

# Kinetics and mechanism of 5-hydroxymethylfurfural oxidation and their implications for catalyst development

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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.

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## 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 Fig. 1.

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

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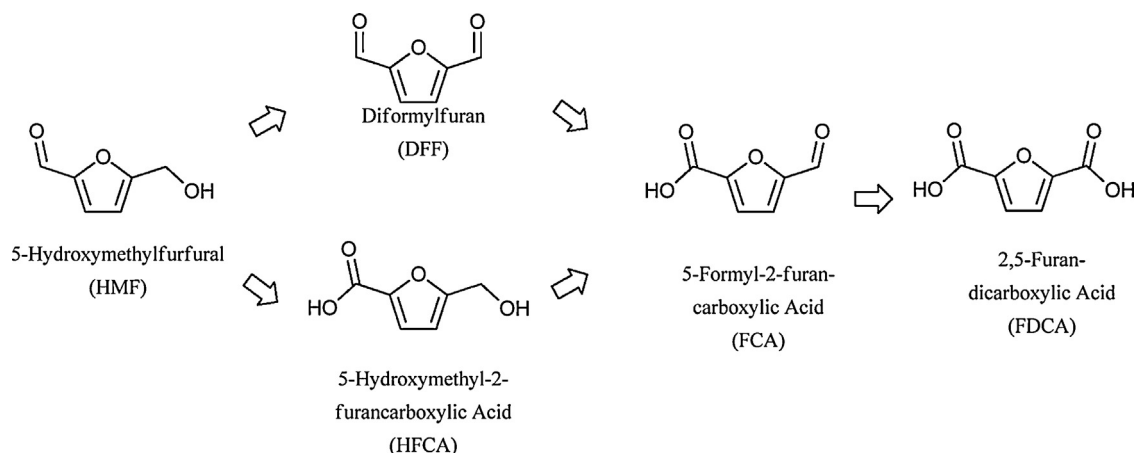


Fig. 1. The general reaction scheme for 5-hydroxymethylfurfural oxidation.

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<sub>2</sub> 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

### 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

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