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Oxidation of 5-hydroxymethylfurfural over supported Pt, Pd and Au catalysts

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ABSTRACT

Supported Pt, Pd, and Au catalysts were evaluated in the aqueous-phase oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) at 295 K and high pH in a semibatch reactor. The intermediate reaction product 5-hydroxymethyl-2-furancarboxylic acid (HFCA) was formed in high yield over Au/C and Au/TiO_2 at 690 kPa O_2, 0.15 M HMF and 0.3 M NaOH, but did not continue to react substantially to FDCA at the specified O_2 pressure and base concentration. In contrast, the final reaction product FDCA was formed over Pt/C and Pd/C under identical conditions. The initial turnover frequency of HMF conversion was an order of magnitude greater on Au catalysts compared to either Pt or Pd. Increasing the O_2 pressure and NaOH concentration facilitated the conversion of HFCA to FDCA over the supported Au. The significant influence of base concentration on the product distribution indicates an important role of OH^- in the activation, oxidation and degradation of HMF.

1. Introduction

The rising cost, diminishing supply and environmental impact of fossil fuels have spawned increased interest in the production of sustainable alternative energy and chemical feedstocks. While much attention is paid to renewable energy such as wind, solar and geothermal, none of those renewable sources can be used to produce organic chemicals currently derived from fossil fuels. However, carbon-containing molecules found in renewable biomass could potentially serve as a sustainable feedstock for the chemical industry.

The molecule 5-hydroxymethylfurfural (HMF) is one of the many potential platform chemicals for biorenewable chemicals production [1] because it is formed by dehydration of fructose and glucose [2–4]. For example, a high yield biphasic method of HMF synthesis from fructose (80% HMF selectivity at 90% fructose conversion, from 10 to 50 wt% fructose) has been reported [5]. In addition, glucose can be converted catalytically in ionic liquids to HMF [6]. One reason HMF is considered to be an important platform chemical is that it can be oxidized to 2,5-furandicarboxylic acid (FDCA). A recent study commissioned by the U.S. Department of Energy identified FDCA as one of 12 potentially useful building blocks for value added chemicals from biomass [7]. For example, FDCA is a possible replacement monomer for terephthalic acid used to produce polyethylene terephthalate (PET). Fig. 1 shows the structural similarity of terephthalic acid and FDCA. Gandini et al. have shown polymers of FDCA to have many properties similar to PET [8].

The oxidation of HMF has been studied over a variety of catalysts in the past two decades. Early work by Verdeguer et al. investigating the oxidation of HMF over Pt/Pb catalysts demonstrated a need for high pH in the reaction solution [9]. They also found that the production of FDCA occurred in two stages; the aldehyde side chain was first oxidized to a carboxylic acid, producing 5-hydroxymethyl-2-furancarboxylic acid (HFCA), which was followed by the oxidation of the hydroxymethyl side chain to produce FDCA. Interestingly, Verdeguer et al. also found that hydroxide base was more effective in producing FDCA than carbonate base, which favored production of HFCA.

The oxidation of HMF over Pt/Al_2O_3 catalysts was also investigated by Vinke et al. at lower pH (pH = 9) [10]. Although FDCA was eventually formed, the intermediate product 5-formyl-2-furancarboxylic acid (FCA) was observed. The intermediate product HFCA appeared at higher pH [10]. The investigation reports that the reaction rate is independent of pH between pH 8 and 11, and that the rate is greater over Pd than over Pt. Transition metals can deactivate in high concentrations of dioxygen, presumably by over oxidization of the metal catalyst. However, Vinke et al. suggest that a strong interaction between HMF and the surface of Pt prevents over oxidation of the metal. Thus, they speculate that the rate limiting step of HMF oxidation is the adsorption of O_2 on the catalyst.

Partenheimer and Grushin report the results of HMF oxidation over various metal bromide catalysts (Co/Mn/Zn/Br) in an acetic acid solution [11]. At lower temperatures (323–348 K), the main product was reported to be 2,5-diformylfuran (DFF) in moderately

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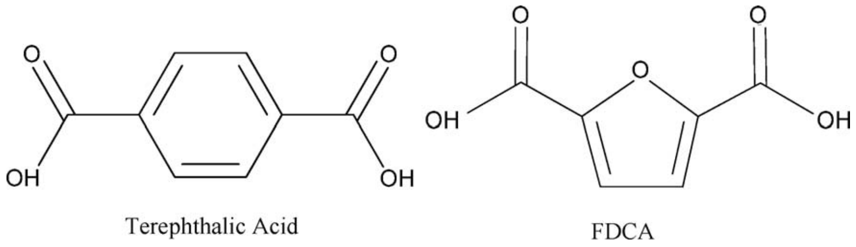

Fig. 1. FDCA is a potential biorenewable replacement monomer for terephthalic acid in polyethylene terephthalate plastics.

high yield (57%) while at elevated temperatures (373–498 K), the main product was FDCA in a yield of ~60%. Similarly, Navarro et al. reported the production of DFF from HMF using vanadyl-pyridine complexes in both homogeneous and heterogeneous forms and in various solvents such as toluene, trifluorotoluene and dimethylsulfoxide (DMSO) solutions [12]. At the moderate temperature of 388 K, DFF was produced in >99% selectivity. It is important to note that the experiments utilized a very high catalyst loading (mol substrate/mol metal = 10). Evidently, the nature of the catalyst surface and the composition of the solvent both play key roles in the effectiveness of HMF oxidation. Although there have been attempts to produce FDCA directly from fructose, success has been limited [13–15].

Very recently, oxidation of HMF over supported gold catalysts has been observed. Taarning et al. reported the oxidation of HMF in methanol over Au/TiO_2 at 403 K in the presence of a small amount of base [16]. Although a majority of the ester product formed at room temperature was derived from HFCA, increasing the temperature to 403 K resulted in the selective formation of the ester of FDCA. Gorbanev et al. also reported HMF oxidation in an aqueous solution over a commercial Au/TiO_2 catalyst, but performed the reaction with 20 equiv. of base [17]. In that study, the yield of FDCA increased significantly when the dioxygen pressure was raised from 1000 kPa to 2000 kPa. Their optimized conditions produced a 71% yield of FDCA with full HMF conversion.

Casanova et al. also investigated HMF oxidation over Au/TiO_2, Au/CeO_2, Au/C and Au/FeO_2 catalysts in liquid water [18]. The Au/TiO_2 and Au/CeO_2 catalysts proved to be most effective for HMF oxidation to FDCA. At their optimized conditions of 403 K, 1000 kPa O_2 and 4:1 NaOH:HMF, >99% yield of FDCA was obtained after 8 h over Au/CeO_2. Interestingly, at lower temperatures, HFCA was the major product at complete conversion of HMF.

To the best of our knowledge, the reactivity of Pt, Pd and Au catalysts has never been directly compared under identical conditions. Moreover, the influence of reaction conditions on the turnover frequency of Au-catalyzed HMF oxidation has not been reported previously. Thus, we have investigated the oxidation of HMF in water over several supported Pt, Pd and Au metal catalysts. Water was chosen as a green solvent to minimize environmental impact. Sodium hydroxide was used to facilitate the reaction because an earlier report indicated that hydroxide was more effective than carbonate [9]. The influence of concentration of hydroxide base on the rate of oxidation and the effect of O_2 pressure on rate and product selectivity over supported Au were also explored.

2. Experimental methods

2.1. Catalyst preparation

A gold on carbon catalyst was prepared through the formation of a gold sol and the subsequent deposition of the gold sol onto a carbon support [19]. The sol was prepared by adding 0.075 g of $HAuCl_4\cdot 4H_2O$ [~50 wt% Au, Aldrich] to 1500 cm^3 of deionized water along with 0.00375 g polyvinyl alcohol [Acros]. The colloid was reduced by adding 0.1 M $NaBH_4$ [Aldrich] dropwise in 4:1 molar ratio of $NaBH_4$:Au. Following reduction, the sol was ruby red in color. Five grams of carbon lampblack [Fisher Scientific] was suspended in 100 cm^3 of deionized H_2O and sonicated for 1 h and subsequently added to the sol. The sol–carbon slurry was stirred for 1 h prior to filtration. The filtrate was clear in color, indicating the Au sol had deposited on the support. The catalyst was washed with several liters of water to remove any residual chlorine and dried overnight at 403 K in air. The catalyst was subsequently reduced in flowing N_2 and H_2 gases in a 9:1 ratio at 150 $cm^3\,min^{-1}$ for 6 h at 573 K. The Au catalyst was stored in a refrigerator and used without any additional pretreatment. Metal weight loading was determined by ICP analysis performed by Galbraith Laboratories, Knoxville, TN.

Gold standard catalysts were obtained from the World Gold Council. A 1.6 wt% Au on TiO_2 catalyst (Type A, Lot. No. Au–TiO_2 #02-8) and a 0.8 wt% Au on C (Type C, Sample 40D) catalyst were used in this study. The platinum and palladium catalysts used here were both 3 wt% metal on activated carbon, supplied by Aldrich. Both the Pd and Pt catalysts were reduced in H_2 (UHP, Messer Gas) flowing at 150 $cm^3\,min^{-1}$ for 6 h at 573 K and cooled under flowing H_2. The catalysts were refrigerated and used without further pretreatment.

2.2. Oxidation reactions

The aqueous phase oxidation of 5-hydroxymethylfurfural (HMF) [Acros, ≥98% purity] was carried out in a 50 cm^3 Parr Instrument Company 4592 batch reactor equipped with a glass liner. Dioxygen was UHP, supplied by Messer Gas.

In all reactions, 7.0 cm^3 of the reactant solution (0.15 M HMF and 0.3 M NaOH) was added to the reactor along with the appropriate amount of catalyst. The reactor was purged with flowing O_2 and then pressurized to the desired value. A constant pressure was maintained by a continuous O_2 feed. Samples of the product solution were acquired by removing the top of the reactor, taking the sample, flushing the reactor with O_2 and repressurizing. The maximum O_2 transport rate from the gas to the liquid was determined by oxidation of sodium sulfite [20], and the HMF oxidation rate was kept significantly below this limit when quantitative rates were measured. The oxidation of sodium sulfite at the standard agitation speed and 690 kPa O_2 resulted in a maximum gas–liquid transfer rate of 4×10^{-7} mol $O_2\,s^{-1}$.

The samples from the oxidation reactions were filtered using PTFE 0.2 μm filters and diluted with deionized H_2O in a 1:3 sample to water ratio. The analysis was conducted using a Waters e2695 high performance liquid chromatograph [HPLC] at 308 K equipped with refractive index and UV/vis detectors. The HPLC utilized either a Waters Atlantis C_{18} column and deionized H_2O flowing at 1 $cm^3\,min^{-1}$ or a Bio-Rad Aminex HPX-87H column and 5 mM H_2SO_4 flowing at 0.5 $cm^3\,min^{-1}$ to perform the separation. The retention times and calibrations for observed products were determined by injecting known concentrations.

Table 1
Catalyst characterization results.

Catalyst	Metal loading (wt%)	Mean metal particle size (nm)	Surface average diameter (nm)[a]	Dispersion
Pt/C	3.04[b]	2.5[c]	–	0.40
Pd/C	2.9[b]	3.3[c]	–	0.32
Au/C (WGC)	0.8[d]	10.5[e]	18.8[f]	0.05[g]
Au/C (sol)	0.77[b]	3.0[h]	8.8[h]	0.11[g]
Au/TiO_2	1.6[d]	2.6[e]	–	0.38[i]

[a] Surface average diameter = $(\sum d^3/\sum d^2)$.
[b] From ICP analysis (Galbraith Labs, Knoxville, TN).
[c] Inverse of dispersion (determined via H_2 chemisorption).
[d] From ICP analysis provided by the World Gold Council.
[e] From TEM analysis provided by the World Gold Council.
[f] From TEM analysis [23].
[g] Inverse of surface average diameter, used to normalize rates for exposed Au atoms for Au/C (WGC) and Au/C (sol).
[h] From TEM analysis, this work.
[i] Inverse of mean particle diameter (nm), used to normalize rates for exposed Au atoms for Au/TiO_2.

2.3. Chemisorption of H_2

The dispersion of Pt and Pd was determined using a Micromeritics ASAP 2020 automated adsorption system. The Pt/C catalyst was heated to 648 K at 4 K min^{-1} under flowing H_2 (UHP, Messer Gas) and reduced at that temperature for 1.5 h. The sample was subsequently evacuated for 2 h at 648 K and then cooled to 308 K for analysis. The Pd/C catalyst was heated to 473 K at 4 K min^{-1} under flowing H_2. The sample was evacuated and held for 2 h at 473 K before being cooled down to 373 K for analysis. The analysis was carried out at 373 K in the pressure range of 0.06–0.6 atm to avoid formation of the β-phase hydride [21].

2.4. Scanning transmission electron microscopy

High-angle annular dark field (HAADF) imaging was performed using a JEOL 2010F FASTEM field emission gun scanning transmission electron microscope operated at 200 kV. The Au/C catalyst sample was suspended in ethanol by grinding in an agate mortar and pestle, and deposited on a holey carbon support film on Cu TEM grids. The images were recorded and analyzed using Digital Micrograph software.

3. Results and discussion

3.1. Catalyst characterization

The Au metal loadings and particle sizes for the catalysts are listed in Table 1. A typical STEM image of the Au/C (sol) and the particle size distribution (Fig. 2) sample indicated that the majority of particles are about 3 nm in diameter, with a small number of particles larger than 4.0 nm. The mean particle size determined by evaluating 792 particles over five different regions of the sample was 3.0 nm. The surface average diameter for the Au/C (sol) sample was 8.8 nm, which corresponds to an estimated dispersion (fraction of metal at the surface) of 0.14 (determined as the inverse of the surface average diameter) [22]. Although a mean particle size of 10.5 nm was provided by the WGC for their Au/C, the Au/C (WGC) catalyst has been previously imaged by Ketchie et al. [23]. The particle size distribution reported that work resulted in a mean particle diameter of 12.2 nm, which compares well to that provided by the WGC. However, the surface average diameter for Au/C (WGC) was 18.8 nm, corresponding to a dispersion of about 0.05. Because the Au/TiO_2 catalyst was not imaged independently, the mean particle size of 2.6 nm provided by the WGC was used to estimate a dispersion of 0.38. Chemisorption of H_2 was used to determine the dispersion for the Pt/C and Pd/C catalysts as 0.40 and 0.32, respectively.

3.2. Oxidation reactions

The oxidation of HMF in an aqueous solution under 690 kPa O_2 at 295 K did not occur in 6 h over Pt/C or Au/C (WGC) without the presence of base. Thus, NaOH was added to the reaction medium to provide the basic environment. It should be noted that HMF in the presence of NaOH in water reacted to form undesirable decomposition products such as formic acid and 2,5-bis(hydroxymethyl)furan. Therefore, the concentration of base was optimized so that side

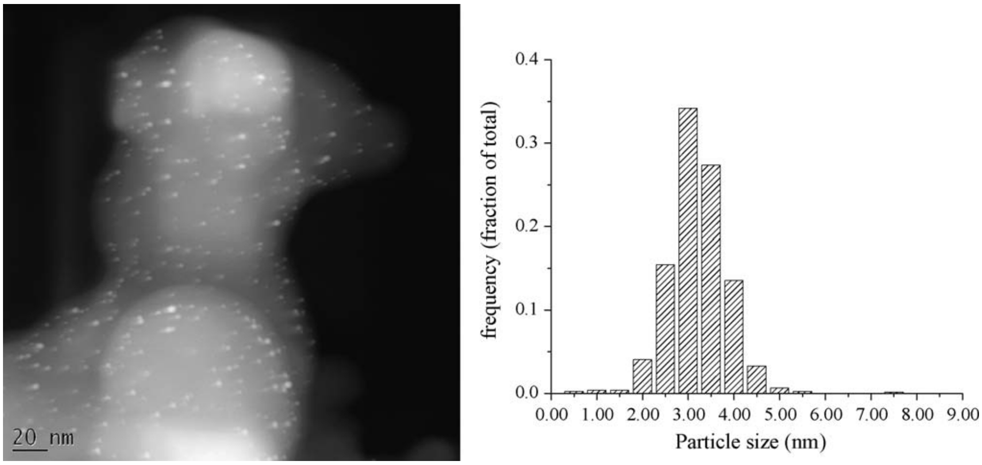

Fig. 2. STEM image of Au/C (sol) catalyst. The accompanying particle size distribution indicates a mean particle size of 3.0 nm.

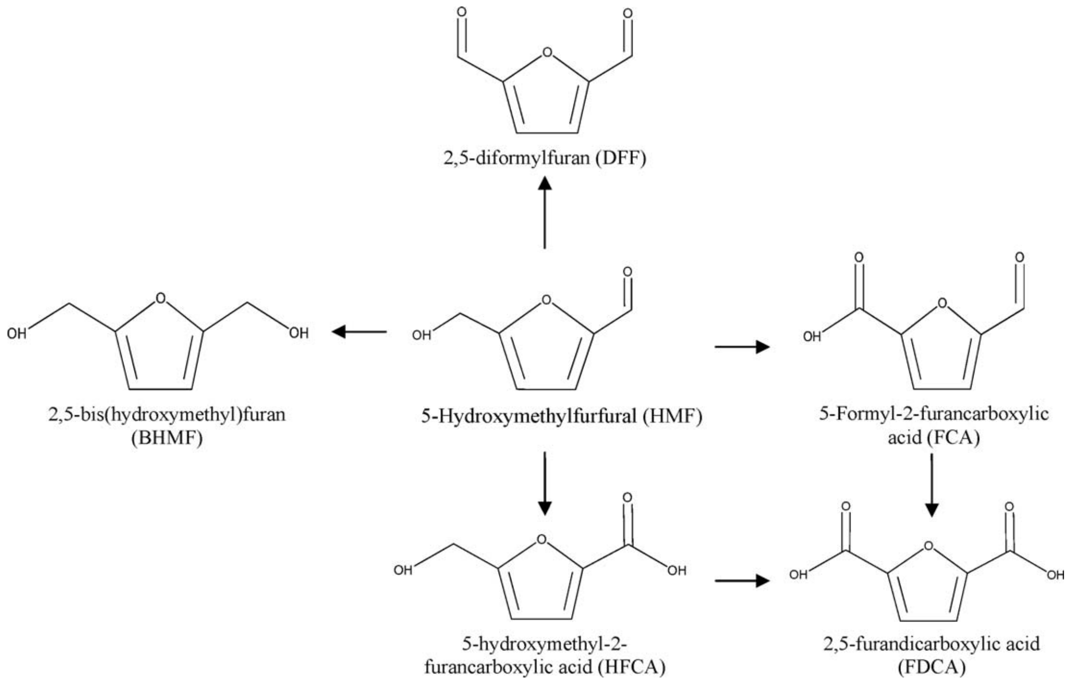

Fig. 3. Products of HMF oxidation.

reactions were minimized while oxidation proceeded. A concentration of 0.3 M NaOH (NaOH:HMF 2:1) was chosen. The background conversion of HMF in NaOH solution without catalyst was 10% over 0.5 h.

The oxidation products of HMF are depicted in Fig. 3. The product 2,5-bis(hydroxymethyl)furan (BHMF) was formed in the Cannizzaro reaction, which is a disproportionation reaction induced by high concentration of the base. A typical reaction profile for HMF oxidation over supported Pt is reported in Fig. 4. The oxidation of HMF proceeded through HFCA and FCA to FDCA. The oxidation of HMF over Pd and Au catalysts apparently proceeded through HFCA because FCA was not observed in the course. In general, the product distributions reported here are consistent with those discussed earlier [9,10,17,18].

All catalysts were investigated for the oxidation of 0.15 M HMF in 0.3 M NaOH at 690 kPa O_2 and 295 K and a catalyst loading equivalent to metal:substrate = 6.7×10^{-3}. The results of these runs after 6 h (high HMF conversion) can be seen in Table 2. Although the conversion of HMF was 100% after 1 h over all three Au catalysts, the major product was HFCA, even after 6 h. In contrast to Pt and Pd, Au did not readily oxidize the alcohol side chain under these reaction conditions. Despite the complete conversion of HMF after 1 h, the relative concentrations of FDCA and HFCA were virtually unchanged between 1 h and 6 h. After 6 h, additional feed solution (0.15 M HMF, 0.3 M NaOH) was added to the reactant mixture to yield a new HMF concentration in the reactor of 0.05 M, which was readily oxidized to HFCA in less than 1 h. These results conclusively demonstrated that the Au catalyst did not deactivate significantly during HMF oxidation. Because the product selectivity was nearly the same for all of the Au catalysts tested, the reaction path was not affected by the carbon or titania support.

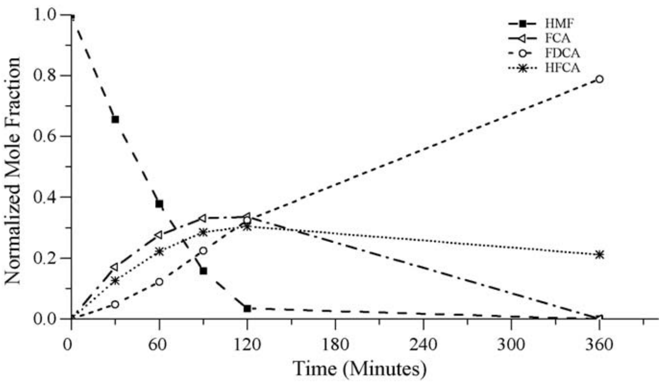

Fig. 4. Sample reaction profile for oxidation of HMF over Pt/C. Reaction conditions: 0.15 M HMF, 0.3 M NaOH, 295 K, 690 kPa O_2.

While the time to reach complete conversion of HMF over Pt was much longer than for Au or Pd, the desired product (FDCA) was obtained in majority (S_{FDCA} = 79%). Oxidation of HMF over Pd also yielded a majority of FDCA (S_{FDCA} = 71%).

The catalyst loadings for the runs in Table 2 were selected to give high conversions in relatively short reaction times. However, the flux of O_2 through the gas–liquid film was very near the mass transfer limit. Therefore, the amount of catalyst loaded into the reactor was lowered in order to obtain rate data unaffected by gas–liquid transport effects. The results of those reactions are summarized in Table 3. It should be noted that the amount of catalyst used for the results in Table 3 was substantially lower for the Pd and Au catalysts relative to the amount used for Table 2.

Although the metal loadings were much lower for the Au catalysts, the major product was still HFCA. Nevertheless, Au catalysts were substantially more active in converting HMF than either Pt or Pd. The turnover frequency on Au ranged from 2 to 5 s^{-1} whereas

Table 2
Oxidation of HMF over supported Pt, Pd and Au catalysts.[a]

Catalyst	Conversion (%)	S_{FDCA} (%)	S_{HFCA} (%)
Pt/C	100	79	21
Pd/C	100	71	29
Au/C (WGC)	100	8	92
Au/C (sol)	100	7	93
Au/TiO_2	100	8	92

[a] Reaction conditions: 0.15 M HMF solution in 0.3 M NaOH, metal:HMF = 6.67×10^{-3} mol/mol, T = 295 K, P = 690 kPa O_2. S refers to selectivity after 6 h.

Table 3
Turnover frequencies and product selectivities during HMF oxidation over supported Pt, Pd and Au catalysts.[a]

Catalyst	Metal:HMF	TOF[b] (s^{-1})	Conversion (%)	S_{FDCA} (%)	S_{HFCA} (%)	S_{BHMF} (%)	S_{FCA} (%)
Pt/C	6.67×10^{-3}	0.08	50	16	33	1	50
Pd/C	2.00×10^{-3}	0.15	50	18	80	2	–
Au/C (WGC)	8.70×10^{-4}	5.0	50	–	95	5	–
Au/C (sol)	5.48×10^{-4}	2.3	50	21	77	2	–
Au/TiO_2	3.57×10^{-4}	1.6	50	3	84	13	–

[a] Reaction conditions: 0.15 M HMF solution in 0.3 M NaOH, T = 295 K, P = 690 kPa O_2.
[b] TOF is calculated from the moles of HMF consumed in 30 min, normalized by the surface metal atoms in the reactor. Conversion of HMF was typically less than 20% after 30 min.

Table 4
The influence of O_2 pressure on reaction and selectivity of HMF oxidation over Au/TiO_2 catalyst.[a]

P (kPa)	TOF[b] (s^{-1})	Conversion (%)	S_{FDCA} (%)	S_{HFCA} (%)	S_{BHMF} (%)
690	1.6	50	3	84	13
2000	1.2	50	28	69	3
3000	1.4	50	36	64	–

[a] Reaction conditions: 0.15 M HMF and 0.3 M NaOH, T = 295 K, metal:HMF = 3.57×10^{-4}.
[b] TOF is calculated from the moles of HMF consumed in 30 min, normalized by the surface metal atoms in the reactor. Conversion of HMF was typically less than 20% after 30 min.

the TOF on Pd and Pt was 0.15 and 0.08, respectively. The Pd catalyst was slightly more active than the Pt catalyst for HMF oxidation, which is consistent with the findings reported by Vinke et al. [10]. The high activity of Au catalysts relative to Pt and Pd has also been observed for the oxidation of octanol [24]. Moreover, Ketchie et al. reported Au to be significantly more active than Pd for glycerol oxidation in basic solution [25]. Interestingly, the Au/C (sol) catalyst did produce some FDCA under these conditions (selectivity = 21% at 50% HMF conversion).

The effect of O_2 pressure on reaction rate and product selectivity over the Au/TiO_2 catalyst was investigated and the results are summarized in Table 4. The turnover frequency was independent of the O_2 pressure in the range investigated. However, as the pressure of O_2 increased from 690 kPa to 2000 kPa to 3000 kPa, the selectivity for FDCA increased from 3% to 28% to 36% at 50% conversion, which agrees with the trend noted by Casanova et al. between 100 kPa and 1000 kPa over their Au/CeO_2 [18]. In contrast, Gorbanev et al. reported the selectivity for the diacid increased as the O_2 pressure increased from 1000 kPa to 2000 kPa but then remained constant to 3000 kPa [17]. Their selectivity to the diacid over a Au catalyst at 2000 kPa O_2 was 78%, which was much higher than that observed here.

It should be noted that the amount of catalyst and concentration of base used in Table 4 were much less than those in Ref. [17]. Therefore, we reproduced the conditions used in Ref. [17] and compare our results in to those published previously in Table 5. The product selectivity on both the AuTiO$_2$ and the Au/C catalyst was similar to that reported by Gorbanev et al. [17]. The selectivity to diacid (FDCA) was enhanced by substantially increasing the base concentration. Evidently, the aldehyde side chain is readily oxidized over Au at lower concentrations of base, but higher concentrations (20 equiv.) were needed to oxidize the alcohol side chain. Likewise, Casanova et al. report higher selectivity to FDCA when a 4:1 ratio of NaOH:HMF was used, instead of a 2:1 ratio [18]. This finding is consistent with previous work on glycerol oxidation over supported Au catalysts in which high base concentration is thought to deprotonate the alcohol and facilitates its conversion to aldehyde [23]. Casanova et al. also observe the need for high base concentration to produce FDCA from HMF. Moreover, they report that the sequential reaction of intermediate HFCA to FDCA is greatly accelerated by increasing the reaction temperature to values greater than 373 K and emphasize that the slow reaction of HFCA to FDCA limits the overall rate [18].

While high pH is necessary to oxidize the alcohol side group of HMF or HFCA, high pH can also lead to degradation of products. A reaction utilizing a lower metal:HMF ratio (used for runs in Table 4) and a high NaOH concentration (used for runs in Table 5) was conducted over Au/TiO_2 to elucidate the role of base concentration on product distribution. Although the selectivity to diacid in this experiment (56% conversion of HMF, 8% selectivity to FDCA) was lower than that reported in Table 4, the major product was BHMF at high base concentration. Continued reaction to ~100% conversion resulted in the formation of formic acid and other degradation products. Evidently, high base concentrations can be detrimental to selectivity because of undesirable side reactions, even at 295 K. To avoid degradation of HMF in concentrated base solution, a high Au catalyst loading (such as that used for the experiments reported in Table 5) is needed to rapidly oxidize HMF to HFCA, an intermediate product that is stable in base.

It should be noted that no evidence for leaching of Au into solution was observed. A sample of the reaction mixture at the end of the reaction catalyzed by Au/C (sol) was filtered with a PTFE 0.2 μm filter to remove solid catalyst, and tested for trace Au by ICP analysis performed by Galbraith Laboratories, Knoxville, TN. The

Table 5
Selectivity of HMF oxidation on Au catalysts at high base concentration.[a]

Catalyst	Reaction time = 6 h[b]		Reaction time = 22 h[b]	
	S_{FDCA}	S_{HFCA}	S_{FDCA}	S_{HFCA}
Au/C (sol)	31	69	72	28
Au/TiO_2	32	68	80	20
Au/TiO_2[c]	50	50	78	19

[a] Reaction conditions: 0.1 M HMF in 2.0 M NaOH, metal:HMF = 8.0×10^{-3}, P = 2000 kPa O_2.
[b] Conversion of HMF was 100%.
[c] Data from Gorbanev et al. [17].

ICP analysis determined the Au concentration in the liquid to be <0.2 ppm.

4. Conclusion

This work presents a comparison of the rate and product distribution for HMF oxidation over supported metal catalysts, Pt/C, Pd/C, Au/C and Au/TiO_2. The rate of oxidation of HMF over Au catalysts was an order of magnitude greater under the standard conditions of 295 K, 690 kPa O_2, 0.15 M HMF and 0.3 M NaOH. However, the rapid conversion of HMF over the Au catalysts was to the intermediate product HFCA, formed by oxidation of the aldehyde side chain of HMF. Under identical conditions, Pt and Pd were able to effectively oxidize the HFCA to FDCA, which indicates Pt and Pd can activate the alcohol side chain of HFCA whereas Au cannot. For a gold sample to catalyze the formation of FDCA from HFCA, high pressures of O_2 and high concentrations of base were required, although the effect of base appeared to be more important than the O_2 pressure. Indeed, the rate of oxidation on Au/TiO_2 was independent of O_2 pressure. From our previous work on Au-catalyzed glycerol oxidation [23], we speculate that OH^- is required to activate the alcohol and form an aldehyde intermediate, which can subsequently oxidize to the carboxylate in the presence of OH^-, Au catalyst and O_2. Evidently, Pt and Pd provide an alternative catalytic route to dehydrogenate the alcohol side chain that is unavailable on Au.

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