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COMMUNICATION

Base-free conversion of 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid over Ru/C catalyst

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The catalytic conversion of 5-hydroxymethyl furfural (HMF) to 2,5-furandicarboxylic acid (FDCA) over commercial Ru/C catalyst in base-free aqueous solution was studied with 88% FDCA yield. A self-catalyzed system using FDCA for the dehydration of fructose to HMF followed by base-free conversion of HMF to FDCA was also demonstrated with 53% overall yield.

Today, over 90% of the world's organic chemicals are produced from petroleum, and 85% of crude oil is used for the production of transportation fuel.[1] Due to the depletion of fossil resources and global warming concern, considerable attention was focused on the conversion of renewable biomass to chemicals and fuels.[2] Among these chemicals, 2,5-furandicarboxylic acid (FDCA) has received significant attention[3] as potential replacement for terephthalic acid for the production of poly(ethylene terephthalate) (PET).[4,5] A FDCA-based polymer poly(ethylene-2,5-furandicarboxylate) (PEF) has been prepared and investigated, which showed comparable properties to PET.[6] FDCA was also listed as one of the 12 key value-added chemicals from biomass by the US Department of Energy.[7]

FDCA can be prepared by oxidation of HMF, while HMF is prepared by acid-catalyzed dehydration of sugars or cellulose.[4b,8] HMF could be oxidized to FDCA with stoichiometric oxidants,[8a] metal catalysts,[3f,9] or enzyme.[10] Among these, the catalytic conversion of HMF with oxygen is more attractive. The most studied catalysts are Au,[9b,11] and Pt,[3a,9b,9d,12] usually with base additive and at elevated temperature. High or even quantitative yield of FDCA can be obtained. However, the product obtained from these catalytic systems under basic condition is the salt form of FDCA which cannot be directly used in polymer industry.[6b,13] The separation of FDCA from aqueous system usually requires the addition of strong mineral acids such as HCl and H_2SO_4 pH =1, where FDCA will then be precipitated from the solution as white precipitate.[14] In contrast, the conversion of HMF to FDCA under base-free conditions would eliminate the need to convert FDCA salt to FDCA, making the system greener with less waste generated.

The base-free conversion of HMF to FDCA has been investigated using homogenous $Co(OAc)_2/Mn(OAc)_2/HBr$ catalysts in acetic acid system with 60% yield under rather harsh reaction conditions (125 °C, 70 bar air).[15] The base-free conversion of HMF to FDCA in a bench-scale flow reactor with Pt/ZrO_2 was also studied,[16] but low HMF concentration was necessary to avoid FDCA precipitation. Very recently, the conversion of HMF to FDCA in base-free condition has also been demonstrated with carbon nanotube supported Au-Pd alloy nanoparticles catalyst[17] as well as a free-standing Pt nanoparticle catalyst.[5] Ru is the least expensive catalyst when compared to Au, Pt and Pd.[9b] Hence, Ru catalyst has also been investigated in the HMF oxidization reaction under basic condition, to give diformyl furan (DFF)[18] or FDCA slats.[19] Here, we report the conversion of HMF to FDCA in aqueous solution under base-free condition with commercial Ru/C catalyst. Under optimized conditions, 88% yield of FDCA was directly obtained as white precipitate. Reaction pathway and various co-catalysts were also studied in this system. Interestingly, FDCA itself could also promote the dehydration of fructose to HMF, where 65% HMF yield was obtained. The obtained HMF was further converted to FDCA under the base-free conditions with an overall yield of 55%.

In fact, our study for the conversion of HMF to FDCA with Ru/C catalyst started with the addition of equivalent amount of base. As shown in Table 1, it was found that stronger base led to lower FDCA yield. For example, when NaOH was used as base, it gave only 69% FDCA yield. The color of the reaction mixture turned brownish due to the degradation of HMF at higher pH.[20] To minimize this side effect, weak bases were tested in the reaction system.

It is clear that the weaker the base used, the higher the FDCA yield was obtained. Eventually, the system with $CaCO_3$ additive gave highest yield of 95%. $CaCO_3$ remained as solid in

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the initial stage of the reaction and was gradually dissolved as it reacted with FDCA to form FDCA calcium salt. The addition of $CaCO_3$ acted more like a neutralizer to FDCA, rather than a base to promote the reaction from HMF to FDCA. The initial pH value of the solution with $CaCO_3$ is 5.6. This indicates that pH>7 is not necessary for this reaction. Therefore, a base-free condition was tested.

Table 1. The conversion of HMF to FDCA with different bases.

Entry	Base	Conv. (%)	Yield (%)	Observation
1	NaOH	100	69	Brown solution
2	K_2CO_3	100	80	Clear solution
3	Na_2CO_3	100	93	Clear solution
4	HT	100	90	Clear solution
5	$CaCO_3$	100	95	Clear solution

Reaction conditions: 1 mmol HMF, 10 ml H_2O, equiv. base, 0.1 g Ru/C (5 mol%), 0.2 MPa O_2, 120 °C, 5 h.

In a typical reaction, 1 mmol of HMF, 10 ml water, 0.2 g Ru/C catalyst (10 mol%), and O_2 were loaded into a 50 ml parr reactor. The reaction mixture was then conducted under different conditions. As shown in Table 2, the best result was obtained at 120 °C, 0.2 Mpa O_2 after 10 hours, with 88% FDCA yield. There is no other products could be identified by crude product NMR analysis. However, it has been observed weight increase of catalyst that indicated some insoluble by-product formed. Pure FDCA was directly obtained as white precipitate, as shown in Figure S1. NMR analysis confirmed that the white precipitate is pure FDCA (Figure S2). The pH of the solution at the end of the reaction was 2.4, indicating the formation of FDCA diacid.

As the catalyst loading was decreased (Ru/C 0.1 g, 5 mol%), the reaction became slower and stopped at FFCA or DFF intermediates after 5 h at 120 °C (Figure S3). Further study showed that it is due to the FDCA precipitation which blocked the active site of Ru, and slowed down the reaction. To confirm this, FDCA with Ru/C was collected by filtration. FDCA precipitate was washed away with methanol. Then, Ru/C was added back into the reaction. The reaction then resumed at 120 °C and completed within 5 h. When 10 mol% catalyst was applied, reaction completed after 10 h without washing of catalyst.

To test the recyclability of the catalyst, we have conducted 6 rounds of experiments. After each round of reaction, the catalyst was washed with methanol and used for the next round of reaction. Experiments showed that for the first 3 rounds, no catalyst deactivation was observed. For the 4th and 5th rounds, slightly slow reaction rate was observed, which may be due to the oxidation of Ru species. Therefore the catalyst was re-activated by H_2/Ar, and, the catalyst resumes its original catalytic performance, as shown in Table S1. To further study the stability of the catalyst, recyclability of Ru/C catalyst within kinetic-controlled region (5 h, half of completion time) was tested. At 5 h, HMF was fully converted to FDCA/FFCA mixture. As shown in Figure 1, with more runs of reaction, the yield of FDCA kept on decreasing while the FFCA kept on increasing. However, the total yield of FDCA and FFCA is almost constant. This indicates that there is some deactivation of Ru/C catalyst occurred during recycle experiment, but only the second step reaction was affected. ICP-MS testing showed 3.4% of Ru species leached to the solution after 5 rounds of reaction, which should not be the main cause for catalyst deactivation. TEM results showed there's no obvious change for Ru particles (Figure S4). However, after 5 rounds reaction, we have also noticed some weight increase of catalyst, which should be due to some unknown impurities. After re-activation of the Ru/C catalyst (Table S1, entry 6), the catalyst resumed a full conversion. So it was believed that the impurities and/or the oxidation of the Ru species is the main reason for catalyst deactivation.

Table 2. Base-free conversion of HMF to FDCA over Ru/C

Entry	Temp. (°C) /O_2 Pressure (MPa)	Conv. (%)	FDCA (%)	FFCA (%)	DFF (%)
1	80 /0.2	100	14	85	0
2	100 /0.2	100	60	37	0
3	120 /0.1	100	87	0	0
4	120 /0.2	100	88	0	0
5	120 /0.5	100	88	0	0

Reaction conditions: 1 mmol HMF, 10 ml H_2O, 0.2 g Ru/C (10 mol%), O_2, 10 h.

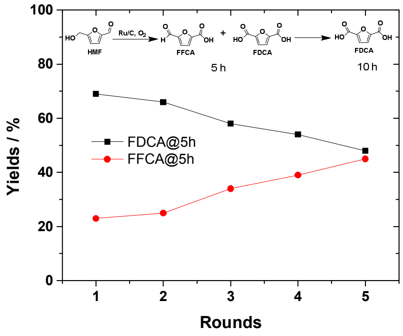

Fig 1. Recycle of Ru/C catalyst at 5h (half of completion time).

The kinetics of the reaction was also studied, as shown in Figure 2. At the initial stage of reaction, DFF and FFCA are increased quickly and then slowly decreased after 1 h reaction. Concurrently, FDCA was produced after 1 h which clearly indicated the reaction pathway where the conversion of HMF to FDCA proceeded via the formation of DFF and FFCA intermediates. A similar behaviour was also demonstrated in the Au/Pd-CNT system.[17] During this process, Ru catalysed the oxidation of -OH to -CHO, and further oxidized -CHO to -COOH. It showed that the conversion of HMF to DFF/FFCA is a fast reaction which was completed within 2 hours, with nearly quantitative overall yield. However, the conversion of the

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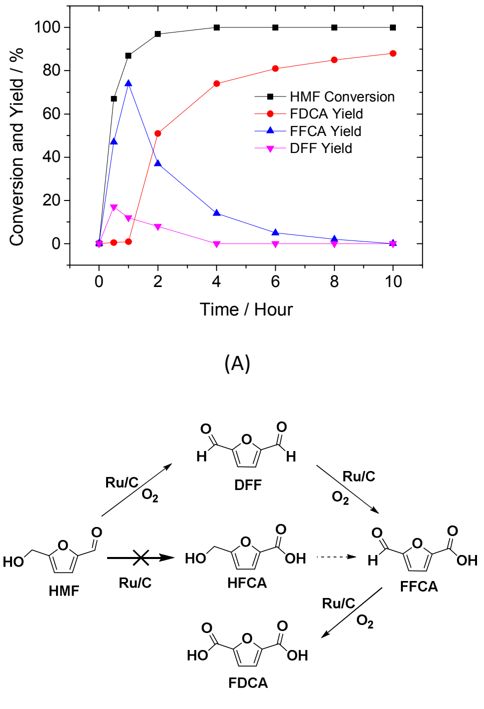
remaining -CHO to -COOH became slower, requiring 8 hours to complete. During the reaction, no HFCA was detected, suggesting the oxidation of HMF always occurred from the –OH side rather than –CHO, as shown in Figure 2B.

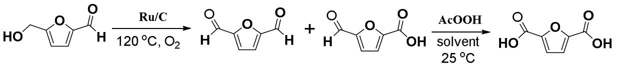


(A)

(B)

Fig. 2 (A) Kinetics study from HMF to FDCA. (B) Reaction pathway from HMF to FDCA. Reaction conditions: 1 mmol HMF, 0.2 g Ru/C, 10 ml water, 0.2 MPa O_2, 120 °C.

From Figure 2, we understand that for the reaction of HMF to FDCA, the conversion of -OH to -CHO is a fast step while the oxidation of -CHO to -COOH is the rate-limiting step. To make the reaction faster, the key is to accelerate the reaction from –CHO to -COOH. Although the conversion of -CHO to -COOH is very fast with the existence of base, it is a challenge under base-free condition. Herein, a one-pot two-step reaction with peracetic acid as oxidant[21] for the second step was proposed, as illustrated in Scheme 1.



Scheme 1: Two-step reaction for the production of FDCA

For the first step, HMF was fully converted to DFF/FFCA in 1.2 h in water system, with 84% FFCA and 13% DFF. When the reaction was conducted in other organic solvents like MeCN, HOAc, and MeOH, excellent selectivity towards DFF was obtained, as shown in Table S2. After the first step, Ru/C catalyst was removed. DFF/FFCA intermediates were recovered by evaporation and re-dissolved in ^{t}BuOH/EtOAc mixture solution (5/5, v/v),[21] peracetic acid was added through a syringe pump at room temperature over 12 h. An overall 95% FDCA yield was obtained as white precipitate, as shown in Figure S5.

Although the one-pot two-step reaction using peracetic acid achieved excellent FDCA yield under mild reaction conditions, peracetic acid was used as an oxidant which will be sacrificed during the reaction. Alternatively, transition metal co-catalysts were also screened in the Ru/C base-free system. $Co(OAc)_2$ and $Mn(OAc)_2$ have been used in the catalytic conversion of HMF to FDCA.[15] $Co(OAc)_2$ and/or $Mn(OAc)_2$ were then added into current reaction system as a co-catalyst of Ru/C. As shown in Table S3, the addition of $Co(OAc)_2$ and/or $Mn(OAc)_2$ have no significant effect on FDCA yield. This may be due to the fact that $Co(OAc)_2$/$Mn(OAc)_2$ was used in HOAc solution, while water was being used in the current reaction system.

It has been demonstrated here that HMF was converted to FDCA by Ru/C catalyst in the base-free condition. HMF is a biomass-derived product and is typically prepared by acid catalyzed sugar dehydration.[8b] Strong acids like HCl,[8c] and Amberlyst-15,[22] have been successfully used for this process. Since FDCA being an acid itself has a pKa of 2.28, it will be interesting and useful if FDCA can be used as acid catalyst to promote the conversion of sugar to HMF, then further oxidized to FDCA. In this way, no additional acid will be used in the reaction system, forming a closed self-catalyzed system to convert sugars to FDCA.

The conversion of fructose to HMF using FDCA as acid catalyst was studied in *i*PrOH/H_2O or THF/H_2O systems.[8c,23] As shown in Figure 3, the reaction rate in *i*PrOH/H_2O is faster than in THF/H_2O, where 64% HMF yield was obtained after 30 mins, with full fructose conversion and full recovery of FDCA. While for THF/H_2O, the full conversion of fructose occured after 2 h, with 51% HMF yield. Together with Sn-beta or $AlCl_3$, FDCA was also tested in glucose dehydration. As shown in Table S4, glucose was almost fully converted after 170 °C for 30 mins. The best HMF yield of 30% was obtained for Sn-Beta (2 h), and 35% for $AlCl_3$ (5 h).

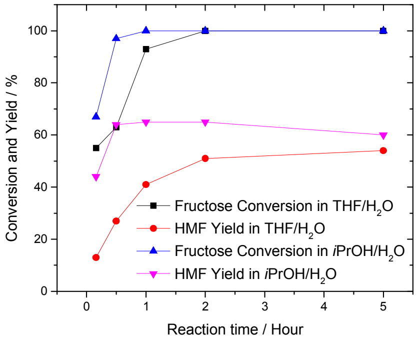


Fig. 3 FDCA promoted conversion of fructose to HMF. Reaction conditions: 1 mmol fructose, 1 mmol FDCA, *i*PrOH/H_2O (4.85/0.15 ml), or THF/H_2O (4.5/0.5 ml), 170 °C.

The HMF formed was then further oxidized to FDCA. After the conversion of fructose to HMF in *i*PrOH/H_2O, the solvent

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was removed by evaporation and the crude HMF together with FDCA was obtained. The HMF was recovered by water extraction using the method we reported earlier (5 ml x 2, 0.64 mmol, >99% HMF recovery).[14b] The HMF in aqueous solution was then directly transferred to a Parr reactor for the oxidation reaction. Under base-free conditions with Ru/C catalyst, the reaction was conducted and completed in 15 hours with an overall FDCA yield of 53% obtained (83% yield in the second step). It should be noted that the Ru/C catalyzed oxidization reaction of freshly synthesized HMF (from sugar) is slower than the reaction of pure commercial HMF (15 h *vis* 10 h), which may be due to some minor water soluble impurities in the freshly synthesized HMF solution.

In conclusion, the base-free conversion of HMF to FDCA over commercially available Ru/C catalyst in water was investigated. FDCA yield of 88% was obtained with full HMF conversion. Under base-free condition with Ru/C catalyst, the oxidation process prefers the DFF/FFCA pathway rather than HFCA pathway. The oxidization of –OH to –CHO of HMF was much faster (<2h), while further conversion of the remaining–CHO to –COOH was the rate-limiting step (8h). To further accelerate this reaction, a one-pot 2-step method was proposed where HMF was first converted to FFCA and DFF intermediates, and it was further oxidized to FDCA by the titration with peracetic aicd at room temperature. In this way, 95% FDCA was obtained. Finally FDCA promoted conversion of fructose and glucose to HMF was also studied, and the freshly obtained HMF was further oxidized to FDCA. An overall FDCA yield of 53% was obtained from fructose under base-free condition. The lower price of Ru catalyst and base-free reaction condition make this method a very competitive process for the FDCA production.

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‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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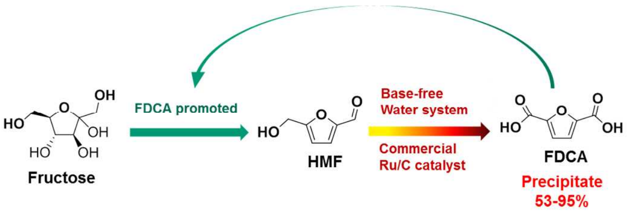

The catalytic conversion of 5-hydroxymethyl furfural (HMF) to 2,5-furandicarboxylic acid (FDCA) over commercial Ru/C catalyst in base-free aqueous solution was studied with up to 88% FDCA yield.