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

Sara E. Davis[a], Levi R. Houk[b], Erin C. Tamargo[a], Abhaya K. Datye[b], Robert J. Davis[a,*]

[a] Department of Chemical Engineering, University of Virginia, 102 Engineers Way, Charlottesville, VA 22904-4741, USA
[b] Center for Microengineered Materials and Department of Chemical & Nuclear Engineering, University of New Mexico, Albuquerque, NM 87131-0001, USA

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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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* Corresponding author. Tel.: +1 434 924 6284; fax: +1 434 982 2658.
E-mail address: rjd4f@virginia.edu (R.J. Davis).

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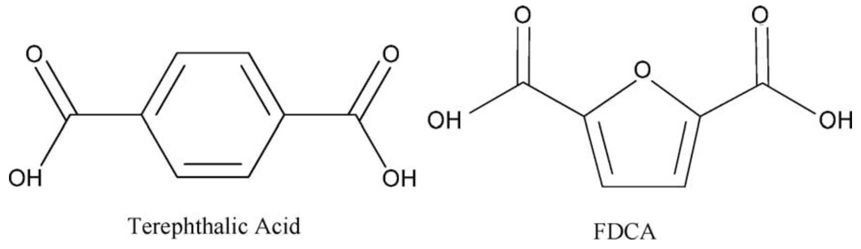

Fig. 1. FDCA is a potential biorenewable replacement monomer for terephthalic acid in polyethylene terephthalate plastics.

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.