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Aerobic Oxidation of HMF-Cyclic Acetal Enables Selective FDCA Formation with CeO_2-Supported Au Catalyst

Minjune Kim,[a] Yaqiong Su,[b] Atsushi Fukuoka,[a] Emiel J.M. Hensen,*[b] and Kiyotaka Nakajima*[a,c]

Dedication ((optional))

Abstract: The utilization of 5-(hydroxymethyl)furfural (HMF) for the large-scale production of essential chemicals has been largely limited by the formation of solid humin as a by-product, which prevents continuous operation of step-wise batch-type processes and continuous flow-type processes. The reaction of HMF with 1,3-propanediol produces an HMF-acetal derivative that exhibits excellent thermal stability. Aerobic oxidation of the HMF-acetal with a CeO_2-supported Au catalyst and Na_2CO_3 in water gives a 90-95% yield toward furan 2,5-dicarboxylic acid, an increasingly important commodity chemical for the biorenewables industry, from concentrated HMF-acetal solutions (10-20 wt%) without humin formation. The stability of the six-membered acetal ring suppresses thermal decomposition and self-polymerization of HMF in concentrated solutions. Kinetic studies supported by density functional theory calculations identify two crucial steps in the reaction mechanism, i.e., the partial hydrolysis of the acetal into 5-formyl-2-furan carboxylic acid involving OH^- and Lewis acid sites on CeO_2, and subsequent oxidative dehydrogenation of the in situ generated hemiacetal involving Au nanoparticles. The present results represent a significant advance over the current state of the art, overcoming an inherent limitation of the oxidation of HMF to an important monomer for biopolymer production.

Large-scale production of commodity chemicals from renewable feedstock has received significant attention as a means of diminishing our current dependence on fossil fuel resources and developing a sustainable chemical industry.[1-8] For instance, several chemical and biological technologies have been successfully developed for the production of polylactic acid, a biodegradable polyester synthesized from food crop-derived starch or woody biomass-derived cellulose.[7-9] A variety of bio-based furans, diols, and dicarboxylic acids are potential building blocks for the production of essential polymers as replacements for petroleum-derived alternatives. Furan-2,5-dicarboxylic acid (FDCA), identified as one of the top 10 bio-based chemicals by the U.S. Department of Energy,[10] has been widely recognized as a suitable replacement for petroleum-derived terephthalic acid for polymer applications.[11] FDCA or its methyl ester with bio-based ethylene glycol can be polymerized into poly(ethylene 2,5-furandicarboxylate) (PEF) as a furan analog to poly(ethylene terephthalate) (PET). PEF is superior to PET in terms of its low permeability for gases such as oxygen and carbon dioxide, excellent processing properties due to high glass transition and low melting temperatures, and high tensile strength;[11,12] therefore, PEF is expected to play a key role for the large-scale production of completely bio-based and value-added plastics.

Owing to the potential of FDCA, a number of chemocatalytic strategies have already been reported for the conversion of 5-(hydroxymethyl)furfural (HMF) to FDCA by aerobic oxidation.[13-19] HMF is one of the key intermediates derived from bio-based glucose through acid-catalyzed dehydration[20-23] and can be converted to useful furans including FDCA.[24,25] Supported metal catalysts, such as Au, Pt, and Ru listed in Table S1, have been successfully employed for FDCA production in water in the presence of a base additive or with a basic support to give high FDCA yields. However, aerobic oxidation has so far been exclusively studied in dilute HMF (0.5-2.1 wt%) solutions, which significantly hampers practical FDCA production on an industrial scale. This limitation can be attributed to the highly reactive hydroxymethyl (-CH_2OH) and formyl (-CHO) groups in HMF, which induce complex side reactions such as condensation and polymerization, even in pure HMF.[26] As a result, chemical transformation in concentrated HMF solutions is accompanied by the formation of solid by-products called humins. Here, we propose a step-wise reaction system for FDCA production that involves the acetalization of HMF with 1,3-propanediol to stabilize the reactive formyl group, followed by aerobic oxidation using a highly active supported Au catalyst in water in the presence of a base additive.

Three different HMF-acetals were first synthesized by reacting HMF with methanol (MeO-HMF), ethylene glycol (EG-HMF), and 1,3-propanediol (PD-HMF) to identify the most thermally stable derivative to be used for FDCA formation. High-purity acetal compounds were synthesized in two different step-wise manners (see the supporting information). HMF and the three acetal derivatives were heated at 473 K for 2 h in a pressure-resistant glass tube to determine the extent of thermal degradation and self-condensation (Figure 1). More than 80% of HMF decomposed in the first 1 h and the color of the solid changed from yellow to dark brown, which indicated the formation of a polymerized species. Heat treatment for 1 h also degraded 96% of MeO-HMF through thermal decomposition of the dimethyl acetal moiety, which resulted in a 71% yield of an unidentified by-product (humin) and 25% HMF. In this case, the by-product formation can be explained by the degradation of free HMF evolved in situ. The amount of EG-HMF decreased by 72% in the first 1 h, which indicated that the five-membered ring

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acetal formed with ethylene glycol is easily degradable, as was the case with the dimethyl acetal. Unlike MeO-HMF and EG-HMF, PD-HMF had excellent stability at 473 K and more than 75% of this acetal remained intact after 2 h. Such thermal stability makes the six-membered ring acetal of HMF formed with 1,3-propanediol a promising intermediate for selective FDCA formation. Scalable production of PD-HMF can be achieved by simply heating HMF in pure 1,3-propanediol at 333 K for 6 h giving a PD-HMF yield of 86%.

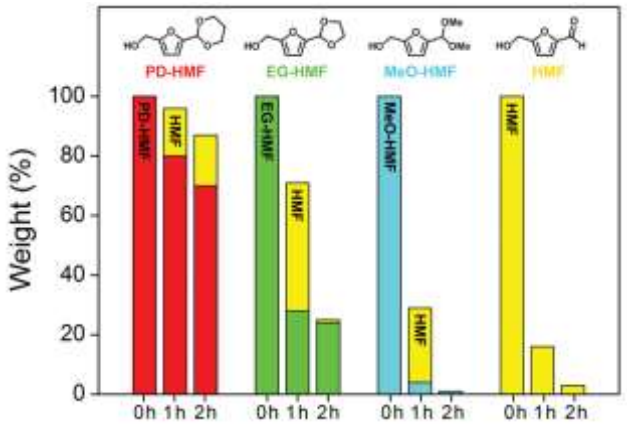
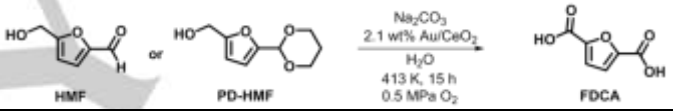


Figure 1. Stability of HMF and its acetal derivatives (PD-HMF, EG-HMF, and MeO-HMF) at 473 K. These compounds were evacuated at 298 K for 2 h in a pressure-resistance NMR tube to remove water contamination. The tubes were sealed and then heated at 473 K for 2 h. The molar loss of these compounds was determined by ^{1}H NMR analysis using benzoic acid as an internal standard.

The aerobic oxidation of HMF and PD-HMF in water was examined in the presence of Na_2CO_3 as a base additive at a pressure of 0.5 MPa O_2 (Table 1). The oxidation catalyst used in this study was 2.1 wt% Au on a CeO_2 support (Figure S1), because a similar material was reported to be highly active and selective for HMF oxidation to FDCA (Table S1).[17,28] When the oxidation was performed using dilute HMF or PD-HMF (1 wt%) solutions in water, FDCA yields for both reactants exceeded 90% (entries 1 and 2). This confirms the utility of the supported Au catalyst for the efficient oxidation of the cyclic acetal of PD-HMF into the carboxylic acid. When the concentration of the HMF or PD-HMF reactants was increased to 10 wt%, the results were very different. The FDCA yield from HMF decreased to 28%, whereas it remained as high as 80% with PD-HMF as the reactant. The FDCA yield by PD-HMF oxidation could be further increased to 94% by optimization of the base concentration (entry 6); however, a similar increase in the base concentration did not further improve the FDCA yield from HMF (entry 5). It was noted that the higher FDCA yield is largely due to a more complete mass balance, which indicates that by-product formation is significantly suppressed in the presence of two equivalents of base relative to PD-HMF. A further increase of the PD-HMF concentration to 20 wt% only slightly affected the FDCA yield (91%) (entry 7). These results demonstrate that the cyclic HMF-acetal with 1,3-propanediol reported here is a promising intermediate for selective FDCA production from highly concentrated solutions in excess of 10 wt%.

Several control experiments were further conducted to evaluate the stability of HMF and PD-HMF. The reactions in entries 5 and 6 were performed at 413 K for 1 h in the absence of O_2 (oxidant). For HMF, this led to significant by-product formation (entry 8), affording a high HMF conversion (47%) and a low mass balance (53%). The low mass balance and FDCA yield observed in entries 3 and 5 are mainly due to the formation of humins due to the rapid degradation of HMF at high concentrations, which even occurs in the absence of oxygen (entry 8). Acetal compounds will generally undergo hydrolysis in acidic or neutral water to form an aldehyde and an alcohol. Hydrolysis of PD-HMF will lead to HMF that will be involved in complex side reactions, which results in various soluble and insoluble by-products. However, almost all PD-HMF remained unreacted under the same conditions (entry 9). This high stability of PD-HMF toward hydrolysis, even at high concentration (10 wt%) and high temperature (413 K), is strongly related to the selective FDCA formation observed in entries 6 and 7.

Table 1. Catalytic activity of Au/CeO_2 toward aerobic oxidation of HMF or PD-HMF in the presence of Na_2CO_3 in water.[a]



Entry	C.[b] /wt%	Substr.	Base /equiv	Conv.[c] /%	Yield /%		M.B[e] /%
					FDCA	Others[d]	
1	1	HMF	0.2	>99.9	91	5	96
2		PD-HMF		>99.9	95	3	98
3	10	HMF	0.2	>99.9	28	25	53
4		PD-HMF		>99.9	80	10	90
5	10	HMF	2.0	>99.9	28	28	56
6[f]		PD-HMF		>99.9	94	3	97
7	20	PD-HMF	2.0	>99.9	91	0	91
8[g]	10	HMF	2.0	47	0	0	53
9[g]		PD-HMF		2	0	0	98

[a] Reagents and conditions: HMF or PD-HMF, 50 mg; Catalyst, Au (2.1 wt%)/CeO_2; catalyst weight, 50 mg (molar ratio of HMF/Au=78 and PD-HMF/Au=53); Na_2CO_3, 0.2 or 2.0 equiv to HMF and PD-HMF on a molar basis; H_2O (solvent), 0.25, 0.5, and 5 mL; Oxygen pressure, 0.5 MPa; Temperature, 413 K; Time, 15 h; Stirring rate, 500 rpm (Table S2). [b] Substrate concentration, [c] Conversion of HMF or PD-HMF estimated by HPLC (Figure S2), [d] Sum of detectable furan-based intermediates (hydroxymethylfuran carboxylic acid, diformylfuran, and formylfuran carboxylic acid) and cyclic acetal compounds of diformylfuran and formylfuran carboxylic acid, [e] Mass balance, [f] pH values of the reaction mixture before and after the reaction was estimated to be 11.4 and 9.7, respectively, [g] 1 h of reaction time and Ar gas atmosphere.

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Reaction pathways for the oxidation of HMF and PD-HMF from concentrated solutions of 10 wt% were investigated. Figure 2A shows time courses for HMF conversion and product yields. Oxidation starts from the formyl group and results in 5-hydroxymethyl-2-furan carboxylic acid (HMFCA). FDCA is subsequently obtained in two steps; the first step involves oxidation of the hydroxymethyl group in HMFCA to form 5-formyl-2-furan carboxylic acid (FFCA). This pathway is consistent with that reported in the literature for supported Au catalysts.[17-19] However, aside from this desired pathway, the reaction also involves heavy humin formation. The yield of these undesired products increases steeply in the first hour to 50% and becomes constant at 70% after 5 h. The kinetic traces in Fig. 2A were fitted using pseudo-first-order reaction kinetics. The rate constant for by-product formation from HMF (k_1 = 0.5 h^{-1}) is much larger than that for HMFCA formation (k_2 = 1.1 h^{-1}). By-products can also be formed from FFCA because of its reactive formyl group (Figure S3); however, the reaction rate constant for this pathway is relatively small (k_4 = 0.1 h^{-1}). Instead, FFCA will be rapidly converted to FDCA (k_5 = 1.9 h^{-1}).

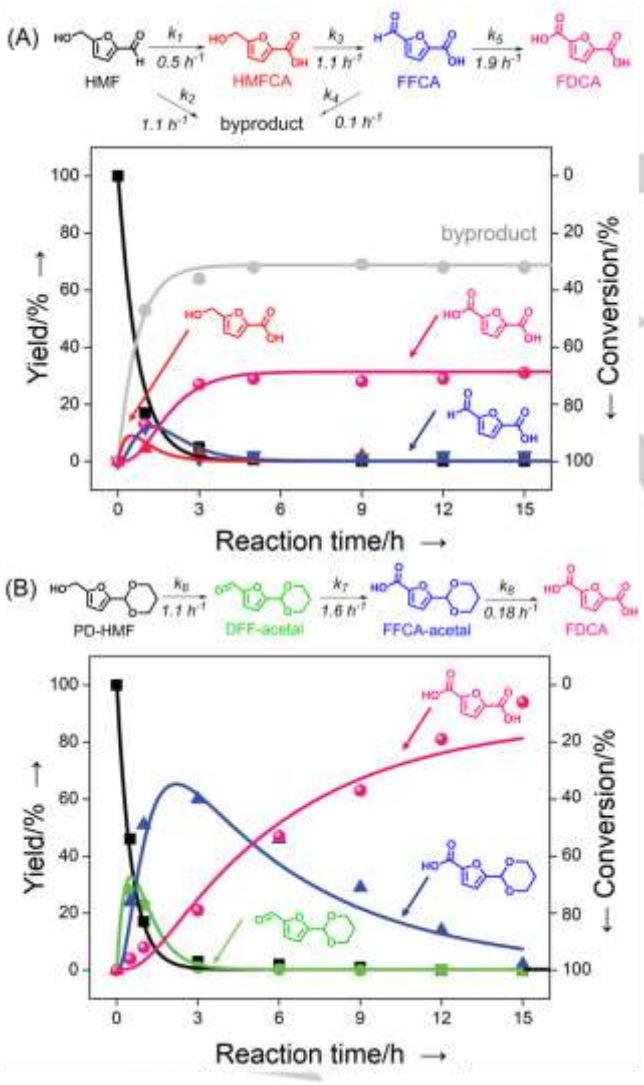

Figure 2. Time courses for FDCA formation from (A) HMF and (B) PD-HMF with CeO_2-supported Au catalyst. Time course lines were modeled with the assumption of a pseudo-first-order reaction using all plotted data. Reagents and conditions: HMF or PD-HMF, 100 mg; Catalyst, Au (2.1 wt%)/CeO_2; Catalyst weight, 100 mg (molar ratio of HMF/Au=78 and PD-HMF/Au=53); Na_2CO_3, 2.0 equiv to HMF and PD-HMF on a molar basis; H_2O (solvent), 1 mL; Oxygen pressure, 0.5 MPa; Temperature, 413 K; Stirring rate, 500 rpm (Table S2). (A) HMF conversion (black line and symbols), byproduct yield (gray line and symbols), HMFCA yield (red line and symbols), FFCA yield (blue line and symbols), FDCA yield (pink line and symbols). (B) PD-HMF conversion (black line and symbols), DFF acetal yield (green line and symbols), FFCA-acetal yield (blue line and symbols), FDCA yield (pink line and symbols).

Figure 2B shows corresponding time courses for conversion and product yields in the oxidation of PD-HMF. All intermediates were confirmed by ^{1}H NMR measurements in the presence of dimethyl formamide as an internal standard (Figures S3, S4, and S5). Oxidation starts at the hydroxymethyl moiety in PD-HMF due to the protection of the reactive formyl group with the six-membered ring acetal. The cyclic acetal was completely preserved during oxidation of the hydroxymethyl moiety (Figure S6), and PD-HMF was oxidized to FFCA-acetal via diformylfuran (DFF)-acetal. Oxidation of the cyclic acetal took place from the FFCA-acetal and produced FDCA with 94% yield after 15 h. On the basis of these observations, we can outline the reaction path for the oxidation of PD-HMF to FDCA (Figure 2B) and fit the kinetic traces using a pseudo-first-order model. As expected, the slow step in the overall reaction is the oxidation of FFCA-acetal to FDCA (k_8 << k_6, k_7).[28] When FFCA-acetal was used as a substrate, a similar reaction rate constant was determined (Figure S7), which means that the oxidation of FFCA-acetal can be identified as the rate-determining step in PD-HMF oxidation. An important aspect of the novel chemistry explored here is the high stability of the six-membered ring acetal. It is apparent that the high FDCA yield is achieved by excluding a cascade reaction consisting of the deprotection of FFCA-acetal and subsequent oxidation of the formyl group. Instead, FDCA is formed by direct oxidation of the cyclic ring acetal. Quantum-chemical calculations were performed to explore the possibility of the direct oxidation of FFCA-acetal into FDCA.

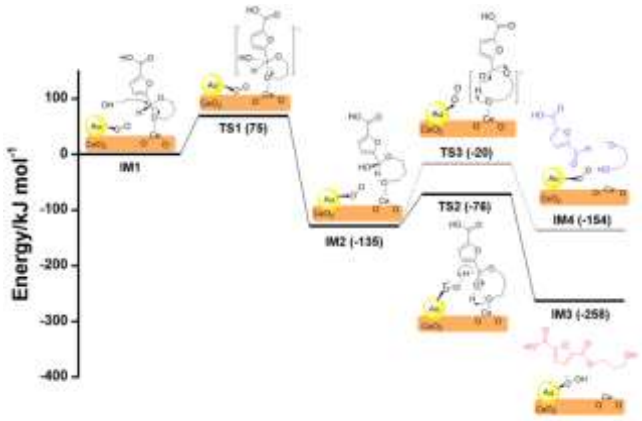

Figure 3. Computed reaction energy diagram for the rate-determining step during the oxidation of PD-HMF to FDCA over the CeO_2-supported Au catalyst.

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Figure 3 shows the computed reaction energy diagram for the conversion of FFCA-acetal to FDCA on a surface model including an Au cluster on the most stable (111) termination of CeO_2 (Figures S8-S10). FFCA-acetal can be stabilized through the coordination of one of the oxygen atoms of the cyclic acetal group to Lewis acid centers on the CeO_2 surface (IM1). Nucleophilic attack of an OH^- ion from the solution promotes partial hydrolysis of the cyclic acetal (IM1 → IM2), which results in the hemiacetal form of FFCA-acetal with a relatively low activation barrier of 75 kJ mol^{-1} (TS1). Oxidative dehydrogenation of IM2 facilitated by molecularly adsorbed O_2 on the Au cluster yields the FDCA-monoester with 1,3-propanediol (IM3). The activation energy barrier for this step (TS2) is estimated to be 59 kJ mol^{-1}. These first two steps are highly exothermic. In contrast, the complete hydrolysis of the hemiacetal form (IM2 → IM4), which leads to deprotection and the formation of free FFCA, is energetically much less favorable with a less stable transition state TS3 (E_a = 115 kJ mol^{-1}). Desorption from the CeO_2 surface and facile hydrolysis of the FDCA-ester yields FDCA. The outcomes of these density functional theory (DFT) calculations are supported by the experimental results; free FFCA was not detected in the reaction mixture by ^{1}H NMR spectroscopy measurements. The activation barrier of 75 kJ mol^{-1} for the first step that produces the hemiacetal is in good agreement with the experimental apparent activation energy (78.6 kJ mol^{-1} in Table S3).

Finally, high stability of the six-membered ring acetal in PD-HMF was studied compared to the five-membered ring acetal in EG-HMF. Competitive acetalization of HMF and trans-acetalization of EG-HMF and PD-HMF were examined with ethylene glycol (EG) and 1,3-propanediol (PD) using a solid Brønsted acid catalyst (Table S4). The results suggest that the formation of the six membered ring acetal is thermodynamically favored over that of the five membered ring acetal. This was also supported by DFT calculations (Figure S11).

In summary, protection of the aldehyde group of HMF with 1,3-propanediol is proposed as an approach to prevent undesired decomposition and self-polymerization, and to achieve efficient downstream conversion of the resultant PD-HMF. We have demonstrated that FDCA can be obtained in high yield from concentrated solutions of PD-HMF by aerobic oxidation in the presence of a Au/CeO_2 catalyst. This case presents a significant advance over the conventional oxidation of HMF that gives only reasonable FDCA yields in dilute solutions. Considering the rapid formation of FDCA at elevated O_2 pressure (Figure S12) and the high reusability of Au/CeO_2 (Figure S13), the technology developed here is promising for practical HMF conversion to FDCA. In addition, 80% of 1,3-propanediol can be recovered from PD-HMF after 15 h of the oxidation reaction (Table 1, entry 6). Small amounts of oxidized products (3-hydroxypropionic acid and 3,3'-oxydipropionic acid) were detected by GC. The use of bio-based 1,3-propanediol and a further increase of the amount of recovered 1,3-propanediol are required for large-scale production of FDCA via PD-HMF. We expect that the concept of a water-stable six-membered ring cyclic acetal can also be applied to other reactions such as selective HMF formation from glucose and fructose resulting in signifcicantly lower humin formation.

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Keywords: biomass conversion • heterogeneous catalysis • furan 2,5-dicarboxylic acid • acetalization • supported Au catalyst

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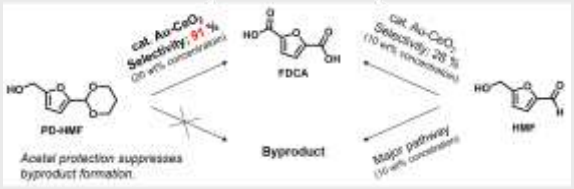

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