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# An effective strategy for high-yield furan dicarboxylate production for biobased polyester applications

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**ABSTRACT:** A unique strategy for the formation of furan-2,5-dicarboxylic acid (FDCA)derived esters with methanol and ethylene glycol in concentrated solutions was reported using a six-membered ring acetal of (5-hydroxymethyl)furfural (HMF) with 1,3-propanediol, in order to improve the economics for the production of polyethylene 2,5-furandicarboxylate (PEF), a biobased polyester. Aerobic oxidative esterification with methanol and ethylene glycol in the

presence of a CeO<sub>2</sub>-supported Au catalyst gave 80-95% yields of methyl furan-2,5-dicarboxylate and bis(2-hydroxyethyl) furan-2,5-dicarboxylate from concentrated HMF-acetal solutions (10-20 wt%). Kinetic studies combined with density functional theory (DFT) calculations are used to identify two key steps for the conversion of the cyclic acetal ring to the corresponding methyl ester: (i) partial hydrolysis of the acetal ring by OH<sup>-</sup> ions and (ii) subsequent oxidation of the hemiacetal in solution by molecular  $O_2$  on Au nanoparticles. These results not only represent a significant contribution to cutting-edge conversion technology for renewable biomass feedstocks to PEF-based applications, but also to opportunities for the efficient conversion of substrates with a reactive formyl group in high yield.

**KEYWORDS:** biomass conversion, biobased polymer, oxidative esterification, acetal functionality, supported Au catalyst

# **1. INTRODUCTION**

Renewable feedstocks are essential for the transformation of the chemical industry to the sustainable production of commodity chemicals.<sup>1-4</sup> Chemo-catalytic conversion of non-edible biomass to value-added chemicals will be a main contributor to comply with sustainable development goals. FDCA synthesized from lignocellulose biomass is widely recognized as a suitable replacement for petroleum-derived terephthalic acid in plastics applications.<sup>5,6</sup> Polymerization of the dimethyl ester of FDCA with ethylene glycol forms PEF, which possesses physical, mechanical, and thermal properties superior to polyethylene terephthalate (PET).<sup>7</sup> PEF is a promising 100% renewables-based polymer derived from plants that can replace the giant of the plastic industry, PET (global annual production >50 MT).<sup>5,8-14</sup> PEF has better barrier

properties and higher tensile strength than PET; therefore, less additives are required, which makes this next-generation polyester also a better recyclable product. Despite its great potential, efficient PEF production systems that use heterogeneous catalysts are limited to dilute solutions  $(\leq 5 \text{ wt\%})$ ,<sup>15-18</sup> which results in low productivity and high energy costs during work-up.





**Figure 1.** Schematic illustration of the present and proposed pathways for the production of PEF from cellulosic biomass. High-quality PEF can be synthesized by self-condensation of bis(2-hydroxyethyl) furan-2,5-dicarboxylate (HEFDC). The conventional process involves three steps to synthesize HEFDC from HMF: aerobic oxidation of HMF (Step 1), esterification of FDCA with methanol (Step 2), and transesterification of methyl furan-2,5-dicarboxylate (MFDC) with ethylene glycol (Step 3). The proposed process here enables the synthesis of MFDC (Step 4) and HEFDC (Step 5) in a one-pot reaction system by aerobic oxidative esterification from PD-HMF with methanol and ethylene glycol, respectively.

The production of PEF is based on the polycondensation of two biobased monomers, methyl furan-2,5-dicarboxylate (MFDC) and ethylene glycol (Figure 1). However, to achieve commercially interesting chain lengths, the condensation by-products must be removed. A typical strategy is to first react MFDC with ethylene glycol to bis(2-hydroxyethyl) furan-2,5-dicarboxylate (HEFDC), followed by self-condensation to a high-molecular weight product.<sup>12,13</sup> Direct polymerization of FDCA with ethylene glycol is less preferred because the use of FDCA causes undesirable side-reactions, including decarboxylation, and produces low-quality PEF with impurities.<sup>5,12</sup> Cost-competitive and practical PEF production thus relies heavily on the efficient production of MFDC and HEFDC from concentrated HMF solutions. An attractive alternative to the conventional oxidation-esterification route of MFDC with FDCA as an intermediate is the oxidative esterification of HMF in methanol, which would lower the energy cost due to the smaller number of reaction steps and the ease of product purification (Figure 1). While easily separable and reusable heterogeneous catalysts have already been successfully applied for this reaction, a major limitation is that high MFDC yield (95-99%) can only be obtained in dilute

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HMF solutions (0.2-5 wt%, see Table S1).<sup>19-23</sup> At higher concentrations, aerobic oxidation of HMF leads to solid by-products, which drastically limit the product yield.<sup>24-26</sup> Likewise, it would be desirable to prepare HEFDC in a one-pot synthesis from HMF and ethylene glycol through oxidative esterification. Self-polymerization of HEFDC produces high-quality PEF polymer in a single step (Figure 1).<sup>12</sup> An additional benefit of such a solvent-less process is that ethylene glycol can be easily recovered and reused for HEFDC production. However, there are no examples in the literature of HEFDC synthesis from HMF using either homogeneous or heterogeneous catalysts.

To perform these desirable oxidative esterification reactions at commercially relevant HMF concentrations, we exploit the stability of the HMF-acetal with 1,3-propanediol (PD-HMF).<sup>24</sup> This acetal, which is stable in concentrated aqueous solution (10-20 wt%), can be converted with appropriate catalysts into useful products such as FDCA. The stable six-membered ring acetal obtained by reaction with the diol protects the highly reactive formyl group from side-reactions that occur at higher rates with an increase in the HMF concentration. Here we show that aerobic oxidative esterification of PD-HMF with methanol and ethylene glycol in the presence of suitable heterogeneous catalysts can result in successful conversion to MFDC and HEFDC, respectively, in excellent yield.

# 2. EXPERIMENTAL SECTION

### 2.1. Preparation and characterization of a ceria-supported Au catalyst

A ceria-supported Au catalyst was synthesized by the deposition precipitation method.<sup>27</sup> HAuCl<sub>4</sub> (350 mg) was dissolved with deionized water (350 mL) and the pH of the solution was adjusted to 10 by addition of 0.2 M NaOH solution. The solution was mixed with a mixture of H<sub>2</sub>O (50 mL) and CeO<sub>2</sub> (4 g, JRC-CEO-2, a reference catalyst supplied from the Catalyst Society of Japan), and the pH of the mixture was again adjusted to pH 10 with NaOH. After stirring the mixture for 18 h at room temperature, a yellow solid was collected by centrifugation and repeatedly washed with deionized water until no white precipitate was formed in the filtrate by the addition of aqueous AgNO<sub>3</sub> solution. The solid was dried at 353 K for 3 h and then used as an oxidation catalyst for HMF and its acetal derivatives. The Au content of Au/CeO<sub>2</sub> was determined by inductively coupled plasma atomic emission spectroscopy (ICPE-9000, Shimadzu) to be 2.0 wt%. The Au/CeO<sub>2</sub> catalyst with a Au loading of 2.0 wt% was used as the sole oxidation catalyst in this study, because a similar material was reported to be highly active and selective for HMF oxidation to FDCA as well as oxidative esterification of HMF to MFDC.<sup>9,19,24</sup> Parent CeO<sub>2</sub> and the supported Au catalyst were characterized using powder X-ray diffraction (XRD), N<sub>2</sub> adsorption-desorption, and transmission electron microscopy (TEM) measurements. Powder XRD patterns were obtained with a diffractometer (Ultima IV, Rigaku) using Cu Ka radiation (40 kV, 40 mA) over the 2 $\theta$  range of 5–90°. Nitrogen adsorption–desorption isotherms were measured at 77 K with a surface area analyzer (3-FLEX, Micromeritics Instrument Corporation). Prior to measurement, the samples were heated at 473 K for 1 h under vacuum to remove physisorbed water. The Brunauer-Emmett-Teller (BET) surface areas were estimated over a relative pressure  $(P/P_0)$  range of 0.05–0.30. TEM observations were conducted using a microscope (JEM-2100F Jeol Ltd.) without metal deposition on the sample.

# **Catalytic oxidation**

Aerobic oxidative esterification of HMF and its acetal derivatives (MeO-HMF, EG-HMF, PD-HMF) to MFDC was performed with methanol in a Teflon-lined stainless-steel autoclave. A mixture of the substrate (10-200 mg), Au/CeO<sub>2</sub> (10-200 mg, substrate/catalyst = 1), Na<sub>2</sub>CO<sub>3</sub> (2.0 molar equivalents with respect to the substrate), and methanol (0.5-10 g) was stirred in an  $O_2$ atmosphere (pressure 0.5 MPa) at 403 K. These conditions were reported as optimized reaction conditions for aerobic oxidation of PD-HMF in water.<sup>24</sup> Aerobic oxidative esterification of HMF and PD-HMF to HEFDC was also conducted in pure ethylene glycol or in N,N'dimethylformamide (DMF) with ethylene glycol (2.5 molar equivalents with respect to the substrate). For HEFDC formation in ethylene glycol, a mixture of the substrate (HMF or PD-HMF, 100 mg), Au/CeO<sub>2</sub> (100 mg, substrate/catalyst = 1), Na<sub>2</sub>CO<sub>3</sub> (2.0 molar equivalents with respect to the substrate), and ethylene glycol (1 or 2 g) was stirred in an O<sub>2</sub> atmosphere (pressure 1.0 MPa) at 383 K for 24 h. For HEFDC formation in DMF, a mixture of the substrate (HMF or PD-HMF, 100 mg), Au/CeO<sub>2</sub> (100 mg, substrate/catalyst = 1), Na<sub>2</sub>CO<sub>3</sub> (2.0 molar equivalents with respect to the substrate), ethylene glycol (2.5 molar equivalents with respect to the substrate), and DMF as the solvent (0.5-1.0 g) was heated at 383 K for 24 h in an O<sub>2</sub> atmosphere (pressure 1.0 MPa). All reaction mixtures were diluted with ethyl acetate (5 mL) after completion of the reaction to dissolve all products and then analyzed using gas chromatography (Shimadzu, GC-2025) with a flame ionization detector (FID) and InterCap 17 column (GL Sciences Inc.). Chlorobenzene was used as an internal standard.

# Stepwise synthesis of 2-(1,1'-dimethoxymethyl)-5-(1,3-dioxan-2-yl)-furan from diformylfuran

Indium triflate (11 mg, 0.5 mol% with respect to the substrate) was added to a mixture of 2,5diformylfuran (500 mg, 4.5 mmol), alcohol (12.5 mmol), trimethyl orthoformate (1.5 g, 14 mmol), and dichloromethane (45 mL). The mixture was stirred at room temperature overnight and then filtered through a short plug of alumina. After purification of the crude product by column chromatography, 2,5-bis(1,1'-dimethoxymethyl)-furan was obtained in 82% yield. A mixture of 2,5-bis(1,1'-dimethoxymethyl)-furan (200 mg, 0.92 mmol), 1,3-propanediol (1.0 molar equivalent with respect to the substrate), In(OTf)<sub>3</sub> (0.5 mol% with respect to the substrate), and dichloromethane (2 mL) was stirred at room temperature for 1 h to promote transacetalization of the dimethyl acetal moiety with 1,3-propanediol. After flash column chromatography with alumina and 10% ethyl acetate in hexane, 2-(1,1'-dimethoxymethyl)-5-(1,3-dioxan-2-yl) -furan was obtained with 21% yield.

> 5-(1,1'-dimethoxymethyl)-2-(1,3-dioxan-2-yl)-furan: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 6.41 (d, 2H), 5.39 (d, 2H), 3.81 (s, 4H), 3.36 (s, 6H), 1.98 (m, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 150.7, 108.9, 97.9, 62.2, 52.8, 33.9.

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# Synthesis of methyl 2-(1,3-dioxan-2-yl)-furan-5-carboxylate (MFFC-acetal) from methyl 5formyl-furan-2-carboxylate (MFFC) with 1,3-propanediol

Amberlyst-15 (50 mg, H<sup>+</sup> content: 4.6-4.8 mmol g<sup>-1</sup>) was added to a mixture of methyl 5-formylfuran-2-carboxylate (180 mg, 0.71 mmol), 1,3-propanediol (110  $\mu$ L, 1.53 mmol), and dichloromethane (3 mL). After stirring the mixture at 398 K for 12 h, the solid catalyst and solvent were removed by suction filtration and vacuum evaporation, respectively, and the final product was used as MFFC-acetal without further purification.

5-(1,3-dioxan-2-yl)-2-furancarboxylic acid (MFFC-acetal): <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) 7.16 (d, 1H), 6.56 (d, 1H), 5.61 (s, 1H), 4.24 (m, 2H), 3.957 (m, 2H), 3.88 (s, 3H), 2.23 (m, 1H), 1.45 (dd, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) 158.8, 154.8, 143.9, 118.3, 108.9, 95.4, 67.0, 51.8, 25.3.

# Esterification of FDCA with ethylene glycol to synthesize HEFDC

FDCA (500 mg, 3.20 mmol) was placed into a 50 mL round bottomed two-neck glass flask equipped with a reflux condenser. After the addition of benzene (20 mL) and ethylene glycol (0.5 mL, mmol), 1-2 drops of sulfuric acid were added. The reaction mixture was heated at 383 K for 24 h. The final reaction mixture was neutralized with a saturated aqueous solution of NaHCO<sub>3</sub>, and the product was extracted with ethyl acetate (10 mL) three times. After dehydration with anhydrous magnesium sulfate and evaporation of the ethyl acetate, HEFDC was obtained with 54% yield.



#### **DFT** calculations

All DFT calculations were performed adopting the generalized gradient approximation Perdew-Burke-Ernzerhof (GGA-PBE) exchange-correlation functional,<sup>28</sup> as implemented in the Vienna ab initio simulation package (VASP).<sup>29</sup> The valence electrons Ce(5s, 5p, 6s, 4f, 5d), O(2s, 2p), Au(5d, 6s) and C(2s, 2p) electrons were expanded in a plane-wave basis set with a cut-off energy of 400 eV. The projected augmented wave method (PAW) was employed to describe the ion-electron interactions.<sup>30</sup> The DFT+U approach was used, in which U is a Hubbard-like term describing the on-site coulombic interactions.<sup>31</sup> This approach improves the description of localized states in ceria, where standard local-density approximation (LDA) and GGA functionals fail. For Ce, a value of U = 4.5 eV was adopted, which was calculated selfconsistently by Fabris et al.<sup>32</sup> using the linear response approach of Cococcioni and de Gironcoli,<sup>33</sup> and which is within the 3.0-6.0 eV range that provides localization of the electrons left upon the removal of oxygen from ceria.<sup>34</sup> The bulk equilibrium lattice constant (5.49 Å) calculated previously using PBE+U (U = 4.5 eV) was used for ceria.<sup>35</sup> The ceria surface model was a periodic ceria slab with a  $(4\times 4)$  surface unit cell of CeO<sub>2</sub>(111), which is the most thermodynamically stable termination of ceria.<sup>36</sup> The CeO<sub>2</sub>(111) slab model is three Ce-O-Ce layers thick (nine atomic layers) and the vacuum gap was set to 15 Å. For the Brillouin zone integration, a 1×1×1 Monkhorst-Pack mesh was used. The Au<sub>4</sub>/CeO<sub>2</sub>(111) structure was adopted

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to model metallic Au clusters supported on a CeO<sub>2</sub> support. The atoms in the bottom layer were frozen in their bulk position and only the top two Ce-O-Ce layers and the supported Au4 cluster were allowed to relax. The climbing image nudged-elastic band (CI-NEB) algorithm<sup>37,38</sup> was used to identify the transition states in the de-protection of MFFC-acetal species. To simulate the OH<sup>-</sup> anions in the reaction system, an electron was added for each OH<sup>-</sup> anion in the simulated system. The formed charge was compensated with a uniform background of charge with the opposite sign, and the system was then allowed to relax. This treatment of the charged system is generally adopted in the exploration of reaction mechanisms.<sup>39,40</sup>

### **3. RESULTS AND DISCUSSION**

# Aerobic oxidative esterification of HMF and its acetals for the production of MFDC and HEFDC

**Table 1.** Formation of MFDC in methanol (A) and HEFDC with ethylene glycol (B) from HMF and its acetal compounds (MeO-HMF, EG-HMF, and PD-HMF) with a CeO<sub>2</sub>-supported Au catalyst under pressurized oxygen.



Entry	Product	Substrate	Concentration	Solvent	Conversion	Yield	Mass
			/ wt%		(%)	(%)	balance (%)
1 <sup>a</sup>		HMF	1	МеОН	>99.9	91	94
2 <sup>a</sup>			10		>99.9	4	12
3 <sup>a</sup>		MeO-HMF	1	МеОН	>99.9	93	95
4 <sup>a</sup>			10		>99.9	2	9
5 <sup>a</sup>	MEDC	EG-HMF	1	МеОН	>99.9	91	92
6 <sup>a</sup>	MFDC		10		>99.9	76	81
7 <sup>a</sup>		PD-HMF	1	МеОН	>99.9	95	96
8 <sup>a</sup>			10		>99.9	92	95
9a			16.7		>99.9	92	93
10 <sup>a,b</sup>			20		>99.9	82	95
11°		HMF	5	Ethylene	>99.9	46	46
12°	HEFDC	PD-HMF	5	Glycol	>99.9	89	89
13°			10		>99.9	45	45
14 <sup>d</sup>		HMF	10		>99.9	5	5
15 <sup>d,e</sup>		PD-HMF	10	Ethylene Glycol	>99.9	91	91
16 <sup>d</sup>			16.7		>99.9	94	94
17 <sup>d</sup>			20		>99.9	80	80

Reagents and conditions: <sup>a</sup>Substrate (HMF, MeO-HMF, EG-HMF, and PD-HMF), 100 mg; 2 wt% Au/CeO<sub>2</sub> catalyst, 100 mg; Na<sub>2</sub>CO<sub>3</sub>, 2.0 molar equivalents with respect to the substrate; MeOH solvent, 10 g (1 wt% solution), 1.0 g (10 wt% solution), 0.60 g (16.7 wt%), 0.50 g (20 wt%); temperature, 403 K; stirring rate, 500 rpm; oxygen pressure, 0.5 MPa; reaction time, 15 h. <sup>b</sup>Oxygen pressure of entry 10, 1.0 MPa instead of 0.5 MPa. <sup>c</sup>Substrate (HMF and PD-HMF), 100 mg; ethylene glycol, 2.0 g (5 wt% solution) or 1.0 g (10 wt% solution); Au/CeO<sub>2</sub> catalyst, 100 mg; temperature, 383 K; stirring rate, 500 rpm; oxygen pressure, 1.0 MPa; reaction time, 24 h. <sup>d</sup>Substrate (HMF and PD-HMF), 100 mg; Au/CeO<sub>2</sub> catalyst, 100 mg; DMF, 1.0 g (10 wt% solution), 0.60 g (16.7 wt% solution), and 0.50 g (20 wt% solution); ethylene glycol, 0.14 g to HMF and 0.20 g to PD-HMF (2.5 molar equivalents with respect to the substrate); temperature, 383 K; stirring rate, 500 rpm; oxygen pressure, 1.0 MPa; reaction time, 24 h. <sup>c</sup>The amounts of 1,3-propanediol and ethylene glycol were estimated to be 0.43 and 1.17 mmol, respectively, after completion of the reaction. Considering the initial PD-HMF content (0.54 mmol) and theoretical

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value of ethylene glycol consumed in this reaction (0.98 mmol), 80% of 1,3-propanediol and 68% of ethylene glycol can be recovered without degradation and used for the subsequent reaction.

Ceria-supported gold nanoparticles (Au/CeO<sub>2</sub>) are excellent catalysts for the aerobic oxidation of a wide range of functional organic groups and have already found utility in the oxidation of HMF and PD-HMF to FDCA in water, as well as MFDC formation from HMF in methanol.<sup>15-17,19-24</sup> The supported gold catalyst was prepared by a homogeneous depositionprecipitation approach (Figure S1). The many black dots in the TEM image (Figure S1(A)) are Au nanoparticles with an average size of 4.17±0.87 nm (Figure S1(B)) that are highly dispersed on CeO<sub>2</sub> particles. The crystalline structure of the CeO<sub>2</sub> support can be characterized by XRD patterns (Figure S1(C)), in which all diffraction peaks can be assigned to cubic CeO<sub>2</sub> phase. No additional diffractions other than cubic  $CeO_2$  were observed for Au/CeO<sub>2</sub> in Figure S1(C), because the Au nanoparticles cannot be detected by XRD measurement due to their small size. PD-HMF can be obtained by acetalization of HMF with 1,3-propanediol promoted by  $In(OTf)_{3}$ .<sup>24</sup> Table 1 lists the reaction conditions, conversion of substrates, and product yields (MFDC and HEFDC) for the two target reactions. The oxidation of other HMF-acetals with methanol (MeO-HMF) and ethylene glycol (EG-HMF) as reference substrates was also investigated. All reactions were conducted with methanol or ethylene glycol in the presence of Na<sub>2</sub>CO<sub>3</sub> (2.0 molar equivalents with respect to the substrate), the Au/CeO<sub>2</sub> catalyst and application of an oxygen atmosphere (0.5 or 1.0 MPa). When conducted in dilute methanol solution (1 wt%), all substrates can be converted to MFDC with a yield higher than 90% at complete substrate conversion (entries 1, 3, 5, and 7). These results imply that the Au/CeO<sub>2</sub> catalyst can effectively promote oxidative esterification of these substrates with molecular oxygen under the applied reaction

conditions. However, the MFDC yield is strongly dependent on the type of substrate in concentrated solutions (10 wt%). Oxidative esterification of HMF and MeO-HMF afforded only MFDC yields below 5% (entries 2 and 4). The low MFDC yield and mass balance in entry 2 can be attributed to rapid by-product formation during the first 3 h of the reaction, which reaches a yield of 69% (see Figure 3(A) for detail information): A similar poor result obtained in entry 4 indicates that the protection of HMF with dimethyl acetal is also insufficient to prevent byproduct formation. Although the yield obtained from EG-HMF (MFDC yield of 76%, entry 6) is substantially higher, reactions with PD-HMF offered excellent MFDC yields and mass balances in excess of 90% for 10 wt% and 16.7 wt% substrate solutions (entries 8 and 9). These high yields in concentrated solutions can be linked to the high stability of the six-membered ring acetal in the PD-HMF substrate.<sup>24</sup> To confirm this, control experiments were conducted in an Ar atmosphere with MeO-HMF, EG-HMF and PD-HMF to evaluate how fast these compounds degrade under otherwise similar conditions to entries 4, 6 and 8 (Figure 2). Approximately 30% of EG-HMF was lost at 2 h by thermal degradation (B) and this phenomenon was more pronounced for MeO-HMF (ca. 50% at 2 h, (A)). However, most PD-HMF remained unchanged in the reaction mixture after 2 h (C). Despite the high stability of PD-HMF in (C), continuous degradation occurred in the absence of  $Na_2CO_3$ , which led to a decrease of approximately 30% PD-HMF over 2 h (D). Therefore, Na<sub>2</sub>CO<sub>3</sub> (2 molar equivalents with respect to PD-HMF) plays an important role to stabilize PD-HMF in concentrated methanol solution (10 wt%) under the reaction conditions. A similar stabilizing effect of acetalization was already reported in a previous work: the presence of a large amount of base (Na<sub>2</sub>CO<sub>3</sub>) protects the six-membered ring acetal of PD-HMF from ring-opening reaction in water, even at high temperature.<sup>24</sup> In water, the high pH prevents the nucleophilic attack of water on the acetal group, which would lead to

deprotection to produce HMF. We speculate that the large amount of Na<sub>2</sub>CO<sub>3</sub> in methanol also effectively suppresses the nucleophilic attack of residual water contaminated and methanol to the acetal group in PD-HMF (Figures 2C and 2D). Water and methanol would lead to, respectively, unstable HMF and MeO-HMF intermediates. The amount of Na<sub>2</sub>CO<sub>3</sub> to afford a high PD-HMF yield for a 10 wt% PD-HMF solution was optimized. The MFDC yield was found to be optimum for 2 molar equivalents of Na<sub>2</sub>CO<sub>3</sub> with respect to PD-HMF. A lower amount of Na<sub>2</sub>CO<sub>3</sub> resulted in a decreased MFDC yield (Figure S2).



**Figure 2.** Stability tests for three HMF-acetal compounds (PD-HMF, EG-HMF, and MeO-HMF) in 10 wt% solutions. Reagents and conditions: substrate (MeO-HMF, EG-HMF, and PD-HMF), 100 mg; 2 wt% Au/CeO<sub>2</sub> catalyst, 100 mg; Na<sub>2</sub>CO<sub>3</sub>, no or 2 molar equivalents with respect to the substrate; methanol, 1.0 g (A-D), 0.5 g (E); temperature, 403 K; stirring rate, 500 rpm; Ar pressure, 0.5 MPa.

The effect of a further increase in the PD-HMF concentration to 20 wt% was also evaluated, which caused by-product formation and led to an unsatisfactory MFDC yield, even after optimization of inorganic and organic bases in a 0.5 MPa O2 atmosphere (Table S2). After an increase of the O<sub>2</sub> pressure to 1 MPa, a moderate yield (82%) was obtained at complete conversion (entry 10 of Table 1). We attribute this limitation to the low solubility of molecular oxygen and  $Na_2CO_3$  in methanol compared to PD-HMF, which is underpinned by the observation that 27% of PD-HMF was thermally decomposed in a 20 wt% PD-HMF solution in Ar (Figure 2(E)). Therefore, under the optimized reaction conditions the maximum PD-HMF concentration is approximately 16 wt% to allow for selective MFDC production from PD-HMF using Au/CeO<sub>2</sub> as the catalyst in the presence of sufficient Na<sub>2</sub>CO<sub>3</sub> base (two molar equivalents with respect to the substrate) via aerobic oxidative esterification. The solid catalyst can be isolated simply by decantation or filtration and could be reused in subsequent reactions at least three times without significant loss of activity (Figure S3). In addition, the majority of 1,3propanediol and  $Na_2CO_3$  could be recovered after the reaction (entry 8), which is another beneficial aspect from a practical perspective.

This reaction system was extended to the one-pot synthesis of HEFDC in ethylene glycol with the same Au/CeO<sub>2</sub> catalyst at 383 K for 24 h at an O<sub>2</sub> pressure of 1.0 MPa. When the reactions were conducted in 5 wt% solutions of pure ethylene glycol, PD-HMF was clearly superior to HMF in terms of product yield at full conversion, as indicated by a comparison of entries 11 and 12. A further increase in the PD-HMF concentration to 10 wt% resulted in a decrease in HEFDC yield to 45% (entry 13). However, when the oxidative esterification of PD-HMF was performed with 2.5 equivalents of ethylene glycol in N,N'-dimethylformamide (DMF), the HEFDC yields were significantly improved to 80-94%, even in concentrated solutions (10-20

wt%) as shown in entries 15-17. Entry 14 shows that HMF cannot be converted effectively to HEFDC in this reaction system. These results suggest that an excess of ethylene glycol promotes by-product formation with PD-HMF.

Kinetic studies for MFDC formation from HMF and PD-HMF



**Figure 3.** (A) Time course for aerobic oxidative esterification of HMF in methanol with Au/CeO<sub>2</sub> catalyst. HMF conversion, black line and symbols; yield of intermediate 1 (methyl 5-hydroxymethyl-furan-2-carboxylate), orange line and symbols; yield of intermediate 2 (methyl 5-formyl-furan-2-carboxylate), green line and symbols; yield of MFDC, pink line and symbols; yield of by-products, gray line and symbols. (B) Time course for aerobic oxidative esterification of PD-HMF in methanol with Au/CeO<sub>2</sub> catalyst. PD-HMF conversion, black line and symbols; yield of intermediate 3 (2-(1,3-dioxan-2-yl)-5-formyl-furan), red line and symbols; yield of intermediate 4 (2-(1,1'-dimethoxymethyl)-5-(1,3-dioxan-2-yl)-furan), blue line and symbols; yield of MFDC, pink line and symbols. Time course lines were estimated using a pseudo-first-order reaction model.

Reagents and conditions: HMF or PD-HMF, 100 mg; catalyst, 100 mg (Au/HMF = 1.3 mol%, Au/PD-HMF = 2.0 mol%); Na<sub>2</sub>CO<sub>3</sub>, 2 molar equivalents with respect to HMF and PD-HMF; methanol, 1.0 g; temperature, 403 K; stirring rate, 500 rpm; O<sub>2</sub> pressure, 0.5 MPa.

The efficient production of MFDC and HEFDC in concentrated solutions can only be achieved from PD-HMF, as highlighted in Table 1. To reveal the difference between HMF and PD-HMF, the reaction mechanism for MFDC formation in methanol from 10 wt% HMF and PD-HMF solutions was investigated by a kinetic study supported by density functional theory (DFT) calculations. Figure 3(A) shows time courses for HMF conversion and product yields during 15 h of reaction. All intermediates were quantitatively analyzed using gas chromatography. The formyl group in HMF was firstly converted into methyl carboxylate through oxidative esterification, which formed intermediate 1 (methyl 5-hydroxymethyl-furan-2-carboxylate). The

desired product, MFDC, was subsequently obtained in two steps. The first step involves oxidation of the hydroxymethyl group in intermediate 1 to form intermediate 2 (methyl 5formyl-furan-5-carboxylate). This pathway is consistent with that reported in the literature with supported Au catalysts.<sup>9,10</sup> However, the reaction also involves an undesirable pathway for the formation of heavy by-products, so-called humins. The kinetic traces were fitted using pseudofirst-order reaction kinetics. (see SI for the detailed information) The rate constant for by-product formation from HMF ( $k_2 = 0.7$  h<sup>-1</sup>) is much larger than that for intermediate 1 ( $k_1 = 0.3$  h<sup>-1</sup>). While by-products can also be formed from intermediate 2 because of its formyl group, the reaction rate constant for this pathway is negligibly small ( $k_4 = 0.1$  h<sup>-1</sup>) compared to that for the desirable oxidative esterification to MFDC ( $k_5 = 0.6$  h<sup>-1</sup>), which means that intermediate 2 will be rapidly converted into MFDC.

Figure 3(B) shows time courses for PD-HMF conversion and product yields during 15 h of reaction. Contrary to the reaction with HMF, oxidation starts at the hydroxymethyl moiety of PD-HMF due to the protection of the reactive formyl group with the stable six-membered ring acetal, as shown in Figure 2. The hydroxymethyl group is converted to methyl ester in three elementary reaction steps involving oxidation of the hydroxymethyl group in PD-HMF, which results in a formyl moiety (intermediate 3), dimethyl acetal formation by reaction of the formyl group of intermediate 3 with methanol (intermediate 4), and oxidative esterification of the dimethyl acetal moiety in intermediate 4, which results in the methyl ester (intermediate 5). MFDC is formed directly by oxidation of the ring acetal in intermediate 5, which results in 92% MFDC yield after 15 h. On the basis of these observations, the reaction pathway for the oxidation of PD-HMF to MFDC can be outlined in Figure 3(B) and the kinetic traces can also be fit using a pseudo-first-order model. (see SI for the detailed information) While the pseudo-first-

order rate constant for oxidative esterification of the dimethyl acetal intermediate 4 ( $k_8$ = 0.50 h<sup>-1</sup>) is much smaller than the rate constants for the two earlier reaction steps (oxidation of hydroxymethyl group with  $k_6$  = 1.3 h<sup>-1</sup> and subsequent dimethyl acetal formation with  $k_7$ = 2.2 h<sup>-1</sup>), the rate-determining step in the overall reaction is oxidation of the cyclic ring acetal in intermediate 5 with  $k_9$  = 0.22 h<sup>-1</sup>.



**Figure 4.** Oxidative esterification of MFFC-acetal with various water contents in methanol. Reagents and conditions: MFFC-acetal, 10 mg; 2 wt% Au/CeO<sub>2</sub> catalysts, 10 mg (Au/MFFC-acetal = 2.3 mol%); methanol, 1.0 g; water, 0 g (< 10 ppm), 0.10  $\mu$ g (1.3 × 10<sup>-6</sup> molar equivalents with respect to MFFC-acetal), 0.20  $\mu$ g (2.6×10<sup>-6</sup> molar equivalents with respect to MFFC-acetal), 1.0  $\mu$ g (1.3×10<sup>-5</sup> molar equivalents with respect to MFFC-acetal), 10  $\mu$ g (1.3×10<sup>-4</sup> molar equivalents with respect to MFFC-acetal); Na<sub>2</sub>CO<sub>3</sub>, 2 molar equivalents with respect to MFFC-acetal; temperature, 403 K; O<sub>2</sub> pressure, 0.5 MPa; stirring rate, 500 rpm; reaction time, 4

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Further kinetic studies were performed with intermediate 5, methyl 5-formyl-furan-2carboxylate (MFFC) with 1,3-propanediol (MFFC-acetal) as a substrate using a dilute (1 wt%) solution. The conversion of the hydroxymethyl group in PD-HMF to the methyl ester results in the formation of two water molecules, which can promote the final oxidative esterification step. Therefore, oxidative esterification of MFFC-acetal was conducted in dehydrated methanol with various water contents to verify the role of water in the oxidation of the cyclic acetal functional group to methyl carboxylate (Figure 4). When the reactions were performed in small amounts of water less than 0.2  $\mu$ g (2.6×10<sup>-6</sup> molar equivalents with respect to the substrate), the resulting MFDC yields were negligibly small. In contrast, the addition of 1.0 µg water to the reaction mixture resulted in a significant increase of the MFDC yield to 75%. This promotion effect with a small amount of water toward the substrate  $(1.3 \times 10^{-5} \text{ molar equivalents with respect to the})$ substrate) strongly implies that a catalytic amount of water accelerates direct oxidative esterification of the cyclic ring acetal to methyl carboxylate. Free MFFC itself was not detected during the reaction, which suggests that a cascade reaction consisting of the deprotection of MFFC-acetal and subsequent oxidation of the formyl group can be excluded from the reaction mechanism of MFFC-acetal oxidation, even in the presence of water. Therefore, a small amount of water added to the reaction mixture significantly accelerates direct oxidative esterification of the cyclic ring acetal to the methyl ester. These experimental results are important to elucidate the reaction path by theoretical calculations.



DFT calculations to clarify presumable reaction path of rate-determining step

**Figure 5.** Computed reaction energy diagram for the rate-determining step during the oxidative esterification of MFFC-acetal over the Au/CeO<sub>2</sub> catalyst.

The role of water in the direct oxidation of the cyclic ring acetal in MFFC-acetal was investigated using DFT calculations. Figure 5 shows the computed reaction energy diagram for the conversion of MFFC-acetal into MFDC on a surface model that consists of a small Au cluster placed on the most stable (111) surface termination of CeO<sub>2</sub> (Figures S4 and S5). MFFC-acetal can be stabilized through coordination of the cyclic acetal oxygen atom to a Lewis acid site on the CeO<sub>2</sub> surface. Nucleophilic attack by an OH ion formed by reaction of residual water and Na<sub>2</sub>CO<sub>3</sub> in methanol leads to partial hydrolysis of the ring acetal and formation of the corresponding hemiacetal, IM2, with an activation barrier of 71.4 kJ mol<sup>-1</sup>. The alternative path that leads to formation of another acetal intermediate (IM5) with methanol by partial transacetalization of the cyclic ring acetal is less relevant due to the lower stability of IM5 (-92.6

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kJ mol<sup>-1</sup>, see Figures S6 and S7) than IM2 (-140.1 kJ mol<sup>-1</sup>). Oxidative dehydrogenation of IM2 facilitated by molecularly adsorbed O<sub>2</sub> on the gold cluster yields the corresponding ester with 1,3-propanediol (IM3). This step is strongly exothermic ( $\Delta E = -175.9 \text{ kJ mol}^{-1}$ ) and the required activation energy barrier is 67.7 kJ mol<sup>-1</sup>. Complete hydrolysis of the hemiacetal form (IM2  $\rightarrow$  IM4), which results in the formation of free MFFC, is unfavorable due to the much higher activation energy barrier ( $E_a = 111.9 \text{ kJ mol}^{-1}$ ). It was also established that the conversion of hemiacetal IM2 to hemiacetal IM6 with methanol cannot proceed due to a very high activation energy barrier of 223 kJ mol<sup>-1</sup> (Figures S6 and S7). Desorption of IM3 from the surface and subsequent transesterification with methanol in the reaction mixture results in MFDC. The main findings of these DFT calculations are well supported by the experimental results. The computed activation barrier of 71.4 kJ mol<sup>-1</sup> for the first step that produces the hemiacetal is in accordance with the experimental apparent activation energy (68 kJ mol<sup>-1</sup>, see Table S3). The results indicate that the OH<sup>-</sup> anion plays a pivotal role in the highly effective formation of MFDC over the methanol group.

# **4. CONCLUSIONS**

We have demonstrated that selective production of MFDC and HEFDC can be achieved from concentrated PD-HMF solutions by aerobic oxidative esterification in the presence of a  $Au/CeO_2$  catalyst. The protection of the reactive formyl group of HMF by acetalization with 1,3-propanediol suppresses side-reactions that limit the product yield. Partial hydrolysis with *in situ*-formed water leads to the hemiacetal form of the cyclic acetal, which initiates conversion of the stable cyclic acetal to the desired esters with methanol or ethylene glycol. These results confirm PD-HMF as a promising candidate for the cost-effective and large-scale production of MFDC

and HEFDC precursors to PEF. The concept of the protection of reactive formyl groups, a common motive in biobased intermediates, also open new strategies for other downstream applications of the biobased HMF platform for the production of fine and commodity chemicals.

#### ASSOCIATED CONTENT

**Supporting Information**. Experimental procedures, Characterization results of fresh Au/CeO<sub>2</sub>, reuse experiments of Au/CeO<sub>2</sub>, DFT calculations for mechanistic studies, Literature survey for oxidative esterification of HMF using heterogeneous catalysts, effect of base additives on the catalytic activity of Au/CeO<sub>2</sub>, Apparent activation energies for the formation of MFDC from HMF and PD-HMF (PDF file). This material is available free of charge via the Internet at http://pubs.acs.org.

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### **Author Contributions**

M.K. and K.N. designed the study. M.K. performed all experiments including catalyst preparation and characterization, synthesis of all organic compounds written in Methods, and catalytic reactions. Y.S. and E.J.M.H. conducted the DFT calculations. M.K., Y.S., T.A., A.F., E.J.M.H. and K.N. wrote the paper.

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The authors declare no competing financial interest.

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# ABBREVIATIONS

FDCA, furan-2,5-dicarboxylic acid; HMF, (5-hydroxymethyl)furfural; PEF, polyethylene 2,5furandicarboxylate; DFT calculation, density functional theory calculation; PET, polyethylene terephthalate; MFDC, methyl furan-2,5-dicarboxylate; HEFDC, bis(2-hydroxyethyl) furan-2,5dicarboxylate; PD-HMF, HMF-acetal with 1,3-propanediol; XRD, x-ray diffraction; TEM, transmission electron microscopy; BET surface area, Brunauer-Emmett-Teller surface area; DMF, N,N'-dimethylformamide; MFFC-acetal, methyl 2-(1,3-dioxan-2-yl)-furan-5-carboxylate; MFFC, methyl 5-formyl-furan-2-carboxylate; GGA-PBE, generalized gradient approximation Perdew-Burke-Ernzerhof (GGA-PBE); VASP, Vienna ab initio simulation package; PAW method, projected augmented wave method; LDA, local-density approximation; CI-NEB algorithm, climbing image nudged-elastic band algorithm; MeO-HMF, HMF-acetal with methanol; EG-HMF, HMF-acetal with ethylene glycol.

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