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H_2O_2-assisted Selective Oxidation of 5-Hydroxymethylfurfural (HMF) in Water under Mild Conditions

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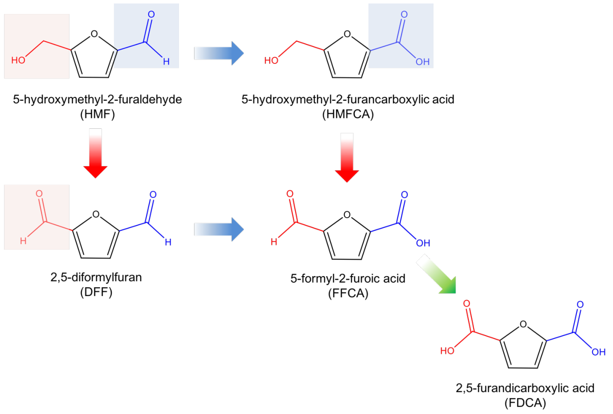
An effective and selective oxidation of 5-hydroxymethylfurfural (HMF) using hydrogen peroxide (H_2O_2) as the liquid oxygen source and activated carbon supported ruthenium (Ru/AC) as the catalyst was demonstrated in this work. This reaction system allows HMF to be oxidized in water and mild reaction conditions efficiently since it has relatively less mass-transfer resistance compared to gaseous oxygen-assisted oxidation systems. In addition, we could selectively control the components of oxidation products by adjusting the reaction conditions. We optimize several reaction parameters such as the reaction temperature (75 °C), times (t = 1 or 6 hr), additive base (sodium carbonate), and the ratios of HMF/catalyst (50 or 10) in order to attain the desired products with the maximum yield. The results showed that 5-formyl-2-furoic acid (FFCA) with a high yield up to 92% could be obtained at the conditions of HMF/catalyst = 50 and t = 1 hr while 2,5-furandicarboxylic acid (FDCA) with the maximum 91.3% yield could be obtained at the conditions of HMF/catalyst = 10 and t = 6 hr. A possible mechanism of such selective oxidation of HMF is also discussed. We envision that the H_2O_2-mediated oxidation systems proposed in this study would be a great benefit to other organic oxidation systems.

5-hydroxymethylfurfural (HMF), a renewable resource from lignocellulosic biomass conversion, is considered as one of the most valued additive chemicals.[1] Comprised of a hydroxyl group, an aldehyde group, and a ring structure, HMF is a platform for converting into useful compounds such as levulinic acid[2] and 2,5-dimethylfuran (DMF)[3] through ring-opening and hydrogenation/hydrogenolysis, respectively. In addition, the aerobic oxidation of HMF to 2,5-furandicarboxylic acid (FDCA) has attracted much attention recently.[4] One of the most important reasons is that FDCA has the potential of replacing terephthalic acid (PTA), an organic diacid compound for synthesizing conventional plastic products such as polyethylene terephthalate (PET),[5] thus can be a renewable building block for polymers.

The conventional aerobic oxidation of HMF to FDCA contains several alcohol and aldehyde oxidation steps with the involvement of the intermediates 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 2,5-diformylfuran (DFF), and 5-formyl-2-furoic acid (FFCA), as shown in **Scheme 1**.[4b] At the first oxidation step, DFF or HMFCA intermediate could be formed based on the catalyst employed.[4b] However, the formation of DFF was more favourable than HMFCA due to the easily oxidized alcohol group. Thus, high selectivity of DFF (over 90%) can be achieved from HMF or via an one-pot conversion of fructose.[6] FFCA, through further oxidation of DFF or HMFCA, is a main chain of FDCA production and also the rate limiting step.[4a, 7] In order to eliminate the intermediates, previous studies usually applied high temperatures (over 120 °C)[8] and pressures (over 2 MPa)[9] in closed systems to increase the solubility of gaseous oxygen. Even though a high yield (over 90%) of FDCA could be obtained in several cases, the utilization of high-pressure gas generates the risk of explosion, which is less favourable for industrial applications.



Scheme1. Oxidation of HMF to FFCA and FDCA through two different pathways.

Very recently, the Ebitani group and others have reported that Au-based catalysts are capable of HMF-to-FDCA aerobic oxidation with high yields under milder conditions.[10] In addition, scientists have found out that by adding bases in the reaction systems aldehyde groups in HMF can be catalysed into acid groups through the nucleophilic attack of OH^- groups, thus high

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yields (over 80%) of FDCA could be obtained even under low pressures (e.g. 1 bar).[11] However, with the presence of bases in the systems, the synthesis of a complicated catalyst such as bi-metals (Bi-Pt/TiO_2,[12] Pt-Pb/Carbon)[13] or those with core/shell structure (Pd/C@Fe_3O_4)[14] that can mediate alcohol/aldehyde oxidation of HMF becomes difficult to achieve. Besides, these systems still involve two-phase (i.e. liquid-gas) reactions that require specially designed reactors and high volume of gaseous oxygen.[4b, 7, 11a] Consequently, an effective, full liquid phase system of HMF conversion would be scientifically challenging but optimum for chemical industries in the future.

Table 1. Optimization of reaction conditions for HMF conversion.

Entry	H_2O (ml)	H_2O_2 (ml)	Na_2CO_3 (ml)	Ru/AC (g)	Conv. (%)	Yield (%)			
						DFF	HMFCA	FFCA	FDCA
1	16	-	-	-	0	-	-	-	-
2	15	-	1	-	8	0	0	0	0
3	15	-	1	0.025	29	3	1	5	0
4	-	15	1	-	93	0	0	0	0
5	-	15	1	0.025	94	14	2	37	0
6	13.5	1.5 (dropwise)	1	0.025	100	0	0	64	3

Reaction condition: 1 bar, 1 h, Ru/AC (2 % Ru, 0.0250 g), HMF (0.3 mmol, 0.0378 g), 0.3 M $Na_2CO_{3(aq)}$, and 35% $H_2O_{2(aq)}$ was used. Final volume of solution = 16.0 ml.

A liquid oxygen source (i.e. hydrogen peroxide or H_2O_2) has been an alternative approach widely applied in industrial manufacture, thanks to its affordable price, safe storage and high active oxygen content.[15] Most of the applications of H_2O_2 are involved as an oxidizing agent for oxidation reaction such as Baeyer-Villiger oxidation reaction,[15b] alcohol oxidation,[16] phenol hydroxylation, [17] oxidation of sulphides and [18] cyclohexane oxidation.[19] Hydrogen peroxide was recently employed in biomass conversion successfully, such as the production of gluconic acid from glucose,[15a] succinic acid from levulinic acid,[20] and oxidation of furfural into maleic acid or furmaric acid.[21] However, difficulties in controlling its selectivity and quickly decomposing in base or metal catalysts are its drawbacks.[15b] Thus, both the selection of catalysts or catalytic system set ups for general oxidation reactions still remain a challenge when H_2O_2 is used as an oxidizing agent.

In this study, we design an aqueous phase catalytic system for HMF oxidation. Instead of using oxygen gas, we choose H_2O_2 as the liquid oxidant to decrease the mass transfer resistance and provide high reactivity. H_2O_2 was chosen as an ideal liquid oxidant among others since it only generates water and oxygen gas after decomposition. This system is operated under atmospheric pressure and temperature below 100 ºC that provides easy and safe controls.

First, we optimized the reaction conditions of HMF oxidation. As comparing Entry 1 with 2 in **Table 1**, it is found that a basic environment could trigger the decomposition of HMF, but no product was found. However, after adding the Ru/AC catalyst (Entry 3), the conversion of HMF was increased and a trace amount of DFF could be obtained. In contrast, as we introduced H_2O_2 to the system (no Ru/AC catalyst), almost all of the HMF was decomposed (conversion was 93%, as presented in entry 4), but there was still no observation of desired products such as DFF, HMFCA, FFCA or FDCA. These results indicate that both base (i.e. Na_2CO_3) and oxidant (i.e. H_2O_2) promote the decomposition of HMF, and the catalysts (i.e. Ru/AC) endorses the conversion of HMF to the desired products. In entry 5, when all of Na_2CO_3, H_2O_2 and Ru/AC were present in the system, we could get 94% HMF conversion but more desired products such as FFCA (37%) and DFF (14%). In such a batch system where a certain amount of H_2O_2 was added in one time, we observed a lot of bubbles generated in the solution, indicating H_2O_2 was quickly decomposed to oxygen gas and water. In contrast of batch system, it is worth of mentioning that a semi-batch system where H_2O_2 was added dropwisely into the system could strongly improve the catalytic conversion of HMF. As shown in Entry 6, when only 1.5 ml of 35% $H_2O_{2(aq)}$ was added dropwisely, we could obtain an increasing yield of 64% for FFCA. This result shows that a continuous involvement of H_2O_2 is crucial to complete the conversion of HMF to the desired products.

We have previously screened many kinds of catalysts (i.e. different metals loaded activated carbon materials) for HMF conversion. As shown in **Table S1**, the results showed that ruthenium (Ru)-loaded activated carbon (i.e. Ru/AC or RuPt/AC) exhibited higher values in HMF conversion and products yield, as compared to other noble metal-loaded AC materials such as Pt/AC, NiPt/AC, CoPt/AC, and PdPt/AC. The recycle ability of the prepared Ru/AC was discussed in **Fig. S1**.

For the reaction environment, we found that as the temperature increased, the conversion of HMF and the yield of products also increased (See **Table S2**). The most suitable reaction temperature is decided to be 75 ºC. Temperatures above 75ºC are not suitable for the presenting aqueous system due to drastic evaporation of the solvent.

The effect of the amount of the base (i.e. Na_2CO_3) in this reaction system was also studied (See **Table S3**). It is shown that when the reaction was conducted without any base, both the HMF conversion and the product yield were relatively low. This result reveals the importance of the Na_2CO_3 base in this system, and the conversion of HMF was not high in the absence of a base. When the HMF/Na_2CO_3 ratio was 1: 0.5, the presence of DFF in the solution indicated that the efficiency of HMF oxidation was not strong enough, since DFF is one of products after an oxidation step (**Scheme 1**). Further increasing the base makes the reaction of DFF move forward, thus resulting in higher FFCA yield. The highest FFCA yield appeared when the ratio is 1: 1. However, the yield of FDCA did not change much as the ratio was increased.

As for the effect of H_2O_2 concentration, we found that the conversion of HMF was low when the reaction was performed in absence of H_2O_2 (See **Table S4**). About 9% of FFCA yield was observed after reaction, indicating that there were a few amounts of HMF oxidized by the Ru/AC catalyst. In this case, few oxygen gas dissolved in the solution could be used as the oxidant. When increasing the H_2O_2 concentration to 5%, the HMF conversion was greatly increased to 100%, and the yield of FFCA was also increased to 79%. Although there was still 5% of DFF at this condition, which implies the oxidation efficiency was not high enough, we could overcome this problem by simply increasing the concentration of of H_2O_2 to 10%. These results indicate that the presence and liquid oxygen source (i.e. H_2O_2) and its concentration are critical in our oxidation system.

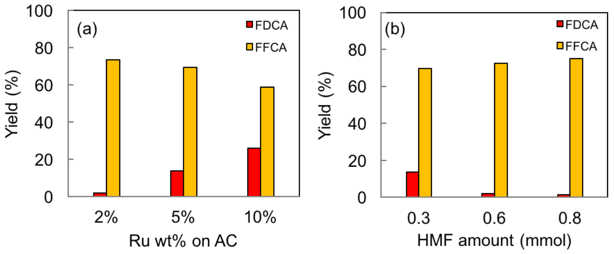

Figure 1. Effects of (a) the amount of Ru and (b) the amount of HMF on the yields of FFCA and FDCA.

Based on our optimization of reaction conditions, we found that FFCA could be synthesized quickly from HMF but the FFCA-to-FDCA reaction was relatively slower. This feature makes it possible to selectively stop the reaction for desired products (i.e. FFCA or FDCA), because both of them are precious block chemicals. Two factors were found to be critical for selective production of FFCA and FDCA. As shown in **Fig. 1(a)**, on one hand, we found the amounts of Ru (wt%) on AC affected the selective oxidation of HMF to FFCA or FDCA. More Ru on AC (from 2% to 10%) would result in higher FDCA yields (i.e. from 1.7% to 26.0%). On the other hand, when increasing the amount of HMF (from 0.3 to 0.8 mmol), more FFCA could be obtained (from 69.5% to 75.0%), as shown in **Fig. 1(b)**. Because FFCA is the intermediate of HMF-to-FDCA, more amounts of Ru on AC (i.e. more catalysts) would catalyze the conversion, and more HMF (i.e. more reactants) would lead to incomplete conversion when the catalyst amount and reaction time are limited. We further adjust both HMF and Ru wt% and use the HMF/Ru ratio to study the selective oxidation of HMF. As shown in **Table S5 and S6**, when we fixed the HMF/Ru ratio at 20, the similar product compositions proved that HMF/Ru molar ratio is the key factor for determining product selectivity in our system. In other words, the effect of adding less reactant gives almost the same results as adding more catalyst. We believe that the amount of HMF that one mole of Ru could react per unit time should be a constant in our system. When HMF/Ru was decreased to 10, given that more catalysts could provide more active sites, HMF would convert to FFCA and then further convert to FDCA. In contrast, when the HMF/Ru ratio was increased to 60, the reactant HMF was not completely consumed (i.e. trace amount of HMF remained). As a result, we control the HMF/Ru ratio at 50 to ensure complete conversion of HMF, and we can obtain FFCA in 84% yield within 1 hour. For getting FDCA, we extended the reaction time to 6 hours, and FDCA with the highest yield of 91% could be obtained under 75 ºC and atmospheric pressure, as shown in **Fig. 2**. We also checked our catalysts through FT-IR analysis to prove that our product will not be adsorbed in the pore of Ru/AC after reaction, as shown in **Fig. S2**.

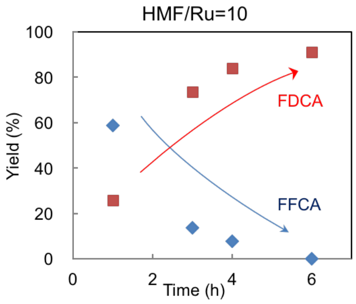

Figure 2. Yields of FFCA and FDCA at various time periods at a molar ratio of HMF/Ru = 10. Reaction condition: 75 ºC, Ru/AC (10 wt% Ru, 25 mg), H_2O (13.5 ml), HMF/Na_2CO_3 = 1 : 1, and 35% $H_2O_{2(aq)}$ was added dropwise with the rate = 1.6 ml/h. Conversions of HMF in this figure are all 100%.

Table 2. Effects of different bases and reaction times on the HMF oxidation.

Entry	Time (h)	Base source	Conv. (%)	Yield (%)			
				DFF	HMFCA	FFCA	FDCA
1	1	$NaHCO_3$	100	0	0	92	3
2		Na_2CO_3	100	0	1	84	3
3		NaOH	100	0	1	57	12
4	3	$NaHCO_3$	100	0	0	67	27
5		Na_2CO_3	100	0	0	61	29
6		NaOH	100	0	0	40	29

Reaction condition: 75 ºC, 1 bar, 1 h, Ru/AC (5 % Ru, 25 mg), HMF (0.3 mmol, 0.0378 g), Na^+/HMF= 2, water was added until total volume = 14.5 ml. Finally, 10% $H_2O_{2(aq)}$ was added dropwisely with the rate = 1.6 ml/h.

To demonstrate the high efficiency of our system using liquid oxygen source (i.e. H_2O_2), we compare our results with that using gaseous oxygen as the oxidant. As shown in **Table S7**, the system using gaseous oxygen while remaining other reaction conditions the same could only produce trace amount of FDCA. This result indicated that the oxygen molecules generated from H_2O_2 would interact with the reactant (i.e. HMF) and catalyst (i.e. Ru/AC) more efficiently than gaseous oxygen molecules that are required to be dissolved in solution prior to reaction.

It is reported that strong base would facilitate the production of FDCA, but at the same time HMF is easily decomposed to other side products in strong alkaline environment.[18] Therefore, it is important to find out the most suitable base for our system. We used different bases including sodium bicarbonate ($NaHCO_3$, pKa = 10.3), sodium carbonate ($NaCO_3$, pKa = 10.33) and sodium hydroxide (NaOH, pKa = 13.8), and the results are listed in **Table 2**. For the cases of 1 hour reaction, it could be found that the base with lower pKa (i.e. $NaHCO_3$) gives a higher FFCA yield, and the one with higher pKa (i.e. NaOH) resulted in more FDCA. However, NaOH was too strong so about 30% of HMF was degraded instead of oxidation. Consequently, a weak base like $NaHCO_3$ is more suitable in our system. When we further extended the reaction time to 3 hours, the amount of FFCA decreased and the amount of FDCA increased, indicating the successful FFCA-to-FDCA conversion.

To further improve the yield of FDCA, we came out an idea that is to separate the HMF-to-FDCA reaction into a sequential HMF-to-FFCA and FFCA-to-FDCA reaction. In the first HMF-to-FFCA reaction we used $NaHCO_3$ (i.e. the weak base) to synthesize FFCA with a high yield. After that, for the second FFCA-to-FDCA reaction, we then added NaOH (i.e. the strong base) into the solution. The strong base can provide more Na^+ ions that can prevent the catalyst from deactivating and more OH^- ions that can promote the FFCA-to-FDCA reaction. The results are shown in **Table 3**. From entry 1 and 2, low yields of FDCA indicated that $NaHCO_3$ was not strong enough for the deionization of FDCA. In addition, in entry 6, even we removed the used Ru/AC catalyst and added fresh Ru/AC catalyst for the FFCA-to-FDCA reaction, we only observed a little improvement of the FDCA yield, indicating that fresh Ru/AC catalyst was still deactivated and lost the efficiency very soon when the FDCA was formed. However, when we used NaOH as the base for the FFCA-to-FDCA reaction, we can convert most of the FFCA into FDCA within 2 hours (Entry 3, 4, 5). As comparison, if we introduce fresh Ru/AC catalyst and NaOH into the system at the same time, FDCA yield of 76% could be obtained (Entry 7) in a total 3-hour reaction. Consequently, we can conclude that a strong base such as NaOH is necessary for the FFCA-to-FDCA reaction.

Table 3. Sequential reaction conditions for HMF-to-FDCA conversion.

Entry	1st step		2nd step			Conv. (%)	Yield (%)	
	base	time (h)	catalyst replacement	base	time (h)		FFCA	FDCA
1	$NaHCO_3$	1	-	-	2	100	67	27
2			-	$NaHCO_3$	2	100	68	31
3			-	NaOH	2	100	23	63
4			-	NaOH	4	100	14	77
5			-	NaOH	5	100	11	82
6			fresh	-	2	100	53	44
7			fresh	NaOH	2	100	10	76

Reaction condition: 75 ºC, 1 bar, HMF (0.3 mmol, 37.8 mg), Na^+/HMF= 2 in each step of reaction, water was added until total volume = 14.5 ml. Finally, 10% $H_2O_{2(aq)}$ was added dropwisely with the rate = 1.6 ml/h.

In conclusion, we propose an effective liquid-phase oxidation system for selective HMF oxidation to either FFCA or FDCA with high yields. Compared to other metal catalysts, we found that ruthenium (Ru)-based catalysts show the best performance with the presence of our liquid oxidant, hydrogen peroxide (H_2O_2). No gas flow is required during the reaction; instead, we added hydrogen peroxide dropwisely into the system. We found the main factors affecting product composition are the molar ratio of HMF to Ru and the reaction time. We can selectively produce FFCA or FDCA by simply adjusting these two factors. The reactions are in low temperature, atmospheric pressure, weak base environment, and short reaction time with high catalytic efficiency, and the catalysts are easy to synthesize, which make this reaction system more feasible for industrial FDCA production in the future.

Experimental Section

Chemicals Hydrogen peroxide solution (H_2O_2, 35% w/w) is purchased from Showa. Ruthenium (III) chloride hydrate ($RuCl_3 \cdot nH_2O$, 38% - 42% Ru basis) and other materials are all purchased from Sigma-Aldrich.

Preparation of catalysts At first, 0.2 g of grinded activated carbon was mixed with 15 ml of water and stirred for 20 min. Then, ruthenium chloride was dissolved in water to form a clear solution, and the solution was added to the activated carbon solution. After stirring for another 20 min, the solution was moved to a rotating evaporator to remove the water gradually under reduced pressure and 30 °C. When most of the water was removed (i.e. powder-formed activated carbon could be observed), the temperature was increased to 70 °C and held for 30 min to further drying of the samples. The material was then reduced to metal state by calcination under hydrogen gas flow. We use mixed gas containing 95% of nitrogen and 5% of hydrogen with a flow rate of 60 ml/min. The temperature was raised from 20 °C to 450 °C within 90 min, and held at 450 °C for 4 h. The reduced Ru-on-activated carbon (denoted as Ru/AC) was then collected after cooling. The oxidation state of Ru in the synthesized Ru/AC samples was examined with XPS measurement (**Fig. S3**).

Oxidation of HMF In a typical oxidation reaction of HMF, 0.0378 g of HMF (0.3 mmol) and 0.0250 g of catalyst was prepared in a two-neck round bottom flask. Then 13.5 ml of de-ionized water and 1 ml of 0.3 M sodium carbonate (Na_2CO_3) aqueous solution were added. After that, the round bottom flask containing the reaction media was then put into an oil bath to control the reaction temperature. A rubber stopper was used to cap the vial and a needle was inserted on it for maintaining the pressure at 1 atm (i.e. open system). Finally, to start the reaction, 1.5 ml of $H_2O_{2(aq)}$ was added to the solution dropwisely in a rate of 1.6 ml/h by syringe pump. The reaction was carried out at various times under stirring. The shortest reaction time was one hour because we examined that all $H_2O_{2(aq)}$ could be consumed within one hour.

Analysis of products After reaction, the catalyst was separated from the solution by filtration, and then the solution was directly analyzed by High Performance Liquid Chromatography (HPLC), which was equipped with RI detector and a Transgenomic COREGel 87H3 (300 mm × 7.8 mm) column. The retention time for HMF, HMFCA, DFF, FFCA, and FDCA are 36.5, 24.5, 47.3, 28.6, and 20.7 minute, respectively. The yield of products is defined as the mole of product produced over the mole of reactant added. The conversion of HMF is defined as the mole of HMF consumed after the reaction over the mole of HMF added.

$$\text{Yield (\%)}=\frac{\text{mole of product produced}}{\text{mole of HMF added}}\times 100\%$$

$$\text{Conversion (\%)}=\frac{\text{mole of HMF consumed}}{\text{mole of HMF added}}\times 100\%$$

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Keywords: Selective oxidation • 5-hydroxymethyl furfural (HMF) • Hydrogen peroxide • 5-formyl-2-furoic acid (FFCA) • 2,5-furandicarboxylic acid (FDCA)

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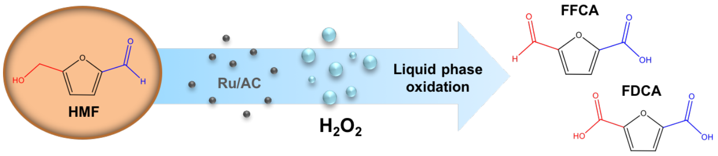

Selective Oxidation of 5-Hydroxymethylfurfural (HMF): We propose an effective liquid-phase oxidation system for selective HMF oxidation to either FFCA or FDCA with high yields using Ru/AC and H_2O_2 as the catalyst and oxidant, respectively.

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Selective Oxidation of 5-Hydroxymethylfurfural (HMF) in Wate under Mild Conditions