

Selective oxidation of 5-formyloxymethylfurfural to 2, 5-furandicarboxylic acid with Ru/C in water solution

Zhihao Si*, Xin Zhang*, Miao Zuo*, Tao Wang*, Yong Sun^{*,†}, Xing Tang*, Xianhai Zeng^{*,**}, and Lu Lin^{*,**}

*Xiamen Key Laboratory of Clean and High-valued Applications of Biomass, College of Energy, Xiamen University, Xiamen 361102, China

**Fujian Engineering and Research Center of Clean and High-valued Technologies for Biomass, Xiamen University, Xiamen 361102, China

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Abstract—2, 5-furandicarboxylic acid (FDCA) is a one of the most promising biomass-derived chemicals to substitute the non-renewable terephthalic acid as the monomer for producing polyethyleneterephthalate. At present, the oxidation of HMF is regarded as a prevalent way to prepare FDCA. Nevertheless, the isolation and storage of HMF is still a challenge. Herein, based on the higher stability of 5-formyloxymethylfurfural (FMF) than 5-hydroxymethylfurfural (HMF), we present an effective preparation route to prepare FDCA by substituting HMF with FMF as feedstock. A complete conversion of FMF and a 93.55% selectivity of FDCA were obtained in the mixed solvent of water and 1, 2-dioxane using Ru/C as catalyst and O₂ as oxidant. An improved process was developed for preparing FDCA using FMF as feedstock. The investigation of conversion pathway showed that FMF and HMF were simultaneously oxidized to 2, 5-diformylfuran (DFF) in a case of the existence of the reversible equilibrium between FMF and HMF. Then DFF was oxidized to 5-formyl-2-furancarboxylic acid (FFCA). Subsequently, FFCA was oxidized to FDCA. In this process, the oxidation of FFCA to FDCA was determined as the rate-determining step. Furthermore, appropriate alkalinity favored the selectivity of FDCA and the conversion of FMF.

Keywords: 5-Formyloxymethylfurfural, 2, 5-Furandicarboxylic Acid, Oxidation, Ru Supported Catalyst

INTRODUCTION

The current problems of environmental pollution prompted us to search for a green alternative to the conventional petrochemicals [1-3]. Under this background, comprehensive utilization of the biomass has attracted much attention of researchers, because of its irreplaceable advantages, such as abundance and renewability. In general, biorefinery is regarded as the most promising and feasible measure to utilize biomass resource, including biological treatment, thermolysis and chemical conversion [4-6]. One of the most important and attractive biorefinery process is converting carbohydrates to 5-hydroxymethylfurfural (HMF), the versatile biomass based platform chemicals hydrolyzed from cellulose [7]. As a research hotspot, the preparation methods of HMF have been studied in detail by the global researchers. And the downstream reactions of HMF have also been extensively studied, basically including the reduction to obtain 2, 5-bis(hydroxymethyl)furan (BHMF) [8], the oxidation to get the 2, 5-diformylfuran (DFF) and the deep oxidation to achieve 2, 5-furandicarboxylic acid (FDCA) [9].

In industry, terephthalic acid is an important monomer for producing polyethyleneterephthalate (PET plastic). Being the similar aromatic structure, FDCA is considered as a most potential alternative to replace terephthalic acid [10]. According to previous reports,

HMF was invariably used as feedstock for producing FDCA [11-13]. To achieve an excellent FDCA yield, noble-metal catalysts were usually the preferred choice. As reported, Au/HY achieved over 99% FDCA yield in water under the conditions of 60 °C and 0.3 MPa O₂ [14]. When using Pt/CNT as catalyst, 98% FDCA yield was obtained in water with complete HMF conversion [15]. Gorbanev et al. [16] reported that the supported Ru(OH)_x catalyst performed well in aerobic oxidation of HMF to FDCA under a moderate oxygen pressure. Considering the high cost, scarcity and long-term availability of noble metals, a new tendency of using non-noble catalyst arose in recent years. Han et al. [3] used MnO_x-CeO₂ composite catalysts in the oxidation of HMF to FDCA, achieving a 91% yield of FDCA.

Although a great deal of excellent results were obtained in the oxidation of HMF to FDCA, the isolation and storage of HMF is still a challenge. Property of instability results in no commercial HMF products in the market, which has been one bottleneck to realize the low-cost production of FDCA from HMF. It is worthwhile to point out here that FMF is more stable, less polar and more hydrophobic than HMF, favoring its isolation from the reaction mixture by extraction and vacuum distillation. Our lab has developed the preparation process of FMF with the purity of 98.8% based on the one-pot pathway from cellulose and two-step pathway from fructose [17,18]. The prepared FMF in our lab remains a good purity of 97.8% after a storage of 90 days (Fig. 1). Based on these advantages of FMF, it was regarded as a promising platform chemical. In this study, we attempt to validate possibility of using FMF as feed-

[†]To whom correspondence should be addressed.

E-mail: sunyong@xmu.edu.cn

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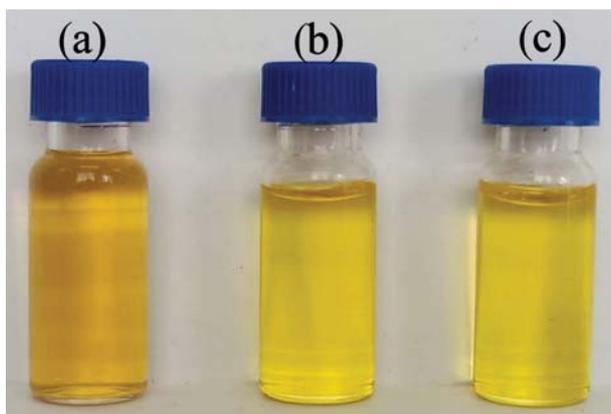


Fig. 1. Color change of FMF during storage. (a) FMF stored 9 months, (b) FMF stored 3 months, (c) Fresh FMF.

stock to produce FDCA like HMF do. Some catalysts usually used to oxidize HMF to FDCA were screened for the oxidation of FMF. Some influencing factors, such as reaction solvent and reaction parameters, were investigated. More importantly, the reaction pathway of FMF to FDCA was revealed in detail.

1. Materials

HMF, FDCA, FFCA, HMFCFA, DFF, 1, 4-dioxane, dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), acetonitrile, phosphonitric chloride trimer, Ru/C (5 wt% Ru, containing 60-70% water), Pd/C (5 wt% Pd, containing 40-60% water), Pt/C (5 wt% Pt, containing water less than 80%), ruthenium chloride hydrate (35.0-42.0% Ru basis), as well as MnO_2 , Fe_2O_3 , Co_3O_4 , ZSM-5, were purchased from Aladdin Chemical Technology Co. Ltd. (Shanghai, China). All reagents used in this study were analytical grade. FMF was prepared in our laboratory.

2. Preparation of Ru Supported Catalysts

The Ru supported catalysts were prepared with the impregnation method. In short, Ru was loaded on several supports respectively by the impregnation with $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ aqueous solution, then the reduction procedure of the RuCl_3 was performed with the flow of H_2/N_2 (10 vol% H_2) mixture gas at 350 °C. The loading of Ru to support was kept at 5 wt%. The nitrogen doped carbon support (NC) was prepared using the method reported by other researchers [19].

3. Characterization

The specific surface area and pore distribution of the catalysts were determined using Micromeritics ASAP 2020 HD88. Prior to the measurement of adsorption, the samples were degassed under vacuum at 373 K for 4 h.

4. Typical Reactions and Product Analysis

The oxidation reactions of HMF and FMF were performed using a 20 mL stainless steel reactor with magnetic stirring. In a typical experiment run, 0.154 g FMF (1mmol) or 0.126 g HMF (1 mmol), 2 g 1,4-dioxane, 8 g H_2O , a certain amount of catalyst and alkali were added in the reactor firstly, followed by filling with O_2 (purity >98%), then the reactor was heated in an oil bath to the target temperature for a certain amount of time. After the reaction was finished, the reactor was cooled to room temperature in cold water, and the supernatant was separated for subsequent analysis.

HPLC analysis of reaction products, such as FDCA, HMFCFA, FFCA, HMF and DFF was performed using high-performance liquid chromatography (HPLC, Waters 2695 Separation Module) equipped with Bio-Rad Aminex HPX-87H ion exclusion column (300×7.8 mm). The column oven temperature was 60 °C and the mobile phase was 0.005 M H_2SO_4 at a flow rate of 0.6 mL·min⁻¹. Moreover, the gas products were analyzed using Agilent 7890B Gas Chromatograph.

The product conversion and yield were calculated according to the following equations:

$$\text{Carbon balance} = \text{FDCA Yield} + \text{FFCA yield} + \text{HMFCFA yield} + \text{HMF yield} + \text{DFF yield} + \text{FMF yield} \quad (1)$$

$$\text{FDCA yield} = \left(\frac{\text{Mole of FDCA in the products}}{\text{Initial mole of reactant}} \right) \times 100\% \quad (2)$$

$$\text{FFCA yield} = \left(\frac{\text{Mole of FFCA in the products}}{\text{Initial mole of reactant}} \right) \times 100\% \quad (3)$$

$$\text{HMFCFA yield} = \left(\frac{\text{Mole of HMFCFA in the products}}{\text{Initial mole of reactant}} \right) \times 100\% \quad (4)$$

$$\text{HMF yield} = \left(\frac{\text{Mole of HMF in the products}}{\text{Initial mole of reactant}} \right) \times 100\% \quad (5)$$

$$\text{DFF yield} = \left(\frac{\text{Mole of DFF in the products}}{\text{Initial mole of reactant}} \right) \times 100\% \quad (6)$$

$$\text{FMF yield} = \left(\frac{\text{Mole of FMF in the products}}{\text{Initial mole of reactant}} \right) \times 100\% \quad (7)$$

RESULTS AND DISCUSSION

1. Reaction Pathways for the Aerobic Oxidation of FMF

Usually, the FDCA can hardly dissolve in most common solvents. Therefore, the preparation of FDCA required the assistance of alkali to form organic salt, which facilitates the dissolution of FDCA in water, promoting the reaction efficiency. In addition, study in subsequent section on the effect of reaction temperature showed the conversion of FMF was too fast at 140 °C. To grasp more information about the distribution of intermediates generated in the oxidation of FMF, the declined reaction temperature was required to lower the reaction rate. In experiments, we compared the oxidation behaviors of FMF in NaHCO_3 solution with different alkalinity at 100 °C (Fig. 2). When 4 mole equivalent NaHCO_3 was used in the reaction, except for FDCA, the intermediates, such as HMF, DFF, FFCA and HMFCFA, were detected. From Fig. 3 in subsequent chapter, we found that FFCA was dominant among all the intermediates till 10 h. Furthermore, it was generated rapidly in initial 15 min, verifying the conversion of FMF to FFCA was rapid reaction and the oxidation of FFCA to FDCA was the rate-determining step. Compared with reaction using 4 mole equivalent NaHCO_3 , we found the generation rate of FFCA from FMF was faster, as well as the conversion rate of FFCA to FDCA, when 2 mole equivalent NaHCO_3 was used in the reaction. It appeared that the excess alkalinity was unfavorable for the oxidation of FMF. To confirm this assumption, the experiments without NaHCO_3 were performed. To our surprise, the intermediates HMF and DFF be-

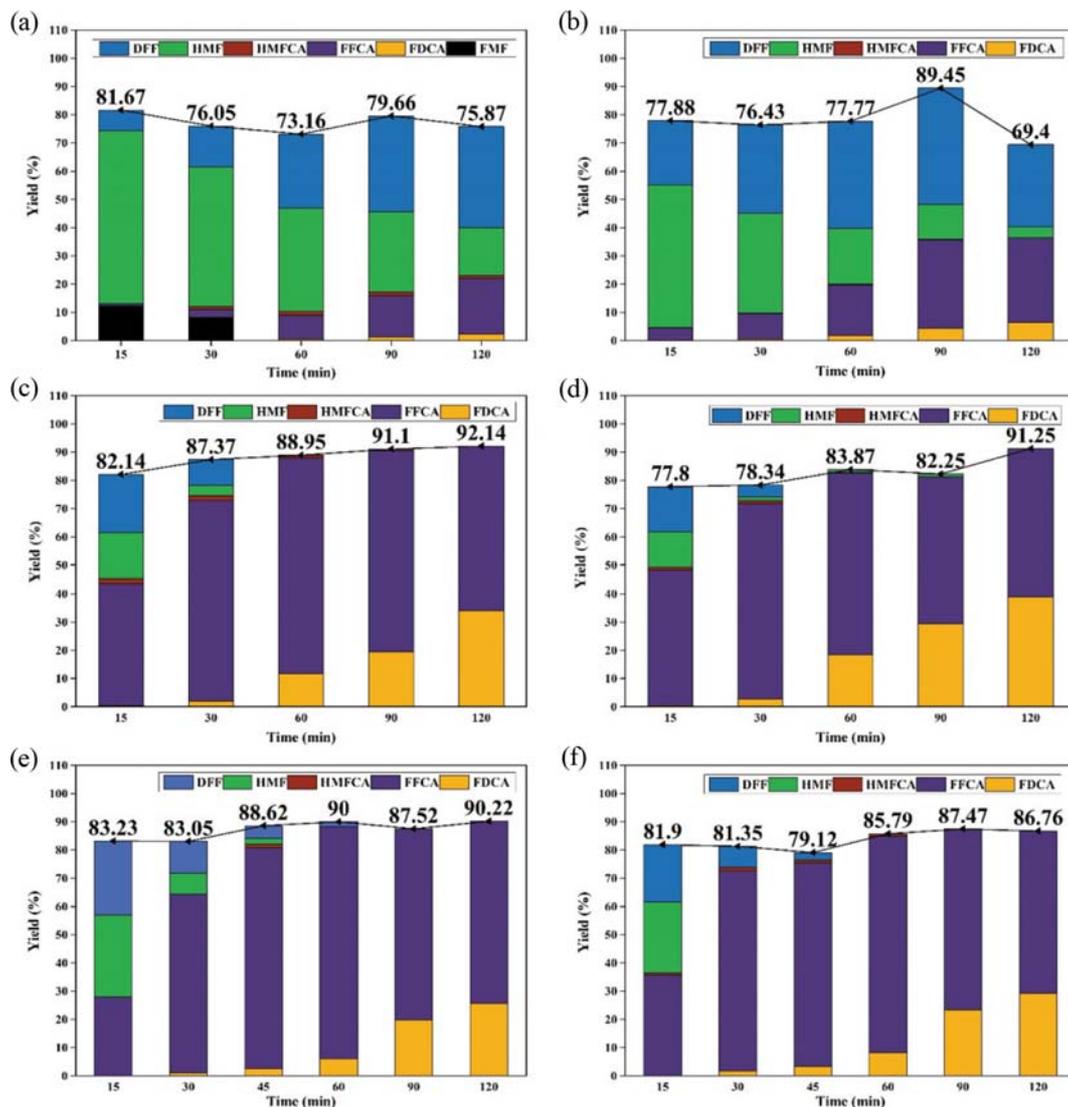


Fig. 2. Production distribution and carbon balance of the oxidation of FMF and HMF to FDCA with different equivalent NaHCO_3 . Reaction conditions: 10 g mixed solvent of 1, 2-dioxane and H_2O (w/w, 2: 8), 0.1 g Ru/C (mole ratio of FMF/Ru=20), 100 °C, 1 MPa O_2 , 500 rpm, completed FMF conversion in each reaction except for marked out. (a) 1 mmol FME, no NaHCO_3 ; (b) 1 mmol HMF, no NaHCO_3 ; (c) 1 mmol FME, 2 equivalent NaHCO_3 ; (d) 1 mmol HMF, 2 equivalent NaHCO_3 ; (e) 1 mmol FME, 4 equivalent NaHCO_3 ; (f) 1 mmol HMF, 4 equivalent NaHCO_3 .

came dominant, suggesting that the insufficient alkalinity also did not benefit the formation of FFCA. Furthermore, the following oxidation of FFCA to FDCA also was influenced, leading to the low yield of FDCA. Especially, the formation of FFCA and FDCA was drastically affected by alkalinity due to the carboxyl in these chemicals. The possible cause was the alkalinity affected the dispersing of intermediates and FDCA in the reaction solution.

By comparison with HMF as feedstock, the change trend of products distribution was similar to that using FMF as feedstock. No matter adding 2 or 4 mole equivalent NaHCO_3 into the reaction, the yield of intermediate DFF using FMF as feed stock was always slightly more than that using HMF as feedstock. Furthermore, the carbon balance in the reaction using FMF as feedstock was slightly more than that using HMF as feedstock. Moreover, the yield of intermediate FFCA using FMF as feedstock was more

than that using HMF as feed stock after 30 minutes. These results indicated that FMF could be directly oxidized to FFCA or indirectly oxidized via HMF to FFCA due to the existence of reversible equilibrium between HMF and FME.

During the reaction, both DFF and HMFCFA were found as intermediates. Some literatures reported that the oxidation of HMF to FDCA underwent DFF or HMFCFA [13,20]. To confirm the conversion pathway in this reaction, DFF or HMFCFA was used as feedstock to produce FDCA (Table 1). The results showed that DFF performed better than HMFCFA, confirming that primary conversion pathway underwent the intermediate DFF in this reaction, whereas the secondary pathway was the oxidation of HMFCFA.

Therefore, in view of the analysis above and previous studies [20-22], a possible reaction mechanism for this oxidation reaction was proposed as illustrated in Scheme 1. The most important differ-

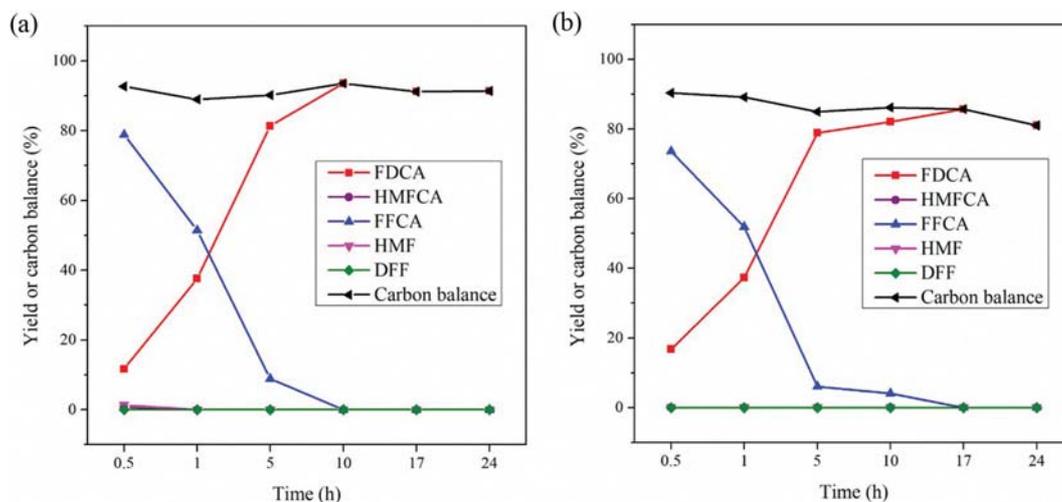


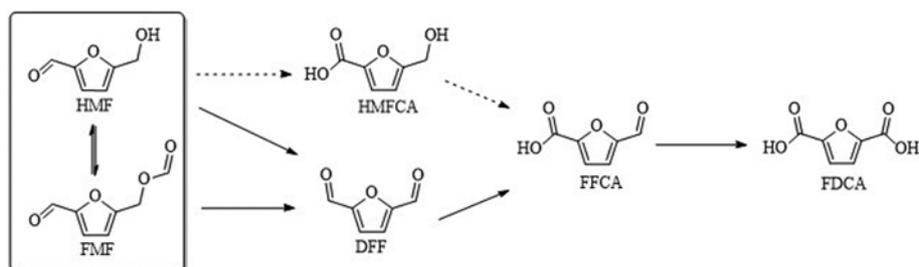
Fig. 3. Effect of reaction time on the oxidation of FMF to FDCA. Reaction condition: (a) 1 mmol FMF or (b) 1 mmol HMF, 10 g mixed solvent of 1, 2-dioxane and H₂O (w/w, 2:8), 0.1 g Ru/C (the mole ratio of substrate/Ru=20), 4 mole equivalent NaHCO₃, 1 MPa O₂, 120 °C, 750 rpm, complete FMF/HMF conversion in 0.5 h for each reaction.

Table 1. Comparison between using DFF and HMFCFA as reactant^a

Entry	Reactant	Yield (%)			Carbon balance (%)
		FDCA	HMFCFA	FFCA	
1	DFF	9.17	0	83.80	92.97
1	HMFCFA	5.52	54.27	38.20	97.99

^aReaction condition: 1 mmol DFF or HMFCFA, 10 g mixed solvent of 1, 2-dioxane and H₂O (w/w, 2:8), 0.1 g Ru/C (mole ratio of FMF/Ru=20), 4 mole equivalent NaHCO₃, 100 °C, 1 MPa O₂, 30 min, 500 rpm

ence is the conversion of FMF. Initially, FMF and HMF existed in the reaction together through the reversible equilibrium. Next, FMF could be oxidized to DFF directly. And it could also be indirectly oxidized to DFF through intermediate HMF, which was a rapid reaction. Meanwhile, the oxidation of a small amount of HMF to HMFCFA was determined as the secondary reaction pathway, since it was detected in the reaction. Subsequently, DFF and HMFCFA were oxidized to FFCA. Finally, FFCA was oxidized to FDCA, furthermore, the oxidation of FFCA to FDCA was the rate-determining



Scheme 1. Proposed mechanism for the oxidation of FMF to FDCA.

Table 2. Effect of different catalysts on the oxidation of FMF to FDCA^a

Entry	Catalyst	Yield (%)					Carbon balance (%)
		FDCA	HMFCFA	FFCA	HMF	DFF	
4	Pd/C	67.77	19.57	5.59	0	0	92.93
5	Ru/C	81.35	0	8.83	0	0	90.18
6	Pt/C	77.69	0	0	0	0	77.69
7	MnO ₂	0	1.53	1.58	53.88	2.8	59.79
8	Fe ₂ O ₃	0	1.10	1.19	64.41	4.39	70.99
9	Co ₃ O ₄	0	1.05	0.8	67.68	5.16	74.69
10	MoO ₃	0	0.78	0.86	68.2	2.64	72.48

^aReaction condition: 1 mmol FMF, 0.1 g dry non-noble catalysts or 0.1 g dry noble catalysts (5%), 4 mole equivalent of NaHCO₃, 120 °C, 1 MPa O₂, 5 h, 750 rpm, 10 g mixed solvent of 1, 2-dioxane and H₂O (w/w, 2:8), complete FMF conversion in each reaction

Table 3. Effect of the catalyst support to the FDCA yield^a

Entry	Catalyst	Yield (%)					Carbon balance (%)
		FDCA	HMFCa	FFCA	HMF	DFE	
1	Ru/ZSM-5 ^b	0	1.20	4.32	41.88	4.39	51.79
2	Ru/ZSM-5 ^c	0	0.77	2.34	64.06	4.56	71.73
3	Ru/C	81.35	0	8.83	0	0	90.18
4	Ru/NC ^d	13.62	0	74.58	0	1.21	89.41

^aReaction condition: 1 mmol FME, 0.1 g dry catalysts, 4 mole equivalent of NaHCO₃, 120 °C, 1 MPa O₂, 5 h, 750 rpm, 10 g mixed solvent of 1, 2-dioxane and H₂O (w/w, 1 : 4), complete FME conversion in each reaction.

^bSi/Al=45-80

^cSi/Al=150-300

^dThe support NC was prepared using method reported by other researchers [19].

ing step.

2. Catalyst Screening

As the experiment results collected in Table 2, several catalysts, usually used in the oxidation of HMF, were employed in the oxidation of FME under the optimized condition of 120 °C, 5 h and 1 MPa O₂. The results showed the Ru/C catalyst presented the much better selectivity for the oxidation of FME to FDCA with the yield of 81.3% and the carbon balance of 90.2%. By comparison, the non-noble metal oxide catalysts used in this reaction presented hardly any catalytic activity for the oxidation of FME to FDCA, the resulting by-product 5-HMF inferred that these metal oxides were more inclined to hydrolyze FME. Owing to the high activity of Ru/C compared with other catalysts, Ru/C was screened as the catalyst for the oxidation of FME to FDCA in the following study.

Subsequently, several Ru-based catalysts with different supports were tested in the oxidation of FME to FDCA. From the results in Table 3, it can be seen that there was no FDCA produced when using ZSM-5 as catalyst support, HMF was the main product instead, which suggested ZSM-5 appeared not to favor the improvement of Ru for the oxidation of FME to FDCA. It is well known that ZSM-5 is a kind of acid molecular sieves, therefore, it was supposed that acidity of ZSM-5 improve the hydrolysis of FME to HMF and influence following oxidation. In addition, the specific surface area analysis of the catalysts showed the commercial Ru/C had the obviously larger surface area, which may contribute to the higher yield of FDCA (Table 4).

Table 4. Physicochemical properties of catalysts

Entry	Catalyst	Langmuir surface area (m ² /g)	Median pore width (nm) ^d
1	Ru/ZSM-5 ^a	478.06	0.37
2	Ru/ZSM-5 ^b	512.69	0.38
3	Ru/C	1901.71	0.51
4	Ru/NC ^c	1626.04	0.52

^aSi/Al=45-80

^bSi/Al=150-300

^cThe support NC was prepared using method reported by other researchers [19].

^dHK pore size distribution.

3. Effect of the Reaction Conditions on the Oxidation of FME to FDCA

3-1. Effect of Solvent

According to previous reports [23,24], solvent presented significant effect on the reaction pathway or the oxidation rate of HMF, therefore several common solvents were employed for further examination (Table 5). Considering previous experiment result that most organic solvent performed bad in the oxidation of FME to FDCA, therefore the mixed solvents, such as THF/water, DMSO/water, acetonitrile/water and 1, 4-dioxane/water, were tested in our experiments. The results showed 1, 4-dioxane/water mixture performed

Table 5. The effect of different solvent composition and ratio on FDCA yield^a

Entry	Solvent	Yield (%)				
		FDCA	HMFCa	FFCA	HMF	DFE
1	DMSO : H ₂ O (w/w, 1 : 4)	86.90	0	0	0	0
2	THF : H ₂ O (w/w, 1 : 4)	73.94	0	2.25	0	0
3	Acetonitrile : H ₂ O (w/w, 1 : 4)	66.31	0	5.01	0	1.42
4	1,4-Dioxane : H ₂ O (w/w, 1 : 9)	90.23	0	0	0	0
5	1,4-Dioxane : H ₂ O (w/w, 1 : 4)	91.34	0	0	0	0
6	1,4-Dioxane : H ₂ O (w/w, 3 : 7)	90.08	0	0	0	0
7	1,4-Dioxane : H ₂ O (w/w, 1 : 1)	91.02	0	0	0	0

^aReaction condition: 1 mmol FME, 0.1 g Ru/C (mole ratio of FME/Ru=20), 4 mole equivalent NaHCO₃, 120 °C, 1 MPa O₂, 24 h, 750 rpm, complete FME conversion in each reaction.

much better in the selectivity of FDCA, even under the condition that the mass ratio of 1, 4-dioxane/water substantially ranged from 1 : 9 to 1 : 1. Owing to the alkalinity of NaHCO_3 , FDCA was prone to form the salt of FDCA, especially at the presence of water. Therefore, the addition of water facilitated the conversion of FMF and generation of FDCA.

3-2. Effect of Reaction Time

The effect of the reaction time on the conversion of FMF to FDCA was presented in Fig. 3(a). It was found that FMF was completely converted within 0.5 h, along with the appearance of the main product FFCA. As prolonging the reaction time to 10 h, the yield of FDCA climbed to 93.55%. During the reaction, except for FFCA, only few other intermediates, such as HMF, DFF and HMFC, were detected. In addition, further prolonging the reaction time bring hardly any positive effect on the yield of FDCA. It seemed that FMF was firstly oxidized to FFCA, followed by the oxidation of FFCA to FDCA. It also suggested that the oxidation of FFCA to FDCA was the rate-determining step in this reaction. By comparison the conversion of HMF to FDCA (Fig. 3(b)), the carbon balance and the yield of FDCA using FMF as feedstock was slightly higher than that of HMF. It might be ascribed to FMF is more stable than HMF.

3-3. Effect of Reaction Temperature

The reaction temperature also influenced the product selectivity greatly. As seen in Fig. 4, during the reaction temperature rose from 80 °C to 160 °C, the highest FDCA yield of 92.58% was obtained at 140 °C in 5 h. What's more, the relatively low temperature had little effect on the oxidation of FMF to FFCA, whereas the oxidation of FFCA to FDCA was greatly dependent on the higher reaction temperature. Notably, when the reaction temperature was lower than 100 °C, the low carbon balance showed that some undesired intermediates not detected were possibly produced.

3-4. Effect of O_2 Pressure

The effect of O_2 pressure was also investigated in this study. The

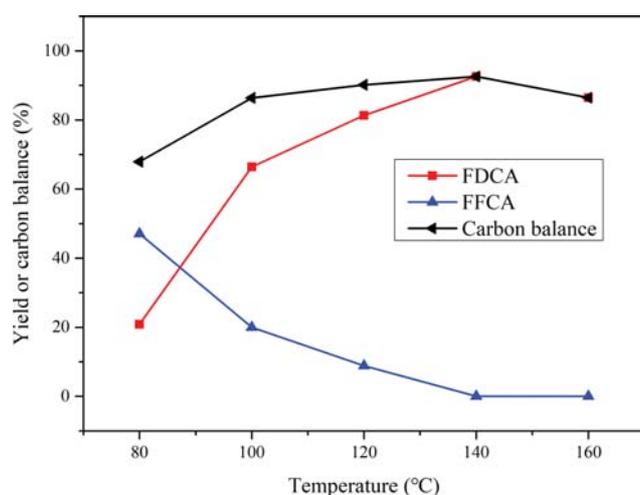


Fig. 4. Effect of the reaction temperature to the FDCA yield. Reaction condition: 1 mmol FME, 2 g 1,2-dioxane and 8 g H_2O , 0.1 g Ru/C (mole ratio of FMF/Ru=20), 4 mole equivalent NaHCO_3 , 1 MPa O_2 , 5 h, 750 rpm, complete FMF conversion in each reaction.

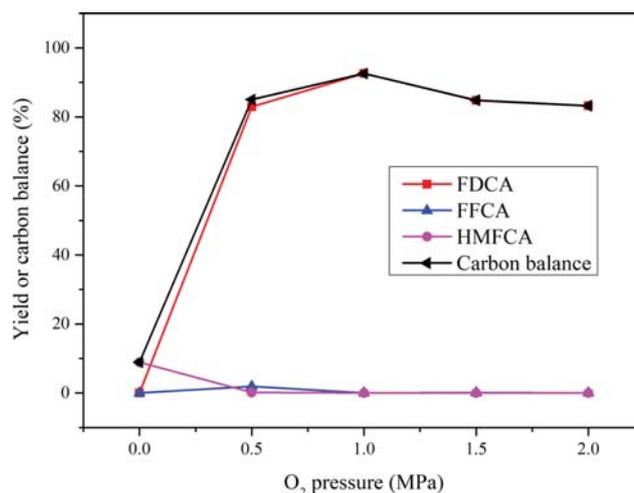


Fig. 5. Effect of the reaction O_2 pressure to the FDCA yield. Reaction condition: 1 mmol FME, 10 g mixed solvent of 1, 2-dioxane and H_2O (w/w, 2 : 8), 0.1 g Ru/C (mole ratio of FMF/Ru=20), 4 mole equivalent NaHCO_3 , 140 °C, 5 h, 750 rpm, complete FMF conversion in each reaction.

results were presented in Fig. 5. When the pressure rose to 1 MPa, the yield of FDCA substantially increased. However, continually increasing O_2 pressure resulted in a slight decrease in the yield of FDCA. Finally, the yield of FDCA remained at around 83% level. Moreover, the solution after reaction turned brown when high pressure O_2 was used. The probable reason is that a little humin dissolved in the solution was produced by side reaction. These results inferred the excessive O_2 possibly caused some side reaction, along with a decline in the FDCA yield.

CONCLUSION

We developed an efficient method to produce the promising biomass-derived chemical FDCA from FME, which is more stable and easier to separate by distillation than HMF. The FDCA selectivity of 93.55% and complete conversion were achieved in the mixed solvent of water and 1, 2-dioxane, when using Ru/C as catalyst and O_2 as oxidant. The investigation of conversion pathway of FMF to FDCA showed that FMF and HMF were simultaneously oxidized to DFF due to the reversible equilibrium between FMF and HMF, which was a rapid reaction; then DFF was oxidized to FFCA as the primary conversion pathway and HMFCA to FFCA as the secondary reaction pathway. Finally, FFCA was oxidized to FDCA. The oxidation of FFCA to FDCA was the rate-determining step. Furthermore, appropriate alkalinity favored the selectivity of FDCA and the conversion of FME.

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