3}$ mmol]	$Pd(OAc)_2$ [×10 ⁻³ mmol]	4 Å molecular sieves/ AlCl₃•6 H₂O [w/w]	PVP/AICI₃•6H₂O [w/w]	FFA [mol%]	HMF [mol%]	Conversion [%]
1 ^[b]	0	35.7	0	0	89.6	0	100.0
2	0	44.6	0	0	2.2	1.4	88.8
3	0	44.6	150	0	3.1	1.0	80.9
4	4.1	0	0	0	0	23.4	98.2
5	4.1	0	150	0	0	23.6	98.7
6	4.1	0	150	15	0	48.1	99.0
7	4.1	44.6	150	15	40.6	5.2	100.0
8	4.1	44.6	150	0	19.8	1.2	97.8
9	4.1 ^[c]	44.6	150	0	15.3	5.7	98.6
10 ^[d]	4.1	44.6	0	0	7.1	14.0	99.0
11 ^[e]	4.1	44.6	0	0	5.8	14.9	99.8
12	4.1	44.6	0	0	7.6	13.9	99.5
13	0	0	0	15	0	1.5	28.2
[a] Reaction conditions: 0.3 mmol of fructose 2 mL of 1.4-diovane 150°C 4 h under N atmosphere. [h] HME used as the starting material. [c] Anhydrous							

[a] Reaction conditions: 0.3 mmol of fructose, 2 mL of 1,4-dioxane, 150 °C, 4 h, under N₂ atmosphere. [b] HMF used as the starting material. [c] Anhydrous AlCl₃ used instead of AlCl₃-6 H₂O. 1,4-Dioxane was dewatered before use. [d] 0.2 mmol of water added before the reaction. [e] 0.6 mmol of water added before the reaction.

ChemCatChem 2016, 8, 1379-1385



molecular sieves produced FFA as the main product with a yield of 40.6% and the complete conversion of fructose (Table 1, entry 7), which implies that most of the HMF produced was decarbonylated to FFA in the one-pot reaction.

Effect of AICl₃·6H₂O on the one-pot reaction

We performed experiments by varying the amount of $AlCl_3 \cdot 6H_2O$ to investigate its role on the one-pot reaction. To reduce the impact of PVP on the dehydration process, we performed the one-pot reactions in the absence of PVP.

If 2.1×10^{-3} mmol of AlCl₃·6H₂O was used, the FFA yield increased from 3.1% (without AlCl₃·6H₂O) to 14.6%, and 53.5% of fructose was converted (Figure 1). Small amounts of HMF (3.3%) and FA (4.4%) were detected as the main byproducts,



Figure 1. Effect of the amount of AlCl₃•6 H₂O used on the yields of FFA and HMF. Reaction conditions: 0.3 mmol of fructose, 2 mL of 1,4-dioxane, 44.6×10^{-3} mmol of Pd(OAc)₂, 4 Å molecular sieves/Pd(OAc)₂ (w/w) = 15, 150 °C, 4 h, N₂ atmosphere.

and furan (2.1%), furfural (0.8%), formaldehyde (1.1%), 5-methylfurfural (5-MF, 0.3%), and 2-methylfuran (2-MF, 0.7%) were detected as the minor byproducts. No levulinic acid (LA) or insoluble humin-like byproducts were observed, which indicates that no rehydration or serious condensation of HMF occurred in the 1,4-dioxane medium. The unbalanced carbon may be ascribed to the formation of some soluble oligomers, the existence of which has been confirmed by using gel permeation chromatography (GPC), the analysis of which showed the presence of byproducts with a molecular mass of 302 (Table S1).^[17] As no oxidant was present in the catalytic system, the FA byproduct was not derived from the further oxidation of formaldehyde but from the direct decomposition of fructose as a result of the presence of HCl derived from the hydrolysis of $AICI_3 \cdot 6H_2O$.^[13b] Furthermore, the lower yield of furfural than formaldehyde indicated the further transformation of furfural to other byproducts. In a control experiment, we studied the possible reaction of furfural and FA in the presence of Pd(OAc)₂, and we observed both furan (26.9%) and FFA (3.8%) as the products. That is, there were two pathways for furfural conversion: to furan by decarbonylation by Pd(OAc)₂ and to FFA by hydrogenation by FA. Thus, the yield of FFA obtained experimentally from the one-pot deoxygenation of fructose was possibly the sum of the decarbonylation of the HMF intermediate and the hydrogenation of furfural, although the latter might make a very low contribution. Moreover, the trace amount of 5-MF and 2-MF detected in the one-pot reaction were derived from the hydrogenation of HMF and FFA with FA, respectively, as we have determined from control experiments.

An increase of the amount of AlCl₃·6H₂O led to an increase in the FFA yield, which reached a maximum of 19.8% (4.1× 10^{-3} mmol of catalyst) and then decreased to 13.0% (8.2× 10⁻³ mmol of catalyst), and the conversion of fructose was 100%. A higher amount of AlCl₃·6H₂O led to a further decrease of the FFA yield to 6.2% (20.5×10^{-3} mmol of catalyst). In comparison, the yield of HMF increased monotonically, which suggests the dominant role of AlCl₃·6H₂O on the dehydration of fructose. Furthermore, the yield of furfural increased, which implies that the addition of AlCl₃·6H₂O also promoted the direct decomposition of fructose to furfural. However, the yield of FA increased first and then decreased, which was accompanied by a decrease of the yield of FFA and an increase the yields of both 2-MF and 5-MF. These results illustrate that the FA formed earlier was consumed by further reaction with HMF and FFA to produce 5-MF and 2-MF. In addition, it was observed that the color of the reaction mixture became deeper as the amount of AlCl₃·6H₂O increased. GPC analysis of the resulting mixture showed the presence of oligomerized byproducts with a molecular mass of ~331 (Table S1).^[17]

Effect of Pd(OAc)₂ on the one-pot reaction

We used 4.1×10^{-3} mmol of AlCl₃·6H₂O as the dehydration catalyst to further investigate the effect of the Pd(OAc)₂ dosage on the product yields (Figure 2). A substantial increase of the FFA yield and decrease of the HMF yield was observed with an increase of the amount of Pd(OAc)₂ used, which confirms the crucial role of Pd(OAc)₂ on the decarbonylation of HMF. A maximum FFA yield of 19.8% was obtained if 44.6×10^{-3} mmol of Pd(OAc)₂ was used. A further increase of the Pd(OAc)₂ dosage



Figure 2. Effect of the amount of $Pd(OAc)_2$ used on the yields of FFA and HMF. Reaction conditions: 0.3 mmol of fructose, 2 mL of 1,4-dioxane, 4.1×10^{-3} mmol of AlCl₃·6 H₂O, 4 Å molecular sieves/AlCl₃·6 H₂O (w/w) = 150, 150 °C, 4 h, N₂ atmosphere.



beyond 44.6×10^{-3} mmol decreased the yields of FFA and furfural and increased the yields of 2-MF and furan. At the same time, the yield of FA decreased continuously. These results suggest that a higher amount of Pd(OAc)₂ promoted the hydrogenation of FFA to 2-MF and the decarbonylation of furfural to furan accompanied by the consumption of FA formed earlier.

Effect of water on the one-pot reaction

The presence of water is unfavorable for the decarbonylation of aldehydes.^[15a] In our system, we investigated the possible influence of water on the tandem dehydration and decarbonylation of fructose to FFA by the removal or addition of water from the catalytic system. As AlCl₃·6H₂O contains water in the crystal, we replaced it with anhydrous AlCl₃ as the dehydration catalyst. The results shown in Table 1 indicated that the total yields of FFA and HMF were comparable over AlCl₃·6H₂O (entry 8) and anhydrous AlCl₃ catalysts (entry 9), but the yield of FFA over anhydrous AlCl₃ was slightly lower. Clearly, the decarbonylation efficiency of the anhydrous AlCl₃/Pd(OAc)₂ catalytic system was lower than that of the AlCl₃·6H₂O/Pd(OAc)₂ system, most probably because of the decrease of the dehydration rate caused by the absence of water of crystallization in the AlCl₃ catalyst. For comparison, we added a certain amount of water into the catalytic system before the one-pot reaction, but no 4 Å molecular sieves were added to remove water. Moreover, we performed another control experiment in which no 4 Å molecular sieves were added if AlCl₃·6H₂O was used as the dehydration catalyst (Table 1, entry 12). A comparison of the data shown in entries 10, 11, and 12 revealed a decrease of the yield of FFA with the increase of the water dosage, whereas the total yields of FFA and HMF almost did not vary. This result indicated that the presence of water was unfavorable for the decarbonylation reaction, possibly because the dehydration rate was decreased. We infer that some hydrolyzed Al species and HCl coexisted in the aqueous system caused by the hydrolysis of AlCl₃·6H₂O. If we used HCl as the dehydration catalyst instead of AlCl₃·6H₂O, we found that the total yields of FFA and HMF increased as the amount of HCI used increased, but these yields were still lower than those over AlCl₃·6H₂O, even if we used three molar equivalents of HCl relative to AlCl₃·6H₂O (Table S2).^[17] This indicates that the hydrolyzed AI species and Pd(OAc)₂ were more active than HCI and Pd(OAc)₂ for the one-pot catalytic deoxygenation of fructose.^[18] Additionally, the yields of furfural and FA increased if the amount of HCl was increased, which demonstrates the ease of fructose decomposition in the presence of a large amount of Brønsted acid.[13]

We tried to remove the water that existed in the solvent and was formed during the dehydration step by adding 4 Å molecular sieves. If the amount of 4 Å molecular sieves increased, we found that the yield of FFA increased from 7.6% (without molecular sieves) to 19.8% (molecular sieves/ AlCl₃·6H₂O = 150, w/w) and then decreased to 17.1% (molecular sieves/AlCl₃·6H₂O = 250, w/w; Figure 3). In contrast, the yield of HMF exhibited the opposite trend. A decrease of the HMF yield accompanied by the increase of the FFA yield if the

CHEMCATCHEM Full Papers



Figure 3. Effect of the amount of 4 Å molecular sieves used on the yields of FFA and HMF. Reaction conditions: 0.3 mmol of fructose, 2 mL of 1,4-dioxane, 4.1×10^{-3} mmol of AlCl₃·6 H₂O, 44.6×10^{-3} mmol of Pd(OAc)₂, 150 °C, 4 h, N₂ atmosphere.

amount of 4 Å molecular sieves was increased revealed the promotion effect of the 4 Å molecular sieves on the tandem decarbonylation of the HMF intermediate to FFA. The slight increase of the HMF yield together with the decrease of the FFA yield if the ratio of 4 Å molecular sieves to AlCl₃·6H₂O was further increased to 250 (w/w) might imply the possible adsorption of FFA on the molecular sieves, but this was excluded immediately as the molecular size of FFA (~7 Å) is larger than the mean pore size of the 4 Å molecular sieves (~4 Å). Moreover, the fact that no HMF or FFA was detected in the washing liquor from the molecular sieves after the reaction also supported this deduction. Therefore, the decreased yield of FFA in the presence of a larger amount of 4 Å molecular sieves was most probably because of the relatively lower dehydration rate caused by the reduction of the catalytically active AI species after the removal of water. Furthermore, the color of the reaction mixture became lighter after the addition of 4 Å molecular sieves into the AlCl₃·6H₂O/Pd(OAc)₂ system. The yields of the byproducts FA, furfural, and 5-MF also decreased if an increased amount of 4 Å molecular sieves was used. These results demonstrate the alleviation of side-reactions such as the direct decomposition of fructose and the polymerization of any reaction intermediates by 4 Å molecular sieves by the removal of water from the reaction mixture. A similar water-removal role was observed for 5 Å molecular sieves, which have a similar pore size to 4 Å molecular sieves (Table S3).^[17]

Effect of PVP on the one-pot reaction

We investigated the role of PVP on the one-pot deoxygenation of fructose. PVP itself had nearly no activity for the dehydration of fructose (Table 1, entry 13). However, the addition of PVP into the $AlCl_3 \cdot 6H_2O/4$ Å molecular sieves system resulted in an increase of the HMF yield from 23.4 to 48.1% (Table 1, entry 5 vs. entry 6), which illustrated the synergetic role of PVP on the dehydration of fructose. Furthermore, the yields of FFA and HMF were 19.8 and 1.2%, respectively, with a total yield of 21.0% if no PVP was used (Figure 4). After the addition of PVP,



Figure 4. Effect of the amount of PVP used on the yields of FFA and HMF. Reaction conditions: 0.3 mmol of fructose, 2 mL of 1,4-dioxane, 4.1×10^{-3} mmol of AlCl₃·6 H₂O, 44.6×10^{-3} mmol of Pd(OAc)₂, 4 Å molecular sieves/AlCl₃·6 H₂O (w/w) = 150, 150 °C, 4 h, N₂ atmosphere.

both the yields of FFA and HMF were increased to a total yield of 44%, which indicated the role of PVP to accelerate the deoxygenation of fructose. The total yield of FFA and HMF almost did not vary as the amount of PVP used was increased. In contrast, the yield of FFA increased firstly to reach a maximum of 40.6% (PVP/AlCl₃· $6H_2O = 15$, w/w) and then decreased to 32.3% with a further increase of the PVP/AICl₃·6H₂O ratio to 20 (w/w). However, the yield of HMF exhibited the opposite trend, that is, it decreased first to reach a minimum value of 3.4% and then increased. The increase of the FFA yield together with the decrease of the HMF yield suggests that FFA was formed from HMF as the intermediate. In addition, these results also implied that PVP might influence the rate of the dehydration reaction, that is, a higher amount of PVP accelerated the dehydration of fructose, which further promoted the subsequent decarbonylation of HMF to produce FFA as the final product. However, a larger amount of PVP beyond 15 (PVP/ AlCl₃·6H₂O, w/w) in the catalytic system increased the viscosity of the reaction mixture, which hindered the mass and heat transfer within the catalytic system and thus disfavored the one-pot deoxygenation.

In the absence of PVP, 5-MF and 2-MF were formed in yields of 0.2 and 1.6%, respectively. Significantly, after the addition of PVP, no 5-MF was detected regardless of the amount of PVP, which indicates that the hydrogenation of HMF was inhibited completely by the addition of PVP. If the amount of PVP used was increased, we observed a decreased yield of 2-MF, which illustrates the inhibiting effect of PVP on the hydrogenation of FFA. That is, the reactivity of HMF and FFA were both inhibited by PVP.

To discern the role of PVP on the dehydration reaction, we recorded the FTIR spectra of fructose and HMF, respectively, after mixing with PVP in 1,4-dioxane at 150 °C for 4 h (see Supporting Information for experimental details).^[17] No clear interaction between fructose and PVP was observed (Figure S2).^[17] However, clear downshifts of the peaks at $\tilde{\nu}$ = 3400 and 1334 cm⁻¹ by 15 cm⁻¹ were observed in the spectrum of HMF after mixing with PVP compared with the spectrum of blank

CHEMCATCHEM Full Papers



Figure 5. FTIR spectra of a) HMF and b) HMF and PVP after mixing in 1,4-dioxane at 150 $^{\circ}$ C for 4 h. c, d) magnified view of the bracketed regions in a and b, respectively.

HMF (Figure 5). The two bands are assigned to the stretching and twisting vibrations of HMF hydroxyl groups, the decrease of which demonstrates the weakening of the O-H bond. It is generally accepted that the frequency of the donor X-H stretching vibration will downshift after the formation of hydrogen bonds (HB) with acceptor Y (X-H...Y).^[19] Therefore, the downshifts in the IR spectra are indicative of the occurrence of HB between HMF and PVP, in which the HMF O-H acts as a HB donor to the PVP molecule. This HB interaction is illustrated in Figure S3.^[17] Such a binding of PVP with the HMF intermediate may protect HMF from the side-reaction of the hydrogenation reaction, which inhibits the formation of 5-MF (similar for 2-MF inhibition). Moreover, the stabilization of the HMF hydroxyl group by PVP may contribute to the synergetic role of PVP in the dehydration of fructose. In addition, PVP could be separated together with AlCl₃·6H₂O, 4 Å molecular sieves, and Pd(OAc)₂ from the reaction mixture by centrifugation at room temperature. We will focus on the recycling issue in future work.

Product evolution with time

We analyzed the samples from the reaction mixture at specified time intervals to reveal the product evolution in the process of FFA formation in the presence of PVP. HMF formed quickly and reached a maximum yield of 42.8% at 30 min with a fructose conversion of 93.9% (Figure 6). As the reaction progressed, the yield of HMF decreased to trace after 4 h, which accompanied an increase of the FFA yield from 3.4 (30 min) to 40.6% (4 h). Fructose was almost fully converted after 2 h. The consumption of HMF and the formation of FFA with time confirmed the feasibility of the tandem dehydration and decarbonylation directly from fructose in one pot. Otherwise, the yields of furfural and FA decreased over the whole reaction period. Meanwhile, detectable amounts of furan and 2-MF were observed as byproducts after 2 h, which indicated the decarbonylation of furfural to furan by Pd(OAc)₂ and the hydrogenation of FFA to 2-MF with FA. No 5-MF was detected in the presence of PVP, which illustrates the stabilization of the HMF intermediate by PVP.



Figure 6. Product evolution with time in the presence and absence of PVP. Reaction conditions: 0.3 mmol of fructose, 2 mL of 1,4-dioxane, 4.1×10^{-3} mmol of AlCl₃·6 H₂O, 44.6×10^{-3} mmol of Pd(OAc)₂, 4 Å molecular sieves/AlCl₃·6 H₂O (w/w) = 150, PVP/AlCl₃·6 H₂O (w/w) = 15, 150 °C, 4 h, N₂ atmosphere.

Proposed reaction network in the one-pot reaction

A possible reaction network for the one-pot deoxygenation of fructose is proposed and is shown in Scheme 1. In 1,4-dioxane medium, fructose was dehydrated to HMF rapidly under the catalysis of $AlCl_3$ - $6H_2O$. The rate of the dehydration reaction



Scheme 1. Possible reaction network for the one-pot deoxygenation of fructose to FFA.

was enhanced by adding PVP as an additive. The formed HMF was decarbonylated to FFA by Pd(OAc)₂, and the decarbonylation efficiency was enhanced by the presence of 4 Å molecular sieves, which removed water formed in the foregoing dehydration step. The addition of 4 Å molecular sieves also inhibited the direct decomposition of fructose to furfural and FA. Furfural, once formed, could be decarbonylated to furan by Pd(OAc)₂. FA acted as a hydrogen source for the hydrogenation of HMF and FFA to 5-MF and 2-MF, respectively, which could be inhibited or partly restrained by the addition of PVP because of the stabilization of the hydroxyl group by PVP.

Conclusions

We developed a one-pot approach to convert fructose directly to furfuryl alcohol (FFA) by tandem dehydration and decarbonylation using an AlCl₃·6H₂O/Pd(OAc)₂ catalyst combination. AlCl₃·6H₂O behaves as an effective Lewis acid to catalyze the dehydration of fructose to 5-hydroxymethylfurfural (HMF), and subsequently, Pd(OAc)₂ catalyzes the removal of a CO moiety from HMF to produce FFA selectively. Dehydration and decarbonylation were promoted by the addition of poly(1-vinyl-2pyrrolidinone) (PVP) and 4 Å molecular sieves, respectively, to give a high FFA yield of 40.6% based on fructose. The formation of the byproducts formic acid and furfural by fructose decomposition was restrained by 4 Å molecular sieves by the removal of water from the catalytic system. The unwanted consumption of HMF by hydrogenation was inhibited by PVP because of the formation of intermolecular hydrogen bond between HMF and PVP. This research highlights a catalytic system to transform renewable carbohydrates into fine chemicals by tandem dehydration and decarbonylation without the separation or purification of the HMF intermediate. Our future work will focus mainly on the development of multifunctional and water-tolerant catalysts for the direct deoxygenation of carbohydrates to low-oxygen-content furan compounds. Additionally, the formation of the formic acid byproduct should be further reduced as its presence could lead to various side-reactions.

Experimental Section

Materials

HMF (98%), FFA (98%), furfural (98%), 5-MF (98%), 2-MF (98%), and Pd(OAc)₂ (47.5 wt% Pd) were purchased from J&K Chemical Co. Ltd. Fructose (BR grade) was supplied by REGAL Co. Ltd. 4 Å molecular sieves (1–2 mm, beads) were purchased from Alfa Aesar. FA (98%) was purchased from Sigma Aldrich. Anhydrous AlCl₃ was obtained from Tianjin Fuchen Chemical Regents Factory. 1,4-Dioxane, furan, PVP (K30), nitrobenzene, and AlCl₃·6H₂O used in the experiments were all of analytical grade, obtained from Kolong Chemical Company (Chengdu, China), and used without further purification.

Catalytic reactions

All of the catalytic reactions were performed in a pressure tube heated in a temperature-controlled oil bath with magnetic stirring. Typically, a 35 mL reaction tube was charged with fructose (60 mg), AlCl₃·6 H₂O (1 mg), Pd(OAc)₂ (10 mg), 4 Å molecular sieves (150 mg), PVP (15 mg), and 1,4-dioxane (2 mL) in turn. The mixture was heated to 150 °C and incubated for the required reaction time. After the reaction, the mixture was cooled gradually to RT. The solid catalysts were separated from the mixture by centrifugation.

Product analysis

HMF, FFA, furan, 5-MF, and 2-MF from the liquid products were analyzed quantitatively by using GC (FILI, GC-9700) equipped with an Innowax capillary column (30 m \times 0.25 mm), a flame ionization de-



tector (FID), and a ZB-2020 integrator. Typical conditions for GC analysis were as follows: injector temperature of 260 °C, detector temperature of 270 °C, and nitrobenzene was used as the internal standard. Byproducts such as FA and furfural were analyzed quantitatively by using HPLC (Dionex, UltiMate 3000 Series) with a dionex PG-3000 pump, an aminex column HPX-87 column (Bio-Rad) (50 °C), a Shodex 101 refractive index detector (35 °C), and a variable wavelength detector using H₂SO₄ (5 mM) as the mobile phase at a flow rate of 0.6 mL min⁻¹. The product yields were calculated based on external standard curves constructed with authentic samples. The conversion of fructose and the product yields were defined as follows [Eqs. (1)–(4)]. The relative errors of the quantification results were estimated to be \pm 1.7%.

Conversion of fructose [mol %] =

(moles of fructose reacted)/(moles of starting fructose) \times 100 % (1)

Yield of FFA [mol %] =

(moles of FFA produced)/(moles of starting fructose) \times 100 %

Yield of HMF [mol %] =

(moles of HMF produced)/(moles of starting fructose) \times 100 % (3)

Yield of byproducts (FA, furfural, furan, 5-MF, and 2-MF) [mol %] =

(moles of byproducts formed)/(moles of starting fructose) \times 100 %

Acknowledgements

This work was supported by the National Nature Science Funding of China (No. 21536007), the Special Research Fund for the Doctoral Program of Higher Education of China (No. 20120181130014), and the Science and Technology Program of Sichuan (No. 2013JY0015).

Keywords: aluminum • biomass • carbohydrates • multicomponent reactions • palladium

- [1] J. R. Rostrup-Nielsen, Science 2005, 308, 1421-1422.
- [2] a) G. W. Huber, J. N. Chheda, C. J. Barrett, J. A. Dumesic, *Science* 2005, 308, 1446–1450; b) J. N. Chheda, G. W. Huber, J. A. Dumesic, *Angew. Chem. Int. Ed.* 2007, 46, 7164–7183; *Angew. Chem.* 2007, 119, 7298–

7318; c) A. Corma, S. Iborra, A. Velty, *Chem. Rev.* **2007**, *107*, 2411–2502; d) D. M. Alonso, J. Q. Bond, J. A. Dumesic, *Green Chem.* **2010**, *12*, 1493–1513.

- [3] a) M. Shiramizu, F. D. Toste, Angew. Chem. Int. Ed. 2012, 51, 8082–8086; Angew. Chem. 2012, 124, 8206–8210; b) S. Dutta, ChemSusChem 2012, 5, 2125–2127.
- [4] a) Y. Román-Leshkov, J. N. Chheda, J. A. Dumesic, *Science* 2006, *312*, 1933–1937; b) T. Wang, M. W. Nolte, B. H. Shanks, *Green Chem.* 2014, *16*, 548–572; c) H. B. Zhao, J. E. Holladay, H. Brown, Z. C. Zhang, *Science* 2007, *316*, 1597–1600; d) J. N. Chheda, Y. Roman-Leshkov, J. A. Dumesic, *Green Chem.* 2007, *9*, 342–350; e) S. Hu, Z. Zhang, Y. Zhou, B. Han, H. Fan, W. Li, J. Song, Y. Xie, *Green Chem.* 2008, *10*, 1280–1283; f) J. B. Binder, R. T. Raines, *J. Am. Chem. Soc.* 2009, *131*, 1979–1985; g) S. Hu, Z. Zhang, J. Song, Y. Zhou, B. Han, *Green Chem.* 2009, *11*, 1746–1749; h) X. Qi, M. Watanabe, T. M. Aida, R. L. Smith Jr., *Green Chem.* 2009, *11*, 1327–1331.
- [5] a) O. O. James, S. Maity, L. A. Usman, K. O. Ajanaku, O. O. Ajani, T. O. Siyanbola, S. Sahu, R. Chaubey, *Energy Environ. Sci.* 2010, *3*, 1833; b) M. M. Antunes, P. A. Russo, P. V. Wiper, J. M. Veiga, M. Pillinger, L. Mafra, D. V. Evtuguin, N. Pinna, A. A. Valente, *ChemSusChem* 2014, *7*, 804–812.
- [6] L. D. Lillwitz, C. Lake, US 4089871A, 1978.
- [7] F. M. A. Geilen, T. vom Stein, B. Engendahl, S. Winterle, M. A. Liauw, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2011**, *50*, 6831–6834; *Angew. Chem.* **2011**, *123*, 6963–6966.
- [8] Y.-B. Huang, Z. Yang, M.-Y. Chen, J.-J. Dai, Q.-X. Guo, Y. Fu, *ChemSusChem* 2013, 6, 1348–1351.
- [9] J. Mitra, X. Zhou, T. Rauchfuss, Green Chem. 2015, 17, 307-313.
- [10] a) B. Liu, Z. Zhang, RSC Adv. 2013, 3, 12313–12319; b) G. A. Halliday,
 R. J. Young, V. V. Grushin, Org. Lett. 2003, 5, 2003–2005; c) Y. Liu, L. F.
 Zhu, J. Q. Tang, M. Y. Liu, R. D. Cheng, C. W. Hu, ChemSusChem 2014, 7, 3541–3547; d) X. Xiang, L. He, Y. Yang, B. Guo, D. Tong, C. Hu, Catal.
 Lett. 2011, 141, 735–741; e) Z.-Z. Yang, J. Deng, T. Pan, Q.-X. Guo, Y. Fu,
 Green Chem. 2012, 14, 2986; f) W. Ghezali, K. D. O. Vigier, R. Kessas, F.
 Jerome, Green Chem. 2015, 17, 4459–4464.
- [11] R. F. Perez, M. A. Fraga, Green Chem. 2014, 16, 3942-3950.
- [12] G.-Y. Jeong, A. K. Singh, S. Sharma, K. W. Gyak, R. A. Maurya, D.-P. Kim, NPG Asia Mater. 2015, 7, e173.
- [13] a) J. Zhang, E. Weitz, ACS Catal. 2012, 2, 1211–1218; b) T. D. Swift, C. Bagia, V. Choudhary, G. Peklaris, V. Nikolakis, D. G. Vlachos, ACS Catal. 2014, 4, 259–267.
- [14] a) V. Nikolakis, S. H. Mushrif, B. Herbert, K. S. Booksh, D. G. Vlachos, J Phy. Chem. B 2012, 116, 11274–11283; b) T. D. Swift, C. Bagia, V. Nikolakis, D. G. Vlachos, G. Peklaris, P. Dornath, W. Fan, AlChE J. 2013, 59, 3378–3390; c) S. K. R. Patil, J. Heltzel, C. R. F. Lund, Energy Fuels 2012, 26, 5281–5293.
- [15] a) A. Modak, A. Deb, T. Patra, S. Rana, S. Maity, D. Maiti, *Chem. Commun.* 2012, 48, 4253–4255; b) Akanksha, D. Maiti, *Green Chem.* 2012, 14, 2314–2320.
- [16] a) Y. Yang, C. W. Hu, M. M. Abu-Omar, *Green Chem.* 2012, *14*, 509–513;
 b) Y. Yang, C.-W. Hu, M. M. Abu-Omar, *ChemSusChem* 2012, *5*, 405–410;
 c) Y. J. Pagán-Torres, T. Wang, J. M. R. Gallo, B. H. Shanks, J. A. Dumesic, *ACS Catal.* 2012, *2*, 930–934.
- [17] See Supporting Information for details.
- [18] M. F. He, H. Q. Fu, B. F. Su, H. Q. Yang, J. Q. Tang, C. W. Hu, J. Phys. Chem. B 2014, 118, 13890-13902.
- [19] T. Steiner, Angew. Chem. Int. Ed. 2002, 41, 48–76; Angew. Chem. 2002, 114, 50–80.

Received: November 23, 2015 Published online on February 23, 2016

(2)