



Glycerol electro-oxidation on bismuth-modified platinum single crystals



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ABSTRACT

Herein we describe the role of Bi adatom irreversibly adsorbed on platinum single-crystal electrodes toward the oxidation of glycerol. Our results show that the presence of bismuth on the Pt(111) electrode improves the activity of the reaction, by preventing the adsorption of poisoning intermediates such as carbon monoxide, as well as the selectivity to dihydroxyacetone, while on the Pt(100)/Bi_{ir} electrode, the presence of a strongly bound glycerol-related adsorbate and a small amount of linearly bonded carbon monoxide causes a decrease in the activity. Significantly, the presence of bismuth on Pt(100) does not change its tendency to produce only glyceraldehyde as the primary product of the oxidation of glycerol. The increase in the selectivity to DHA on Pt(111)/Bi_{ir} is attributed to the interaction of the Bi adatom with the enediol intermediate, an adsorbed intermediate that exists on Pt(111) but not on Pt(100). The enediol is the key intermediate in the isomerization reaction between glyceraldehyde and dihydroxyacetone, and the stabilization of this intermediate by the interaction with the bismuth enhances the rate of the isomerization reaction toward the thermodynamically most stable isomer, namely dihydroxyacetone.

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1. Introduction

The oxidation of organic compounds derived from biomass has attracted increasing attention due to its possible application in fuel cells and because some compounds can be used to produce valuable chemicals [1,2]. Glycerol, a surplus by-product from the production of biodiesel, can be oxidized to CO₂ yielding 14 electrons, making its use as fuel in a Direct Alcohol Fuel Cell (DAFC) very attractive [1,3]. Furthermore, glycerol can be oxidized to functionalized feedstock such as dihydroxyacetone (DHA), glyceric acid (GEA) and tartronic acid (TA), all commercially useful compounds [2]. DHA, a product of secondary alcohol oxidation, is especially interesting because it is widely used in the cosmetic industry as self-tanning agent. It is currently produced by microbial oxidation, a method that requires a low glycerol concentration and a long operation time [4].

Previous results have shown that glycerol can be converted into DHA by using an electrochemical approach [5,6]. Our recent work on Pt single crystal electrodes showed that the selectivity of the electrochemical oxidation of glycerol to DHA is sensitive to the surface structure and that this sensitivity is related to the initial mode through which glycerol binds to the surface, as also confirmed by Density Functional Theory calculations [6].

In heterogeneous catalysis several mono- and bi-metallic catalysts (Pd, Pt, Au and Pt–Bi, Au–Pt, Au–Ag) have been considered promising for the selective conversion of glycerol to DHA [7–9]. Also homogeneous catalysts have been reported for the selective glycerol oxidation to DHA [10].

It has been demonstrated that the modification of the surface composition of noble metal electrodes constitutes a convenient approach to enhance their electrocatalytic properties [11–13]. The deposition of a certain amount of adatoms can enhance the electrocatalytic activity of a given electrode and improve its selectivity. Specifically, the effect of the adsorption of p-block metal promoters, such as Bi and Sb, on Pt electrodes, toward the electro-oxidation of organic compounds such as formic acid and ethylene glycol has been widely studied [12–17].

More recently, Kwon et al. [5,18] showed that the electro-oxidation of glycerol to DHA can be achieved with almost 100% selectivity by making use of adatom species on a Pt/C electrode. It was observed that in the absence of promoters, the primary alcohol oxidation is dominant; however, with bismuth or antimony in solution, the oxidation of secondary hydroxyl groups is preferred. A similar selectivity enhancement was reported for the selective electro-oxidation of sorbitol (C6 polyol) to glucose and fructose [19].

However, the role of promoters, such as Bi, in enhancing the activity and selectivity of catalytic oxidation reactions is still not clear. Many works discuss the enhanced activity based on the

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so-called third-body effect, in which Bi blocks the formation of poisonous species during the oxidation of small organic molecules [11,20,21]. In addition, electronic and bifunctional catalytic effects have been suggested [22,23]. However, there is currently no good understanding of how Bi and Sb steer the selectivity of polyol oxidation.

This paper discusses the effect of irreversibly adsorbed bismuth (Bi_{ir}) on the activity and selectivity of glycerol oxidation on Pt single-crystal electrodes. Our results show that the presence of adatom does not change the pathway toward the oxidation of primary and secondary hydroxyl groups of the glycerol molecule, compared to the unmodified electrodes [6]. However, the presence of Bi on Pt(111) enhances the activity and selectivity to DHA, while on Pt(100), the presence of bismuth causes a decrease in the overall activity, although the efficiency to primary alcohol oxidation is improved. This observation gives important hints about the mechanism of the selectivity enhancement for glycerol oxidation by Bi and other p-block metal promoters.

2. Experimental section

2.1. Experimental conditions, electrodes and reactants

All experiments were carried out at room temperature ($20^\circ \pm 1^\circ \text{C}$) in a single classical three-electrode cell, which was cleaned by a standard procedure to remove all organic traces. For the preparation of the solutions, high-purity perchloric acid (70%, Merck Suprapur), glycerol (GLY) (85%, analytical grade), bismuth (III) oxide (98%, Sigma-Aldrich) and ultrapure water from a Millipore system ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) were used. The counter and reference electrodes were a Pt wire and a reversible hydrogen electrode (RHE), respectively. The working electrodes were Pt(111) and Pt(100) purchased from icryst, with a geometric area of 0.0402 and 0.0366 cm^2 , respectively. Prior to each experiment, the working electrode was flame annealed and cooled down in a $\text{H}_2 + \text{Ar}$ atmosphere, after which it was protected with a droplet of water saturated with the cooling gases to prevent the contamination and reconstruction of the surfaces during the transfer to the electrochemical cell [24]. Next the electrode was characterized in an O_2 -free 0.5 M perchloric acid solution to ensure that the surface has been properly prepared and the cell and solution were completely clean.

The bismuth adlayer was prepared by an irreversible adsorption technique, which consists in bringing the electrode into contact with a Bi^{3+} containing solution (10^{-5} – 10^{-4} M) at open circuit potential for different adsorption times [11]. By changing the immersion time, different Bi coverages can be achieved. According to the literature [11], the charge density associated with the surface process and the blockage of the hydrogen and anion adsorption reactions on the bare Pt sites are proportional. The adatom coverage of the surface (θ) was therefore estimated using the following equation:

$$\theta = \frac{Q_{\text{Ad}}}{nQ_{\text{Pt}(hkl)}}$$

where Q_{Ad} is the charge density involved in the adatom oxidation process, $Q_{\text{Pt}(hkl)}$ is the charge density corresponding to the transfer of one electron per Pt atom on the surface [$241 \mu\text{C cm}^{-2}$ for Pt(111) and $209 \mu\text{C cm}^{-2}$ for Pt(100)], and n is the number of electrons transferred in the oxidation of one Bi adatom (i.e. $n = 3$) [11,25].

After preparation, the modified electrode was rinsed with ultrapure water and transferred to the electrochemical cell containing the supporting electrolyte (0.5 M HClO_4). The presence of irreversibly adsorbed bismuth on the Pt(111) and Pt(100) electrodes

was investigated by cyclic voltammetry recorded from 0.05 to 0.9 V vs. RHE at 10 mV s^{-1} . The potential was controlled by a Potentiostat/galvanostat ($\mu\text{Autolab Type III}$). After characterization of the Bi coverage, the electrode was transferred to the cell containing a deaerated 0.1 M GLY + 0.5 M HClO_4 solution for the glycerol electro-oxidation measurements, with the potential scanned from 0.05 V to 0.9 V at 1.0 mV s^{-1} . For all the electrochemical experiments, prior to bringing the work electrode in contact with the solution, a potential of 0.1 V vs. RHE was applied.

For the adsorbate formation from glycerol on Pt(111)/ Bi_{ir} and Pt(100)/ Bi_{ir} , the electrode was held at 0.2 V vs. RHE with the working electrode immersed in the working electrolyte for 1 min. After adsorption, the electrode was rinsed in O_2 free ultrapure water to remove excess of alcohol and then transferred to another electrochemical cell, which contained the pure electrolyte (0.5 M HClO_4). CO stripping measurements were also performed on Pt(111)/ Bi_{ir} and Pt(100)/ Bi_{ir} for comparison with the adsorbate stripping. For these experiments, CO gas was bubbled during 5 min into the cell containing pure electrolyte with the potential kept at 0.1 V vs. RHE. Next, excess CO was removed from the solution by bubbling argon for 10 min. The oxidative stripping of the resulting adsorbates and CO was performed in a clean supporting electrolyte by sweeping potential between 0.06 V and 0.9 V at 10.0 mV s^{-1} .

2.2. HPLC experiments

High Performance Liquid Chromatography (HPLC) was used to detect the liquid products produced during the electrochemical oxidation of the glycerol [26]. The reaction products were collected during the cyclic voltammetry with a small Teflon tip (0.38 mm inner diameter) positioned close (10 μm) to the center of the electrode surface, which was connected to a PEEK capillary with inner/outer diameters of 0.13/1.59 mm. Before sample collection, the tip and capillary were cleaned with ultrapure water and supporting electrolyte. The sample volume collected in each well was 60 μL on a 96-well microtiter plate (270 μL /well, Screening Devices b. v.) using an automatic fraction collector (FRC-10A, Shimadzu). The flow rate of sample collection was adjusted to 60 $\mu\text{L}/\text{min}$ with a Shimadzu pump (LC-20AT). After collecting samples, the microtiter plate was covered by a silicon mat to prevent the evaporation of collected samples. The samples were collected each 60 mV, in the potential range between 0.06 V and 0.9 V vs. RHE at 1.0 mV s^{-1} on Pt(111)/ Bi_{ir} and Pt(100)/ Bi_{ir} electrodes. The collected samples were analyzed by high-performance liquid chromatography (Prominence HPLC, Shimadzu). The microtiter plate with the collected samples was placed in an auto sampler (SIL-20A) holder and 30 μL of sample was injected into the column. The column configuration was an Aminex HPX 87-H (Bio-Rad) together with a Micro-Guard Cation H cartridge (Bio-Rad) in series with a Sugar SH1011 (Shodex) column and diluted sulfuric acid (0.5 mM) was used as the eluent. The temperature of the column was maintained at 70°C in a column oven (CTO-20A), and the separated compounds were detected with a refractive index detector (RID-10A). The expected products were analyzed separately to produce standard calibration curves at 70°C (i.e., glyceraldehyde, dihydroxyacetone, glyceric acid, glycolic acid, formic acid, oxalic acid, mesoxalic acid, hydroxypyruvic acid and tartronic acid).

2.3. OLEMS experiments

The volatile products of the reaction were detected using online electrochemical mass spectroscopy (OLEMS) with an evolution mass spectrometer system (European Spectrometry systems Ltd) [27]. The porous Teflon tip (inner diameter, 0.5 mm) was positioned close ($\approx 10 \mu\text{m}$) to the center of the electrode. Before the experiments, the tip was dipped into a 0.2 M $\text{K}_2\text{Cr}_2\text{O}_7$ in 2 M

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