

Towards an intensified process of biomass-derived monomers: The influence of HMF by-products on gold-catalyzed synthesis of 2,5-furandicarboxylic acid

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ABSTRACT

The utilization of biomass and development of intensified processes are essential to establish a sustainable production of chemicals in the future. Herein, we report on a strategy that allows to directly convert the biomass-derived platform molecule 5-(hydroxymethyl)furfural over Au/ZrO₂ in aqueous medium to 2,5-furandicarboxylic acid, a renewable building block for bio-based polymers like polyethylene furanoate. The focus lies on identifying the influence of HMF synthesis by-products, like unconverted sugars, levulinic acid, formic acid as well as remaining inorganics on the synthesis of FDCA, to save the intermediate step of HMF purification. These components were added to the reaction mixture individually and in combination to study their effect. Although most of these substances lowered the FDCA yield, the reaction conditions could be optimized to produce FDCA quantitatively. Only the addition of levulinic acid led to a severe deterioration of the production of FDCA, which was attributed to poisoning of the catalyst. Going to a realistic technical scenario, the direct oxidation of impure HMF from unconcentrated sugar syrup in high FDCA yield was demonstrated. Catalyst stability was investigated in the presence of sugars. Based on these studies, highly needed recommendations for the HMF synthesis were developed to establish a more sustainable, technically feasible and intensified process for direct FDCA production from sugars at industrial scales.

KEYWORDS

Biorefinery, biomass, intensification, HMF, FDCA, by-products, gold, deactivation

INTRODUCTION

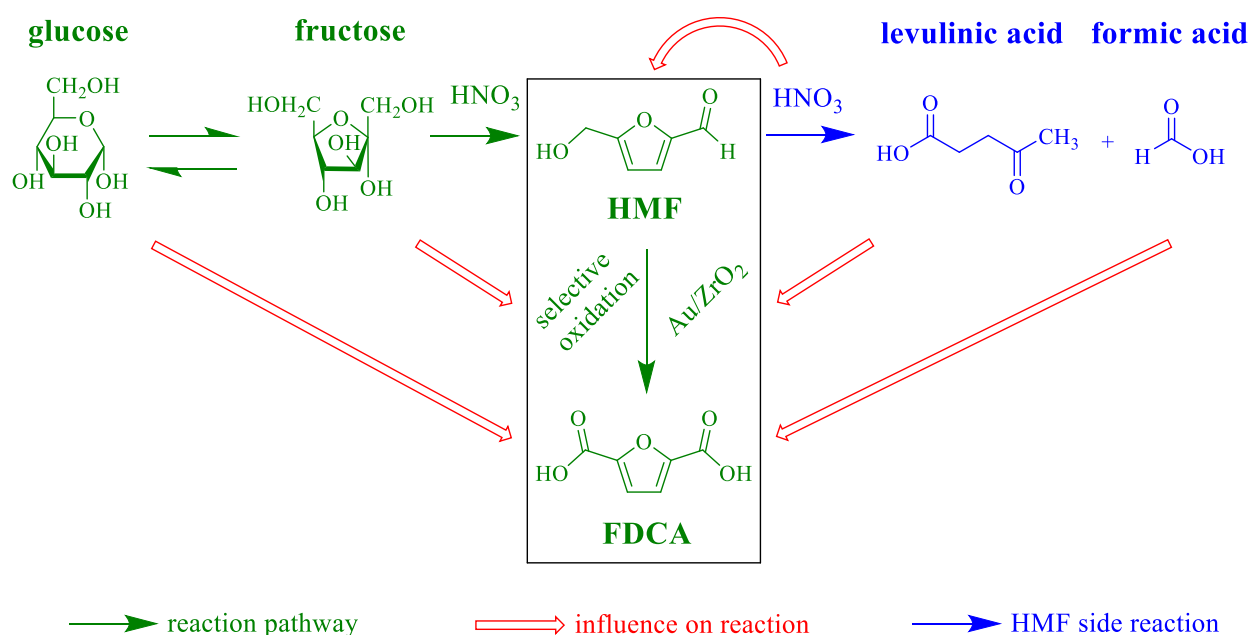
Increasing emissions of greenhouse gases and dwindling reserves of fossil resources make the use of more abundant and renewable feedstocks like biomass unconditionally necessary.¹⁻⁴ For a sustainable production of biopolymers, for example, the synthesis of bio-derived monomers can be realized *via* the top value added platform molecules, like 5-(hydroxymethyl)furfural (HMF), which can be obtained from all kind of carbohydrate-containing biomass *via* hydrolysis and dehydration.⁵⁻⁸ Among various conversion strategies, notably the selective oxidation to the building block 2,5-furandicarboxylic acid (FDCA) gained increasing interest due to its potential to replace terephthalic acid. Terephthalic acid is a fossil-based monomer for the production of polyethylene terephthalate (PET), which is commonly used for food packaging.^{5,9} Polymers such as polyethylene furanoate (PEF) can be synthesized from FDCA and it shows superior material properties, such as reduced oxygen permeability or better mechanical properties compared to PET.¹⁰⁻¹¹ Avantium demonstrated that PEF can be used instead of PET industrially.¹² However, the high demand for plastics is still a huge challenge for researchers to develop a sustainable FDCA synthesis at larger scales.

Among the reported processes, like biocatalytic, electro-catalytic and homogeneously catalyzed processes, the heterogeneously catalyzed reactions are advantageous due to better process management, easy recovery of the catalysts and higher sustainability.¹³ In the latter case, various reaction systems were investigated, using numerous catalyst concepts, solvents and oxidants.¹³ According to the principles of Green Chemistry¹⁴ safer solvents like water should be applied instead of harmful organic solvents. On the other hand, FDCA shows a poor solubility in water, which might lead to precipitation onto the catalyst surface thus deactivating the catalysts. To avoid precipitation of FDCA, a homogeneous base is often added to increase FDCA solubility and more importantly, to promote oxidation, since mechanistic studies¹⁵ over Au catalysts revealed that hydroxide ions are incorporated in the oxidation product, thus directly participating the catalytic cycle. For example, Gorbanev *et al.*¹⁶ achieved 71 % FDCA yield

after 18 h under optimized conditions at room temperature, 20 equivalents (eq.) of NaOH with respect to HMF and 20 bar oxygen pressure over Au/TiO₂ in aqueous medium.

In the production of HMF, however, several by-products like unconverted sugars, levulinic acid and formic acid or so-called humins are obtained.¹⁷ The yield of HMF and concentration of by-products depend heavily on the reaction system and conditions.¹⁸ Although higher HMF yields are possible in organic solvents, HMF synthesis should follow sustainability principles of Green Chemistry¹⁴ also using water as a solvent, for example.^{6, 19} Yet, the extraction of HMF in water seems to be very problematic because of its highly polar character.²⁰ Directly using the product solution from HMF synthesis for further transformations, like the FDCA synthesis, would offer a great advantage, because the same solvent can be used without intermediate HMF purification. This will save costs and energy consumption, important in view of sustainability. Therefore, investigating the direct synthesis of FDCA starting from realistic mixtures of HMF produced from biomass would provide insightful information in optimizing the overall process.

Scheme 1. Schematic representation of the present study involving HMF synthesis from glucose with possible side reactions that produce levulinic and formic acid and the influence of these compounds on the selective oxidation to FDCA.



Only a few publications describe a direct FDCA synthesis from sugars.²¹⁻²⁷ Usually FDCA is produced starting from hexoses followed by acid-catalyzed dehydration to HMF and subsequent oxidation to FDCA (**Scheme 1**). Among these studies, however, organic multiphase solvents face long reaction times due to mass transfer limitations implying the difficulty of HMF extraction. More importantly, the drawback of organic solvents like methyl isobutyl ketone (MIBK) or dimethyl sulfoxide (DSMO) is the potential harm to environment and human health violating the principles of Green Chemistry.¹⁴ In addition, the separation of these solvents to isolate HMF is not easy. The boiling point of both are rather high compared to water, therefore a distillation needs a lot of energy, and HMF might be thermally degraded. Thus, for both HMF and FDCA synthesis, sustainable single-phase reactions using more sustainable solvents e.g. pure aqueous medium are desired.²⁵⁻²⁷ However, the possibly increased formation of by-products subsequently affecting the performance of FDCA synthesis is disadvantageous.²⁴⁻²⁵ Starting from sugar-derived HMF solutions, the FDCA yield is lower in comparison starting from pure HMF indicating a negative effect of by-products.²⁴⁻²⁵ Although the direct synthesis of FDCA from sugars has been reported, there is, to the best of our knowledge, no study on the individual influence of specific by-products on the oxidation of HMF. Revealing these influences is imperative to draw the interrelations in the direct FDCA synthesis strategy and to establish a feasible commercial process.

Since gold catalysts have been identified to be highly active in HMF oxidation,^{16, 28} we report a novel approach focusing on the influence of HMF by-products on the gold-catalyzed FDCA synthesis. Selective oxidation of HMF over Au/ZrO₂ has been performed in water using air as oxidant. In this study, the general influence and concentration dependency of the by-products glucose (GLU), fructose (FRU), levulinic acid (LA) and formic acid (FA) as well as sodium nitrate (NaNO₃) on FDCA synthesis have been examined. After optimization of reaction conditions, oxidation reactions of a technically impure HMF synthesis solution from biomass

and stability tests have been conducted. Based on this study, a recommendation for the HMF synthesis from sugars has been developed.

EXPERIMENTAL SECTION

Materials. All chemicals were used in analytical grade and have been used without further purification. Alfa Aesar: ZrO_2 1/8" pellets, $H AuCl_4 \cdot 3 H_2O$, Merck: NaOH, $NaNO_3$, 5-hydroxymethyl-2-furancarboxylic acid (HFCA), HCl (36 %), ethyl acetate, Sigma-Aldrich: HMF, levulinic acid, FDCA, DMSO- d_6 , VWR Chemicals: D(+)-glucose, D(-)-fructose, formic acid, Air Liquide: synthetic air. A technical HMF solution was received by hydrolysis of unconcentrated sugar syrup according to reference²⁹.

Catalyst synthesis. Au/ ZrO_2 was synthesized *via* deposition-precipitation (dp) similar to the procedure reported in reference²⁸. Briefly, the ZrO_2 support (calcined at 400 °C, 4 h) was suspended in water and stirred for 30 min at room temperature. Afterwards, an aqueous solution of $H AuCl_4 \cdot 3 H_2O$ was slowly introduced to the suspension and stirred for another 60 min. Then, the pH value was adjusted to 9 using 0.05 M NaOH and the mixture was heated to 80 °C for 2 h. After 1 h at the desired temperature, the pH value was checked and adjusted by additional NaOH. Finally, the solution was stirred over night at room temperature and the resulting catalyst was filtered, washed (200 mL) and dried at 110 °C for 2 h, followed by calcination in air at 350 °C for 2 h and reduction in hydrogen (10 vol.-% H_2 in N_2 , at 350 °C, 2 h, 3 $L_N \text{ min}^{-1}$).

Catalyst characterization. Inductively coupled plasma optical emission spectroscopy (ICP-OES) was used to determine the metal loading of catalyst and the concentration of metals in the reaction solution (Agilent 720/725-OES spectrometer). For this purpose, catalyst samples (25 mg) were dissolved in a mixture of sulfuric (2 mL) and nitric acid (6 mL) in a microwave oven. The resulting solution was sprayed at a rate of 1.3 mL min^{-1} into an argon plasma (15 $L_N \text{ min}^{-1}$).

X-ray diffraction (XRD) measurements were conducted on rotating sample holders and recorded on a PANalytical X'Pert Pro instrument using Cu-K- α radiation (wavelength = 1.5406 Å) at diffraction angles 2θ from 20° to 80° and a step size of 0.017°. The support was measured in a calcined state, and the catalyst after calcination, reduction and after catalytic reactions.

The specific surface area of the catalysts was determined *via* N₂-physisorption following the Brunauer-Emmet-Teller (BET) method. The adsorption experiments were performed on a Rubotherm BELSORP-mini II instrument. Firstly, the sample was heated to 300 °C for 2 h under reduced pressure and subsequently adsorption of N₂ was performed at - 196 °C.

Organic residues on recycled catalysts were identified by infrared (IR) spectroscopy using a Varian FT-660-IR spectrometer (Agilent). For this purpose, the catalyst samples were grinded with potassium bromide (KBr), pressed into a pellet and measured in the transmission mode.

Catalytic tests and analysis of reaction solutions. All reactions were carried out in home-built, magnetically stirred, stainless steel batch autoclaves with a total volume of 75 mL (52 mL Teflon® insets, max. temperature of 350 °C at 200 bar) equipped with heating sleeves. Firstly, the reactant mixture was introduced to the inlet using glucose, fructose and sodium nitrate as solids and 0.2 M HMF, 2.5 M NaOH, 0.25 M levulinic acid, 0.25 M formic acid solutions resulting in a total volume of 10 mL. Then the catalyst (98.5 mg, theoretical molar HMF/Au-ratio of 100 at 2.0 wt.-% metal loading) was added to the solution. The autoclaves were closed, purged three times with synthetic air, pressurized and heated to the desired reaction temperature. After the reaction, the product mixtures were cooled to room temperature in an ice bath, depressurized and the catalyst was removed by decantation. The resulting product solution was filtered (0.45 μ m Teflon® filter) and the product composition analyzed with high performance liquid chromatography (HPLC) using a Hitachi Primaide instrument (Bio-Rad Aminex HPX-87H column, 4 mM sulfuric acid, 50 °C, 50 bar, 0.5 mL min⁻¹) for calculating conversion, selectivity and yield. In addition, the HMF related carbon balance was calculated.

The catalyst was dried at 110 °C over night and reused in some reactions to study the durability. During this recovering process, a slight loss of catalyst occurred. Hence, the amount of reactants and the total volume were adjusted to the recovered catalyst mass in order to maintain the same molar ratios during the subsequent experiment.

Product characterization. The separated product was analyzed *via* NMR spectroscopy. ^1H (250 MHz) and ^{13}C (63 MHz) NMR spectra were recorded using a Bruker Avance 250 spectrometer. Product samples (20 mg) were dissolved in 0.5 mL DMSO- D_6 and the resonance signals at 2.5 ppm (^1H , DMSO- D_6) and 39.8 ppm (^{13}C , DMSO- D_6) served as reference for the chemical shift δ .

RESULTS AND DISCUSSION

Catalyst characterization. The prepared Au/ZrO₂ catalyst had a metal loading of 1.6 wt.-% based on ICP-OES, which corresponds to a slightly lower deposition efficiency of 80 %. The XRD patterns of the calcined and reduced catalyst were similar to the pure support material, indicating that the support material was stable in the preparation process. In addition, the absence of characteristic gold reflections points to the presence of highly dispersed small gold nanoparticles, as desired for this study for high catalytic efficiency (**Figure S1**). These results are in line with a previous report²⁸, in which the presence of gold particles with a mean size of 3.7 nm was determined *via* transmission electron microscopy (TEM). No change in the specific surface area of the supported catalyst (96 m² g⁻¹) also indicated that the metal particles did not block any pores of the support material.

Catalytic activity of Au/ZrO₂ in selective oxidation of HMF. First, the catalytic activity of the Au/ZrO₂ catalyst was tested in the oxidation of pure HMF. At reaction conditions of 100 °C, 4 eq. NaOH and 10 bar air, HMF was quantitatively converted after 5 h, which gave FDCA in 100 % yield (**Table 1, entry 1**). The closed carbon balance indicates total carbon utilization and that no degradation of HMF occurred.

Table 1. Influence of GLU, FRU, LA, FA and NaNO₃ on the product distribution of selective oxidation of HMF over Au/ZrO₂. Reaction conditions: 100 °C, 4 eq. NaOH, 10 bar air, 5 h, 98.5 mg of catalyst, 0.1 M HMF in 10 mL, eq. = molar HMF equivalents.

entry	reaction mixture	conversion / %		yield / %		carbon balance / %
		HMF	by-product	HFCA	FDCA	
1	HMF	100	-	0	100	100
2	+ 1 eq. GLU	100	95	47	24	71
3	+ 1 eq. FRU	100	100	48	5	52
4	+ 0.25 eq. LA	56	7	54	0	98
	+ 0.25 eq. FA		100			
5	+ 0.25 eq. NaNO ₃	100	-	0	12	12

General influence of by-products on the selective oxidation of HMF. As stated above (**Scheme 1**), using biomass as a feedstock for HMF synthesis usually leads to some by-products and remaining, unreacted sugars in the technical solution.^{17,29} In order to allow direct synthesis of FDCA without purification of HMF, we individually studied the influence of typical by-products such as GLU, FRU, LA, FA and NaNO₃ under the same reaction conditions. In the presence of GLU the FDCA yield decreased from 100 % to 24 % and the formation of the intermediate 5-hydroxymethyl-2-furancarboxylic acid (HFCA) with a yield of 47 % was observed (**Table 1, entry 2**). In addition, the reduced HMF related carbon balance further confirmed undesired side reactions, probably due to the formation of humins.¹⁷ 95 % of GLU was isomerized to FRU and transformed to unidentified by-products due to the low stability of GLU in alkaline solution³⁰ or converted over the gold catalyst. Side reactions from sugar degradation can be very complex forming numerous different products.²⁹⁻³¹ Some degradation products like glycolaldehyde could be identified (Figure S2), but not in significant

concentration. No further distinct signals were observed in the HPLC chromatograms suggesting the formation of humins rather than products obtained from a catalytic conversion. For example, no formation of gluconic acid was observed although gold catalysts have been reported to be active in glucose oxidation.³² When FRU was added to the reaction solution, the same trend was observed (**Table 1, entry 3**) with a lower FDCA yield of 5 % and a carbon balance of 52 %. In this reaction, FRU was completely transformed to humins. No formation of FDCA was observed in the presence of LA and FA or their respective carboxylates under the alkaline reaction conditions, which were added combined as the rehydration of HMF leads to equimolar amounts of both by-products, lowering the conversion of HMF to 56 % (**Table 1, entry 4**). However, HFCA was formed in a high yield of 54 % (96 % selectivity). The conversion of LA was 7 % and no FA was detected in the reaction solution, which probably decomposed to form H₂ and CO₂.³³⁻³⁴ The addition of NaNO₃ led to a FDCA yield of 12 % and a carbon balance of 12 % while no formation of the intermediate HFCA was observed (**Table 1, entry 5**).

These results demonstrate the emerging challenge of the reaction, when changing from pure to a technical solution of HMF. Possible reasons for lower catalytic activity could be that sugar degradation products like glycolaldehyde and particularly humins lead to deactivation of gold catalyst by adsorbing on the surface or by blocking the surface.³⁵ IR spectra of the recovered catalyst uncovered that hardly any organic residues were found when GLU was added to the reaction mixture (**Figure S3**). Hence, competitive adsorption of the hydroxymethyl group may be responsible for the lower catalytic activity. In fact, FRU showed a more pronounced inhibition on HMF oxidation compared to GLU. FRU includes two hydroxymethyl groups while GLU has one hydroxymethyl functionality. Thus, more active sites may be blocked for HMF oxidation at same molar concentrations of these sugars. The lower reaction rate at the same time allows HMF to polymerize to humins resulting in a lower carbon balance. Competitive adsorption might also be the reason for lower catalytic activity in case of LA, FA

and NaNO_3 . In case of LA and FA, the HMF conversion was deteriorated probably due to partial neutralization of the hydroxide ions by the added acids, leading to a reduced degradation of HMF.

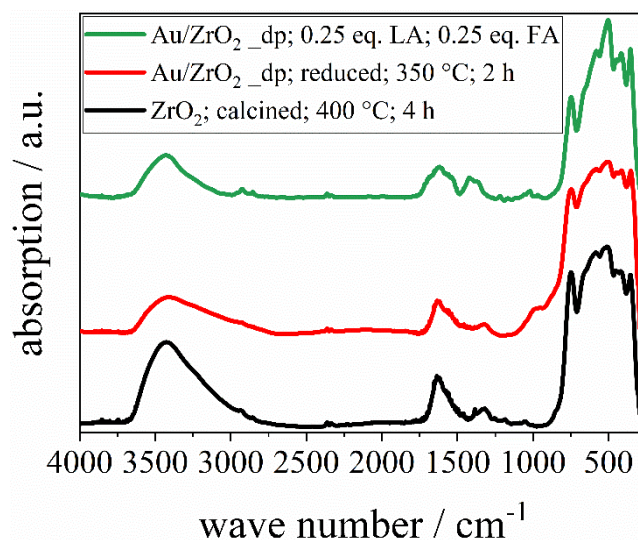


Figure 1. Normalized IR absorption spectra of recovered Au/ZrO_2 after the reaction in the presence of 0.25 equivalents (eq.) of LA and FA, in reduced state before reaction and of calcined ZrO_2 support.

Moreover, organic residues were found on the spent catalyst based on IR spectroscopy (**Figure 1**), which can most likely be attributed to the addition of LA, since HMF degradation products were formed only to minor extent and gold catalyst are reported to be active in FA conversion to H_2 and CO_2 .^{34, 36}

The presented results show the individual effect of each by-product in the FDCA synthesis from a technical solution of HMF. These observations could possibly explain the longer reaction times and lower yields in the studies of direct and single-phase solvent FDCA synthesis in water.^{25, 27}

Concentration dependency of glucose and fructose. Depending on the feedstock, reaction system and conditions in HMF synthesis, various conversions of used sugars can be achieved resulting in varying molar concentrations.¹⁸ Thus, in order to extend the study to a broader

representation of the technical scenario, the influence of the sugar concentration on the oxidation, different amounts of GLU and FRU were added to the reaction mixture.

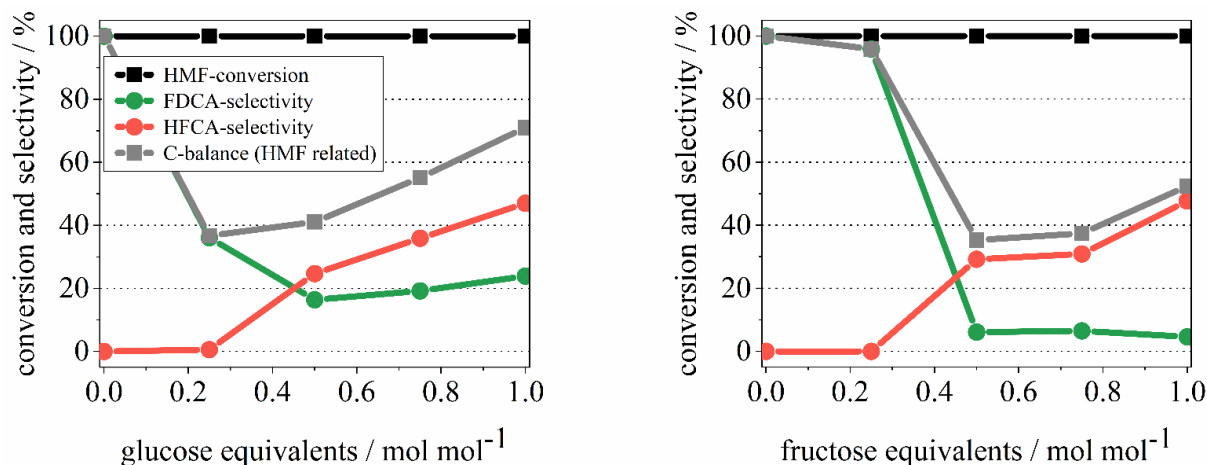


Figure 2. Influence of the GLU (left) and FRU (right) concentration on the oxidation of HMF over Au/ZrO₂. Reaction conditions: 100 °C, 4 eq. NaOH, 10 bar air, 5 h, 98.5 mg of catalyst, 0.1 M HMF in 10 ml.

The HMF conversion was 100 % in all cases. However, the FDCA yield decreased to 16 % with increasing GLU concentrations until 0.5 eq. (**Figure 2, left**). At higher concentrations, HFCA was formed as the main product. Moreover, the formation of gluconic acid was observed at 0.25 eq. with a yield of 12 %. Interestingly, the FDCA yield slightly increased to 24 % with further increase of GLU concentration and the carbon balance increased from 37 % at 0.25 eq. to 71 % at 1 eq. On other hand, the conversion of GLU decreased from 95 % at 1 eq. to 82 % at 0.25 eq. resulting in a reduced GLU conversion at low concentrations and indicating that GLU adsorption is favoured over HMF. A slightly different behavior was observed when FRU was added to the reaction mixture (**Figure 2, right**). At a concentration of 0.25 eq. no significant influence on HMF oxidation occurred. Furthermore, gluconic acid emerged at 0.25 eq. with high yield of 52 %. A pronounced decrease in FDCA yield (6 %) and the carbon balance (35 %) were observed in the presence of 0.5 eq., which also led to the production of intermediate HFCA

in 29 % yield. As in the case of GLU, a further increase of the FRU concentration led to an increase in HFCA yield (48 %) as well as the carbon balance (52 %). Conversely, above 0.5 eq. the FDCA yield was not affected by the increasing concentration.

The formation of the intermediate HFCA above 0.5 eq. of GLU or FRU indicated a slower reaction rate of HMF oxidation. This is probably due to adsorption competitively to HMF, since Au-based catalyst are active in GLU oxidation.³² Temporarily, active sites seem to be blocked for longer time, which led to strong decrease of FDCA yield and enhanced formation of humins. Comparing GLU and FRU, the addition of FRU led to a stronger decrease of FDCA formation, which might be attributed to the presence of the additional hydroxymethyl group in FRU. However, no influence was observed at 0.25 eq. of FRU giving high yield of gluconic acid and indicating its fast oxidation over gold catalyst under these conditions. The increase of the sugar concentration did not promote HMF condensation and polymerization. This can be explained by chemical effects and dilution regarding GLU and its reaction products. As reported³⁷ several degradation products like acids with various functionalities are obtained from GLU in basic media. These degradation products could influence the formation of humins derived from HMF.³¹ Moreover, the lower HMF amount fraction ($\text{mol}_{\text{HMF}} \text{mol}_{\text{mix}}^{-1}$) with the addition of sugars could be an additional reason. For instance, the base induced Cannizzaro reaction of HMF requires the collision of two molecules of HMF for disproportionation reaction.^{16, 35, 38} Also the condensation of HMF shows a reaction order higher than one, because two molecules have to collide.³⁹ The likelihood of collision is probably reduced in the presence of sugars. However, the polymerization to humins is not sufficiently clarified and characterized yet.^{17, 31}

Optimization of reaction conditions in the presence of glucose. Next, the influence of the reaction temperature, added base and air pressure was studied in the presence of GLU to investigate whether high FDCA yields can be achieved under more demanding conditions. As GLU is often the chosen feedstock for chemical syntheses due to its availability also from non-food or hard lignocellulosic biomass, the reaction conditions were optimized in the presence of

GLU as a model process.⁵ More importantly, HMF yields are lower starting from GLU, which represents the worst case and the highest improvement potential.⁶

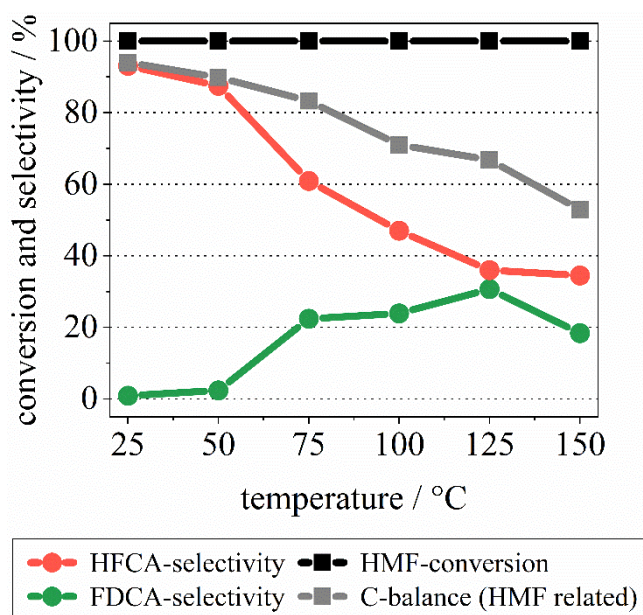


Figure 3. Influence of reaction temperature on HMF oxidation over Au/ZrO₂ in the presence of glucose. Reaction conditions: 4 eq. NaOH, 1 eq. GLU, 10 bar air, 5 h, 98.5 mg of catalyst, 0.1 M HMF in 10 mL.

HMF was always converted to 100 % at all tested temperatures (**Figure 3**). At room temperature, the HFCA yield was 93 % while FDCA was produced in 1 % yield. Enhancing the reaction temperature led to an increase in FDCA yield with a maximum of 31 % at 125 °C. Further increase led to lower FDCA and HFCA yield in line with a decreasing carbon balance. GLU conversion was in the range of 16 % to 96 % with increasing temperature while no gluconic acid was formed, suggesting a strong temperature dependency for GLU conversion and a degradation to humins rather than a catalytic conversion to further products as the HPLC chromatograms did not show distinct products formed in high concentration.

At room temperature, the high HFCA and low FDCA yield indicate a slow oxidation rate of HFCA to FDCA, which was identified to be rate-limiting step in this process.¹⁵ The constantly decreasing carbon balance can be attributed to the thermal instability of HMF in alkaline

aqueous solution.⁴⁰ As a compromise between a sufficiently high reaction rate to FDCA and decreasing carbon balance, a reaction temperature of 125 °C was used for further studies.

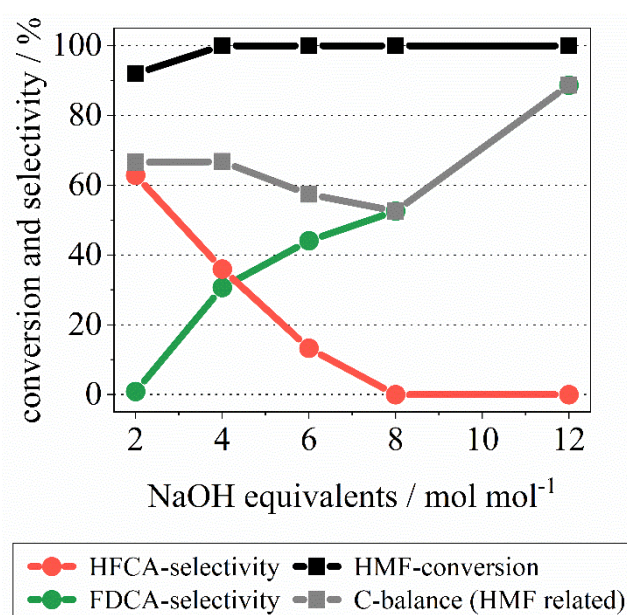


Figure 4. Influence of NaOH equivalents on HMF oxidation over Au/ZrO₂ in the presence of glucose. Reaction conditions: 125 °C, 1 eq. GLU, 10 bar air, 5 h, 98.5 mg of catalyst, 0.1 M HMF in 10 mL.

When studying the influence of the amount of added base, the HMF conversion was 92 % but no formation of FDCA was observed at 2 eq. of NaOH (**Figure 4**). Increasing the amount of base showed a strong promoting effect on HMF oxidation, which led to quantitative HMF conversion and a constantly increase in FDCA yield to 89 % at 12 eq. of NaOH. In order to keep the reaction rate high and, at the same time, use moderate excess of base, 8 eq. of NaOH were used for further tests.

Air was used as an oxidant in this study, which is more sustainable but more challenging than pure oxygen. Increasing air pressure from 10 to 30 bar thus led to an enhanced and quantitative FDCA yield while glucose conversion increased simultaneously from 91 % to 98 % (**Figure 5**). The quantitative production of FDCA despite the high GLU conversion suggests that the

resulting by-products including possible formation of humins formed from GLU degradation do not affect FDCA formation to a major extent under these optimized reaction conditions.

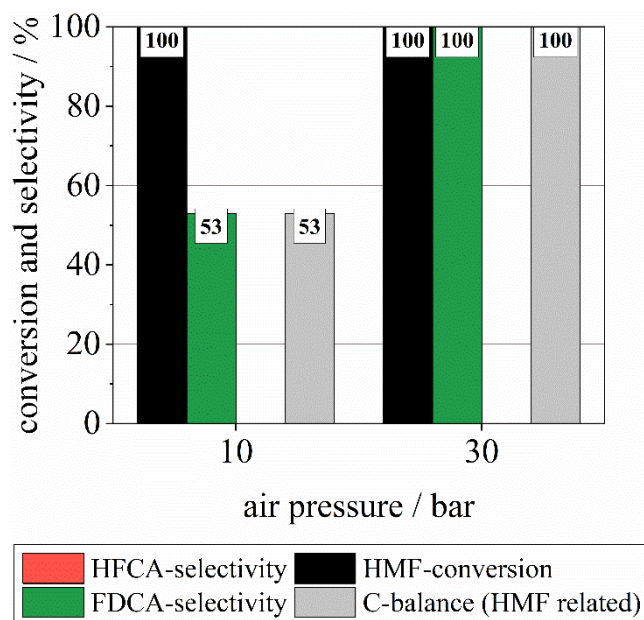


Figure 5. Influence of air pressure on HMF oxidation over Au/ZrO₂ in the presence of glucose. Reaction conditions: 125 °C, 8 eq. NaOH, 1 eq. GLU, 5 h, 98.5 mg of catalyst (HMF/Au = 100), 0.1 M HMF in 10 mL.

Effects of optimized reaction conditions on further by-products. At reaction conditions of 100 °C, 4 eq. NaOH and 10 bar air the FDCA yield was 24 % in the presence of GLU, the formation of HFCA indicated incomplete oxidation and HMF was partially polymerized. The optimization led to a complete conversion of HMF to FDCA giving 100 % yield and leading to total HMF related carbon utilization. In the next step, the influence of other by-products was studied under the reaction conditions previously optimized for GLU (**Table 2**).

The optimized reaction conditions led to a lower FDCA yield of 78 % in the oxidation of pure HMF (**Table 2, entry 1**). When FRU was added to the reaction mixture FDCA was obtained in 94 % yield (**Table 2, entry 3**). Like for GLU, the carbon balance increased upon addition of FRU to the reaction mixture. Upon further extension of the studies, when LA was tested at the

same conditions it led to minimal formation of FDCA in 2 % yield, which identifies LA as a critical by-product (**Table 2, entry 4**). The yield of intermediate HFCA was almost the same as with the initial conditions (**Table 1, entry 4**) with 58 %, however, the selectivity decreased to 67 % together with a carbon balance of 73 %. In the case of NaNO₃, the optimized reactions conditions led to an increased FDCA yield from 12 % to 100 % (**Table 2, entry 5**).

Table 2. Catalytic results of the selective oxidation of HMF under optimized reaction conditions in the presence of GLU, FRU, LA, FA and NaNO₃ over Au/ZrO₂ catalyst. Reaction conditions: 125 °C, 8 eq. NaOH, 30 bar air, 5 h, 98.5 mg of catalyst, 0.1 M HMF in 10 mL, eq. = molar HMF equivalents.

entry	reaction mixture	conversion / %		yield / %		carbon balance / %
		HMF	by-product	HFCA	FDCA	
1	HMF	100	-	0	78	78
2	+ 1 eq. GLU	100	98	0	100	100
3	+ 1 eq. FRU	100	100	0	94	94
4	+ 0.25 eq. LA	87	7	58	2	73
	+ 0.25 eq. FA		100			
5	+ 0.25 eq. NaNO ₃	100	-	0	100	100

Due to harsher reaction conditions a rapid degradation of pure HMF occurred since the increased reaction temperature and amounts of base promote instability of pure HMF. In contrast, a more closed carbon balance was observed in the presence of FRU. This might be accounted to the presence of sugars in relatively high concentrations of 1 eq. preventing the formation of humins due to chemical effects to some extent and the relative dilution of HMF in the mixture (**Figure 2**). Hence, FDCA yield increased when FRU was added because HMF

degradation was reduced. However, a lower FDCA yield compared to the addition of GLU indicated the inhibiting effect of the additional hydroxyethyl group of FRU. Despite higher HMF conversion (87 %) no relevant different behavior was observed under optimized reaction conditions when LA and FA were added to the reaction solution. Among the catalytic results of all by-products the addition of LA significantly prevented the formation of FDCA independently from the studied reaction conditions. Interestingly, aldehyde oxidation of HMF to HFCA was not affected while alcohol oxidation of HFCA to FDCA seemed to be prevented. One possible explanation could be that the carbonyl group of LA strongly adsorbs on gold active sites which activate alcohol oxidation.³⁴ As LA was mainly unconverted, these active sites were probably blocked for further alcohol oxidation of HFCA. To further investigate this assumption, we performed reactions with GLU and FRU in combination with LA and FA to underline the deactivation of alcohol oxidation of added sugars (**Table 3**).

Table 3. Influence of by-product combination on the selective oxidation of HMF over Au/ZrO₂ in the presence of GLU or FRU with LA and FA. Reaction conditions: 125 °C, 8 eq. NaOH, 30 bar air, 5 h, 98.5 mg of catalyst, 0.1 M HMF in 10 mL, eq. = molar HMF equivalents.

entry	reaction mixture	conversion / %		yield / %		carbon balance / %
		HMF	by-product	HFCA	FDCA	
1	HMF	54		28	0	74
	+ 1 eq. GLU		14			
	+ 0.25 eq. LA		4			
	+ 0.25 eq. FA		100			
2	HMF	78		34	0	56
	+ 1 eq. FRU		56			
	+ 0.25 eq. LA		5			
	+ 0.25 eq. FA		100			

HMF conversion dropped to 54 % and 78 %, respectively, when GLU (**Table 3, entry 1**) and FRU (**Table 3, entry 2**) were added to the reaction solution together with LA and FA. No formation of FDCA was observed in both cases. The conversion of GLU and FRU were majorly reduced from 98 % to 14 % and from 100 % to 56 % respectively when LA was added to the solution, which itself remained unconverted with 4 % and 5 %.

The sole formation of HFCA in hand with a reduced conversion of added sugars was observable in these reactions. Thus, a deactivation of alcohol oxidation sites which convert HFCA to FDCA, GLU and FRU can be concluded due to stronger adsorption of LA.⁴¹

Oxidation of technical HMF solution obtained from biomass. Based on the optimized reaction conditions, we studied a technical unpurified HMF solution which was produced from unconcentrated sugar syrup as feedstock (cf. experimental, reference²⁹) in a next step. The detailed analysis showed that HMF concentration amounted to 0.07 mol L⁻¹ with additional components, especially FRU (0.73 eq.), FA (0.1 eq.), LA (0.08 eq.), as well as inorganic constituents like nitrate (0.46 eq.). After addition of the alkaline solution (2.5 M NaOH) biomass derived HMF with a molar concentration of 0.06 mol L⁻¹ and total volume of 12.2 mL was oxidized over the Au/ZrO₂ catalyst (67.1 mg to maintain the same theoretical HMF/Au-catalyst ratio as in previous reactions). This resulted in almost complete HMF conversion (97 %), with a high FDCA yield of 74 %. The rather low concentration of LA could have benefited the reaction towards a high FDCA formation. Additionally, FDCA could be easily isolated by acidifying the reaction mixture (HCl, pH = 1) and extraction by ethyl acetate. Evaporation of the solvent under reduced pressure resulted in solid FDCA (**Figures S3-4**).

Catalyst stability and reusability in the presence of sugars. The reusability of the recovered Au/ZrO₂ was studied by using it in subsequent reactions. Au/ZrO₂ showed rapid deactivation in the oxidation of pure HMF under the reaction conditions that were optimized for the oxidation of HMF in the presence of GLU (**Figure 6**). The FDCA yield decreased to 14 % already in the second run. Interestingly, the deactivation was less pronounced in the

presence of GLU and FRU. The FDCA yield dropped to 45 % in the second and to 40 % in the third catalytic run in the presence of GLU and 57 % in the second and 50 % yield in a third reaction in the presence of FRU.

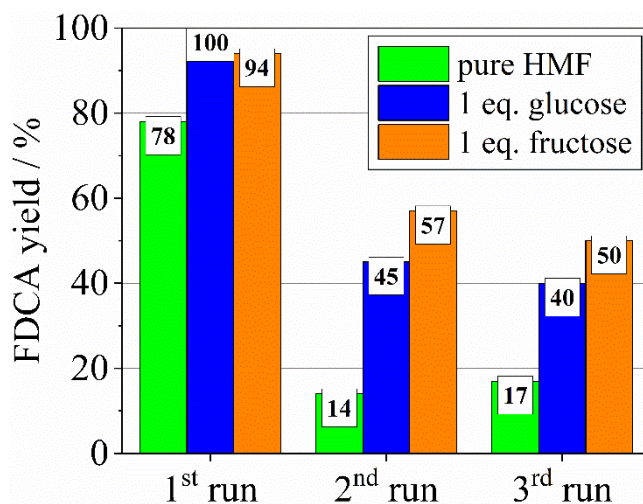


Figure 6. Reusability of Au/ZrO₂ in HMF oxidation of pure HMF and in the presence of glucose and fructose. HMF-conversion was 100 % and no formation of intermediate HFCA was observed in all reactions. Reaction conditions: 125 °C, 8 eq. NaOH, 30 bar air, 5 h, 0.1 M HMF. Amount of HMF and H₂O was adjusted to recovered catalyst mass

Considering earlier reports in literature, there are three possible explanations for the fast decrease in FDCA yield. A first deactivation pathway is due to sintering³⁵ considering the crucial role of particle size in Au catalysis.⁴²⁻⁴³ Hence, we measured XRD patterns of the recovered catalyst after the third run. In all cases, reflections of Au emerged indicating an increase in crystal size, i.e. sintering of Au particles (**Figure S6, A**) as no reflections were observed in the XRD pattern of the fresh catalyst. Thus, XRD uncovers particle growth as one possible deactivation pathway. Another reason for decreasing activity might be leaching of Au. ICP-OES analysis of resulting solution using pure HMF revealed leaching of gold after each run with a concentration < 2 μg mL⁻¹ corresponding to an overall metal loss of 4 % after the third reaction. Interestingly, when the sugars were added, no leaching of gold was observed. Further studies including, for example, *in situ* X-ray absorption spectroscopy may allow further

insight into the difference of metal leaching observed under the different reaction conditions.⁴⁴ Besides sintering and leaching, catalyst deactivation could be also attributed to fouling by organic residues.³⁵ Thus, we measured IR spectra of recovered catalyst in the presence of GLU. It was found that intensified absorption bands occurred (**Figure S6, B**) which indicated the presence of organic residues, probably humins,⁴⁵ contributing to deactivation upon re-use. The identification of these residues and possible formation pathways by surface intermediates may be investigated during the reaction in future, for example by attenuated total reflection IR (ATR-IR) spectroscopy.⁴⁵⁻⁴⁶

In summary, three possible routes of deactivation, sintering of Au particles, metal leaching and fouling may be the reason for decreasing FDCA yields upon re-use. The increase of particle size of gold is probably the main reason for deactivation in the presence of by-products, whereas leaching will play an additional role if only HMF is present. In addition, organic residues might contribute to deactivation. In future, these deactivation pathways including the mechanism may be studied in more detail using *in situ* characterization tools.

HMF synthesis recommendation. Based on the presented results, a highly needed HMF synthesis recommendation was developed:

- use water as a solvent

Although higher HMF yields are possible in organic solvents, water provides more sustainability.^{6, 14} A direct synthesis of FDCA in water in high yields is technically feasible despite the possibly increased presence of by-products which occur when water is used in HMF synthesis.

- prefer HMF selectivity over quantitative sugar conversion

In the interest of HMF synthesis, a high single pass sugar conversion is desired. But if a higher differential selectivity towards HMF can be achieved at a moderate sugar conversion, unconverted sugars like GLU and FRU at high concentrations of 1 eq. can be tolerated in FDCA synthesis under optimized reactions conditions.

- avoid further dehydration of HMF to LA

LA at a concentration of 0.25 eq. was identified as the most critical by-product which led to rapid catalyst deactivation preventing the formation of FDCA due to poisoning. Hence, the formation of LA must be avoided in HMF synthesis. However, at lower concentrations of 0.08 eq. its deactivation effect was negligible. Studies show that the formation of LA is highly dependent on the pH and can be minimized at a pH of 3.⁴⁷

CONCLUSION

The direct FDCA synthesis from a HMF product solution offers great advantages for an intensified process chain: same solvent and no intermediate HMF purification. Pursuing the presented synthesis strategy allowed to emphasize the by-product effects on FDCA synthesis in order to develop rational recommendations for a highly needed HMF synthesis. The individual study on the influence of by-products like GLU, FRU, LA, FA and remaining inorganics on the oxidation of HMF showed that especially the presence of LA in high concentrations needs to be prevented. While compounds like the sugars compete with HMF in the oxidation reaction, acids have probably two effects: they act as a buffer in solution and block the surface irreversibly so that HMF condensates and polymerizes due to lower reaction rates. In addition, the production of further side products may occur, like the formation of gluconic acid that was observed in some reactions along with the degradation to humins. Such an influence of by-products should be deepened in order to develop more efficient processes. Optimization of the reaction conditions in the presence of GLU allowed a total HMF related carbon utilization and quantitative FDCA production at 125 °C, in the presence of 8 equivalents of NaOH and 30 bar air pressure within 5 h. Catalyst reusability tests showed no additional negative effects due to the presence of the sugars. Going from a model mixture to a technical and thus, impure HMF solution from unconcentrated sugar syrup, the gold-catalyzed oxidation to FDCA in high yields was successful simplifying the process tremendously. The

concentration of the critical by-product LA was found to be low enough so that it hardly disturbed. Overall, the presented results contribute to an understanding of a continuous FDCA synthesis for commercialization of bio-derived monomers. As a next rewarding step, the development of a continuous and direct synthesis of FDCA would be valuable.

ASSOCIATED CONTENT

Supporting Information (SI). The following files are available free of charge.

XRD patterns of the as-prepared Au/ZrO₂ catalyst, representative HPLC chromatograms of calibrated compounds and the reaction solution in the presence of one equivalent of GLU, IR spectra of the spent Au/ZrO₂ catalyst after reaction and recycling in the presence of one equivalent of GLU, ¹H and ¹³C NMR spectra of the extracted reaction product and XRD patterns of the recycled Au/ZrO₂ catalyst in the presence of impurities.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript. || These authors contributed equally.

Funding

This work was funded and supported by KIT. In addition, we acknowledge funding from the FNR-project (KEFIP, FKZ: 22010718).

Notes

The authors declare no conflicts of interest.

ACKNOWLEDGMENT

We are thankful to Dominik Neukum (catalyst synthesis), Sonja Habicht, Veronika Holderied (HPLC), Armin Lautenbach (ICP-OES), Angela Deutsch (BET), Dr. Thomas Zevaco (FT-IR), Dr. Silke Behrens (XRD), Philipp Treu, Dr. Stephan Pitter (NMR) and AVA Biochem BSL AG (HMF solution from unconcentrated sugar syrup).

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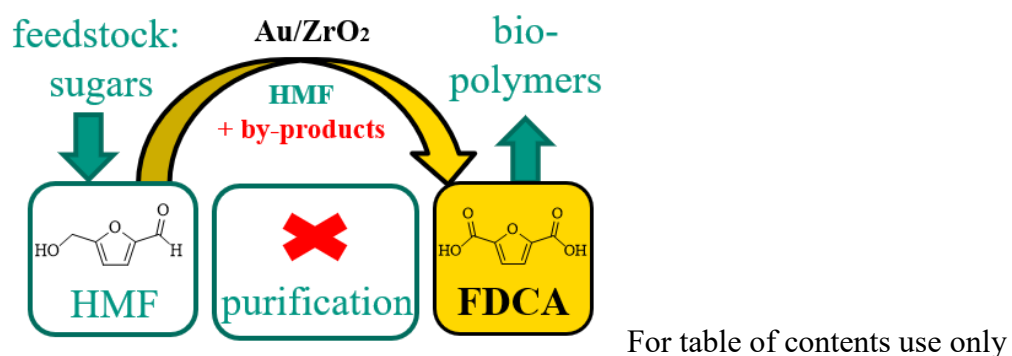
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TOC/Abstract Graphic



Synopsis

The development of an intensified FDCA synthesis from biomass contributes to the commercialization of bio-based monomers.