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Author: Sara E. Davis Angelica Benavidez Robert W. Gosselink Johannes H. Bitter Krijn P. de Jong Abhaya K. Datye Robert J. Davis



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**Authors**: Sara E. Davis,<sup>a</sup> Angelica Benavidez,<sup>b</sup> Robert W. Gosselink,<sup>c</sup> Johannes H. Bitter,<sup>c</sup> Krijn P. de Jong,<sup>c</sup> Abhaya K Datye,<sup>b</sup> and Robert J. Davis<sup>a</sup>\*

<sup>a</sup>Department of Chemical Engineering, University of Virginia, 102 Engineers Way, Charlottesville, VA 22904-4741, USA

<sup>b</sup>Department of Chemical and Nuclear Engineering, University of New Mexico, 1 University of New Mexico, MSC 01 1120, Albuquerque, NM 87131-0001 USA

<sup>c</sup>Inorganic Chemistry and Catalysis, Debye Institute for Nanomaterials Science, Utrecht University, Universiteitweg 99, 3584 CG Utrecht, Netherlands

\*Corresponding Author: Robert J. Davis Department of Chemical Engineering University of Virginia 102 Engineers Way Charlottesville, VA 22904-4741, USA phone: 434-924-6284 FAX: 434-982-2658 email: rjd4f@virginia.edu

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#### Abstract

The reaction mechanism of 5-hydroxymethylfurfural (HMF) oxidation in neutral aqueous solution with O<sub>2</sub> to 5-hydroxymethyl-2-furancarboxylic acid (HFCA) and 2,5-furandicarboxylic acid (FDCA) was evaluated over a 3 wt% Pt/activated carbon catalyst in a semibatch reactor and confirmed that the mechanism was the same as that determined at high pH. In addition, the reaction kinetics of intermediate HFCA oxidation to FDCA over supported Pt at high pH were investigated. The combination of reaction kinetics and isotopic labeling studies using <sup>18</sup>O-labeled H<sub>2</sub>O and O<sub>2</sub> was used to suggest a reaction mechanism in which H<sub>2</sub>O inserts oxygen into the product and O<sub>2</sub> scavenges electrons from the metal catalyst. Carbon nanofibers (CNF) containing excess acid or base groups were also used as supports for Pt and Au nanoparticles and evaluated as catalysts in HMF oxidation. Although the CNF-supported samples catalyzed HMF oxidation at rates similar to other carbon-supported Pt and Au catalysts, the CNF support with basic groups improved the ability of supported Au to form FDCA from HMF under mild conditions.

### 1. Introduction

The development of biomass-derived fuels and chemicals to replace fossil fuels and petrochemicals continues to be of great interest. One such biomass-derived molecule is 2,5-furandicarboxylic acid (FDCA), which has been identified as one of the top 12 value-added chemicals from biomass by the U.S. Department of Energy because of its potential as a replacement monomer in the production of plastics [1]. The diacid FDCA is structurally similar to terephthalic acid, the monomer used in PET plastic production. Recently, Avantium announced large scale production of FDCA-based polymers for bottles and other polymer applications [2]. Diacid FDCA is an oxidation product of 5-hydroxymethylfurfural (HMF), which is derived from fructose dehydration.

The oxidation of HMF has been investigated under a variety of reaction conditions utilizing both homogeneous and heterogeneous catalysts [3-15]. In early work, Verdeguer et al. studied the oxidation of HMF over Pt catalysts with Pb promoters and noted the need for high pH in the reactant mixture when the oxidation was performed at moderate temperatures [14]. That work also demonstrated hydroxide bases improved reaction rates more than carbonate bases. The base concentration not only affects the rate of HMF oxidation but also influences the product distribution, especially when Au catalysts are used. The general scheme of HMF oxidation is presented in Figure 1.



Figure 1. The general reaction scheme for 5-hydroxymethylfurfural oxidation

Previous reports indicated that oxidation of HMF at near room temperature (295 K) and with small quantities of base (2:1 NaOH to HMF or 8% sodium methoxide relative to HMF) over Au produced a majority of the monoacid, hydroxymethylfurancarboxylic acid (HFCA) [6, 13]. In one case, simply raising the temperature to 403 K resulted in further oxidation to the diacid product FDCA [13]. Increasing the amount of base (20:1 NaOH:HMF) and catalyst used also facilitated the subsequent oxidation of HFCA to FDCA [6, 7]. Similarly, Casanova et al. reported that the optimized conditions of 403 K, 1000 kPa O<sub>2</sub>, and 4:1 NaOH:HMF produced >99% yield

FDCA after 8 h over Au/CeO<sub>2</sub> [4]. At the same pressure and solution concentrations but at lower temperature (298 K), HFCA was the major product after complete conversion of HMF.

The literature indicates that the aldehyde group, which is highly reactive in high concentrations of NaOH, is rapidly oxidized to the acid in the presence of a metal catalyst [6]. Since Au is unable to activate the alcohol group, high concentrations of OH<sup>-</sup> are required to oxidize the alcohol to an aldehyde, which is subsequently oxidized to acid rapidly [6]. In contrast, supported Pt and Pd catalysts produced a majority of the diacid product, FDCA, at a relatively low concentration of NaOH (2:1 NaOH:HMF), which is likely the result of higher alcohol reactivity on those metals compared to Au [6]. The turnover frequency, or TOF, of HMF oxidation over Pt and Pd catalysts is reportedly lower than that over Au catalysts, however.

The mechanism for HMF oxidation over Au and Pt catalysts at high pH was recently investigated through the use of isotopically-labeled dioxygen and water [16]. The source of oxygen insertion was shown to be H<sub>2</sub>O rather than O<sub>2</sub> in all cases. The role of dioxygen was proposed to be as electron scavenger, closing the catalytic cycle and allowing the reaction to proceed.

The high pH reaction conditions typical of HMF oxidation is unfavorable economically and environmentally, leading to interest in developing reaction conditions that allow for FDCA production in neutral solution. The use of a solid base support for the metal catalyst is one potential way to replace the need for homogeneous base in the reaction. For example, some investigators explored hydrotalcites as solid base supports for Au catalysts in the aqueous oxidation of HMF to FDCA [8, 17]. Others have reported leaching of hydrotalcite during reaction, likely the result of the product acid reacting with the Mg<sup>2+</sup> component of the support

during HMF oxidation [17-19]. Hydrotalcite therefore appears to serve as a stoichiometric replacement for the homogeneous base rather than as a true catalytic material. If a solid base material is to be used to replace homogeneous base, the interaction between basic sites on the catalyst and product acid FDCA must be considered. In addition, the very low solubility of the product acids HFCA and FDCA in neutral water must also be addressed, as products may precipitate and/or inhibit access to the metal catalyst [10, 20].

Lilga et al. reported on the base-free oxidation of HMF to FDCA over a  $Pt/ZrO_2$  catalyst in a flow reactor [10]. Apparently, the oxidation proceeds over Pt in the absence of homogeneous base at a relatively higher temperature (373 K) than commonly used in previous studies. The group utilized low concentrations of HMF (0.5 – 3 wt%) to keep the product FDCA within its solubility limit, ultimately realizing 98% yield of FDCA (373 K, 1035 kPa O<sub>2</sub>).

Since the pH of the reaction medium drops as the reaction proceeds, a molecular understanding of the mechanism of base-free HMF oxidation is desired to complement earlier studies performed under highly basic conditions.

Likewise, the impacts of NaOH concentration, O<sub>2</sub> pressure, and temperature on the rate of transformation as well as the product distribution during HMF oxidation are needed to guide catalyst development.

Structural characteristics of the catalyst support are also important, especially when dealing with relatively large molecules typical of biomass transformations. For example, a low surface area support with large pores may be desirable to enhance the transport of bulky substrates to the active metal particles located in the interior of the support pellets. Although carbon has been widely used as a catalyst support, the microporosity of activated carbon can

hinder internal mass transfer [21]. Reproducibility issues also plague the synthesis of activated carbon, which is detrimental to applications in catalysis [21]. To ameliorate some of the transport problems, non-microporous supports, such as carbon nanofibers (CNF), may be beneficial. An added benefit of CNFs is that their synthesis is highly reproducible and provides a relatively uniform product. The CNF materials can be functionalized with various surface groups, forming both acidic and basic sites, and can be used alone as catalysts or as supports for catalytically-active metal nanoparticles.

The acidic sites on oxy-functionalized CNF (CNF-ox) prepared by an oxidative treatment in acid have been studied in detail, as has their influence on the synthesis of supported Pt and Ni nanoparticles [22-24]. Nitrogen-containing CNFs (CNF-N) are reported to be solid base catalysts [25-28]. For example, Van Dommele et al. demonstrated the effectiveness of nitrogen-containing carbon nanotubes as solid base catalysts for the Knoevenagel condensation [26]. Likewise, Gong et al. studied the electrocatalytic activity of nitrogen-containing carbon nanotubes for oxygen reduction reactions for fuel cell applications [27]. Moreover, CNF-N materials have been investigated recently as catalyst supports for several different metals. Liu et al. highlighted the high dispersion and stability of Pd nanoparticles supported on CNF-N in the hydrodechlorination of chlorobenzene [28]. The lone electron pair of pyridine species on the functionalized nanofibers is thought to interact with Pd, enabling a high dispersion of metal nanoparticles and preventing their aggregation. Similarly, Villa et al. report on Pd and Au-Pd catalysts supported on CNF and CNF-N [29]. The metals supported on nitrogen-functionalized CNFs had smaller metal particle sizes and therefore higher overall catalytic activity for liquid-phase alcohol oxidation.

In this contribution, we investigate the reaction mechanism of HMF oxidation over supported Pt at neutral or lower pH to verify the generality of the mechanism determined

previously under basic conditions. Isotopic labeling studies and detailed reaction kinetics provide the basis for additional catalyst development with acid- and base-functionalized carbon nanofibers as novel supports for Pt (and Au) particles.

#### 2. Experimental Section

#### **2.1 Catalyst Preparation**

The carbon nanofibers (CNF) used in this work were grown over a Ni/SiO<sub>2</sub> catalyst. First, a Ni/SiO<sub>2</sub> (5-wt% Ni) was prepared via homogeneous deposition-precipitation using SiO<sub>2</sub> (Degussa, Aerosil 200), Ni(II)NO<sub>3</sub>•6H<sub>2</sub>O (Acros, 99% purity), and urea (Acros) [30]. The resulting catalyst was used to grow fibers by flowing CO/H<sub>2</sub>/N<sub>2</sub> at 823 K as previously described [30]. The material containing both CNF and Ni/SiO<sub>2</sub> catalyst was subsequently refluxed three times in 1.0 M KOH solution for 1 h each time to remove SiO<sub>2</sub>, and then washed with deionized H<sub>2</sub>O until the effluent was pH neutral. Next, the material was refluxed twice in 65% HNO<sub>3</sub> for 1 h each time to remove Ni and introduce oxygen into the CNF. The material was washed again with deionized H<sub>2</sub>O until the effluent was pH neutral and dried in air at room temperature overnight. This material is referred to as CNF-ox. Toebes et al. used this procedure to produce CNF with a residual nickel content of <0.5 wt%, and the trace nickel was located inside graphitic envelopes, making it unavailable for catalysis. [31]

Some of the CNF-ox material was further treated in NH<sub>3</sub> to replace oxygen-containing groups with nitrogen-containing groups [28]. The CNF-ox sample was heated to 1123 K under flowing NH<sub>3</sub> (60 cm<sup>3</sup> STP min<sup>-1</sup>), held under these conditions for 100 minutes, and cooled under flowing NH<sub>3</sub>. The resulting materials are referred to as CNF-N.

The CNF materials were subsequently used to support Pt and Au nanoparticles. The Pt catalysts were prepared using an impregnation method [32]. In brief, 0.16 g H<sub>2</sub>PtCl<sub>6</sub>·6(H<sub>2</sub>O) was dissolved in 30 cm<sup>3</sup> distilled, deionized H<sub>2</sub>O, to which 2.0 g of CNF-ox or CNF-N was added. The mixture was stirred at room temperature for 18 h. The catalysts were filtered from solution, washed several times with H<sub>2</sub>O, and dried overnight in air at 403 K. The resulting catalysts were reduced in 100 cm<sup>3</sup> min<sup>-1</sup> flowing H<sub>2</sub> (UHP, Messer gases) at 673 K, cooled in H<sub>2</sub>, exposed to air and stored in a refrigerator. The supported Pt catalysts were used without further pretreatment.

The Au catalysts were synthesized using a sol method [33]. First, an Au sol was prepared by dissolving 0.04 g HAuCl<sub>4</sub>•3(H<sub>2</sub>O) (Aldrich) in 1000 cm<sup>3</sup> deionized H<sub>2</sub>O along with a 2 wt% polyvinyl alcohol (Acros) solution in a ratio of Au:PVA = 1:1 w:w. The colloid was reduced by adding 0.1 M aqueous solution of NaBH<sub>4</sub> (Aldrich) dropwise in 3:1 molar ratio of NaBH<sub>4</sub>:Au. Following reduction, the sol was ruby red in color. The CNF support was added to the sol and the mixture was acidified to pH = 2 with H<sub>2</sub>SO<sub>4</sub>. The Au sol-CNF mixture was stirred for 4 h to allow the Au to deposit on CNF. The Au/CNF sample was recovered by filtration and washed with several liters of H<sub>2</sub>O. The filtrate was clear in color, confirming the Au sol had deposited on the support. The catalyst was dried in air at 333 K overnight and subsequently treated in N<sub>2</sub> and H<sub>2</sub> (9:1 ratio) flowing at 150 cm<sup>3</sup> min<sup>-1</sup> for 4 h at 573 K. The resulting Au catalyst was exposed to air and stored in a refrigerator. As with the Pt catalysts, the Au samples were used without any additional pretreatment. Metal weight loading (Au or Pt) was determined by ICP analysis performed by Galbraith Laboratories, Knoxville, TN.

In addition, 3 wt% Pt on activated carbon (Aldrich) was also used in this study. It was reduced in H<sub>2</sub> (UHP, Messer Gas) flowing at 150 cm<sup>3</sup> min<sup>-1</sup> for 6 h at 573 K and cooled under

flowing H<sub>2</sub>. After exposure to air, the catalyst was refrigerated and used without further pretreatment.

#### 2.2 Catalyst Characterization

#### 2.2.1 Chemisorption of $H_2$

The dispersion of Pt was determined using a Micromeritics ASAP 2020 automated adsorption system. The Pt catalysts were heated to 473 K at 4 K min<sup>-1</sup> under flowing H<sub>2</sub> (UHP, Messer Gas) and reduced for 1.5 h. The samples were evacuated for 2 h at 473 K and then cooled to 308 K for analysis. No H<sub>2</sub> uptake was observed on the bare CNF-ox or CNF-N materials.

### 2.2.2 Physisorption of $N_2$

The surface area of CNF-ox was also determined using a Micromeritics ASAP 2020 automated adsorption system. The CNF-ox material was heated to 473 K and held under vacuum for 16 h. The material was cooled to 77 K for  $N_2$  adsorption.

#### 2.2.3 Titration

The amount of acid and base sites on the carbon materials, with and without metals, was determined by titration with NaOH and HCl using a Titralab TIM 845 system [24, 26]. To evaluate the acid site density, a solution of 0.01 M NaOH and 0.1 M KCl was used as titrant. The solid material (0.05 g) was dispersed in 60 cm<sup>3</sup> of 0.1 M KCl and titrated to pH 5 and pH 7.5, corresponding to the amount of strongly acidic groups and the total amount of acidic groups, respectively. To quantify the base site density, a solution of 2.0 mM HCl was used as titrant. To 50 cm<sup>3</sup> of 0.1 M KCl, 0.1 g of the solid material was added, and the mixture was titrated to pH 7.

High-angle annular dark field (HAADF) imaging was performed using a JEOL 2010F FASTEM field emission gun scanning transmission electron microscope operated at 200kV. The catalyst samples were 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.

### **2.3 Oxidation Reactions**

The aqueous phase oxidation of HMF (Acros, ≥98% purity) or HFCA (ChemBridge, 95% purity) was carried out in a 50 cm<sup>3</sup> Parr Instrument Company 4592 batch reactor equipped with a glass liner. In all reactions, 7.0 cm<sup>3</sup> of the reactant solution was added to the reactor along with the appropriate amount of catalyst. The reactor was purged with flowing O<sub>2</sub> (UHP, Messer Gas) and then pressurized to the desired value. A constant pressure was maintained by a continuous O<sub>2</sub> feed. Samples of the product solution were acquired by removing the top of the reactor, taking the sample, flushing the reactor with O<sub>2</sub> and repressurizing. The maximum O<sub>2</sub> transport rate from the gas to the liquid was determined by oxidation of sodium sulfite [34], and the reactant oxidation rate was kept significantly below this limit when quantitative rates were measured. The samples from the oxidation reactions were filtered using PTFE 0.2 µm filters and diluted with deionized H<sub>2</sub>O in a 1:3 sample:water ratio. The analysis was conducted using a Waters e2695 high performance liquid chromatograph (HPLC) at 303 K equipped with refractive index and UV/vis detectors. The HPLC utilized a Bio-Rad Aminex HPX-87H column and 5mM H<sub>2</sub>SO<sub>4</sub> flowing at 0.5 cm<sup>3</sup> min<sup>-1</sup> to perform the separation. The retention times and calibrations for observed products were determined by injecting known concentrations.

#### 2.3.1 Mass spectrometry

Mass spectrometry was performed using a Waters Micromass ZQ quadrupole mass spectrometer (in both electronegative and electropositive modes, depending on the molecule being ionized) using a direct injection of the product mixture. Prior work in our lab indicated that exchange of oxygen between the water and the product can occur during HPLC analysis [35]. This exchange process was avoided by direct injection of the product into the mass spectrometer. Known compounds in aqueous solution were directly infused into the mass spectrometer to obtain reference spectra. The electronegative mode was best to ionize HFCA, FCA, and FDCA. The parent peak for HFCA appeared at a mass-to-charge ratio (m/z) of 141 (mass of HFCA, 142, minus 1, since H<sup>+</sup> was removed during ionization). In the case of FDCA, a prominent peak appeared at m/z of 155, which corresponds to the mass of FDCA minus one proton removed during ionization. The peak for FCA appeared at 139, which corresponds to the mass of FCA, 140, minus 1, as 1 H<sup>+</sup> was removed during ionization. The electropositive mode was best to ionize HMF. The peak for HMF appeared at 127, corresponding to the mass of HMF plus 1 H<sup>+</sup> added during ionization.

### 3. Results and Discussion

### 3.1 Mechanism of base-free HMF oxidation over commercial Pt/C

In our previous work, the mechanism of HMF oxidation at high pH was based on isotopic labeling studies over Au and Pt catalysts [16]. In brief, the oxidation of HMF proceeds by the rapid, reversible hydration of the aldehyde moiety to a geminal diol in solution. This reaction is greatly accelerated by NaOH. The second step is a hydrogen transfer from the geminal diol on the catalyst surface to form a carboxylic acid, thus depositing two electrons on the metal. The

hydroxymethyl group is subsequently oxidized on the metal surface to an aldehyde, again depositing two electrons on the catalyst. The aldehyde undergoes reversible hydration to a geminal diol, as in the first step. Finally, a hydrogen transfer step produces the second carboxylic acid, again depositing two electrons on the metal surface. The role of O<sub>2</sub> in HMF oxidation is to scavenge electrons from the metal catalyst surface, thus closing the catalytic cycle and allowing the reaction to continue. The presence of peroxide in solution during the reaction suggests that O<sub>2</sub> is sequentially reduced to peroxide and eventually to hydroxide, analogous to the previously published mechanism of glycerol oxidation on Au [35]. Hydroxide ions in solution and on the metal surface facilitate geminal diol formation and hydrogen abstraction from the alcohol moiety. An investigation into the mechanism of HMF oxidation in neutral solution is presented here to determine if the pH change influences the mechanism of oxygen insertion.

To confirm that the products of HMF oxidation did not exchange O appreciably with liquid water, unlabeled HFCA, FCA, and FDCA were dissolved separately in  $H_2^{18}$ O in the presence of Pt/C and heated to reaction temperature for the duration of a reaction experiment. The same type of control experiment was conducted with HMF, though the duration was 4 h because 100% conversion of HMF is realized in 4 h during a reaction. All experiments were performed under N<sub>2</sub> rather than O<sub>2</sub> to minimize oxidation.

Significant conversion of HFCA, even in an inert environment, was observed in a control experiment utilizing unlabeled water (60% conversion of HFCA in 18 h, with 83% selectivity to FCA and 17% selectivity to FDCA). The parent peaks of unlabeled HFCA and FCA (142 g mol<sup>-1</sup> and 140 g mole<sup>-1</sup>, respectively) are 2 mass units apart, which would cause a problem in the analysis if <sup>18</sup>O were incorporated. The mass to charge ratio is the same for HFCA containing no <sup>18</sup>O and FCA with one <sup>18</sup>O incorporated (m/z = 141); thus, it is impossible to distinguish between

the two compounds directly injected into the mass spectrometer. As this is the expected outcome (exchange in the aldehyde group due to reversible hydration in water, but no exchange in the acid group), an exchange experiment utilizing HFCA would not yield useful results and was therefore not performed. The exchange experiment utilizing FCA resulted in some oxidation, even under inert atmosphere, but the only product was FDCA. The parent peaks of FDCA (m/z = 155) and FCA (m/z = 139) are separated by 16 mass units, so peak overlap was not a concern in the analysis. Likewise, HMF and its oxidation product, HFCA, are separated by 16 mass units. The FDCA control experiment did not result in any conversion of FDCA.

To confirm that the alcohol moiety does not exchange <sup>18</sup>O with water under our reaction conditions, ethanol was tested as substrate (0.3 M ethanol, 18 h and 348 K; pressure 1034 kPa to keep substrate in liquid phase). No scrambling of oxygen was observed between ethanol and  $H_2^{18}$ O; thus, exchange between the hydroxymethyl group of HFCA and  $H_2^{18}$ O was not expected. An exchange experiment for the dialdehyde product, DFF, was not performed because of the known reactivity of aldehydes in water.

The mass spectrum of the mixture from the HMF exchange experiment in  $H_2^{18}O$  displayed a prominent peak at m/z = 129, corresponding to HMF with incorporation of one <sup>18</sup>O. Thus, scrambling of one oxygen atom in HMF with water must be accounted for when analyzing the final product. The oxygen atom that was most likely exchanged with water was that of the highly reactive aldehyde group, presumably the result of reversible hydration.

The spectrum from the FCA control experiment showed a prominent peak at m/z = 141, indicating incorporation of one <sup>18</sup>O atom from H<sub>2</sub><sup>18</sup>O in FCA. An additional smaller peak was seen at m/z = 143, suggesting the exchange of two <sup>18</sup>O atoms. Thus, the scrambling of at least

one oxygen atom, and possibly two, in FCA must be taken into account when analyzing the final product FDCA. Very little exchange of oxygen between FDCA and  $H_2^{18}O$  was observed.

Although some oxygen scrambling with  $H_2^{18}O$  was observed with molecules that have an aldehyde group, some details about the oxidation mechanism can still be gleaned. If oxygen insertion occurred through dioxygen, HMF oxidation under  ${}^{18}O_2$  in unlabeled water would be expected to produce FDCA containing two  ${}^{18}O$  atoms (incorporated during the oxidation of the aldehydes to acids). If no label is found in the product, then oxygen addition utilized  $H_2O$  as an oxygen source.

The mass spectra of the FDCA products from HMF oxidations under  ${}^{18}O_2$  in unlabeled water and under unlabeled dioxygen in  $H_2{}^{18}O$  can be seen in Figure 2.



Figure 2. Mass spectra (electrospray negative mode) of major product, FDCA, from base-free HMF oxidation over Pt/C catalyst. Striped bars indicate experiments conducted in <sup>18</sup>O<sub>2</sub> and H<sub>2</sub><sup>16</sup>O; solid bars indicate experiments conducted in <sup>16</sup>O<sub>2</sub> and H<sub>2</sub><sup>18</sup>O. m/z of unlabeled FDCA = 155. Reaction conditions: T = 348 K, P = 345 kPa O<sub>2</sub>; HMF:Pt = 100; 0.15 M HMF. HMF conversion = 100%.

As shown in Figure 2, the reaction performed under  ${}^{18}O_2$  did not incorporate  ${}^{18}O$  into the diacid product FDCA (m/z 155), whereas the reaction conducted in H<sub>2</sub> ${}^{18}O$  incorporated four  ${}^{18}O$  atoms into FDCA (m/z 163). Incorporation of four labeled  ${}^{18}O$  atoms cannot be explained by oxygen scrambling between reaction intermediates and labeled water. Since we have shown that FDCA does not exchange O with H<sub>2</sub>O under the conditions of this study, the oxidation of HMF likely proceeds with H<sub>2</sub>O to form FDCA, analogous to the mechanism of HMF oxidation at high pH proposed previously [16].

We propose that the oxidation of HMF in base-free solution proceeds, like the high pH case, via geminal diol formation due to reversible hydration of aldehyde in water (accounting for two of the <sup>18</sup>O atoms incorporated into FDCA). Oxidation of the geminal diol to carboxylic acid likely occurs on the catalyst surface, depositing two electrons on the metal surface. Subsequent activation of the alcohol moiety, on the catalyst surface, to form an aldehyde deposits two more electrons on the metal surface. The next step is the reversible hydration of aldehyde to geminal diol in solution, accounting for the other two <sup>18</sup>O atoms found in the product acid. Finally, the geminal diol is oxidized on the metal surface, depositing a two more electrons on the metal surface on the metal surface. Consistent with earlier work, we propose that the role of dioxygen in HMF oxidation in base-free solution is to scavenge electrons from the metal surface, being reduced to peroxide and other species, closing the catalytic cycle in the process. It should be noted that a small amount of HMF can be oxidized to dialdehyde DFF instead of HFCA under base-free conditions, but the subsequent oxidation of DFF still yields the final product FDCA by analogous steps.

#### 3.2 Reaction kinetics of HMF and HFCA oxidation over commercial Pt/C

With the mechanism of HMF oxidation at low pH established as the same as that at high pH, the kinetics will provide additional insight into the reaction and will help guide catalyst development. Though the influence of temperature, substrate concentration, O<sub>2</sub> pressure, and base concentration on the product distribution during HMF oxidation has been widely investigated and reported in the literature, there are few reports on the effects of these parameters on reaction rates. To the best of our knowledge, there have not been any reports on the influence of these parameters on the Pt-catalyzed oxidation rate of HFCA, the main intermediate of HMF oxidation to FDCA. Generally, the first step of HMF oxidation is oxidation of the aldehyde moiety to carboxylic acid, HFCA. In contrast, the first step in oxidation of HFCA is oxidation of the alcohol moiety to aldehyde. Since the mechanism of reaction over Pt is the same at neutral and high pH, we chose to perform the kinetics studies at high pH to increase the solubility of the various reaction products. A commercially-available 3 wt% Pt/C catalyst (Aldrich) having a dispersion of 98% determined by H<sub>2</sub> chemisorption was used to test the influence of the various reaction conditions.

The effect of substrate concentration was investigated over the range of 0.05 M to 0.15 M. All other reaction parameters (295 K, 690 kPa O<sub>2</sub>, 0.30 M NaOH concentration, 0.01 or 0.02 g 3 wt% Pt/C depending on substrate) were held constant for each experiment. Initial reactant concentrations were chosen based on standard conditions in previous work (0.15 M substrate, 0.30 M NaOH) [6]. To ensure an excess of NaOH was available throughout the reaction, the range of initial substrate concentrations was kept below 0.15 M. Because the rate of HMF conversion was greater than that of HFCA, the catalyst loading in the HMF oxidation experiments was 0.01 g whereas 0.02 g was used in the HFCA experiments. Turnover

frequencies derived from initial rates and metal dispersion of the fresh catalyst are plotted versus initial substrate concentration for both HMF and HFCA oxidation in Figure 3.



Figure 3. Turnover frequencies of HMF and HFCA oxidation as a function of initial substrate concentration confirm zero order behavior. Reaction conditions: 0.30 M NaOH, 295 K, 690 kPA O<sub>2</sub>, 0.01 g 3 wt% Pt/C (HMF) or 0.02 g 3 wt% Pt/C (HFCA)

The oxidation rates of both HMF and HFCA were zero order in substrate concentration over the range investigated. This finding is in agreement with Vinke et al., who investigated HMF oxidation over Pt/Al<sub>2</sub>O<sub>3</sub> [15]. In general, zero order behavior suggests the Pt catalyst surface is highly covered with adsorbed reactant.

The influence of initial NaOH concentration was also probed. The initial substrate concentration 0.15 M was chosen for both HMF and HFCA, and the rest of the conditions were held constant, as described earlier (295 K, 690 kPa O<sub>2</sub>, 0.01 or 0.02 g Pt/C depending on substrate ). Turnover frequencies are plotted as a function of NaOH concentration in Figure 4.



Figure 4. Turnover frequencies of HMF and HFCA oxidation as functions of initial NaOH concentration. Reaction conditions: 0.15 M HMF or HFCA, 295 K, 690 kPA O<sub>2</sub>, 0.01 g 3 wt% Pt/C (HMF) or 0.02 g 3 wt% Pt/C (HFCA)

The rate of HMF oxidation was first order with respect to NaOH concentration in the range 0.15 M - 0.6 M NaOH. It should be noted that the low end of the concentration range, 0.15 M, represents a 1:1 ratio of NaOH:HMF, and thus formation of acid product will lower the pH

during the reaction. Moreover, the oxidation of HMF proceeds through the main intermediate HFCA. Therefore, the initial oxidation rate, based on the consumption of HMF, is attributed to the rate of oxidation of the aldehyde moiety to acid, i.e. HMF to HFCA.

The influence of NaOH concentration on the rate of HFCA oxidation over Pt was not the same as its influence on HMF oxidation. A run utilizing 0.15 M NaOH resulted in very little conversion of HFCA (5% conversion in 3 h), presumably because the 1:1 stoichiometry of NaOH:HFCA of this experiment suggests that all of the NaOH was consumed in neutralizing the acid groups of HFCA. Although the oxidation of HFCA over Pt in absence of base is possible [10], the temperature for these reactions was not sufficiently high. At higher NaOH concentrations (above 0.30 M NaOH, 2:1 NaOH:HFCA), the reaction rate was nearly zero order in NaOH concentration.

The results here indicate that the oxidation of the aldehyde moiety of HMF depends on NaOH concentration, whereas the oxidation of the alcohol moiety of HFCA does not, above 2:1 NaOH:HFCA. Aldehydes in aqueous solution are recognized to undergo rapid, reversible hydration to geminal diols and the reaction is accelerated at high pH [36]. Previous work indicated that the oxidation of HMF proceeds through hydration of aldehyde in solution and subsequent dehydrogenation of the geminal diol on the catalyst surface to produce carboxylic acid [16]. This work demonstrates that this step of HMF oxidation follows a first order dependence on NaOH concentration. The higher concentration of OH<sup>-</sup> in solution likely facilitates the hydration to geminal diol, which subsequently dehydrogenates to the carboxylic acid on the Pt catalyst. Above a critical concentration (2:1 NaOH:HFCA, or 0.30 M NaOH in this case), however, there is no dependence of HFCA oxidation rate (the second oxidation step in

HMF oxidation to FDCA) on NaOH concentration, suggesting the Pt surface is the key catalytic component of the reacting system.

The effect of  $O_2$  pressure in the range 690 – 3000 kPa on HMF oxidation rate was investigated previously over a Au/TiO<sub>2</sub> catalyst and reported to be zero order. The relationship between HMF oxidation rate and  $O_2$  pressure, and between HFCA oxidation rate and  $O_2$  pressure over Pt, however, has not been probed. Thus, the  $O_2$  pressure was varied between 690 kPa and 2070 kPa and the initial turnover frequencies were evaluated (Figure 5).



Figure 5. Turnover frequencies of HMF and HFCA oxidation as function of O<sub>2</sub> pressure. Reaction conditions: 0.15 M HMF or HFCA, 0.30 M NaOH, 295 K, 0.01 g 3 wt% Pt/C (HMF) or 0.02 g 3 wt% Pt/C (HFCA)

In both cases, the  $O_2$  pressure was increased by 300%, but the rate of oxidation increased by only 20% for HMF oxidation and 10% for HFCA oxidation. Thus, the rates of HMF and HFCA oxidation were nearly zero order in  $O_2$  over the range of 690 to 2070 kPa. This result is not surprising, given the proposed mechanism for HMF oxidation, in which the role of  $O_2$  is simply to scavenge electrons from the catalyst surface. Recent work by Ide and Davis investigating diol oxidation over Pt also reports a zero order dependence on dioxygen pressure over the range 5 – 20 bar [37].

The temperature dependence of both HMF and HFCA oxidation was established and overall activation energies for both HMF and HFCA oxidation were calculated. The oxidation of HMF was investigated at temperatures between 273 K and 308 K to keep the oxidation rate below the known external mass transfer limit in our system. Likewise, oxidation of HFCA was investigated between 295 K and 323 K. Arrhenius-type plots from HMF and HFCA oxidation are shown in Figure 6.



Figure 6. Arrhenius plots of HMF and HFCA oxidation. Reaction conditions: 0.15 M HMF or HFCA, 0.30 M NaOH, 690 kPa O<sub>2</sub>, 0.01 g 3 wt% Pt/C (HMF) or 0.02 g 3 wt% Pt/C (HFCA)

The apparent activation energy of HMF oxidation was calculated to be 29.0 kJ mol<sup>-1</sup> in this study, which is lower than 37.2 kJ mol<sup>-1</sup> reported by Vinke et al. over  $Pt/Al_2O_3$  (reaction conditions: constant pH = 9.0, p(O<sub>2</sub>) = 0.2 atm (p(total) 1.0 atm), 1.0 g 5 wt%  $Pt/Al_2O_3$ , 0.1 M HMF) [15].

The overall activation energy of HFCA oxidation was 29.6 kJ mol<sup>-1</sup>, which is surprisingly similar to that of HMF oxidation. Ide and Davis also report the activation energy of 1,6-

hexanediol oxidation over supported Pt to be 35 kJ mol<sup>-1</sup> and that of 1,3-propanediol to be 34 kJ mol<sup>-1</sup> [37].

#### 3.3 Mechanistic implications

The oxidation of HMF to diacid is comprised of two parts: aldehyde oxidation and alcohol oxidation. The kinetics of aldehyde oxidation were investigated by using HMF as substrate. Aldehyde oxidation occurs by rapid, reversible hydration of the aldehyde to a geminal diol (on the catalyst or in solution), followed by hydrogen transfer from the geminal diol to metal surface, forming a carboxylic acid. Gaseous dioxygen is reduced by scavenging electrons from the metal surface and eventually regenerating hydroxide.

The rate of HMF oxidation showed zero order dependence on HMF concentration, which suggests that the metal surface is saturated in some form of the substrate. We attribute the first order dependence of the rate on NaOH concentration to the reversible hydration of aldehyde to geminal diol, which is accelerated by base.

The oxidation of the alcohol group in HFCA was zero order in substrate concentration, NaOH concentration, and O<sub>2</sub> pressure. This rather counterintuitive finding may be explained by a kinetic model recently proposed by Ide and Davis in their study of alcohol oxidation over Pt at low pH [37]. In their model, there are two types of non-competing sites on the Pt catalyst: one accessible to all species involved in the reaction and one accessible only to hydrogen atoms. In the dehydrogenation of hydrocarbons over transition metals, H atoms preferentially reside on high coordination 3- and 4-fold sites, which are likely to be inaccessible to larger molecules. We suspect a similar phenomenon occurs in the oxidation of HMF.

The implication of their kinetic mechanism of alcohol oxidation at low pH, which is also zero order in substrate and  $O_2$ , is that the measured rate is essentially the rate of C-H activation of adsorbed alkoxide to form aldehyde. If C-H activation were the common step being evaluated in all of these reactions tested (HMF, HFCA, other alcohols), then the similarity of the activation energy for the reactions studied here (~30 kJ mol<sup>-1</sup>) and elsewhere (~35 kJ mol<sup>-1</sup>) [37] is expected.

The other implication of this work involves the nature of the metal catalyst. Since Pt can activate C-H bonds by itself whereas Au is ineffective at that reaction, there is clearly a more important role of base in the case of Au catalysts compared to Pt catalysts.

### 3.4 Carbon nanofibers as supports for Pt and Au nanoparticles

Recognizing the important difference between Pt and Au catalysts as a function of pH, we decided to test the role of functionalized supports on the oxidation catalysis. As discussed earlier, recent work has shown hydrotalcite as a support enables Au catalysts to oxidize HMF to diacid without additional base. However, the hydrotalcite is consumed in the reaction and is not a true catalytic material. In our work, we chose to use functionalized (acid and base) carbon nanofibers as novel supports for the reaction.

The oxidation of HMF was therefore investigated over Pt and Au supported on carbon nanofibers that were functionalized with either oxygen- or nitrogen-containing groups. Table 1 summarizes the physical and chemical properties of the freshly prepared (reduced) materials. The BET surface area for the CNF-ox support materials was found to be 170 m<sup>2</sup>, in agreement with other reports (180-200 m<sup>2</sup> g<sup>-1</sup>) [22, 23].

Catalyst	Weight loading metal (%) <sup>a</sup>	Metal Dispersion (%)	Metal Avg Diameter (nm) <sup>b</sup>	Metal Surface Avg Diameter (nm) <sup>c</sup>	Strong acid sites (mmol kg <sup>-1</sup> ) <sup>d</sup>	Total acid sites (mmol kg <sup>-1</sup> ) <sup>d</sup>	Total base sites (mmol kg <sup>-1</sup> ) <sup>e</sup>
Pt/CNF-N	2.3	$100^{\mathrm{f}}$	0.7	0.9	-	•-	26.0
Pt/CNF-ox	0.42	83 <sup>f</sup>	1.6	2.2	0.0	45	-
Au/CNF-N	0.71	19 <sup>g</sup>	3.7	5.4	-	-	20.7
Au/CNF-ox	0.60	18 <sup>g</sup>	4.4	5.7	59	134	-
CNF-N	0	-	-	-	- 6	-	8.9
CNF-ox	0	-	-	-	164	333	-

Table 1. Results from characterization of CNF materials

<sup>a</sup>determined via ICP analysis

<sup>b</sup>determined via TEM analysis

 $^{c}\Sigma d^{3}/d^{2}$ 

<sup>d</sup>determined by dispersing 0.05 g of material in 50 cm<sup>3</sup> 0.1 M KCl solution and titrating with 0.01 M NaOH and 0.1 M KCl solution. Strong acid sites determined by titration to pH = 5; total acid sites determined by titration to pH = 7.5

<sup>e</sup>determined by dispersing 0.1 g of material in 50 cm<sup>3</sup> 0.1 M KCl solution and titrating with 2.0 mM HCl solution

<sup>f</sup>determined via H<sub>2</sub> chemisorption

<sup>g</sup>calculated as inverse of surface average diameter

The final metal loading of the Pt/CNF-ox catalyst was much lower than that of Pt/CNF-N

(0.42 wt% and 2.3 wt %, respectively), although the synthesis procedures were identical and the

intended loading was 3 wt% Pt for both. Expectedly, the presence of acidic or basic surface

groups on the support material affected the uptake of H<sub>2</sub>PtCl<sub>6</sub>(aq) onto CNF. In the case of Au on

CNF, the metal weight loadings were similar between the two catalysts (0.71 wt% Au/CNF-N

and 0.60 wt % Au/CNF-ox) but both were less than the nominal 1 wt% that was targeted. The

acidic and basic surface functionalization did not have a substantial influence on the uptake of

Au onto CNF materials, presumably because the synthesis procedure involved the adsorption of

a pre-reduced Au sol onto the fibers instead of impregnation of unreduced metal precursors as was the case with Pt.

Results from titration of the acid and base sites are presented in Table 1. The initial pH of a 0.1 M KCl solution after adding CNF-ox was between 4 and 5, indicating that CNF-ox possessed acid sites. The materials were titrated to two endpoints, pH 5 and pH 7.5, to count sites of various acid strength. Strong acid groups, or those titrated to pH 5, are generally attributed to carboxylic acids [38]. The acid sites titrated between pH 5 and pH 7.5 are considered to be fairly weak. From the titration of the CNF-ox support material, approximately half of the acid groups present on the surface are attributed to carboxylic acid groups (333 mmol kg<sup>-1</sup> total acid groups with 164 mmol kg<sup>-1</sup> strong acid groups). The addition of either Pt or Au to CNF-ox decreased the total concentration of acid groups as well as the concentration of strong acid groups. The Au/CNF-ox sample exposed 134 mmol kg<sup>-1</sup> total acid groups with 59 mmol kg<sup>-1</sup> attributed to strong acid groups, while Pt/CNF-ox contained 45 mmol kg<sup>-1</sup> total acid groups with no strong acid groups. Although the loading of Pt (0.42 wt%) was slightly lower than the loading of Au on CNF-ox supports (0.60 wt % Au), the addition of Pt consumed the acid groups substantially more than the addition of Au. This result may be related to the much higher dispersion of Pt on CNF-ox (83%) compared to Au (18%).

The loss of acidic sites that occurred during synthesis of Pt and Au catalysts supported on CNF-ox may result from the deposition of metal and its reduction at elevated temperatures. The same trend was noted by Plomp et al. during Pt/CNF-ox synthesis via a homogeneous deposition-precipitation method [24]. Dihydrogen dissociated on metal nanoparticles might migrate to the support during the reduction of Pt [26, 32]. Dihydrogen may also assist in the

decomposition of oxygen-containing groups [32]. Acidic sites may also anchor metal particles to the carbon surface, as noted in other works involving Pt/CNF-ox [22, 23].

The low uptake of Pt by CNF-ox during impregnation may be because of the lack of basic sites. Basic sites on carbon are reportedly the strongest anchoring sites for the H<sub>2</sub>PtCl<sub>6</sub>(aq) utilized in this synthesis method and are responsible for strong adsorption of  $PtCl_6^{2-}$  (aq) on C [32, 39]. Basic sites incorporated in the CNF-N material via ammonia treatment were added at the expense of acidic sites, which is consistent with the results in Table 1 [28]. The basic Pt/CNF-N material therefore had a higher loading of Pt than the acidic Pt/CNF-ox (2.3 wt% and 0.42 wt%, respectively), likely because of the greater concentration of strong anchoring sites for PtCl<sub>6</sub><sup>2-</sup> (aq).

The basic nanofibers, CNF-N, were titrated with 2 mM HCl to determine the number of exposed basic sites. The initial pH of the material suspended in solution was between pH 8.5 and 9.1, confirming that they were overall basic. As seen in Table 1, the number of basic sites was higher on the supported catalysts (20.7 mmol kg<sup>-1</sup> on Au/CNF-N and 26.0 mmol kg<sup>-1</sup> on Pt/CNF-N) than on bare CNF-N (8.9 mmol kg<sup>-1</sup>). The higher number of basic sites on the supported catalysts does not indicate that the metal nanoparticles are basic, but rather that the material likely has acidic and basic sites. This method of titrating acidic and basic sites measures a net acidity or basicity; i.e., CNF-N materials have more exposed basic sites than acidic sites. The higher number of basic sites on the supported catalysts may be attributed to the removal of residual acid groups during reduction of the catalysts by H<sub>2</sub> as described above, or could possibly indicate some anchoring of metal particles on residual acidic sites.

Electron microscopy of all supported metal catalysts revealed small, well-dispersed metal particles. Images of the support materials and all catalysts are seen in Figure 7. In particular, the Pt catalysts had very small particles (average diameters 0.7 nm for Pt/CNF-N and 1.6 nm for Pt/CNF-ox) but were larger than the Pt particles on CNF materials. The Au catalysts contained metal particles of about the same size (average diameters 3.7 nm for Au/CNF-N and 4.4 nm for Au/CNF-ox). Evidently, the nature of the surface groups did have a large influence on loading but not on the final metal particle size of supported Pt and Au catalysts.



Figure 7. TEM images of [a] CNF-ox support, [b] CNF-N support, [c] Pt/CNF-ox, [d] Pt/CNF-N,

[e] Au/CNF-ox, and [f] Au/CNF-N

### 3.4 Catalytic activity of CNF-supported catalysts

Platinum and gold supported on CNF were tested as catalysts in the oxidation of HMF in NaOH solution and the rates were compared to rates reported over other Pt/C and Au/C catalysts. As discussed earlier, the loading of catalyst was adjusted to keep the rate of conversion of substrate below the external (gas-to-liquid O<sub>2</sub>) mass transfer limit. The turnover frequency (TOF) at a particular loading of each catalyst is reported in Table 2. It should be noted that, in control experiments, the bare support materials CNF-N and CNF-ox did not exhibit catalytic activity for HMF oxidation.

Table 2. Reaction rates over metal catalysts supported on CNF materials<sup>a</sup>

Catalyst	HMF:Metal <sub>surf</sub>	TOF(s <sup>-1</sup> ) <sup>b</sup>
Pt/CNF-ox	325	0.04
Pt/CNF-N	800	0.07
Au/CNF-ox	30000	3.6
Au/CNF-N	13900	2.0

<sup>a</sup>All reactions: 0.15 M HMF, 0.30 M NaOH, 690 kPa O<sub>2</sub>, 295 K

<sup>b</sup>TOF calculated at 0.5 h based on consumption of HMF per mole of surface metal.

The TOFs obtained over the Pt catalysts were fairly similar,  $0.04 \text{ s}^{-1}$  for the CNF-oxsupported catalyst and  $0.07 \text{ s}^{-1}$  for the CNF-N-supported catalyst. Apparently, the presence of acidic or basic surface groups on CNF-supported Pt catalysts did not significantly influence the rate of HMF oxidation. In our previous work, the rate of HMF oxidation over a commercial 3 wt% Pt/C (Aldrich) catalyst under the same reaction conditions was  $0.08 \text{ s}^{-1}$  [6].

The CNF-supported Au catalysts exhibited much higher TOFs than the Pt catalysts, (2.0 s<sup>-1</sup> over Au/CNF-N and 3.6 s<sup>-1</sup> over Au/CNF-ox), which is typical for HMF oxidation over Au compared to Pt [6]. The presence of surface groups on the CNF supports did not seem to significantly influence the rate of HMF oxidation over Au. The TOFs obtained over the CNF-supported catalysts were similar to those seen in our previous work for Au catalysts at the same reaction conditions (2.3 s<sup>-1</sup> over a 0.77 wt% Au/C synthesized via a sol method, 5.0 s<sup>-1</sup> over a 1 wt% Au/C catalyst obtained from the World Gold Council, and 1.6 s<sup>-1</sup> over a 1.6 wt% Au/TiO<sub>2</sub> also obtained from the World Gold Council) [6].

The product distribution is compared in Table 3. Both Pt catalysts produced mostly HFCA near 50% conversion of HMF, with the Pt/CNF-ox demonstrating slightly lower HFCA selectivity (62%) than the Pt/CNF-N catalyst (76%). The Pt/CNF-ox catalyst was slightly more selective to the intermediate FCA (33%) than the Pt/CNF-N catalyst (16%), and both catalysts had less than 10% selectivity to the final product FDCA. Although there was some influence on selectivity to the intermediate products FCA and HFCA, it does not appear that the acidic or basic properties of Pt/CNF-N and Pt/CNF-ox had a significant effect on the selectivity to the diacid.

Catalyst	Conversion (%)	S <sub>HFCA</sub>	S <sub>FCA</sub>	S <sub>FDCA</sub>
Pt/CNF-ox	53	62	33	5
Pt/CNF-N	48	76	16	8
Au/CNF-ox	50	100	0	0
Au/CNF-N	50	100	0	0

Table 3. Product selectivity during HMF oxidation over CNF-supported metal catalysts<sup>a</sup>

<sup>a</sup>Reaction conditions: HMF:Pt<sub>surf</sub> = 325; CNF-N: HMF:Au<sub>surf</sub> = 13,900; CNF-ox: HMF:Au<sub>surf</sub> = 30,000; 0.15 M HMF in 0.3 M NaOH, 690 kPa O<sub>2</sub>, 295 K

At low catalyst loadings (HMF:Au = 13,900 for Au/CNF-N and HMF:Au = 30,000 for Au/CNF-ox), selectivity to the intermediate HFCA was 100% over supported Au at all levels of conversion, for reactions utilizing 2:1 NaOH:HMF. Increasing the catalyst loading to a ratio of HMF:Au = 1400 increased the selectivity to the diacid FDCA significantly over the Au/CNF-N catalyst, though the same behavior was not observed over the Au/CNF-ox catalyst. The product distributions at different catalyst loadings are compared in Figure 8.



Figure 8. Selectivity to monoacid HFCA and diacid FDCA during HMF oxidation over Au catalysts. Reaction conditions: 0.15 M HMF, 0.30 M NaOH, 295 K, 690 kPa, HMF:Au<sub>surf</sub> = 1400.

After 24 h and 100% conversion of HMF, the selectivity to FDCA was 62% over the Au/CNF-N catalyst, whereas under the same conditions the selectivity to FDCA was just 18% over Au/CNF-ox. For comparison, the product distribution over a previously described 0.77 wt% Au/C<sub>black</sub> catalyst [6] was investigated for the same time period. The selectivity to FDCA was only 18% after 24 h and 100% conversion of HMF. Previous work confirmed that HMF oxidation over Au catalysts at similar conditions resulted in the formation of HFCA as a majority product; Au catalysts in the absence of a high concentration of NaOH were unable to activate the alcohol moiety of HMF [6, 13]. To produce substantial amounts of diacid over Au catalysts, either the NaOH:HMF ratio or the reaction temperature, or both, needed to be greatly increased

[4, 7]. In this work, however, the Au/CNF-N catalyst produced diacid with just 2:1 NaOH:HMF at 295 K, whereas the Au/CNF-ox and Au/C<sub>black</sub> catalysts produced diacid at low levels at the same conditions.

To probe this difference in behavior further, an experiment was conducted using the monoacid HFCA as the substrate and Au/CNF-N as catalyst (0.15 M HFCA, 0.3 M NaOH, HMF:Au<sub>total</sub> = 420, 690 kPa O<sub>2</sub>, 295 K). As expected, 82% conversion of HFCA in 24 h with 100% selectivity to the diacid FDCA was observed. An experiment under the same conditions but utilizing Au/C<sub>black</sub> produced less than 5% conversion of HFCA in 24 h, demonstrating the enhanced activity of Au/CNF-N for producing the diacid FDCA via oxidation of an alcohol group. Finally, a physical mixture of Au/C<sub>black</sub> and bare CNF-N was used in HFCA oxidation (0.15 M HFCA, 0.3 M NaOH, HMF:Au<sub>total</sub> = 420, 0.071 g CNF-N, 690 kPa O<sub>2</sub>, 295 K) and results were about the same as those when Au/C<sub>black</sub> was used alone (7% conversion in 24 h). This experiment confirmed that CNF-N was not influencing the reactivity results through the solution phase. Apparently, the Au nanoparticles must be supported CNF-N to improve HFCA oxidation activity. At this point, we cannot explain definitively the observed synergy of Au on CNF-N for diacid formation but will continue to explore its origins.

Previous studies of Pd catalysts supported on CNF-N for hydrodechlorination reactions suggested that the lone pairs of electrons on nitrogen atoms incorporated in CNF-N attract HCl molecules, removing HCl from the metal surface rapidly and preventing product inhibition [28]. For Pt/CNF or Pt/CNT, (competitive) adsorption on the support has been put forward to affect cinnamaldehyde hydrogenation [40] and aqueous-phase reforming [41], respectively. In our case, perhaps the pyridinic nitrogen species assists in the activation of the alcohol moiety of HMF and HFCA, a reaction that Au is seemingly unable to catalyze unless in presence of high

concentrations of base (20:1 NaOH:HMF) [7] and/or at elevated temperature (4:1 NaOH:HMF and 338 K) [4].

#### 4. Conclusions

The oxidation of HMF over Pt catalyst under the conditions tested in this study was zero order with respect to substrate concentration, first order with respect to NaOH concentration, and had an apparent activation energy of 29.0 kJ mol<sup>-1</sup>. In addition, the oxidation of reaction intermediate HFCA over Pt was also zero order in substrate concentration and O<sub>2</sub> pressure. The HFCA reaction rate was zero order in NaOH concentration above 2:1 NaOH:HFCA, but was influenced by NaOH concentration below this threshold. The observed activation energy of HFCA (alcohol oxidation) was found to be 29.6 kJ mol<sup>-1</sup>, which was surprisingly similar to the observed HMF activation energy. Finally, the mechanism of Pt-catalyzed base-free HMF oxidation in water was found to be the same as that at high pH, wherein the oxidation proceeds through active participation of H<sub>2</sub>O and the role of O<sub>2</sub> is to scavenge electrons from the catalyst surface, thereby closing the catalytic cycle. Based on other studies in the literature and the results reported here, we propose that the measured rate of reaction on Pt is associated with the activation of C-H bonds on the Pt surface to form either adsorbed aldehyde or acid, depending on substrate.

The investigation of HMF oxidation over Pt and Au supported on non-microporous carbon nanofibers produced turnover frequencies that were similar to those measured on microporous catalysts at the same conditions. Acidic or basic surface groups on the carbon nanofibers did not significantly influence the size of Pt or Au metal particles supported on them, although they affected the adsorption of  $H_2PtCl_6$ . The acidic CNF-ox material had a much lower

uptake (0.42 wt%) of Pt than did the basic CNF-N material (2.3 wt%), despite identical synthesis procedures with and intended weight loading of 3 wt%. Presumably, the N-groups present on CNF-N materials have stronger anchoring sites for the negatively charged platinum precursor. Since Au particles were synthesized in solution via a sol method, there was no need for the Au precursor to interact with the functional groups of CNF, and therefore there was no influence of functional groups on the size or loading of the gold particles. Regardless of CNF surface functionalization, particle sizes were the same within the same metal type (approximately 5 nm for Au and 1-2 nm for Pt). The rates of HMF oxidation were not influenced by the presence of acidic or basic sites in either the Pt or Au case. Interestingly, increasing the amount Au/CNF-N (to HMF:Au<sub>surf</sub> = 1400) greatly increased the selectivity to diacid FDCA. Previous work showed that, under these conditions (2:1 NaOH:HMF, 295 K), Au catalysts produced the monoacid HFCA in a majority amount; oxidation of the hydroxymethyl group of HFCA only occurred over Au with much higher NaOH concentrations and/or temperature. This work demonstrated a synergistic effect between Au and CNF-N in close contact that produced a FDCA in a majority amount at mild conditions.

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### Highlights

Kinetics of hydroxymethylfurfural (HMF) oxidation were studied

Kinetics of hydroxymethylfurancarboxylic acid oxidation were investigated

The mechanism of base-free HMF oxidation over Pt was elucidated

Non-microporous carbon nanofibers (CNFs) were functionalized with acid and base sites

Au and Pt catalysts supported on CNFs were characterized and used for HMF oxidation

