Applied Catalysis B: Environmental 147 (2014) 871–878

Contents lists available at ScienceDirect

Applied Catalysis B: Environmental

journal homepage: www.elsevier.com/locate/apcatb

Selective electro-oxidation of glycerol to tartronate or mesoxalate on Au nanoparticle catalyst via electrode potential tuning in anion-exchange membrane electro-catalytic flow reactor

Zhiyong Zhang[a], Le Xin[a], Ji Qi[a], David J. Chadderdon[a], Kai Sun[b], Kayla M. Warsko[a], Wenzhen Li[a,*]

[a] Department of Chemical Engineering, Michigan Technological University, 1400 Townsend Drive, Houghton, MI, 49931, United States
[b] Department of Materials Science and Engineering, University of Michigan, Ann Arbor, MI, 48190, United States

ARTICLE INFO

Article history:
Received 24 May 2013
Received in revised form
16 September 2013
Accepted 2 October 2013
Available online 16 October 2013

Keywords:
Glycerol
Electro-catalysis
Gold nanoparticles
Green chemical production
Selective oxidation

ABSTRACT

A potential-controlled glycerol oxidation to tartronate or mesoxalate was demonstrated on Au nanoparticle catalysts in a self-designed anion-exchange membrane electro-catalytic flow reactor. The investigation clearly shows that by tuning the anode potential from 0.35 to 0.65 V, the selectivity to tartronate dropped from 79% to 26%, while that to mesoxalate increased from 0% to 57%. The tests also indicate that the elongation of reaction time will only increase the glycerol conversion, having little effects on the product distribution. The work may open a new route for the controllable oxidation of biorenewable polyols to valuable chemicals.

1. Introduction

The exploration of sustainable and cost-effective catalytic processes for production of valuable chemicals from biologically derived compounds is in urgent need to replace petrochemical feedstocks [1–6]. However, the complexity of these multi-functionalized structures leads to difficulty limiting oxidation or reduction to the target functional group without affecting the rest. Glycerol is a simple polyol that is massively produced from biodiesel manufacturing, and is considered an ideal biorenewable feedstock for the production of a series of high value oxygenated chemicals [7–14]. On monometallic Pt, Pd, and Au catalysts, it is easy to oxidize one of the primary-OH group, achieving high yield of glycerate (or glyceric acid in low pH aqueous solution) [10,15,16], but further oxidation of another primary –OH, and further the secondary –OH group to obtain tartronate and mesoxalate is far less efficient, due to the over-competition from C–C bond cleavage (yielding glycolate or oxalate). Reasonable selectivities to tartronate and mesoxalate from heterogeneous chemical oxidation of glycerol were obtained under restricted conditions either through low efficient multi-step sequential batch reactions [17,18] or on complicated multi-metallic catalysts (Ce-Bi-Pt-Pd/C [19] or Ce-Bi-Pt/C [17]); however, it is still unclear what is the dominant factor governing the oxidation of different functional groups. As a result, it is still hard to achieve controlled oxidation of different –OH groups or breakage of C–C bond in glycerol oxidation.

Besides heterogeneous catalysis, electro-catalytic oxidation of glycerol has been investigated, heavily focused on the voltammetries combined with spectroscopies or chromatographies in half-cells [14,20–24]. Seminal work has been done by Koper et al. [14,24] through combining the in-situ sample collection ex-situ HPLC analysis technique with linear scan voltammetries, and they successfully captured the products generated on Pt and Au polycrystalline electrodes under a wide range of potentials. Although these fundamental works from Koper et al. demonstrated that the electrode potential can serve as a facile and controlled driven force instead of molecule O_2 or H_2O_2 for the chemical oxidation of glycerol, the products are mainly glycerate and glycolate. No tartronate and mesoxalate were detected on Au, and only trace amount of tartronate was detected on Pt [14,24]. The glycerol electro-oxidation on bimetallic PtBi, PdBi and trimetallic PtPdBi catalysts were also investigated in alkaline electrolyte by Simoes et al. [21,25]. Based on the HPLC analyses after long-term chronoamperometries, at 50% glycerol conversion, the authors detected glycerate and tartronate at 0.55 V, and mesoxalate at 0.85 V, but no product selectivity was reported in their work. Meanwhile, with the

* Corresponding author. Tel.: +1 906 487 2298; fax: +1 906 487 3213.
E-mail addresses: wzli@mtu.edu, liwenzhen@gmail.com (W. Li).

0926-3373/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.apcatb.2013.10.018

assistance of in-situ FTIR techniques, Simoes et al. observed the formation hydroxypyruvate on Au nanoparticles at potentials >0.7 V [20], which is proposed to be an intermediate to mesoxalate [25]. However, weak signals of tartronate and mesoxalate were probed only at very high potentials (>1.2 V vs. RHE) on an Au electrode surface [26]. These results seem to have closed the door to a fine electrochemical manipulation of the glycerol oxidation to deeper-oxidized valuable tartronate (1564 US$ g^{-1}) and mesoxalate (156 US$ g^{-1})[7].

Recently, our group successfully demonstrated that glycerol can be electro-oxidized to tartronate and mesoxalate with simultaneous generation of electric power under anion-exchange membrane fuel cell (AEMFC) working conditions [27,28]. The massive production of tartronate and mesoxalate from electro-oxidation of glycerol also indicated that the carbon cloth based porous electrodes may function differently from glycerol electro-oxidation in a half cell setting (with smooth glassy carbon electrode). Using a similar testing configuration, Vizza et al. also observed the formation of tartronate from glycerol on Pd-based catalysts under a galvanostatic condition [29,30], which further supported that a porous electrode will facilitate the generation of deeper-oxidized products. However, in their works, no mesoxalate was observed, and the controlling factor in glycerol electro-oxidation process remains unclear. On the Au/C nanocatalyst, we recently observed the anode potential can be a key factor determining the degree of glycerol oxidation [28]. However, due to the lack of direct anode potential control, we could not obtain high yield of tartronate without the formation of mesoxalate under AEMFC test conditions.

In order to confirm the predominant effect of anode potential over glycerol oxidation, to distinguish the potential requirement for the generation of tartronate or mesoxalate, and to achieve high yield to tartronate or mesoxalate, in this work, an efficient potential controlled electro-catalytic process was successfully demonstrated on a supported Au nanoparticle (Au/C) catalyst in a delicately-designed anion-exchange membrane electro-catalytic flow reactor. By tuning the anode applied potential, glycerol can be selectively converted to tartronate or mesoxalate, with a switch potential of 0.45 V (vs. Reversible Hydrogen Electrode (RHE)). At an anode potential of 0.4 V and 50 °C, a selectivity of 78% to tartronate was obtained (at a glycerol conversion of 35%) and no mesoxalate was detected; while at 0.65 V, the main product was switched to mesoxalate (55% selectivity at a glycerol conversion of 78%).

2. Experimental

2.1. Chemicals

$AuCl_3$ was purchased from Alfa Aesar. $LiBEt_3H$ (1 M in THF) and 1-octadecene were purchased from Acros Organics. Oleylamine was purchased from Aldrich Chemistry. Glycerol (99.8%) was purchased from Fisher Chemical. Carbon cloth (untreated) was purchased from Fuel Cell Store. FAA anion-exchange membrane (110 μm) was purchased from FumA-Tech. Prior to testing, the FAA anion-exchange membrane was treated as recommended by the manufacturer.

2.2. Synthesis of Au/C catalysts

The preparation of 40 wt% Au/C catalyst was reported in our previous publications [31,32]. Briefly, 151.7 mg of $AuCl_3$ was dissolved in a mixture of 16 ml of octadecene and 4 ml of oleylamine under nitrogen gas flow. The system was then heated to 80 °C, followed by a quick injection of 1.5 ml of $LiBEt_3H$. After holding the temperature constant for 10 min, the Au nanoparticles (NPs) were obtained after quickly cooling down the solution to room temperature and separated by centrifugation. The as-prepared Au-NPs were then dispersed into 50 ml of hexane and slowly dropped into an ethanol dispersion of carbon black (148.0 mg). The final product Au/C catalyst (40 wt%) was obtained after filtration and washed with copious ethanol.

2.3. Physical characterizations

The X-ray diffraction (XRD) analysis of the Au/C catalyst was carried out on a Scintag XDS-2000 diffractometer with a Cu $K\alpha$ source (λ=1.5406 Å). The transmission electron microscopy (TEM) image of Au/C was collected on JEOL JEM-4000FX with an operating voltage of 200 kV. High resolution TEM (HR-TEM) was performed by JEOL 2010F with the operating voltage of 300 kV.

2.4. Single electro-catalytic flow reactor setup and potential controlled glycerol electro-oxidation

The potential controlled electro-oxidation of glycerol was investigated in a self-designed electro-catalytic flow reactor (5.0 cm^2 active cross-sectional area). A Au/C based anode (5.0 mg_{Au} cm^{-2}) and a Pt/C based cathode (1.0 mg_{Pt} cm^{-2}) were firstly prepared by airbrushing on carbon cloth (PTFE-untreated, 381 μm, Fuel Cell Store) that serves as the liquid diffusion layers (LDL), and assembled with a solid anion-exchange membrane (FAA, 110 μm, Fuma-Tech), home-made anode graphite block with serpentine flow pattern and high-density polyethylene cathode chamber. The system was sealed with the assistance of unreactive silicon gaskets (508 μm, Fuel Cell Store) and a torque of 20 N m. During each run, 8.0 ml of glycerol + KOH solution was introduced into a plastic vessel and pumped into the anode at the rate of 1.0 ml min^{-1} through a closed loop by a peristaltic pump (Gilson Minipuls 3), while a KOH solution (the same pH as the anode reactant solution) was cycled through the cathode chamber. The anode applied potential was controlled by potentiostats (Versastat, Princeton Applied Research) through a Hg/HgO/1.0 M KOH electrode embedded in the anode chamber for a certain reaction time. The reactor temperature was controlled at 50 °C. All electrochemical data was collected vs. a Hg/HgO/1.0 M KOH reference electrode and converted to a reversible hydrogen electrode (RHE) by $V_{\mathrm{vs.\,RHE}} = V_{\mathrm{measured\,vs.\,Hg/HgO/1.0\,M\,KOH}} + 0.098 + 0.059 \times$ (pH of electrolyte solution).

2.5. Electro-oxidation of glycerol in half cell with in-situ sample collection

The half cell in-situ sample collection test was conducted at room temperature in a conventional three-electrode-cell setup following the procedure in our previous work [27]. Briefly, 2.0 mg of the as-prepared Au/C catalyst were dispersed in 1.0 ml isopropanol by sonication to form a uniform ink. The working electrode was prepared by drop-casting 40 μl of the ink onto the glassy carbon electrode. 20 μl of 0.05 wt% AS-4 anion conductive ionomer solution (Tokuyama Inc. Japan) was then added on the top to affix the catalyst. A Hg/HgO/1.0 M KOH and a Pt wire were applied as the reference and counter electrodes, respectively. The electrochemical data was also reported versus RHE. A linear staircase scan in N_2-saturated 0.1 M KOH + 0.1 M glycerol was carried out with the increment of 100 mV 10 min^{-1}. In the course of the voltammetry, the products under each potential were in-situ collected through a needle positioned within 0.5 mm to the center of working electrode surface.