Product Distribution of Glycerol Electro-oxidation over Platinum-Ceria/Graphene Nanosheet

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ABSTRACT
Pt and ceria nanoparticles were deposited into graphene nanosheets (Pt–CeO$_{2-x}$/GNS) via a polyol-assisted reduction process and examined as catalysts for the electro-oxidation of glycerol in alkaline solutions. The electrochemical activity of the catalyst was evaluated by cyclic voltammogram and chronoamperometry measurements. The products of glycerol oxidation over the catalyst were analyzed by high performance liquid chromatography. It was found that the Pt–CeO$_{2-x}$/GNS catalyst facilitated the formation of C3 products. The ratio between C3 products and C2 products is 2.6 for the Pt–CeO$_{2-x}$/GNS, which is much larger than that of 0.8 for the GNS supported Pt nanoparticles (Pt/GNS) at $-0.4$ V (vs. SCE.). Notably, a glyceraldehyde selectivity of 52% over the Pt–CeO$_{2-x}$/GNS was obtained at $-0.4$ V. The enhanced activity and selectivity of Pt–CeO$_{2-x}$/GNS catalyst relative to the Pt/GNS catalyst is related to the bifunctional and electronic effects.

Keywords : Glycerol Electro-oxidation, Ceria, Platinum, Selectivity

1. Introduction

Being an important biomass, Glycerol (GLY) can be converted into many value-added fuels and chemicals. Some high value-added products such as glyceraldehyde (GALD), tartaric acid (TA), glyceric acid (GLA) are of particular interest. GALD is used as an ingredient of cosmetics. GLA can be converted into various products such as polymers and biodegradable emulsifiers. TA can be used as a drug-delivery agent to increase the absorption of antibiotic. However, GLY oxidation is a multi-step process and involves many intermediates, which can be easily converted into one another via redox reactions. In industrial, GLY oxidation is conducted using stoichiometric oxidants, such as permanganate, nitric acid or chromic acid. The use of strong and toxic oxidants makes it difficult to control reaction pathway, thus leading to unsatisfactory selectivities towards desired products. Alternatively, GLY electro-oxidation is a totally green process, which affords a promising way to produce high value-added chemicals and intermediates. However, the diverse range of products renders it challenge to control both activity and selectivity during the oxidation process. To this end, considerable work has been devoted to searching for high-performance electrocatalysts. Pt is widely studied for GLY electro-oxidation both in acidic and alkaline media and a great deal of work has been done to improve its product selectivity toward GLY electro-oxidation. For instance, Kim et al. obtained selectivities values of 87% and 50% for GLA and GALD, respectively, from carbon supported Pt catalyst. Zhang et al. synthesized a PtCo/RGO catalyst with a GLA selectivity of 85.9%, which was higher than those of Pt/RGO and Co/RGO. Dai et al. studied GLY oxidation over an AuPt catalyst which showed a selectivity of 70% for lactic acid. In addition, Koper and coworkers studied GLY electro-oxidation on Bi-modified Pt single crystals and found that the presence of Bi improved both activity and selectivity. The presence of Bi in Pt (111) facets prevented the adsorption of poisoning intermediates such as carbon monoxide, leading to superior activity. Lee et al. investigated GLY oxidation in acidic media using a PtSn/C catalyst and suggested that the changes in the electronic structures of Pt arisen from adjacent Sn atoms led to a DHA selectivity of 61.4%. Kwon et al. systematically compared activity and selectivity of Sb, Pb, Sn, and Ir modified Pt/C electrodes. They found that a Sb decorated Pt/C electrode was capable of selectively oxidizing glycerol to DHA with a lower onset potential. Recently, we reported a three-component hybrid consisting of ultrathin Pt nanoparticles supported by ceria decorated graphene nanosheets. The resulting Pt–CeO$_{2-x}$/GNS catalyst showed excellent activity toward alcohol electro-oxidation. Herein, the Pt–CeO$_{2-x}$/GNS was studied as catalysts for the electro-oxidation of GLY in alkaline solutions. The main objective of this work is to reveal the effects of ceria in the product distribution and explore the mechanism/pathways of GLY oxidation. To this end, the products of GLY oxidation over the catalyst were analyzed by high performance liquid chromatography (HPLC). It was found that the interaction between Pt nanoparticles and ceria not only increased the activity toward GLY electro-oxidation but also enhanced the selectivity of C3 products.

2. Experimental

2.1 Synthesis and characterization of catalysts

GNS support was prepared via chemical deposition of methane sheets (<10 layers) with a Brunauer-Emmett-Teller (BET) surface area of 247 m$^2$ g$^{-1}$. The Pt–CeO$_{2-x}$/GNS catalyst was synthesized via a typical polyol-assisted reduction process as reported in the author’s previous work. Briefly, GNS support, ceria (III) nitrate, sodium hydroxide, and chloroplatinic acid were thoroughly mixed in ethylene glycol. The reduction was carried out at 180°C for 30 min. For comparison, GNS supported Pt catalyst (denoted as Pt/GNS) without addition of ceria was also prepared under identical conditions. The nominal weight percentage of Pt in the catalysts is 40% and that of ceria in the Pt–CeO$_{2-x}$/GNS catalyst is 10%. The structures of the catalysts were extensively characterized as reported in the author’s previous work. The morphology of the resulting catalysts was observed by transmission electron microscopy (TEM). The composition of metallic nanoparticles was analyzed by inductively coupled plasma-atomic emission spectrometry.
2.2 Electrochemical measurements

The activity of the catalysts was evaluated by cyclic voltammetry (CV) in a conventional three-electrode cell. A glassy carbon electrode (diameter = 3 mm) was used as a working electrode. A saturated calomel electrode (SCE) and a Pt gauze (effective area: 1 × 1 cm²) electrode were used as reference and counter electrodes, respectively. CVs were recorded in a solution of 0.1 M KOH and 1 M GLY with a scan rate of 50 mV s⁻¹. For product analysis, GLY electro-oxidation was conducted using an H-type cell. The H-type cell consists of two compartments which are separated by an anion exchange membrane (Nafion 112). A graphite paper (10 mm × 10 mm) was used as a working electrode. The catalyst was deposited onto the electrodes via a typical coating process as reported in the authors’ previous work. 25 Briefly, the catalyst powder was dispersed in a solution of Nafion solution (5 wt.%), ethylene glycol, isopropanol and water (volume ratio: 1:9:15:75) by ultrasonication to form a stable suspension. The catalyst suspension was transferred to the graphite using a pipette and then dried at 80°C. The loading of the catalyst on the electrode was ca. 180–200 µg cm⁻². i-t curves were recorded at three different potentials, i.e., −0.4, −0.1 and 0.2 V in a solution of 0.5 M KOH and 0.5 M GLY for 2 h. The volume of the electrolyte in each chamber was 20 mL. The products were collected with a syringe for HPLC analysis after chronoamperometry measurements. Before the test, the electrolyte solution was bubbled with high-pure N₂ gas for 30 min to remove the dissolved oxygen. The electrochemical measurements were performed using a CHI 660E electrochemical station at room temperature. All the potentials reported in this work were referenced to the SCE.

2.3 Product analysis

Product analysis was performed using HPLC (Agilent 1260 Infinity II, Agilent Technologies) equipped with a refractive index detector and a multiple wavelength detector. An Aminex HPX-87H (Bio-Rad) column was used for product separation. 32,33 The eluent was 5 mM sulfuric acid. Typically, 2 mL of aliquot was sampled and mixed with a droplet of 0.5 M H₂SO₄. 20 µL of the sample was injected into the column and the temperature of the column was kept at 65°C. The selectivity (S) of each product was calculated by following equation: $S = c_i / \Sigma c_i$, where $c_i$ is the concentration of product $i$.

3. Results and Discussion

3.1 Structural characterization

Figure 1 shows the TEM images of the as-prepared catalysts. It clearly reveals that ultrathin nanoparticles are intimately immobilized to the GNS support. The average Pt particle size in the Pt/GNS catalyst was determined as 1.8 nm. High-resolution TEM image shown in Fig. 1c reveals the lattice fringes with a space value of 0.23 nm, which can be ascribed to the d-spacing value of (111) planes in face-centered-cubic Pt crystals. Shown in Fig. 1d, large ceria NPs with an average size of 5.6 nm and small Pt NPs with a size of 1.4 nm are noted in the Pt–CeO₂₋ₓ/GNS catalyst. Distinct lattice fringes with spacing values of 0.32 nm, which could be originated from ceria (111) planes, are observed from the high-resolution TEM micrograph (see Fig. 1f). The co-existence of Ce⁴⁺ and Ce³⁺ species in the ceria NPs were confirmed by X-Ray photoelectron spectroscopy and the composition of ceria was calculated to be CeO₂₋ₓ, as reported in our previous work. 31

3.2 Activity of the catalysts

Figure 2 shows the CV curves of the catalysts recorded in a solution of 1 M KOH. Three typical electrochemical processes are observed, including hydrogen adsorption-desorption, Pt surface oxidation-reduction, and the double-layer charging. Compared with the Pt/GNS, the Pt–CeO₂₋ₓ/GNS shows a thicker double-layer zone, which is consistent with the results reported by Tabet-Aoul and Mohamedi. 34 The hydrogen adsorption-desorption of Pt–CeO₂₋ₓ/GNS becomes less-defined in comparison with that of the Pt/GNS, which can be explained from the strong interaction of Pt with ceria. 35 Two peaks in hydrogen adsorption-desorption, indicating that there are two different crystal facets of Pt over the catalysts. 32 Based on the CVs in 1 M H₂SO₄, the electrochemical active surface area (ECSA) of the catalyst was determined using following equation: $ECSA = S / (\nu \times M_{Pt} \times 210 \times 10^{-16})$, where $S$ is the hydrogen adsorption area in the CVs, $\nu$ is the scanning rate 0.05 V s⁻¹ and $M_{Pt}$ is the Pt mass in the catalyst. The ECSA values of the Pt/GNS and Pt–CeO₂₋ₓ/GNS are determined to be 62.9 and 68.6 m² g⁻¹ Pt, respectively, as reported in our previous work. 25

To evaluate the activity of the catalysts, CVs are recorded in 0.1 M KOH + 1 M GLY, as shown in Fig. 3. Notably, the hydrogen adsorption-desorption peaks are significantly suppressed, indicating that the active sites of the catalysts are mainly occupied by the GLY and/or intermediates. 36 The onset potential of the Pt–CeO₂₋ₓ/GNS toward GLY oxidation was negatively shifted in comparison with the Pt/GNS. The Pt–CeO₂₋ₓ/GNS exhibits a forward peak current density of 0.67 mA cm⁻², which is 2.7 times larger than that of the Pt/GNS. The backward peak current density of Pt–CeO₂₋ₓ/GNS is also much larger than that of the Pt/GNS. Notable, in the whole potentials of glycerol oxidation, the Pt–CeO₂₋ₓ/GNS exhibited higher current densities compared with the Pt/GNS.

A close examination on the CVs could reveal that the peak positions of the Pt–CeO₂₋ₓ/GNS are negatively shifted. To further study the electrochemical properties of the catalysts, i-t curves were recorded in 0.5 M KOH + 0.5 M GLY under three potentials of −0.4, −0.1 and 0.2 V as shown in Fig. 4. It shows that the Pt-
CeO$_2$/$GNS$ has higher current densities after 7200 s at all the three different applied potentials as compared with the Pt/GNS. In addition, the current densities are closely related to applied potentials, manifesting that different kinds of products are derived from the oxidation process. The remarkable activity of the Pt–CeO$_2$/$GNS$ could result from the bifunctional and electronic effects as induced by ceria NPs.

3.3 Product analysis

To investigate the products of GLY oxidation, the sample solution after $i$–$t$ tests was collected for HPLC analysis. Five compounds including oxalate acid (OA), TA, GLA, GALD, and GA were obtained from the catalysts as shown in Fig. 5. When the Pt/GNS catalyst was used, GA is the main product as shown in Fig. 5a. The selectivity of GA increases with increasing potentials. A largest GA selectivity of 65.5\% was obtained at $0.2 \text{ V}$. In addition, the selectivity of GA is larger than that of other products at the three potentials. The selectivity of GALD decreases with increasing potentials. GALD selectivities of 30.2, 14.5 and 7.9\% are obtained at the potentials of $0.4$, $0.1$ and $0.2 \text{ V}$, respectively. Similar to the selectivity of GALD, that of OA is also decreases with increasing potentials. The largest OA selectivity is 19.8\% at $0.4 \text{ V}$. Comparatively, the applied potential shows limited effects in the GLA selectivity. The Pt/GNS catalyst possesses TA selectivity no more than 0.4\%. Compared with the Pt/GNS catalyst, the Pt–CeO$_2$/$GNS$ catalyst shows a larger selectivity of GALD at the potential of $0.4 \text{ V}$ as shown in Fig. 5b. The Pt–CeO$_2$/$GNS$ catalyst shows GALD selectivities of 52, 28 and 45\% at the potentials of $0.4$, $0.1$, and $0.2 \text{ V}$, which are 1.7, 1.9 and 5.7 times of those of the Pt/GNS catalyst, respectively. In particular, GA selectivity of the Pt–CeO$_2$/$GNS$ is significantly lower than that of the Pt/GNS catalyst. A larger GA selectivity (10\%) is obtained at $-0.1 \text{ V}$. The Pt–CeO$_2$/$GNS$ yields more OA and GLA as compared with the Pt/GNS. TA selectivity is also small over the Pt–CeO$_2$/$GNS$ catalyst.

For a better comparison, the concentrations of products are comparatively shown in Table 1. A maximum GLA concentration (6.3 mg L$^{-1}$) was obtained from the Pt–CeO$_2$/$GNS$ catalyst at the potential of $0.1 \text{ V}$.
In addition, GLA concentration of the Pt–CeO$_2$/GNS catalyst increases from 4.3 mg L$^{-1}$ at $-0.4$ V to 6.3 mg L$^{-1}$ at $-0.1$ V and then decreases to 2.52 mg L$^{-1}$ at 0.2 V. Such a trend is consistent with that of the Pt/GNS catalyst. Considerable GALD is yield from the Pt–CeO$_2$/GNS catalyst. A maximum GALD concentration 9.47 mg L$^{-1}$ is obtained from the Pt–CeO$_2$/GNS catalyst at $-0.4$ V. GALD concentrations of the Pt–CeO$_2$/GNS catalyst are larger than those of the Pt/GNS catalyst at the three potentials. GA concentrations of the Pt/GNS are much larger than those of the Pt–CeO$_2$/GNS. The Pt/GNS shows GA concentrations of 8.88, 14.32 and 18.63 mg L$^{-1}$ at the potentials of $-0.4$, $-0.1$ and 0.2 V, respectively. It seems that the production of GA from Pt–CeO$_2$/GNS is suppressed. OA concentration of the Pt–CeO$_2$/GNS increases from 4.58 mg L$^{-1}$ at $-0.4$ V to 11.91 mg L$^{-1}$ at $-0.1$ V and then decreases to 8.98 mg L$^{-1}$ at 0.2 V while that of Pt/GNS decreases with increasing potentials. Such differences in potential dependence could be related to the interaction of ceria with Pt, which modifies the binding strength of glycerol and intermediates, thereby regulating their adsorption and desorption. OA tends to be produced at high potentials. Compared with other compounds, the production of TA is negligible for the two catalysts, resulting in concentrations no more than 0.2 mg L$^{-1}$.

For a good comparison, the products derived from GLY electro-oxidation were categorized into C3 compounds (including GLA, GALD and TA) and C2 compounds (including GA and OA). The C3/C2 ratios of those two catalysts are compared as shown in Fig. 6. It can be seen that the Pt–CeO$_2$/GNS possesses the much larger C3/C2 ratios as compared with the Pt/GNS. In particular, the Pt–CeO$_2$/GNS exhibits a largest C3/C2 ratio of 2.6 at $-0.4$ V. The C3/C2 ratios of the Pt/GNS decrease with increasing potentials. The Pt/GNS shows the C3/C2 ratios of 0.8, 0.4 and 0.3 at the potentials of $-0.4$, $-0.1$ and 0.2 V, respectively, which are significantly lower than those of 2.6, 0.9 and 1.2 obtained from the Pt–CeO$_2$/GNS. Based on the C3/C2 ratios results, it can be concluded that the Pt–CeO$_2$/GNS catalyst shows a strong tendency to yield C3 products.

3.4 Reaction pathways

On the basis of HPLC results, the reaction pathway of GLY oxidation over the catalysts is proposed, as shown in Scheme 1. In alkaline media, GLY is first oxidized to GALD in a two-electron transfer step both on the Pt/GNS and Pt–CeO$_2$/GNS catalysts. This process is facilitated by the Pt–CeO$_2$/GNS catalyst, which can be explained by the bifunctional and electronic effects. A combination of the bifunctional and electronic effects can result in a downshift in the d-band center of Pt, reducing the adsorption energy and binding strength of GALD on the Pt surface, which makes GALD easier to desorb from Pt surface and hinders the further decomposition of GALD into two and one carbon products. As a next two-electron transfer step, GALD is further oxidized to GLA. GLA can be further converted into GA by cleavage of a C–C bond. This process is favored on the Pt/GNS, indicating that a relatively strong adsorption of GLA existing on the pure Pt catalyst. In addition, GA and GLA can be further oxidized to OA and TA, respectively, on both the catalysts. It was reported that low levels of TA were detected for the oxidation of GLA over Pt-based catalysts, indicating that the oxidation of GLA to TA may be favored by the C–C bond cleavage.

4. Conclusions

In this work, we studied GLY electro-oxidation over the Pt/GNS and Pt–CeO$_2$/GNS catalysts. Compared to the Pt/GNS catalyst, the Pt–CeO$_2$/GNS catalyst exhibited better performance in terms of higher current densities and lower onset potentials. In addition, HPLC results indicate that the Pt–CeO$_2$/GNS catalyst showed a higher selectivity towards C3 products. The ratio between C3 products and C2 products is 2.6 for the Pt–CeO$_2$/GNS, which is larger than that of the Pt/GNS (0.8) at $-0.4$ V. Notably, a GALD
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