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Aerobic oxidative esterification of 5-hydroxymethylfurfural to dimethyl furan-2, 5-dicarboxylate by using homogeneous and heterogeneous PdCoBi/C catalysts under atmospheric oxygen

Feng Li, Xing-Long Li, Chuang Li, Jing Shi and Yao Fu *

Conversion of platform molecule 5-hydroxymethylfurfural (HMF) into highvalue-added derivatives has attracted significant interest. FDCA and its esters are important derivatives of HMF, which can be used as polyester monomers and pharmaceutical intermediates. In this paper, the oxidative esterification of 5-HMF have been carried out by using homogeneous and heterogeneous PdCoBi/C catalysts under atmospheric oxygen. The effect of reaction conditions on product distribution have been studied under both homogeneous and heterogeneous catalytic conditions. The highest yield of oxidative esterification products were 93% and 96% by using homogeneous and heterogeneous PdCoBi/C catalysts, respectively. The catalysts were characterized by X-ray photoelectron spectroscopy (XPS), powder X-ray diffraction (XRD). The catalytic system had better compatibility according to the substrate extension. A proposed reaction mechanism and the recycle experiments were also carried out.

Introduction

The environmental pollution and energy crisis caused by the consumption of fossil resources were imminent. Exploring sustainable green energies was very urgent and necessary. Biomass resources, as the only renewable carbon resources, could be converted into high value-added fuels and chemicals which was an important way to solve the problems of energy and environment.^[1] Biomass-based polymer materials have dual functions of resource conservation and environmental protection. At present, the widely used biomass-based polymer materials were mainly fatty polymers such as polylactic acid (PLA), ^[2a] polyhydroxy fatty acid (PHA), ^[2b] polyglycolic acid (PGA), ^[2c] polybutylene glycol succinate (PBS) ^[2d], etc. Their mechanical properties and heat resistance were significantly lower than those of petroleum based polymers, such as aromatic polyethylene terephthalate (PET), bisphenol A epoxy resin (Epoxy), which severely limited their application. 2,5furandicarboxylic acid (FDCA) was one of the potential bio-based platform compounds evaluated by the U.S. Department of Energy. It is considered as a "sleeping giant" by DuPont and DSM corporations. ^[3] The novel polyethylene-2, 5-furandicarboxylate (PEF) prepared by polymerization of 2, 5-furandicarboxylic acid

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(FDCA) or its esters and ethylene glycol had excellent material properties. The oxygen isolation rate of PEF was six times higher than that of PET, and the isolation rate of CO_2 and water of PEF was two times higher than that of PET. The glass transition temperature of PEF was 11 degrees higher than that of PET, and the melting temperature of PEF was 40 degrees lower than that of PET. ^[4] FDCA had an aromatic ring system similar to PTA and a diacid structure needed for the synthesis of polyester. It was expected to be an important biomass based polyester material for the synthesis of green, degradable plastics and non-toxic plasticizers. ^[5] Therefore, it is of great significance to study the green and efficient synthesis method of FDCA and its esters.

According to the different sources of raw materials, the methods for preparation of 2, 5-FDCA were mainly divided into the following categories: 1) Preparation by furoic acid through disproportionation reaction or chloromethylation reaction or CO₂ solid-phase reaction. ^[6] 2) Preparation by hexaric acid through oxidation dehydration reaction.^[7] The raw materials were easily isomerized and carbonized under acidic conditions which resulting in low yield; 3) The diglycolic acid was used as the raw material to react with methanol and thionyl chloride to obtain the diglycolic acid dimethyl ester, which was then condensed with trimeric glyoxal dehydrate. But it was expensive and not suitable for largescale industrial production.^[8] 4) Preparation by furan, 2, 5-dimethyl furan, 2-methyl-5-acetyl furan, 5-methyl-2-furfural and other furan based materials through oxidative reaction. Under acidic conditions, the opening of the furan ring was more likely to cause incomplete oxidation, and the synthesis of the raw materials was difficult, which greatly reduced the selectivity of 2, 5-FDCA.^[9] 5) Preparation by 5-HMF obtained from the hydrolysis of hexoses. HMF could be

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further transformed into a wide variety of value-added derivatives. ^[10] The oxidation of HMF was the most studied reaction process at present due to an analogous structure with FDCA, namely similar functional group position.

Traditional pathway for the oxidizing of HMF to FDCA involved an equivalent oxidizing agents such as nitric acid, ^[11a] potassium hypermanganate. ^[11b] etc. However, more waste salt and lower reaction yield were main problems which were not suitable for industrial production. In this direction, homogeneous catalytic system such as Co/Mn/Br catalyst ^[12a] and TEMPO catalysts ^[12b] were developed for the improvement of reaction conditions. However, problems still remained such as reactor corrosion and catalyst recovery difficulties. Therefore, numerous supported metal or metal oxide heterogeneous catalytic systems have been developed (e.g. Au, ^[13] Pd, ^[14] Ru, ^[15] Fe, ^[16] etc.) for the conversion of HMF to FDCA and higher selectivity and yield were obtained. However, due to the special physical and chemical properties of FDCA, its solubility was poor in water and most organic solvents. Purification by conventional crystallization and rectification was difficult, which limited the application scale of FDCA. Furan dicarboxylic acid esters, especially dimethyl furan dicarboxylate (DMFDCA), could be easily separated and purified from reaction due to the lower boiling point and could be used as ideal substitute of FDCA. Therefore, it was of great significance to study the selective one-step oxidation of 5-HMF to DMFDCA. The oxidative esterification of HMF to DMFDCA undergone two reaction pathways: 1) The aldehyde group was converted to 5hydroxymethyl-2-methyl-furoate through oxidative esterification, then the hydroxyl is oxidized to 5-formyl-2-methyl-furoate; 2) The hydroxyl group was first oxidized to DFF, and then aldehyde group was esterified to 5-formyl-2-methyl-furoate. Finally, aldehyde group was oxidized and esterified to obtain DMFDCA.



Scheme 1. The reaction pathways of HMF under the oxidative esterification conditions.

In 2008, Christensen *et al.* realized the catalytic oxidation of 5-HMF to DMFDCA in the presence of sodium methoxide at 130 °C and 4 atm via Au/TiO₂ catalyst with a yield of 98%. ^[17] Corma *et al.* reported the oxidative esterification of 5-HMF with Au/CeO₂ as a catalyst at 130 °C and 10 atm O₂ to obtain a 99% yield. ^[18] Subsequently, Maela Manzoli developed a catalytic system for oxidative esterification of furfural and HMF over Au/ZrO₂ catalyst under 1 atm O₂ that high yields and selectivity were obtained.^[19] In addition to the Au-based catalysts, Fu *et al.* reported that DMFDCA could be prepared via CoxOy-N@C catalyst at (100 °C, 10 atm O₂) with a 96% yield. ^[20] In 2016, high yield of furan-2,5-dimethylcarboxylate (FDMC, 95.6 %) without basic additive was obtained by using CoOx-N/C and α -MnO₂-Cu catalyst (3 atm O₂, 100 °C). ^[21] Recently, Tong *et al.* used MnO₂-Cu catalyst (3 atm O₂, 140 °C), and found that the selectivity of DMFDCA was only 26.5%.

^[22] Stahl *et al.* reported that alcohols could be oxidized to esters or acids with high selectivity by using PdBiTe catalysts. ^[23] Overall, the selective aerobic oxidative esterification of HMF was still under high temperature or certain pressure. Therefore, it was still a challenge to develop a high selectivity catalytic system for oxidizing esterification of 5-HMF to DMFDCA under mild conditions with both normal pressure and low temperature.

Herein, a homogeneous catalytic system and a heterogeneous catalytic system were designed for the selective oxidative esterification of HMF to DMFDCA. The effect of various additives on the product distribution was investigated initially. Based on these studies, the reaction conditions such as catalyst loadings, catalyst proportion, alkali type and alkali amount, *etc.* were screened subsequently. In order to realize the recyclability of catalytic system, the heterogeneous catalyst was prepared. Meanwhile, the characterization of XRD and XPS, *etc.* were carried out for the investigation of structure activity relationship of catalysts. The possible reaction mechanism was also proposed and supported by ¹H-NMR and infrared spectra (IR) analysis of the reaction solutions.

Experimental Section

Materials and reagents

All the chemicals used in the experiments were commercially available. 5-Hydroxymethylfurfural was sponsored by Hefei Leaf Biotech Co., Ltd. Pd/C (10 wt %) was purchased from Alfa Aesar (China) Chemicals Co., Ltd. $ZrO(NO_3)_2$, $Fe(NO_3)_3.9H_2O$, Ni(NO_3)_2.6H_2O, Ce(NO_3)_3, Se, Co(NO_3)_2.6H_2O, Pb(NO_3)_2, Bi(NO_3)_3, K_2CO_3, NaOAc, NaHCO_3, Na_2CO_3, NaOH, KOH, Et_3N, KH_2PO_3, Ethyl benzoate , Conc HCl ,Conc HNO_3 and SOCl_2 were purchased from Sinopharm Chemical Reagent Co.,Ltd. *t*-BuOLi, *t*-PenONa were purchased from Meryer (Shanghai) Chemical Technology Co., Ltd.

Catalyst preparation and characterization

Co(NO₃)₂.6H₂O (146 mg , 5 mmol) and Bi(NO₃)₃ (198mg ,5 mmol) were dissolved in a mixture of 2 mL HCl and 0.2 mL conc HNO₃ while stirred at room temperature for 5 minutes, then added to a flask which mixed with 32 mL of deionized water and 530 mg 10 wt % Pd/C . Reaction was kept at 50 °C for 3 h. After 3 h, 1.2 mL of 30% NaOH solution was added to adjust the mixture alkaline. Then, 0.4 mL of 37% formaldehyde was added, and the mixture was heated to 80 °C under Ar₂ for 16 h. After the mixture was cooled to room temperature, the catalyst was filtered, washed with deionized water for several times until neutral, and dried under vacuum at 70 °C for 48 h to afford heterogeneous catalyst (PdCoBi/C).

Catalysts were characterized by X-ray photoelectron spectroscopy (XPS), X-ray power diffraction (XRD). X-ray photoelectron spectroscopy (XPS) data were obtained with a Thermo Scientific Escalab 250-X-ray photoelectron spectrometer which equipped a hemispherical electron analyzer and an Al K α X-ray source. All binding energies were referenced to C 1s line at 284.7 eV. X-ray power diffraction (XRD) patterns were obtained on X' pert (PANalytical) diffractometer with Ni-filtered Cu-K α radiation, at 40 kV and 40 mA. 2 θ range was 20°~80°. ¹H-NMR and ¹³C-NMR spectra

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were recorded on a Bruker Avance 400 spectrometer at ambient temperature. NMR spectra were analysed with MestReNova software.

Typical experiment and product analysis

20 mol% K₂CO₃, 5 mol% Pd(10 wt% Pd/C), 5 mol% Co(NO₃)₂, 5 mol% Bi(NO₃)₃, 2 mL MeOH were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and agitated under 1 atm O₂. After the mixture was heated to 60 °C , 0.5 mmol 5-HMF was added to the vessel, then reaction was kept at 60 °C under 1 atm for 14 h. After reaction, the mixture was cooled to room temperature, SOCl₂ was added and the mixture was stirred at room temperature for 2 h, 0.5 mmol ethyl benzoate was added as an internal standard. Then the solution was analyzed with HPLC. The conversion of 5-HMF and the yield of products were calculated according to the following formula:

$$Conv/\% = \frac{n_{5-HMF} - n'_{5-HMF}}{n_{5-HMF}} \times 100\%$$
$$Y/\% = \frac{n_{(mole of product)}}{n_{5-HMF}} \times 100\%$$

 n_{5-HMF} : mol of 5-HMF before reaction n'_{5-HMF} : mol of 5-HMF after reaction

Typical heterogeneous experiment and product analysis

20 mol% K_2CO_3 , 5 mol% PdCoBi/C catalyst, and 2 mL MeOH were added to a Schlenk tube equipped with a stir bar. The vessel was evacuated and agitated under 1 atm O_2 . After the mixture was heated to 60 °C, 0.5 mmol 5-HMF was added to the vessel, then reaction was kept at 60 °C under 1 atm O_2 for 14 h. After reaction, the mixture was cooled to room temperature, 0.5 mmol ethyl benzoate was added as an internal standard. Then the solution was analyzed with HPLC. The conversion of 5-HMF and the yield of products were calculated according to the following formula:

$$\begin{split} &\text{Conv}/\% = \frac{n_{5-\text{HMF}} - n_{5-\text{HMF}}'}{n_{5-\text{HMF}}} \times 100\% \\ &\text{Y}/\% = \frac{n_{(\text{mole of product})}}{n_{5-\text{HMF}}} \times 100\% \\ &n_{5-\text{HMF}} \text{: mol of 5-HMF before reaction} \\ &n_{5-\text{HMF}}' \text{: mol of 5-HMF after reaction} \end{split}$$

Results and Discussion

The selective oxidative esterification of HMF to DMFDCA were carried out in the presence of Pd/C catalyst, additives and alkali in methanol solvent under atmospheric pressure oxygen (Table 1). Additives including transition metals, non-metallic elements and metal nitrate were screened initially. Firstly, the additives of zirconyl nitrate with iron nitrate, nickel nitrate, cerium nitrate, selenium, and cobalt nitrate were carried out, but they did not give satisfactory results (Table 1, Entries 1-5). Then the combination of iron nitrate with nickel nitrate, cerium nitrate and selenium were tested, and only small amounts of oxidative esterification products were obtained (Table 1, Entries 6-8). Then cobalt nitrate was combined with selenium or metal salts (Table 1, Entries 9-13). It was found

that the yield of DMFDCA was increased to 42% by using cobalt nitrate and bismuth nitrate as co-additives (Table 1, Entry 10). With above reaction results, it was found that bismuth nitrate and cobalt nitrate have a great effect on this reaction. This might be caused by the formation of geminal diol intermediate state during the reaction, while bismuth atom had strong affinity for oxygen. The formation of Bi-O bond could promote the adsorption of substrate on the catalyst surface to form geminal diol intermediates, which was favorable for the dehydrogenation of geminal diol intermediates to obtain acid by using Pd-based catalysts. Meanwhile, the formation of complexes adsorbed on the metal surface could also inhibit the Pd catalyst acidosis. ^[24] It was found that the conversion of HMF and the selectivity of products were still poor, which might be related to the reaction conditions.

Table 1. The oxidative esterification of HMF with different catalysts^a

но	2.5 mol% Pd/C 2.5 mol% additive A 2.5 mol% additive B 20 mol% K ₂ CO ₃	нооме +	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	Meo	
HMF	MeOH, 60 °C 1 bar O ₂ , 14 h	HMMF	FMF	DMFDCA	

Entry	Additives	Conversion ^b [0/1	Yield ^b [%]		
	A/B	Conversion [%]	HMMF	FMF	DMFDCA
1	ZrO(NO ₃) ₂ /Fe(NO ₃) ₃	32	18	7	6
2	ZrO(NO ₃) ₂ /Ni(NO ₃) ₂	42	25	7	9
3	ZrO(NO ₃) ₂ /Ce(NO ₃) ₂	42	18	8	13
4	ZrO(NO ₃) ₂ /Se	39	10	4	22
5	ZrO(NO ₃) ₂ / Co(NO ₃) ₂	29	12	3	13
6	Fe(NO ₃) ₃ /Ni(NO ₃) ₂	28	10	4	14
7	Fe(NO ₃) ₃ /Ce(NO ₃) ₃	30	18	2	9
8	Fe(NO ₃) ₃ /Se	24	6	3	14
9	Co(NO ₃) ₂ /Se	42	13	4	23
10	Co(NO ₃) ₂ / Bi(NO ₃) ₃	70	25	3	42
11	$Co(NO_3)_2/Ce(NO_3)_2$	48	25	10	12
12	Co(NO ₃) ₂ / Fe(NO ₃) ₃	42	17	6	16
13	Co(NO ₃) ₂ / Ni(NO ₃) ₃	39	20	4	13

[a] Reactions conditions : 0.5 mmol HMF, 2.5 mol% Pd/C catalyst, 2.5 mol% A, 2.5 mol% B, 20 mol% K_2CO_3 as base, 2 mL MeOH, under 1 atm O_2 , 14 h, 60 °C. [b] The yields were determined by HPLC, ethyl benzoate was used as internal standard. HMMF: 5-hydroxymethyl-2-methyl-furoate). FMF: 5-formyl-2-methyl-furoate. DMFDCA: dimethyl furandicarboxylate.

To gain further insight into our reaction, the detailed analysis of reaction conditions were carried out.

Effect of catalyst ratio

The effect of catalyst ratio on product distribution was investigated and the results were shown in **Figure 1**. Without the addition of Pd/C catalysts, no reaction was occurred. It has been reported that Pd/C catalyst could catalyse the conversion of alcohol to carboxylic acid, but the reaction needed an equivalent amount of base.^[25] The yield of DMFDCA was only 30%, and the conversion of HMF was 65% with Pd/C catalyst

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alone. It showed that Pd/C could catalyse the reaction but the yield was lower. There was no oxidative esterification products obtained by using a single $Co(NO_3)_2$ or $Bi(NO_3)_3$ or $Co(NO_3)_2$ and $Bi(NO_3)_3$ co-additives. The conversion of substrate was significantly improved to 94% and 92% by using Pd/C+ $Bi(NO_3)_3$ or Pd/C+ $Co(NO_3)_2$ catalyst system, respectively. This showed that the presence of Co or Bi both promoted the oxidative esterification reaction. ^[26]



Figure 1. Reactions conditions: 0.5 mmol HMF, 20 mol% K_2CO_3 as base, 5% Pd/C as catalyst, $Co(NO_3)_2$ and $Bi(NO_3)_3$ as additives, 2 mL MeOH, 1 atm O_2 , 14 h, 60 °C. The yields was determined by HPLC, ethyl benzoate was used as internal standard. HMMF: 5-hydroxymethyl-2-methyl-furoate. FMF: 5-formyl-2-methyl-furoate. DMFDCA: dimethyl furandicarboxylate.

It was found that HMMF obtained by using Pd/C+ Bi(NO₃)₃ cocatalysts was lower than that obtained by using $Pd/C+Co(NO_3)_2$ cocatalysts, and the yield of DMFDCA was higher than those of Pd/C+ Co(NO₃)₂ co-catalysts. This indicated that the presence of Bi was not only conducive to the conversion of substrate, but also the promotion of oxidative esterification. ^[27] The use of $Bi(NO_3)_3$ alone had no effect on the reaction, but it could greatly increase the catalytic activity and product selectivity combined with Pd/C+ $Co(NO_3)_2$. Comparing with the experimental results in Table 1, the selectivity of products were still poor by using Pd/C+ $Bi(NO_3)_3$ + $Co(NO_3)_2$ co-catalysts and the amount of catalysts were 2.5 mol%. The yield of DMFDCA increased greatly with a yield of 93% and no FMF was observed while increased the amount of catalysts to 5 mol%. On this basis, the catalyst ratio was further investigated (Figure 1). The yield of DMFDCA were 62% and 89% as the ratio of Pd: Co: Bi was 5:5:2.5 and 5:5:7.5, respectively. The yield of DMFDCA was 63% and 87% as the ratio of Pd: Co: Bi was 5:2.5:5 and 5:7.5:5, respectively. The decrease amount of $Co(NO_3)_2$ or $Bi(NO_3)_3$ was not conducive to the increased yield of DMFDCA. The yield of DMFDCA extremely decreased to 53% as the proportion of Pd decreased to 2.5% (Pd: Co: Bi = 2.5:5:5). The results showed that increasing the amount of a single additive could promote the reaction. The yield of DMFDCA was similar as the ratio of Pd: Co: Bi increased from 5:5:5 to 7.5:7.5:7.5, and the optimal ratio of catalysts was 5: 5: 5.

Effect of alkaline species

The alkali strength and alkalinity have important effect on oxidative esterification of alcohols. The effect of bases on the product distribution was investigated and the results were showed in the Figure 2. The weak bases such as sodium acetate, sodium bicarbonate and sodium carbonate were investigated. Only 21% conversion of HMF and 7% yield of the oxidative esterification products were obtained by using sodium acetate as alkali. The yield of DMFDCA increased to 32% by using sodium bicarbonate as alkali. It showed that the rate of oxidation increased with the increase of alkalinity. This was mainly caused by the presence of alkali, which could promote in the hydration of the aldehyde. The hydration of aldehyde group to geminal diol group was lowered with lower reaction pH. ^[24a] As a result, the strong base potassium carbonate was used, and the yield of DMFDCA was significantly increased to 93%. The use of potassium hydroxide only generated small amount of DMFDCA. This might be due to the gradual degradation of HMF (Cannizzaro reaction) under high pH. $^{\left[28\right]}$ The better oxidative esterification yield was obtained by using the stronger organic bases (t-BuOLi, t-PenONa). The weak organic base such as triethylamine, almost could not promote the reaction. Finally, the weakly acidic potassium dihydrogen phosphate (KH₂PO₄) was further investigated and no product was observed. Therefore, the suitable strength of alkali was beneficial for the oxidative esterification of 5-HMF.



Figure 2. Reactions conditions : 0.5 mmol HMF, 5 mol% Pd/C catalyst, 5 mol% Co(NO₃)₂, 5 mol% Bi(NO₃)₃, 20 mol% base, 2 mL MeOH, 1 atm O₂, 14 h, 60 °C. The product yields were determined by HPLC, ethyl benzoate was used as internal standard. HMMF: 5-hydroxymethyl-2-methyl-furoate. FMF: 5-formyl-2-methyl-furoate. DMFDCA: dimethyl furandicarboxylate.

Effect of alkali amounts

The effect of alkali amounts on product distribution was investigated and the results were listed in **Figure 3**. No conversion of HMF was observed in the absence of base, which indicated that alkali played an important role in the oxidative esterification reaction. The conversion of HMF was occurred (25% of conversion) as the alkali amount was increased to 10 mol%. Meanwhile, the yield of oxidative esterification product DMFDCA were 15%, and the yield of

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intermediate HMMF and FMF was 5% severally. It showed that the alkali promoted the oxidative reaction, but the rate of reaction was slower due to the small amount of alkali. Increasing the alkali amount to 20 mol%, HMF was completely converted and the main product was DMFDCA.



Figure 3. Reactions conditions : 0.5 mmol HMF, 5 mol% Pd/C catalyst, 5 mol% Co(NO₃)₂, 5 mol% Bi(NO₃)₃, K₂CO₃ as base, 2 mL MeOH, 1 atm O₂, 14 h, 60 °C. The product yields were determined by HPLC, ethyl benzoate was used as internal standard. HMMF: 5-hydroxymethyl-2-methyl-furoate. FMF: 5-formyl-2-methyl-furoate. DMFDCA: dimethyl furandicarboxylate.

The content of FMF in the mixture was always low. This might mainly due to the fast conversion rate of aldehyde group in the reaction system, which led to the rapid conversion of the intermediate FMF into DMFDCA. The conversion of HMF was complete, but the yield of the oxidative esterification products decreased obviously as the amount of alkali was increased to 50 mol%. It might be that the aldehyde groups belonged to HMF and intermediate FMF were disproportionated with increasing the alkali amount, which led to the reduced selectivity and yield of DMFDCA. ^[28] The yield of oxidative esterification product DMFDCA almost unchanged with the alkali amounts increased to 100 mol%. The yield of DMFDCA increased firstly and then decreased with the alkali amounts increased from 10 mol% to 100 mol%. Increasing the alkali amount not only promoted the oxidative esterification reaction of hydroxyl and aldehyde groups, but also promoted the saponification reaction. Therefore, a suitable alkali amount was beneficial to obtain the higher selectivity of DMFDCA, and an alkali amount of 20 mol% was suitable herein.

Effect of reaction time

The effect of reaction time on product distribution was studied to better analysis the reaction pathway. (Figure 4) The conversion of HMF was about 80% and the generation of HMMF and DMFDCA were observed after 1 h. Among them, the product HMMF, which obtained from the esterification of aldehyde group on HMF, was the major product with a yield of 53%. The yield of DMFDCA was 24%, while the yield of FMF was much lower. This indicated that the aldehyde group of HMF was easier to oxidize and esterify at the initial stage of reaction. This was probably due to the fact that the hemiacetal was easily formed from the aldehyde group in the presence of methanol. It have been reported that the hemiacetal at the benzyl group was more easily oxidized than that of aldehyde group to obtain an esterified product.^[29] This might be the reason

that the intermediate FMF could hardly been detected. It also showed that the oxidative esterification of aldehyde groups was a fast step. The lower yield of MFDCA also showed that the aldehyde group was not easily oxidized in the catalytic system to obtain a carboxyl product. Along with the extension of reaction time, the conversion of 5-HMF was completed, the yield of intermediate HMMF gradually decreased and the yield of DMFDCA increased gradually. The highest yield of oxidative esterification product reached to 96% after 16 h.



Figure 4. Reactions conditions : 0.5 mmol HMF, 5 mol% Pd/C catalyst, 5 mol% Co(NO₃)₂,5 mol% Bi(NO₃)₃, 20 mol% K₂CO₃, 2 mL MeOH, 1 atm O₂, 60 °C. The yields were determined by HPLC, ethyl benzoate was used as internal standard. HMMF: 5-hydroxymethyl-2-methyl-furoate. FMF: 5-formyl-2-methyl-furoate. DMFDCA: dimethyl furandicarboxylate.

Effect of heterogeneous PdCoBi/C catalysts

 Table 2. The optimization of reaction conditions by using heterogeneous

 PdCoBi/C catalysts^a

Entry	Pd: Co:	Conversion ^b [9/1	Yield ^b [%]		
	Bi		HMMF	FMF	DMFDCA
1	1:1:0.5	91	28	7	55
2	1:0.5:1	95	19	3	71
3	0.5:1:1	94	15	10	68
4	1:1:1	99	3	0	96
5	1:1:1.5	97	5	2	89
6	1:1.5:1	97	6	3	86
7	1.5:1:1	98	9	5	82
8 ^c	1:1:1	88	1	1	86
9 ^d	1:1:1	90	62	5	20
10 ^e	1:1:1	97	19	1	76

[a] Reactions conditions: 0.5mmol HMF, 20 mol% K_2CO_3 , 10 mol% PdCoBi/C catalyst, 2 mL MeOH, 1 atm O_2 , 14 h, 60 °C. [b]The yields were determined by HPLC, ethyl benzoate was used as internal standard. [c]. 5 mol% PdCoBi/C catalyst. [d]. no base was used. [e] Air was used instead of O_2 . HMMF: 5-hydroxymethyl-2-methyl-furoate. FMF:5-formyl-2-methyl-furoate.DMFDCA: dimethyl furandicarboxylate.

In order to better study the interaction of the various components in catalyst, the heterogeneous catalysts were prepared according to the literature ^[20c] and the effect of catalyst ratio on product distribution was investigated and the

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results were listed in Table 2. The effect of catalyst ratios had a great effect on product distribution according to the above results. Similar results were found by using heterogeneous catalysts. The highest yield of DMFDCA was 96% as the ratio of Pd: Co: Bi=1:1:1 (Table 2, Entry 4). The yield of DMFDCA decreased to 55% with the ratio of Bi decreased from 1 to 0.5 (Table 2, Entry1), the yield of DMFDCA decreased from 96% to 89% as the ratio of Bi increased from 1 to 1.5 (Table 2, Entry 5). It showed that the ratio of Bi had a great effect on product distribution. Similarly, the ratio of Pd and Co also affected the product yield. The yield of DMFDCA decreased to 71% and 86% with the ratio of Co decreased to 0.5 and increased to 1.5, respectively (Table 2, Entries 2 and 6). The yield of DMFDCA decreased to 68% and 82% with the ratio of Pd decreased to 0.5 and increased to 1.5, respectively (Table 2, Entries 3 and 7). It was shown that increasing the proportion of one metal could not obtain the best reaction effect. The optimal ratio of Pd: Co: Bi was 1:1:1.

The yield of DMFDCA were 86% and 96% with 5 mol% and 10 mol% catalyst loading, respectively (**Table 2, Entries 8 and 4**). Meanwhile, the effect of alkali on product distribution was further investigated in the heterogeneous system. Under the homogeneous system, no oxidative esterification products were formed without alkali (Figure 3). But under the condition of heterogeneous catalysts, 20% yield of DMFDCA was obtained without the addition of alkali (**Table 2, Entry 9**). This showed that the interaction between the three metals was conducive to the occurrence of oxidative esterification reaction. 76% yield of DMFDCA was obtained by replacing oxygen with air (**Table 2, Entry 10**). and used directly for the next cycle. The effect of catalyst circulation on product distribution was listed in **Figure 5**. The conversion of raw materials and the yield of oxidative esterification product gradually decreased with the increased catalyst recycling times. However, only the yield of product HMMF was gradually increased. This might be caused by the loss of the catalyst during the treatment process. After the catalyst was recycled four times, the amount of recycled catalyst was weighed and fresh heterogeneous catalyst was added to 10 mol%. A good catalytic activity and 91% yield of DMFDCA were obtained. Characterization with XRD and XPS analyses of both fresh and used catalysts were conducted. (**Figure S1- Figure S4**) No significant changes of the fresh and used catalysts were found according to the analysis of the XRD spectra and XPS spectra. The catalyst exhibited a better stability.

Scope of substrates

Oxidative esterification of different alcohols in the presence of catalysts were also investigated. It was found that good yields could be obtained with aryl substrates. Substrates containing electrondonating groups (e.g., methoxy, methyl) could be converted to the desired products smoothly with good to excellent isolated yields, while the yield of substrates with electron-withdrawing groups (e.g., nitro) were slightly decreased. With p-chlorobenzyl alcohol as substrate, the oxidative esterification product was obtained with a much lower 70% yield, which might be caused by the dehalogenation reaction in the presence of a strong base. High yield was obtained with furfuryl alcohol as a substrate, indicated that this catalytic system has an excellent compatibility with furan derivatives. Regarding to the fatty alcohols, such as octanol, moderate yield was obtained.

Table 3. The scope of substrates

Catalyst recirculation



Figure 5. Reactions conditions: 0.5 mmol HMF, 20 mol% K₂CO₃, 10 mol% PdCoBi /C (1:1:1) catalyst, 2 mL MeOH, 1atm O₂, 14 h, 60 °C. The yields were determined by HPLC, ethyl benzoate was used as internal standard. Number 5: Fresh heterogeneous catalyst was added to 10 mol% after recycling 4 times. HMMF: 5-hydroxymethyl-2-methyl-furoate. FMF: 5-formyl-2-methyl-furoate. DMFDCA: dimethyl furandicarboxylate.

The recycling experiment was carried out subsequently. (Figure 5) The experimental procedure was carried out as follows: after the reaction, the solution was centrifuged to separate the catalyst, the catalyst was washed with methanol twice, centrifuged



Reactions conditions: 0.5 mmol HMF, 20 mol% K_2CO_3 , 10 mol% PdCoBi/C (1:1:1) catalyst, 2 mL MeOH, 1atm O_2 , 14 h, 60 °C.

Reaction mechanism

A proposed reaction mechanism was carried out according to the previous study of the reaction process (**Scheme 2**). The conversion of HMF might undergo three reaction pathways in the presence of a catalyst, methanol and oxygen: a) the hemiacetal intermediate **E** was obtained through hemiacetal reaction of the aldehyde group on HMF; b) the etherified intermediate **F** obtained through etherification of the hydroxyl

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group on HMF; c) the product DFF obtained from the oxidation of hydroxyl group on HMF. No production of intermediates **F** and DFF were observed through monitoring of the products. This was mainly due to the etherification reaction was difficult to occur under alkaline conditions.



Scheme 2. Possible reaction pathways.

The reason for the main obtained product intermediate E was that acetal and hemiacetal reactions of aldehyde group were easier to carry out in alcoholic solvents. This was also the reason that no DFF product could be detected. The intermediate E was converted to intermediate HMMF more easily due to the active hemiacetal structure. With the occurrence of oxidation reaction, the hydroxyl group in intermediate HMMF undergone further oxidation reaction to obtain the aldehyde product FMF. The intermediate FMF was mostly converted to the oxidative esterification product D under the catalytic system, and only small amount of the aldehyde-based oxidized product C was formed. This showed that intermediate FMF was mainly converted through the hemiacetalization and reoxidation of aldehyde groups, rather than the direct oxidation process. During the reaction process, the oxidation of hydroxyl group to aldehyde group was the rate-limiting step. To further study the mechanism, the ¹H-NMR and the Infrared Spectra (IR) analysis on 0.5 h, 8 h, and 14 h of the reaction mixture were carried out. The characteristic peaks of HMMF and FMF were obviously observed according to ¹H-NMR analysis. The ¹H-NMR characteristic peaks of HMF, HMMF, FMF, and DMFDCA were successfully detected while reaction proceed at 0.5 h. The characteristic peaks of HMMF and FMF extremely decreased after 8 h. When the reaction time prolonged to 14 h, the characteristic peaks of FMF disappeared and very small amount of HMMF was observed. The results were listed in Figure S5-Figure S7 (SI) and corresponding statements have been added and highlighted in manuscript.

According to the Infrared Spectra (**IR**, **SI**, **Figure S8**), the obvious aldehyde peaks of FMF could be observed as the reaction was carried out for 0.5 h. This indicating that the intermediate FMF was generated during the reaction. In combination with the ¹H-NMR analysis, the characteristic peaks of the hydroxyl group was the overlap of HMMF and HMF. When the reaction was prolonged for 14 h, only the characteristic peaks of ester group belonged to FDCA were observed.

The efficient conversion of HMF to oxidative esterification product DMFDCA was carried out with using homogeneous and heterogeneous PdCoBi/C catalysts under atmospheric oxygen. The highest yield of DMFDCA was 93% with 10% Pd/C as catalyst, $Co(NO_3)_2$ and $Bi(NO_3)_3$ as additives, 20 mol% K₂CO₃ as base, 1 atm O₂, 14 h, 60 °C. The highest yield of DMFDCA was 96% with 10 mol% PdCoBi/C (1:1:1) catalyst, 20 mol% K₂CO₃ as base, 1 atm O₂, 14 h, 60 °C. The catalytic system had good compatibility according to the expansion of substrate. It was found that the reduced reaction activity in the circulation was caused by the loss during the treatment according to the XRD spectra and XPS spectra characterization. The oxidation of hydroxyl group to aldehyde group was the rate-limiting step of reaction according to the study of reaction mechanism.

Conflicts of interest

There are no conflicts of interest to declare.

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Conclusions

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