Top Catal (2012) 55:24–32
DOI 10.1007/s11244-012-9777-3

ORIGINAL PAPER

Influence of Reaction Conditions on Diacid Formation During Au-Catalyzed Oxidation of Glycerol and Hydroxymethylfurfural

Bhushan N. Zope · Sara E. Davis · Robert J. Davis

Published online: 7 February 2012
© Springer Science+Business Media, LLC 2012

Abstract The selective oxidation of glycerol and 5-hydroxymethylfurfural (HMF) to diacids over supported gold catalysts (Au/C and Au/TiO_2) in liquid water at mild temperatures was a strong function of the added base such as NaOH. Use of hydrotalcite as a solid base in place of NaOH in the HMF reaction medium facilitated the production of diacid over Au/TiO_2, but extensive leaching of magnesium suggested that hydrotalcite was consumed stoichiometrically in the reaction. Production of diacids from glycerol oxidation over supported Au catalysts was promoted by operating in a continuous flow reactor and by increasing the catalyst loading in a semi-batch reactor. Trace inhibitors formed by conversion of the product monoacid are proposed to account for the generally low selectivity to diacids over gold catalysts.

Keywords Hydroxymethylfurfural · Glycerol · Glyceric acid · Tartronic acid · Furandicarboxylic acid · Gold catalyst · Oxidation

1 Introduction

The need to replace fossil fuels with sustainable, environmentally-benign carbon sources is well documented in recent literature [1–3]. Glycerol is one potential feedstock molecule that can potentially be derived from biomass resources. For example, glycerol can be produced through hydrogenolysis of sugar derivatives obtained from biomass [4, 5]. Glycerol is also a co-product of the transesterification of triglycerides with methanol to form biodiesel fuel (methyl esters of fatty acids) and is obtained in a 1:3 mol ratio (approximately 10 wt% of the total biodiesel produced). Increased biodiesel production, primarily a result of government policy, is expected to result in a glycerol glut [6, 7], so efficient use of glycerol is important for the overall economics of biodiesel synthesis [7]. Various value added chemicals such as glyceric acid, glycolic acid, tartronic acid, mesoxalic acid, hydroxypyruvic acid, and dihydroxyacetone can be obtained through selective oxidation of glycerol [6, 8]. These oxidation products find uses in personal/oral care products, drugs/pharmaceuticals, fuels, polymers, and food additives [9, 10]. The molecule 5-hydroxymethylfurfural (HMF) can also be produced in significant amounts from biomass feedstocks. Dehydration of fructose forms HMF in high yield (80% selectivity to HMF with 90% conversion of fructose) [11], and oxidation of HMF results in 2,5-furandicarboxylic acid (FDCA), which has been identified by the US Department of Energy as one of 12 important building block chemicals [10]. The structure of FDCA is similar to terephthalic acid, a key monomer in polyethylene terephthalate (PET) plastics, and therefore FDCA has the potential to be used in a biomass-derived alternative to PET plastics [10, 12].

Traditional methods for oxidation have utilized organic solvents or inorganic oxidants such as transition metal oxo compounds, halogenated compounds and sulfur oxides [13–15]. Use of metal catalysts during oxidation in liquid water with molecular oxygen provides a sustainable and economical route for alcohol oxidation [16, 17], and oxidation of alcohols over supported Pt-group metals has been discussed extensively in the literature [18]. Catalyst deactivation through over-oxidation of active metal sites, leaching of metal and strong adsorption of byproducts is a major obstacle in their commercial application [6, 18].

B. N. Zope · S. E. Davis · R. J. Davis (✉)
Department of Chemical Engineering, University of Virginia, 102 Engineers Way, Charlottesville, VA 22904-4741, USA
e-mail: rjd4f@virginia.edu

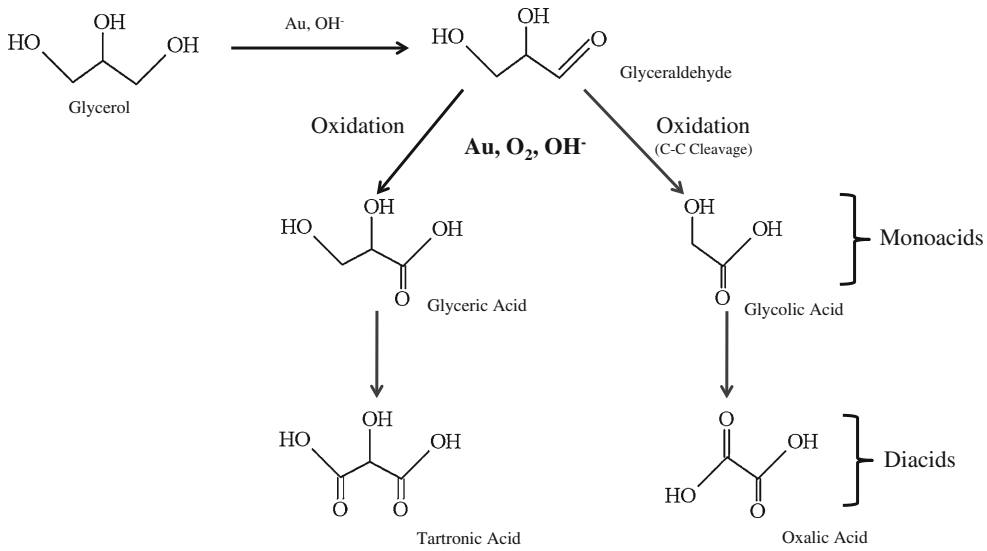
In contrast, supported Au catalysts are more active, selective and stable for oxidation, primarily as a result of the noble nature of Au [18, 19]. However, addition of a base such as NaOH is required for selective oxidation of glycerol and HMF to proceed over supported Au catalysts [20].

The need for base in alcohol oxidation over Au catalysts is a serious limitation of this catalyst system [21]. Indeed, base has been recognized as an essential component of alcohol oxidation with Au catalysts since the initial study by Prati and Rossi [22]. Carrettin et al. also demonstrated that glycerol cannot be oxidized in absence of base over Au catalysts [20, 21, 23]. Recent mechanistic studies with gold catalysts have demonstrated the essential role of hydroxide ions during oxidation of alcohols [24–26]. Hydroxide ions facilitate the initial deprotonation of alcohols, which are weak acids (pKa = 14–18), since a gold catalyst, by itself, cannot activate the hydroxyl group of alcohols at mild temperatures [27]. Ketchie et al. reported that even unsupported Au powder is active for oxidation reactions in the presence of hydroxide ions, further demonstrating the promotional effect of hydroxide ions [28].

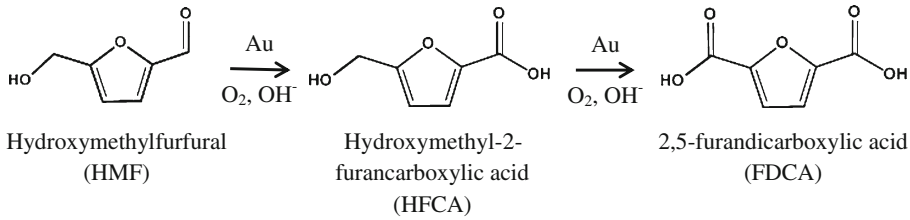
Unfortunately, the use of an inorganic base such as NaOH produces of salts of carboxylic acid products during alcohol oxidation. Neutralization of the product stream and release of the free acid increase the operating cost of the process and produce additional salt byproducts, which are of little value and may have a negative environmental impact. Thus, highly basic catalyst supports have been used as potential replacements of the added inorganic base during aqueous-phase alcohol oxidation [29, 30]. Villa et al. reported that glycerol oxidation activity of Au/$MgAl_2O_4$ spinel-type catalysts was controlled by the Mg:Al ratio, and the Mg:Al ratio superseded the effect of Au particle size [31]. The Mg:Al ratio was supposedly used to control the basicity of the support, but inorganic base (NaOH) was still added to the reaction medium. Takagaki et al. used hydrotalcite (HT) as a support for Au catalysts in glycerol oxidation [32], and reported that only Au/HT catalysts calcined at temperatures above 373 K were active in the reaction; however, the product distribution did not match the majority of studies reporting on glycerol oxidation since glycolic acid (C_2 acid) was the major product. Glyceric acid, which is the major product in most other studies, was not produced during glycerol oxidation over Au/HT [32]. Furthermore, the authors did not report the reaction rate or the turnover frequency on the Au/HT catalysts. In a related study, Gupta et al. explored HMF oxidation over the Au/HT catalysts and observed very high selectivity (>80%) to FDCA during the reaction [30].

Over supported Au catalysts, glyceric acid is generally considered to be the primary product of glycerol oxidation with molecular oxygen in liquid water in the presence of added base whereas glycolic acid (C_2 acid derived from C–C cleavage) is the secondary product. Tartronic and oxalic acid are produced by the sequential oxidation of glyceric and glycolic acid, respectively (Scheme 1). One of the limitations of Au catalysts is the very low selectivity to the diacid products during oxidation of glycerol. Aqueous-phase oxidation of glycerol over supported Au catalysts in a batch reactor system is highly selective (≥90%) towards the monoacid products, i.e., glyceric and glycolic acid [20, 33, 34]. Subsequent oxidation of these primary products to diacid products, such as tartronic and oxalic acid, is slow under the conditions typically used for glycerol oxidation (293–333 K, 1–10 bar O_2 pressure, NaOH:glycerol ratio of 1 to 4 (mol:mol)) [25]. Analogous results are observed during oxidation of HMF. A low selectivity to FDCA (≤10%), the diacid product, is reported during HMF oxidation over supported Au catalysts with low loadings of base (NaOH:HMF mol:mol <4) [35, 36]. Oxidation of HMF to FDCA proceeds through the intermediate primary acid, 5-hydroxymethyl furan carboxylic acid (HFCA) (Scheme 2), which is produced readily under basic conditions. For the oxidation to proceed to a majority of the diacid product, an increase in temperature and/or NaOH concentration is necessary [35–37].

Recent studies have also reported a significant effect of reactor configuration on a three-phase system such as aqueous-phase glycerol oxidation over supported Au catalysts [38–40]. In previous work, we compared the activity and selectivity of glycerol oxidation over a Au/TiO_2 catalyst provided by the World Gold Council (WGC) in both a batch autoclave reactor and a fixed bed continuous up-flow reactor. We observed significant variation in the product distribution of glycerol oxidation in the two reactor systems. Interestingly, the continuous up-flow fixed bed reactor system gave significant selectivity (30%) to diacid products (tartronic and oxalic acid) during glycerol oxidation whereas a semi-batch autoclave reactor system always produced small amounts (~5%) of diacid products, even at nearly complete conversion of glycerol under similar reaction conditions [38]. Other research groups also studied glycerol oxidation in different reactor configurations. The Hutchings research group performed glycerol oxidation over a gold catalyst in a meso-scale structured down-flow slurry bubble column reactor and compared the results to those obtained in a standard batch autoclave reactor [39]. Under their particular conditions, glyceric acid was produced with nearly 100% selectivity at 30% conversion of glycerol in the batch reactor. However, the specific rate in the flow reactor was higher by several orders of magnitude compared to that observed in a batch autoclave at the same temperature and reactant concentration. Moreover, the selectivity of the reaction at 30% conversion of glycerol was about 50% glyceric acid with the remaining 50% being mostly dihydroxyacetone. Diacid



Scheme 1 Reaction pathway of glycerol oxidation over supported Au catalysts



Scheme 2 Sequential oxidation of aqueous HMF over supported Au catalysts in the presence of base

was not produced, despite their claim of higher activity and oxygen availability in their recirculating system [39]. In contrast to Hutchings, but similar to our results, the group of Prati noted increased production of diacid products in their continuous reactor [40]. However, they concluded that decreasing the amount of base promoted consecutive oxidation, which is opposite to our findings. The significantly different findings among three different studies indicate that even a rudimentary understanding of the mechanism of diacid formation remains elusive.

In this study, we have investigated the role of base (both liquid and solid base) in aqueous-phase oxidation of glycerol and HMF over supported Au catalysts. In addition, the influence of reaction conditions (reactor configuration, base concentration, O_2 pressure and catalyst loading) on the formation of diacid products during glycerol oxidation over Au catalysts was elucidated.

2 Materials and Methods

2.1 Materials

The Au/TiO_2 catalyst (1.6 wt% Au, with an average Au particle size 3.5 nm and an estimated dispersion of 0.29, based on Au particle size) and Au/C catalyst (0.8 wt% Au, with an average Au particle size 10.5 nm and an estimated dispersion of 0.05, based on Au particle size) provided by WGC were used as received [41]. The powdered catalysts were used in their original form for the batch and continuous reactor study. Glycerol [Acros, 99.6% purity] and NaOH [Mallinckrodt, 99%] were used to prepare the liquid feed for the reaction. All gases used in the study (dioxygen, dinitrogen, and helium) were of ultra high purity grade [GT&S].

The HT was 4:1 Mg:Al, prepared by a constant-pH coprecipitation method [42]. In short, a 300 mL aqueous solution of 0.36 mol $Mg(NO_3)_2{\cdot}6H_2O$ and 0.09 mol $Al(NO_3)_3{\cdot}9H_2O$ and a 300 mL aqueous solution of 0.09 mol of Na_2CO_3 were added dropwise to 80 mL of deionized water under vigorous stirring for 30 min at 333 K. Dropwise addition of a 4.0 mol L^{-1} NaOH solution maintained the pH of the solution at 10. The slurry was stirred for 24 h at 333 K. The precipitate was recovered, washed with DI water, dried in air at 338 K for 24 h, and finally ground into a powder with particle size between 0.038 mm and 0.075 mm. The HT was stored in a vial and used without further pretreatment.

2.2 Glycerol Oxidation in a Semi-Batch Reactor

Glycerol oxidation was performed in a 50 cm^3 Parr Instrument Company 4592 autoclave reactor equipped with a magnetic stirrer and stir plate. The feed solution (30 mL,

0.3 M glycerol, 0.1–3 M NaOH) and a proper amount of catalyst were added to the reactor that was then sealed, purged with He and heated to 333 K before pressurizing with O_2. Dioxygen was continually fed to maintain constant head pressure (11 bar absolute) in the reactor. The amount of catalyst was adjusted to avoid dioxygen mass transfer limitations from the gas to the liquid in the batch reactor [25]. Samples were periodically removed through the sample diptube and were filtered using a syringe filter (0.2 μm) before analysis in a high pressure liquid chromatograph (HPLC).

The glycerol oxidation experiments with different glycerol:Au ratios were performed by changing the amount of Au catalyst in the initial reaction mixture. These experiments used 5 mL of reaction volume, to save the precious metal catalyst.

The oxidation of glyceric acid was also carried out in the same semi-batch reactor system. The feed solution (30 mL, 0.1 M glyceric acid, 0.2–1 M NaOH) and Au/TiO_2 catalyst (glyceric acid:Au = 2600 mol:mol) were added to the reactor that was then sealed, purged with He and heated to 333 K before pressurizing with O_2. Dioxygen was continually fed to maintain constant head pressure (11 bar absolute) in the reactor.

2.3 Glycerol Oxidation in a Continuous Reactor

Glycerol oxidation was also studied in a continuous upflow fixed bed reactor system, which was described in detail in our previous work [38]. A stainless steel tubular reactor with ½ inch (12.7 mm) OD and 11 mm ID was used with packed catalyst bed at the end of the tube supported by stainless steel frit (20 μm, pressed) on one side and by glass wool on the other. Previous work utilized a stainless steel reactor with ¼ inch OD [38]. In that study, continuous use caused significant pressure drop across the fixed bed of catalyst due to pellets breaking down, which restricted continuous operation to maximum of 40 h. To solve this problem, a large diameter reactor was utilized, which alleviated pressure drop across the catalyst bed. In addition to the Au/TiO_2 catalyst tested previously, a carbon-supported Au catalyst was also studied for glycerol oxidation in the continuous reactor. A packed bed was formed by mixing the Au catalyst powder with silica granules (−4/+16 mesh).

2.4 HMF Oxidation in a Semi-Batch Reactor

To investigate the leaching of Mg and Al from HT catalysts, aqueous HMF (1 mmol HMF in 6 mL H_2O) was added to the batch reactor, which was flushed with helium and pressurized to 3.4 bar. The reactor was heated to 363 K over 30 min, at which point the Au/TiO_2 and HT were added. The reactor was flushed with O_2 and pressurized to 3.4 bar. The Au/TiO_2 and HT, described above, were used without further pretreatment. The reaction product mixture was filtered using a PTFE 0.2 μm filter, and the resulting mixture was analyzed via HPLC. The product mixture was also analyzed by ICP (Galbraith Laboratories, Knoxville, TN) for Mg and Al content.

2.5 Product Analysis

The liquid products of glycerol and HMF oxidation were analyzed using a HPLC equipped with a refractive index detector and a UV–Vis detector. Product separation in the HPLC was carried out using an Aminex HPX-87H column (Bio-Rad) with 5 mM H_2SO_4 as eluent flowing at 0.5 cm^3 min^{-1}. The retention times and calibration curves were found using known concentrations of products.

2.6 Turnover Frequency and Selectivity Calculations

The initial turnover frequencies, or TOF [mol glycerol converted (mol $Au_{surface})^{-1}$ s^{-1}], for glycerol oxidation were calculated from the initial conversion of glycerol, usually within the first 30 min of reaction. Selectivity was defined as moles of product formed divided by moles of C_2 and C_3 products formed. For oxidation of glyceric acid, the TOF was based on the moles of glyceric acid converted in 3 h [mol glyceric acid reacted (mol $Au_{surface})^{-1}$ s^{-1}].

3 Results and Discussion

3.1 Evidence for Hydroxide Consumption and Partial Regeneration During Glycerol Oxidation

In our previous work, the role of O_2 during oxidation was reported to be an indirect one where it does not participate in the reaction via dissociation and addition to the substrate but instead undergoes reduction over the Au catalysts [24]. The mechanism of alcohol oxidation with hydroxide ions involves the deposition of electrons into the Au metal particles and, since metal nanoparticles cannot hold large amounts of negative charge (from the deposited electrons), O_2 is envisioned to scavenge the electrons from the Au surface to complete the catalytic cycle. This O_2 reduction sequence also regenerates some of the OH^- ions consumed during oxidation [24].

To probe experimentally the role of O_2 during oxidation, we measured the OH^- concentration in a glycerol oxidation experiment (0.3 M glycerol, 0.6 M NaOH, Au/TiO_2, 333 K, at 30 min) by means of acid–base titration of the basic product mixture using 0.5 M H_2SO_4 solution and a phenolphthalein indicator. Our measurements indicated

Table 1 Loss of hydroxide ions during glycerol oxidation over Au/TiO_2 in a semi-batch reactor

Time (min)	OH^- (moles) $\times 10^3$	Glycerol (moles) $\times 10^3$	Ratio (OH^-/glycerol) (mol:mol)
0	18	9.42	–
30	12.75	6.69	–
Loss ($t_{0,\ OH^-} - t_{30,\ OH^-}$)	5.25	2.73	1.92

Loss ratio (OH^-:glycerol) from Scheme 3 = 4.0

Reaction conditions: 0.3 M glycerol, 0.6 M NaOH, glycerol:Au = 8,000:1 (mol:mol), 30 mL, 333 K, PO_2 = 11 bar

$$RCH_2OH + \mathbf{OH^-} \rightarrow RCH_2O^- + H_2O$$
$$RCH_2O^- \rightarrow RCH_2O^* + e^-$$
$$RCH_2O^* + OH^* \rightarrow RCHO^* + H_2O$$
$$RCHO + \mathbf{OH^-} \rightarrow RCHOOH^-$$
$$RCHOOH^- \rightarrow RCHOOH^* + e^-$$
$$RCHOOH^* + OH^* \rightarrow RCOOH + H_2O$$
$$(\mathbf{OH^-} + * \leftrightarrow OH^* + e^-) \times 2$$

Scheme 3 Electrochemical balance during glycerol oxidation to glyceric acid [24]

that the ratio of OH^- moles lost to glycerol moles converted was about 2 (mol:mol) (Table 1), which is half of that predicted by the reaction path depicted in Scheme 3. This result indicates that some of OH^- ions are regenerated during alcohol oxidation via reduction of molecular oxygen over the Au catalyst.

3.2 Stoichiometric Consumption of HT During HMF Oxidation

As mentioned earlier, highly basic catalyst supports have been proposed to replace the added inorganic base during aqueous-phase alcohol oxidation [29, 30]. For example, the Ebitani research group developed highly active and selective Au and Pt catalysts with HT as a support for base-free glycerol and HMF oxidation [30, 32, 43].

To explore the role of solid bases in the oxidation reaction, we performed HMF oxidation with Au/TiO_2 with added HT in the reaction medium. Because the oxidation activity of Au/TiO_2 has been studied previously, any differences in the observed activity or selectivity by adding HT would most likely be attributed to a modification of the solution phase since Au is not in contact with the HT. The experimental conditions of Gupta et al. were matched as closely as possible in our reactor setup (1 mmol HMF in 6 mL H_2O, $T = 363$ K, $P = 3.4$ bar, HMF:Au = 150 mol:mol, mass HT = 0.13 g) [30]. After 20 h, the product mixture was filtered, and the resulting mixture was analyzed via HPLC. The reaction was >99% selective to FDCA with 100% conversion of HMF and the carbon balance closing to 95%, which is similar to the results of Gupta et al. [30].

The liquid was recovered and analyzed via ICP (Galbraith Labs, Knoxville, TN) for Mg and Al content. Magnesium was present in a concentration of 0.16 M, indicating significant leaching of Mg into solution. Interestingly, the concentration of FDCA in this solution is also 0.16 M. The equimolar amounts of FDCA and Mg in solution suggest stoichiometric dissolution of the divalent magnesium. The Mg in solution (0.16 M) accounts for 70% of the Mg in the HT added to the reactor. Although this is a high percentage of Mg to leach into solution, a significant pH drop, from 9 to 6, was noted during the course of the reaction. The instability of HT at low values of pH ($5.0 < pH < 9.0$) has been documented in the literature, and results in preferential dissolution of Mg^{2+} [44]. It is likely that the high conversion of HMF to diacid lowered the pH of the solution significantly, thus causing instability and dissolution of Mg^{2+} from the HT catalyst. It should be noted that the Al content of the product was <0.2 mM, which confirmed that Mg was preferentially leached from the HT by the product acid. This incongruent leaching of Mg, but not Al, from the HT catalyst in an acidic environment is also documented in the literature [44].

In an attempt to slow the rate of Mg dissolution, the amount of HT added to the reactor was increased by a factor of 3.75 to help maintain a higher pH throughout the reaction. The initial pH of the reaction medium was nine but it decreased to seven at the end of the reaction. Analysis of the solution from this run also showed preferential leaching of Mg to give a concentration of 0.13 M, which corresponded to 15% of the available Mg in the reactor. The concentration of FDCA at the end of the run was 0.12 M, which is quite similar to the amount of leached Mg, again suggesting stoichiometric dissolution of the Mg from HT.

Evidently, the addition of HT to the reactor served as a stoichiometric reagent rather than a heterogeneous catalyst for HMF conversion. Based on the mechanistic studies with labeled compounds and the observed leaching of Mg from HT, we conclude that solid base supports are most likely to react with the product acid and either deactivate by strong adsorption or dissolve by formation of soluble salts of the product acids.

3.3 Influence of Reactor Configuration on Product Selectivity During Glycerol Oxidation

In addition to the need of added base for activity, gold catalysts are also limited by a low selectivity to the desired diacid products during oxidation of alcohols such as

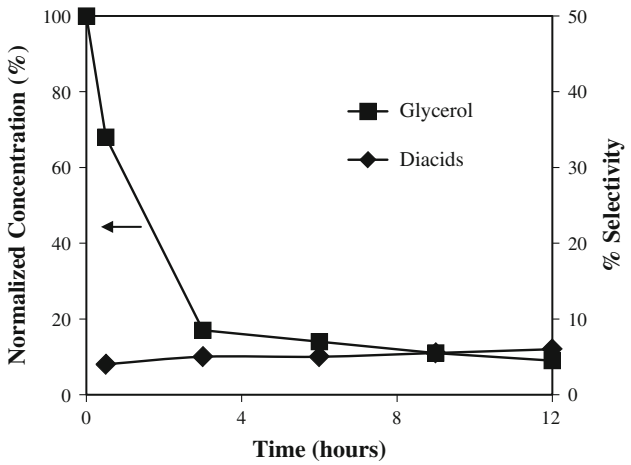


Fig. 1 Oxidation of glycerol over Au/TiO_2 in a semi-batch reactor over 12 h. Reaction conditions: 0.3 M glycerol, 0.6 M NaOH, glycerol:Au = 8,000:1 (mol:mol), 30 mL, at 333 K, PO_2 = 11 bar. Diacids = tartronic + oxalic acid

glycerol and HMF [20]. Oxidation of glycerol over supported metal catalysts under moderate conditions of temperature (293–333 K) and O_2 pressure (1–11 bar absolute) produces monoacids in large quantities (>90% selectivity) [23]. Since tartronic and oxalic acid are subsequent oxidation products of glyceric and/or glycolic acid, the low selectivity to the diacids in a batch reactor, even at high conversions of glycerol, is rather unexpected. In our work, a typical glycerol oxidation experiment was carried out for 3 h. Thus, we performed an experiment for 12 h under standard reaction conditions to allow for subsequent oxidation of the primary products. However, the selectivity to the secondary oxidation products was still less than 10% for the entire course of the reaction (Fig. 1), even at 90% conversion of the glycerol.

In the continuous up-flow fixed bed reactor, under similar conditions of concentration, pressure, temperature and pH, a higher selectivity towards secondary oxidation products tartronic and oxalic acid was observed over both Au catalysts, even at low conversions (Table 2). Our results for Au/TiO_2 in the continuous reactor matched well with those observed with a smaller diameter reactor used in a previous study [38]. In that earlier paper, we performed an in-depth analysis of the mass transfer characteristics in the continuous fixed bed reactor [38]. Although mass transfer limitations in the continuous reactor were not completely eliminated, their influence on the measured rates was not severe. Indeed, we would expect that the existence of gas–liquid–solid mass transfer limitations in the reactor system might limit the over-oxidation of glycerol; however our results showed enhanced oxidation of glycerol to secondary diacid products in the continuous reactor compared to the semi-batch reactor. The turnover frequencies were similar in the semi-batch and continuous reactor for the Au/C catalyst but were somewhat lower in the continuous reactor for the Au/TiO_2 catalyst (Table 2). Thus, the presence or absence of mass transfer artifacts could not account for the different product distribution in the two reactor systems.

3.4 Oxidation of Glyceric Acid

To further understand the oxidation of primary products during glycerol oxidation, we studied oxidation of glyceric acid by itself. Glyceric acid (0.1 M) and NaOH (0.2 M) solution (NaOH:glyceric acid = 2.0 mol:mol) was oxidized over the Au/TiO_2 catalyst in the semi-batch reactor setup, under the conditions described above. No conversion of glyceric acid was observed in 3 h (Table 3). However, the oxidation rate increased with increasing base concentration. Significant conversion (65%) of glyceric acid to the diacid products over 3 h was observed at NaOH:glyceric acid ratio of 20 (mol:mol) (Table 3). This result indicates that a higher concentration of base is needed to further oxidize the primary monoacid products. Thus, we performed a glycerol oxidation experiment at NaOH:glycerol ratio of 10 (mol:mol). The higher base concentration in the

Table 2 Glycerol oxidation over Au catalysts in semi-batch and continuous reactor

Catalyst	NaOH:glycerol (mol:mol)	TOF (s^{-1})	Conversion (%)	Selectivity (%)			
				Glyceric acid	Glycolic acid	Tartronic acid	Oxalic acid
Semi-batch[a]							
Au/C	2.0	6.1	6.8	67	33	0.0	0.0
Au/TiO_2	2.0	4.9	33	64	24	2.0	0.0
			85	69	19	4.0	1.0
Continuous[b]							
Au/C	2.0	4.3	4.7	50	28	12	10
Au/TiO_2	2.0	0.9	18	40	25	13	18

[a] Reaction conditions: 0.3 M glycerol, glycerol:Au = 8,000:1 (mol:mol), 30 mL, at 333 K, PO_2 = 11 bar

[b] Reaction conditions: 0.3 M Glycerol, 333 K, P_{tot} = 11 bar, Q_L = 1 cm^3 min^{-1}, Q_G = 30 cm^3 (STP) min^{-1}, 30 mg Au/C or 55 mg Au/TiO_2

Table 3 Glyceric acid oxidation over Au/TiO_2 in a semi-batch reactor

NaOH: substrate (mol:mol)	TOF (s^{-1})	Conversion (%)	Selectivity (%)	
			Tartronic acid	Oxalic acid
2.0	0.0	0.0	–	–
6.0	0.1	17	85	15
20	0.47	64	86	13

Reaction conditions: 0.1 M glyceric acid, glyceric acid:Au = 2600:1 (mol:mol), 30 mL, at 333 K, PO_2 = 11 bar, 3 h. TOF is calculated at t = 3 h

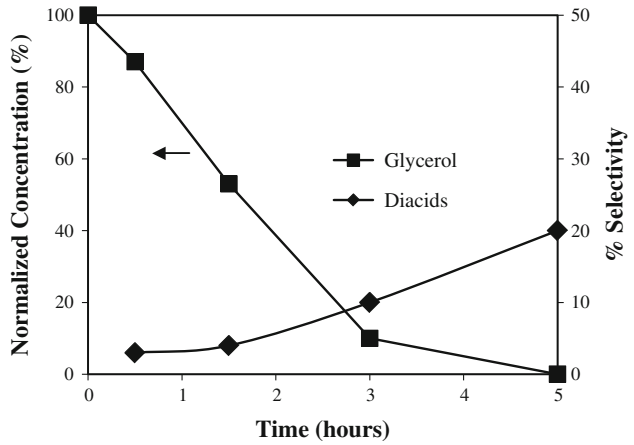


Fig. 2 Oxidation of glycerol over Au/TiO_2 at high base loading in a semi-batch reactor. Reaction conditions: 0.3 M glycerol, NaOH:glycerol = 10 (mol:mol), glycerol:Au = 8,000:1 (mol:mol), 30 mL, at 333 K, PO_2 = 11 bar. Diacids = tartronic + oxalic acid

initial reaction mixture allowed for further oxidation of primary monoacid products to give a higher selectivity (20%) to the diacid products (Fig. 2). As the continuous reactor utilized a lower concentration of base (NaOH:glycerol $\leq$ 2.0 mol:mol), this finding alone cannot account for the high amounts of diacid products formed in the continuous reactor.

3.5 Effect of O_2 Pressure on Glycerol Oxidation

Very few studies report the effect of O_2 pressure on the oxidation of alcohols over supported metal catalysts. Claus et al. observed that O_2 pressure had no influence on the rate of glycerol oxidation in their batch studies [45]. Increasing the O_2 pressure during HMF oxidation has been reported to increase the selectivity of diacid product at the expense of primary monoacid product [35, 36]. Davis et al. reported that increasing the O_2 pressure from 6.9 bar to 30 bar during HMF oxidation increased FDCA, the diacid product, selectivity from 3 to 36%, whereas the selectivity to HFCA, the monoacid product, decreased from 84 to 64%

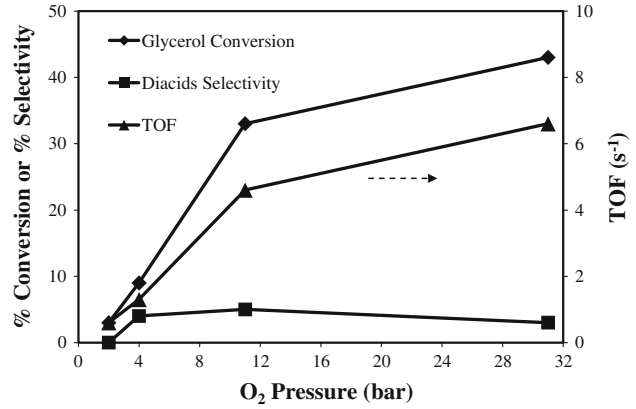


Fig. 3 Effect of O_2 pressure on rate and diacid production during glycerol oxidation over Au/TiO_2 in a semi-batch reactor. Reaction conditions: 0.3 M glycerol, 0.6 M NaOH, 30 mL, glycerol:Au = 8,000:1 (mol:mol), at 333 K. Reaction time = 30 min. Diacids = tartronic + oxalic acid

[35]. Hence, we studied the effect of O_2 pressure on glycerol oxidation over Au/TiO_2 in the semi-batch reactor.

The oxidation experiments were performed as described above but by varying the O_2 pressure from 2 to 31 bar absolute. During our study, we noticed that the TOF for glycerol oxidation increased with pressure (Fig. 3). However, contrary to the results from HMF oxidation discussed above, selectivity to the diacid products during glycerol oxidation remained relatively constant ($\sim$5%) with the change of O_2 pressure from 2 to 31 bar absolute (Fig. 3). Unlike the two terminal OH-groups in glycerol, HMF has one alcohol side-chain and one aldehyde side-chain. Hence, it is difficult to correlate the effect of O_2 pressure on the product distribution during Au-catalyzed glycerol oxidation with that during HMF oxidation. The key point to note here is that increasing O_2 pressure did not favor the production of diacids from glycerol over gold catalysts. Thus, the availability of oxygen was evidently not a key factor in the production of diacids.

3.6 Effect of Au Metal Loading on Product Distribution During Glycerol Oxidation

One of the most apparent differences between the two reactor systems (semi-batch versus continuous) was the fluid to metal ratio in the active reaction zone. The continuous reactor had a very low volume of liquid ($\sim$0.5 mL) in contact with the fixed bed of catalyst at any given time, compared to a 30 mL reactant volume slurried with a small amount of catalyst (14 mg) in the semi-batch reactor. Therefore, the conditions from the fixed bed reactor were better simulated in the semi-batch reactor by increasing the catalyst loading. The glycerol:Au ratio was lowered progressively from 8,000 to 350 (mol:mol) by adding more

Table 4 Effect of catalyst loading on product distribution during glycerol oxidation over Au/TiO_2 in a semi-batch reactor

Glycerol:Au (mol:mol)	Conversion (%)	Selectivity (%)			
		Glyceric acid	Glycolic acid	Tartronic acid	Oxalic acid
8,000[a]	83	61	34	3.4	1.2
3,500	36	64	17	5.0	1.0
3,500	87	64	23	7.0	2.0
2,000	91	63	14	13	2.0
350	27	52	2.0	15	3.0
350	100	50	7.0	25	5.0

Reaction conditions: 0.3 M glycerol, NaOH:glycerol = 2.0 (mol:mol), 5 mL, at 333 K, PO_2 = 11 bar

[a] Reaction volume = 30 mL

Table 5 Effect of product addition on rate of glycerol oxidation over Au/TiO_2 in a semi-batch reactor

Compound added to reaction mixture	Glycerol conversion at 3 h	TOF (s^{-1})	% Decrease in oxidation activity
No additive	85	4.9	–
Glyceric acid[a]	65	1.7	65

Reaction conditions: 0.3 M glycerol, 0.6 M NaOH, glycerol:Au = 8,000:1 (mol:mol), 30 mL, at 333 K, PO_2 = 11 bar, 3 h

[a] 0.3 M glycerol, 0.3 M glyceric acid, 0.9 M NaOH, glycerol:Au = 8,000:1 (mol:mol), 30 mL, at 333 K, PO_2 = 11 bar, 3 h. Adapted from Ref. [47]

catalyst to the semi-batch reactor. The percent selectivity to diacid products increased from 4.6 to 30 as the Au loading was increased (Table 4). At the highest Au loading tested (glycerol:Au = 350 mol:mol), the diacid selectivity matched closely with that seen in the fixed bed reactor (Tables 2, 4).

Even at the lowest glycerol:Au ratio (350 mol:mol) tested, the moles of glycerol were in great excess to the moles of Au (if surface Au atoms are considered instead of total Au atoms, then the glycerol:$Au_{surface}$ = 1200 (mol:mol); as the dispersion of Au/TiO_2 catalyst was 0.29). Therefore, a simple explanation relating the sequential oxidation to the availability of catalyst (due to increased catalyst loading) cannot be justified by these results. Glyceric acid, a strong chelating agent, has been reported to deactivate glycerol oxidation over a Pt–Bi/C catalyst [46]. In a recent study of Au-catalyzed glycerol oxidation, we also observed strong inhibition of Au catalysts by addition of glyceric acid [47]. An experiment in which glyceric acid was present in the initial reaction mixture together with glycerol (0.3 M glycerol, 0.3 M glyceric acid, 0.9 M NaOH) resulted in a TOF for glycerol oxidation of 1.7 s^{-1} (a 65% decrease from the original TOF of 4.9 s^{-1}) (Table 5) [47]. Because simple carboxylic acids do not inhibit the glycerol oxidation rate, we propose that a byproduct species derived glyceric acid strongly inhibited the catalytic activity of the Au catalyst [47].

Since the selectivity to diacid during glycerol oxidation depends on reactor configuration (flow versus semi-batch) and on catalyst loading in the reactor, a likely explanation for the phenomenon of low diacid production in a semi-batch reactor with low catalyst loading is that a species formed by the subsequent conversion of the monoacid product is responsible for preventing its subsequent oxidation to diacid. The flow reactor operates at a stationary state that produces a constant level of monoacid products that are continuously removed by the flowing fluid stream. Thus, there is negligible residence time in the flow reactor for the product monoacid to form the inhibitory byproduct species. In a semi-batch reactor, there is sufficient time and fluid volume to convert the product monoacid to an inhibitory byproduct species that can adsorb onto the catalyst and prevent oxidation. We have recently identified ketonic species as strong inhibitors of the glycerol oxidation reaction and they are likely to be the species that affect sequential oxidation reactions in the semi-batch reactor operating with low catalyst loadings [47]. For a semi-batch reactor with higher catalyst loadings, the tolerance of the system in the presence of these trace inhibitory side products is increased.

4 Conclusions

Diacids are important monomers for the polymers industry because of their bifunctional nature, but many of the acid products and byproducts formed during alcohol oxidation reactions are strong chelating agents and their presence in the reaction mixture can severely inhibit the oxidation activity of Au catalysts. This work has shown that reactor configuration, Au catalyst loading and base concentration can be used to improve the selectivity of Au catalysts for diacid formation during the oxidation of glycerol in liquid water. After comparing the reactivity trends of Au catalysts

for glycerol oxidation in a continuous reactor versus a semi-batch reactor and examining the influence of Au loading in a semi-batch reactor, we propose that the product monoacid forms a trace byproduct species that inhibits both the rate of glycerol oxidation as well as the rate of monoacid oxidation to diacid. Therefore, conditions that slow its formation (continuous reactor) or tolerate its presence (high Au catalyst loadings) are needed to produce diacids effectively. Moreover, high base concentrations presumably facilitate deprotonation of the alcohol group of the monoacid products thus enhancing their oxidation to diacid products. Since solid bases are attractive alternatives to the use of liquid bases that need to be neutralized at the end of the reaction, HT was evaluated as an additive to Au-catalyzed oxidation of HMF in liquid water. Although the product diacid FDCA was formed with high selectivity, elemental analysis of the product solution revealed extensive dissolution of magnesium from the HT.

Acknowledgment This material is based upon work supported by the United States Department of Energy under Grant No. DE-FG02-95ER14549 and the National Science Foundation under Grant Nos. OISE 0730277 and EEC-0813570. RJD acknowledges informative and inspiring discussions with Professor Harold Kung (Northwestern University) about gold catalysis over the past decade.

References

1. Ragauskas A, Williams C, Davison B, Britovsek G, Cairney J, Eckert C, Frederick W, Hallett J, Leak D, Liotta C, Mielenz J, Murphy R, Templer R, Tschaplinski T (2006) Science 311:484
2. Bozell JJ (2008) CLEAN Soil Air Water 36:633
3. Bozell JJ, Petersen GR (2010) Green Chem 12:539
4. Huber GW, Iborra S, Corma A (2006) Chem Rev 106:4044
5. Clark IT (1958) J Ind Eng Chem 50:1125
6. Pagliaro M, Rossi M (2008) The future of glycerol. Royal Society of Chemistry, Cambridge
7. Stelmachowski M (2011) Ecol Chem Eng S 18:9
8. Katryniok B, Kimura H, Skrzynska E, Giradon J-S, Fongarland P, Capron M, Ducoulombier R, Mimura N, Paul S, Dumeignil F (2011) Green Chem. doi:10.1039/c1gc15320j
9. Centi G, van Santen RA (2007) Catalysis for renewables. Wiley, Weinheim
10. Werpy T, Petersen G (2004) Top value added chemicals from biomass volume i: results of screening for potential candidates from sugars and synthesis gas. US Department of Energy Report, Oak Ridge
11. Roman-Leshkov Y, Chheda JN, Dumesic JA (2006) Science 312:1933
12. Gandini A, Silvestre AJD, Pascoal Neto C, Sousa AF, Gomes M (2008) J Polym Sci Part A 47:295
13. Arcadi A (2008) Chem Rev 108:3266
14. Sheldon RA, Arends IWCE, Dijksman A (2000) Catal Today 57:157
15. Sheldon RA, Dakka J (1994) Catal Today 19:215
16. Besson M, Gallezot P (2000) Catal Today 57:127
17. Gangwal VR, van der Schaaf J, Kuster BFM, Schouten JC (2005) J Catal 232:432
18. Mallat T, Baiker A (2004) Chem Rev 104:3037
19. Stephen GJHA, Hashmi K (2006) Angew Chem Int Ed 45:7896
20. Carrettin S, McMorn P, Johnston P, Griffin K, Hutchings GJ (2002) Chem Comm 7:696–697
21. Carrettin S, McMorn P, Johnston P, Griffin K, Kiely CJ, Attard GA, Hutchings GJ (2004) Top Catal 27:131
22. Prati L, Rossi M (1998) J Catal 176:552
23. Carrettin S, McMorn P, Johnston P, Griffin K, Kiely CJ, Hutchings GJ (2003) Phys Chem Chem Phys 5:1329
24. Zope BN, Hibbitts DD, Neurock M, Davis RJ (2010) Science 330:74
25. Ketchie WC, Murayama M, Davis RJ (2007) Top Catal 44:307
26. Zhu JJ, Figueiredo JL, Faria JL (2008) Catal Comm 9:2395
27. Dimitratos N, Villa A, Bianchi CL, Prati L, Makkee M (2006) Appl Catal A 311:185
28. Ketchie WC, Fang Y-L, Wong MS, Murayama M, Davis RJ (2007) J Catal 250:94
29. Villa A, Veith GM, Prati L (2010) Angew Chem Int Ed 49:4499
30. Gupta NK, Nishimura S, Takagaki A, Ebitani K (2011) Green Chem 13:824
31. Villa A, Gaiassi A, Rossetti I, Bianchi CL, van Benthem K, Veith GM, Prati L (2010) J Catal 275:108
32. Takagaki A, Tsuji A, Nishimura S, Ebitani K (2011) Chem Lett 40:150
33. Demirel S, Lehnert K, Lucas M, Claus P (2007) Appl Catal B 70:637
34. Porta F, Prati L (2004) J Catal 224:397
35. Davis SE, Houk LR, Tamargo EC, Datye AK, Davis RJ (2011) Catal Today 160:55
36. Casanova O, Iborra S, Corma A (2009) ChemSusChem 2:1138
37. Taarning E, Nielsen IS, Egeblad K, Madsen R, Christensen CH (2008) ChemSusChem 1:75
38. Zope BN, Davis RJ (2009) Top Catal 52:269
39. Pollington SD, Enache DI, Landon P, Meenakshisundaram S, Dimitratos N, Wagland A, Hutchings GJ, Stitt EH (2009) Catal Today 145:169
40. Villa A, Chan-Thaw CE, Prati L (2010) Appl Catal B 96:541
41. Holliday R Data sheets accompanying gold reference catalysts
42. Xi Y, Davis RJ (2010) Clays Clay Miner 58:475
43. Tsuji A, Rao KTV, Nishimura S, Takagaki A, Ebitani K (2011) ChemSusChem 4:542
44. Jobbágy M, Regazzoni AE (2011) Appl Clay Sci 51:366
45. Demirel-Gulen S, Lucas M, Claus P (2005) Catal Today 102–103:166
46. Wörz N, Brandner A, Claus P (2009) J Phys Chem C 114:1164
47. Zope BN, Davis RJ (2011) Green Chem 13:3484–3491. doi: 10.1039/C1GC15953D