

Role of Ru on Carbon-supported PtRu Catalysts for Electrocatalytic Glycerol Oxidation in Acidic Condition

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Abstract: A series of binary PtRu catalysts with different Pt:Ru atomic ratios in a range from 7:3 to 3:7 are synthesized on carbon support using the colloidal method; they are then used for electrooxidation of glycerol in acidic media. X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and Xray absorption spectroscopy (XAS) analyses are used to investigate the particle size, size distribution, and structural and electronic properties of the prepared catalysts. The addition of Ru content to the Pt-based catalysts caused structural and electronic modifications over the PtRu alloy catalyst formation. The electrocatalytic activities of PtRu/C series catalysts are investigated by using the cyclic voltammetry (CV) technique. Among the prepared catalysts, the Pt₅Ru₅/C catalyst shows enhanced catalytic activity at least 40% higher than that of the Pt/C catalyst, with improved stability for glycerol electrooxidation; these improvements can be attributed to the structural and electronic modifications of the Pt catalysts. Using an electrocatalytic batch reactor, product analysis after the oxidation reaction is performed by high-performance liquid chromatography

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(HPLC) to determine and compare the reaction pathways on the Pt/C and PtRu/C catalysts. To understand different catalytic activities of glycerol oxidation on the PtRu alloy surfaces, density functional theory (DFT) calculations have been performed and discussed with the experimental results.

Introduction

Glycerol is a valuable byproduct in the production of biodiesel and fatty acids.^[1-4] Recently, efforts have been devoted to developing efficient electrochemical conversion technologies to produce value-added chemicals and/or energy from biomass-derived oxygenates such as glycerol.[5-13] The electrocatalytic conversion process of glycerol is a promising technology that can produce valuable chemicals such as dihydroxyacetone, glyceraldehyde, and glyceric acid by selective oxidation reaction^[14-16] and electrical energy by a full oxidization reaction^[17-19]. In particular, full glycerol oxidation has been considered a promising reaction for direct alcohol fuel cells (DAFC), because glycerol is nonflammable and has environment-friendly properties; it also possesses high theoretical energy density, with relatively low price and simple purification steps.^[5,20] It has also been reported that glycerol can be used as fuel for a DAFC in alkaline condition over Pt and Pd-based catalysts.[5,21-27]

The electrooxidation reaction of glycerol can be represented as below; this electrooxidation reaction can take place in a Pt-based catalyst electrode in acidic media^[17,28]:

 $C_3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 14H^+ + 14e^-$ at anode (1)

Compared to the electrooxidation of methanol (CH₃OH + H₂O \rightarrow CO₂ + 6 H⁺ + 6 e⁻), the oxidation process of glycerol (Reaction 1) involves additional complicated reaction steps due to the scission of more C–C and C-H bonds, especially at low temperatures (20 - 120 °C). It also leads to the necessity of additional activation energy for the reaction.^[28,29] Therefore, glycerol oxidation depends on the ability to break the C-C and C-H bonds. Recently, we reported that PtRu-based catalysts showed improved catalytic activity and stability for glycerol electrooxidation in acidic condition.^[17,18] However, more scientific investigation is required to understand why the PtRu combination is so active for glycerol electrooxidation in acidic condition.

We report here an experimental and computational investigation of PtRu/C catalysts used for electrocatalytic glycerol oxidation in acidic electrolyte. PtRu/C catalysts with different

Pt:Ru atomic ratios are synthesized by the colloidal method and characterized by using various physicochemical analyses such as transmission electron microscopy (TEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and X-ray absorption spectroscopy (XAS). The electrocatalytic activities of the PtRu/C catalysts are investigated using the cyclic voltammetry (CV) technique and the chronoamperometry (CA) method; results are analyzed and discussed along with the reaction product analysis by employing high-performance liquid chromatography (HPLC). With the help of density functional theory (DFT) calculations, we also explore the correlation between the catalyst activity for glycerol electrooxidation and the glycerol binding energy in order to gain further insight into the promoting mechanism of Ru to Pt. To the best of our knowledge, this is the first work to demonstrate a glycerol electrooxidation mechanism in acidic condition with reaction product analysis and DFT calculations over Pt-based catalysts.

Results and Discussion

Structural properties of PtRu/C catalyst

Figure 1 presents the TEM images and the corresponding histograms of the particle size distribution of carbon supported Pt_7Ru_3 , Pt_5Ru_5 , and Pt_3Ru_7 nanoparticles with the ETEK commercial Pt/C catalysts, showing the morphology and average particle size distribution. Based on the TEM images, Pt and PtRu nanoparticles can be seen to be finely and uniformly dispersed on the surface of the carbon support, with a uniform metal particle size. The average particle size was estimated with the following equation using the more than 150 different particles visible on the micrographs:

$$d = \frac{\sum n_i d_i}{\sum n_i}$$

where n_i is the number of particles having a diameter of size d_i .^[25] The particle sizes of carbon supported Pt, Pt_7Ru_3 , Pt_5Ru_5 , and Pt_3Ru_7 are estimated to be ca. 2.3, 2.0, 2.0, and 1.7 nm,



Figure 1. TEM images of carbon-supported Pt and PtRu catalysts with different Pt:Ru atomic ratios, together with corresponding histograms of particle size.

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Figure 2. XRD patterns of the Pt/C and PtRu/C catalysts with different Pt:Ru atomic ratios and the selected scan range of the Pt (111) reflection peaks.

respectively, with relatively narrow particle size distribution (see Table 1).

XRD patterns of Pt/C and PtRu/C catalysts with different Pt:Ru atomic ratios are displayed in Figure 2. In the XRD pattern of Pt/C, the characteristic peaks at ca. 39°, 46°, 67°, and 81° exhibit a Pt face-centered cubic (*fcc*) lattice structure corresponding to the (111), (200), (220), and (311) planes, respectively. The diffraction peaks of the PtRu/C catalysts with different Pt:Ru atomic ratios are similar to those of the Pt/C, except that the 2 θ values of the Pt diffraction peaks are gradually shifted to higher values with increasing Ru content, as summarized in Table 1. No distinguishable diffraction peaks for Ru or RuO₂ crystal peaks appeared, suggesting an alloy formation between Pt and Ru through incorporation of Ru atoms into the fcc crystal lattice of Pt.^[30-32] The lattice parameters of the prepared catalysts were calculated using the following equation:

$$a = \frac{\lambda}{2\sin\theta} \times \sqrt{h^2 + k^2 + l^2}$$

where a is the lattice parameter, (*hkl*) are the (220) Miller indices, λ is the wavelength of the X-rays (1.54056 Å), and θ is the diffraction peak position at the (220) plane. The values of the lattice parameters of the PtRu/C catalysts were found to consistently decrease with increasing of the Ru content due to the smaller atomic radius of Ru relative to that of Pt (see Table 1).

Electronic properties of PtRu/C catalyst

XPS was employed to explain the surface oxidation states of the prepared catalysts. Figure 3 shows the Pt *4f* and Ru *3p* regions in the XPS spectra of the Pt/C and PtRu/C series. The core-level binding energies (BEs) and their relative amounts of oxidation states for the Pt *4f* and Ru *3p* are reported in Table 1. It was found that the predominant surface species in the prepared catalysts is the metallic state of zero-valent Pt (Pt⁰); a relatively small amount of the oxidized Pt (Pt²⁺) is present. Also, the BEs of Pt (Pt⁰) 4f_{7/2} for the PtRu/C series were positively shifted compared with that of Pt/C, indicating that the vacancies in the Pt valence band



Figure 3. XPS of Pt 4*f* and Ru 3*p* for the Pt/C and PtRu/C catalysts with different Pt:Ru atomic ratios.

increase due to Ru, leading to more tightly bound electrons in the Pt core levels.^[33] This implies that the Pt electronic structure in PtRu/C was significantly modified by the presence of Ru. It was possible to deconvoluted the Ru $3p_{3/2}$ spectra to the metallic phase (Ru⁰) and to the oxidation states (Ru⁴⁺) in forms of RuO₂

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Figure 4. Pt L₃ edge XANES spectra for the Pt/C and PtRu/C catalysts with different Pt:Ru atomic ratios together with Pt foil as the reference. The inset is a magnified image for the white line intensity.

with different BE values. More than 72% of the surface composition is in metallic state in the PtRu/C series catalysts. The XPS results suggest that on the surface of the binary PtRu/C catalysts the dominant surface phase of Pt and Ru is the metallic state.

Figure 4 shows the normalized XANES spectra obtained at the Pt L₃ edge for the prepared catalysts. Overall XANES shapes of the Pt/C and PtRu/C series are similar to that of the Pt foil, except for the white line (WL) intensity. WL, which is a strong peak above the edge energy position, corresponds to the $2p_{3/2} \rightarrow 5d$ transition at the Pt L₃ edge and is closely related to the density of vacant d orbital states.^[34,35] The WL intensities for all of the carbon-supported catalysts show greater values than that of the Pt foil. And, in case of the PtRu/C catalysts, the WL intensities appear to increase in the order of Pt₇Ru₃/C < Pt₅Ru₅/C < Pt₃Ru₇/C (inset of Figure 4). The increased WL intensities for the PtRu bimetallic catalysts can be attributed to the 5d electron loss of the Pt in the PtRu alloys.^[36,37] The quantitative WL values, with the edge energy analysis, are summarized in Table 1.

| | XRD | | TEM | X | (PS | XANES | |
|------------------------------------|---|--|--|------------------------------|--------------------------------------|---|---|
| Catalysts | 2θ _{max^[a] (°)} | Lattice parameter ^[b] (Å) | Mean particle size ^[c] (nm) | Pt 4f _{7/2} (eV) | Ru 3 <i>p</i> _{3/2} (eV) | E ₀ ^[f] (eV) | WL intensity ^{(ی} (a.u.) |
| Pt foil | - | | | - | - | 11564.0 | 1.26 |
| Pt/C | 67.8 | 3.905 | 2.3 ± 0.42 | 71.05 (60.2) ^[d] | - | 11564.0 | 1.42 |
| | | | | 74.38 (39.8) ^[d] | | | |
| Pt7Ru₃/C | 68.7 | 3.880 | 2.0 ± 0.39 | 71.34 (59.3) | 461.94 (83.3) ^[e] | 11564.0 | 1.42 |
| | | | | 74.67 (40.7) | 464.90 (16.7) ^[e] | | |
| Pt₅Ru₅/C | 68.9 | 3.850 | 2.0 ± 0.43 | 71.30 (60.5) | 462.49 (75.2) | 11564.4 | 1.52 |
| | | | | 74.63 (39.5) | 465.51 (24.8) | | |
| Pt ₃ Ru ₇ /C | 70.3 | 3.826 | 1.7 ± 0.45 | 71.29 (61.0) | 462.01 (72.0) | 11564.4 | 1.56 |
| | | | | 74.62 (39.0) | 464.84 (28.0) | | |

images. [d] Relative % of the Pt^0 and Pt^{2+} species. [e] Relative % of the Ru^0 and Ru^{4+} species. [f] $Pt L_3$ edge energy. [g] White line intensity.



Figure 5. CVs for the electrooxidation of glycerol over the Pt/C and PtRu/C catalysts in 0.5 M H_2SO_4 + 2 M $C_3H_5(OH)_3$ with a scan rate of 50 mV s^1 at room temperature.

Electrocatalytic activity and stability of PtRu/C catalyst

The electrocatalytic activity of the Pt/C and PtRu/C series catalysts was investigated by the cyclic voltammetry (CV) technique in 0.5 M H₂SO₄ with 2 M glycerol at a scan rate of 50 mV s⁻¹, as shown in Figure 5. The current densities were normalized to the geometric area of the electrode. The electrocatalytic test results are summarized in Table 2. By comparing the characteristics of the CVs, the addition of Ru to Pt was found to substantially enhance the catalytic activity for glycerol electrooxidation. First, the onset potentials (indicative of the catalytic activity) of glycerol oxidation in the case of alloyed catalysts showed relatively lower values than that of only the Pt catalyst. The positions of the onset potentials follow the order of $Pt_5Ru_5/C < Pt_7Ru_3/C < Pt_3Ru_7/C < Pt/C$. Second, the forward peak current densities (showing the maximum catalyst performance) of the binary catalysts toward glycerol oxidation are in the order of $Pt_5Ru_5/C > Pt_7Ru_3/C > Pt/C > Pt_3Ru_7/C$. In particular, the peak current density of the Pt₅Ru₅/C catalyst is 1.4 times higher than that of the Pt/C catalyst. Thus, the Pt₅Ru₅/C catalyst exhibited the

| Cotolucto | Eonset ^[a] | E _f ^[b] | If ^[C] |
|------------------------------------|-----------------------|-------------------------------|----------------------|
| Catalysis | (V vs. SHE) | (V vs. SHE) | (mA cm ⁻² |
| Pt/C | 0.635 | 0.893 | 27.5 |
| Pt7Ru3/C | 0.480 | 0.862 | 33.7 |
| Pt₅Ru₅/C | 0.448 | 0.854 | 38.6 |
| Pt ₃ Ru ₇ /C | 0.498 | 0.825 | 21.9 |

most prominent electrochemical performance in terms of the largest forward peak current density and the lowest onset potential. It should be noted that the peak current density of the Pt₃Ru₇/C catalyst is the lowest among the tested catalysts, which may be due to a substantial reduction of available surface Pt active sites by large amounts of Ru.

Figure 6 shows the long term cycle test results for the Pt₅Ru₅/C and Pt/C catalysts in 0.5 M H₂SO₄ with 2 M glycerol at a scan rate of 50 mV s⁻¹. To compare the decay rate, the current density was normalized by the initial current. After 500 cycles, Pt₅Ru₅/C presents a normalized current density ratio of 0.635, which is much higher than that of Pt/C (0.465). This result indicates that the Pt₅Ru₅/C catalyst has stability better than that of the Pt/C catalyst.

Reaction pathways for glycerol electrooxidation over PtRu/C catalyst

In order to understand how the reaction path differs for the Pt/C and Pt₅Ru₅/C catalysts, we conducted electrocatalytic glycerol oxidation using an electrochemical batch reactor featuring a three-electrode system with catalyst-coated carbon paper as the working electrode. Liquid samples after the reaction were analyzed by HPLC. Table 3 shows the glycerol conversion, product selectivity, and mass balance for the electrocatalytic oxidation of glycerol using the batch reactor over the Pt/C and



Figure 6. Long-term cycle stability for the electrooxidation of glycerol over the Pt/C and Pt₅Ru₅/C catalysts in 0.5 M H₂SO₄ + 2 M C₃H₅(OH)₃ with a scan rate of 50 mV s⁻¹ at room temperature.





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| Table 3 Glycerol conversion and product selectivity for electrocatalytic glycerol oxidation using a batch reactor at 60 °C over Pt/C and Pt ₅ Ru ₅ /C catalysts. | | | | | | | | | |
|--|------------------------------|----------------------------------|---------------------------------|---|-----------------------------------|------|------|------|--|
| Catalvst | Feed Solution ^[a] | Applied Potential ^[b] | Mass Bal. ^[c] [%] | Glycerol Conv. ^[d] [%] | Product Selec. ^[d] [%] | | | | |
| System | | | | | DHA | GAD | GLA | GCA | |
| Pt/C | 0.1M Glycerol | 1.1 V | 100.4 | 20.3 | 0 | 42.1 | 57.8 | 0.5 | |
| Pt₅Ru₅/C | 0.1M Glycerol | 1.1 V | 80.4 | 31.5 | 35.0 | 17.1 | 11.1 | 17.2 | |

[a] The 0.1 M glycerol in 0.5 M H_2SO_4 was used as feed solution. [b] The anode applied potential for the electrocatalytic glycerol oxidation was 1.1 V (vs. SHE). [c] Mass balance (bal.) was determined on basis of observed C_2 and C_3 products. [d] Glycerol conversion (conv.) and product selectivity (selec.) were calculated after 7 hours reaction and identified in liquid C_2 and C_3 products; Liquid samples after the reaction were analyzed by HPLC; DHA = dihydroxyacetone, GAD = glyceraldehyde, GLA = glyceric acid, GCA = glycolic acid

Pt₅Ru₅/C catalysts. Results for the electrooxidation of glycerol were obtained at a reaction temperature of 60 °C and 0.1 M glycerol in 0.5 M H₂SO₄ at a fixed potential of 1.1 V (vs. SHE) for 7 hours reaction. Figure 7 exhibits the current-time plots of the Pt₅Ru₅/C and Pt/C catalysts in 0.5 M H₂SO₄ with 0.1 M glycerol. Similar to the CV results (Figure 5 and Table 2), the current density of Pt₅Ru₅/C, determined from chronoamperometry measurement, is much higher than that of Pt/C. As can be seen in Table 3, the glycerol conversion of PtRu/C achieved a value of 31.5 %, which was higher than the value of 20.3 % of Pt/C. As Table 3 indicates, the glycerol oxidation on Pt/C catalyst mainly leads to the formation of glyceraldehyde and glyceric acid. In the case of the Pt₅Ru₅/C catalyst, dihydroxyacetone of 35.0 % was observed, indicating that the production of dihydroxyacetone is favored on the PtRu surface. More oxidized products such as glycolic acid were produced over the PtRu/C catalyst. The mass balance of detectable products decreased from 100.4 % for Pt/C to 80.4 % for PtRu/C. The undetectable carbon was probably C1 molecules (formic acid or CO₂) produced by C-C cleavage

reactions over the PtRu/C. These results demonstrate how the PtRu surface can increase the rate of C-C bond cleavage as well as that of C–H and O–H bond breakage compared to only the Pt surface. It has been reported by several authors^[17,19,38-40] that the modified structural and electronic properties of the Pt may promote the C-C and C-H bond cleavage, thus enhancing the catalytic activity for the alcohol electrooxidation.

Figure 8 shows the possible reaction pathway over the Ptbased catalysts for glycerol electrooxidation in acidic media. The glycerol molecule is primarily oxidized to glyceraldehyde and/or dihydroxyacetone, which are further oxidized to glyceric acid. The glyceric acid is subsequently oxidized to glycolic acid, hydroxypyruvic acid, and tartronic acid. It has been reported that low levels of hydroxypyruvic acid and tartronic acid were detected for the oxidation of glyceric acid over Pt-based catalysts, indicating that the oxidation of glyceric acid to glycolic acid under acidic media may be favored by C–C bond cleavage.^[15] This is consistent with the reaction mechanism on the PtRu/C catalyst, discussed above and shown in Table 3.



Figure 8. Proposed reaction pathways over the PtRu catalyst for electrocatalytic glycerol oxidation in acidic condition. (DHA: dihydroxyacetone, GAD: glyceraldehyde, GLA: glyceric acid, HPA: hydroxypyruvic acid, TTA: tartronic acid, GCA: glycolic acid, OXA: oxalic acid)



Figure 9. Binding modes and energies of glycerol on Pt, Ru, and Pt mixed with Ru surfaces. (a) Glycerol binding on Pt, Pt_eRu_e , and Ru surfaces (from left to right). Pt atoms are shown in blue and Ru atoms are in pink. (b) Glycerol binding energies and (c) average partial charges of surface atoms with respect to Ru contents.

Correlation between catalyst activity and binding energy

First principle DFT calculations were carried out to understand the interactions between glycerol molecules and the metal surface. In Figure 9a, we have drawn optimized structures of the glycerol molecules and metal surfaces for three cases: Pt, Pt₅Ru₅, and the Ru surfaces. Two oxygen atoms of glycerol are close to the surface, indicating that oxygen-metal interaction holds the glycerol to the surface. In addition, as oxygen atoms are bound to the surface, hydrogen atoms in C-H and O-H bonds are also close to the surface. This binding mode will surely be the same for all other oxidized intermediates containing oxygen atoms and implies several chemical bonds are affected by the catalyst. Although the binding modes are the same, binding energies show different behavior. For the mixed surfaces, the binding energies of glycerol decrease as the Ru content increases (Figure 9b). The pure Pt and Ru surfaces also interact with the glycerol molecules. However, their interaction is weaker compared to the case of the mixed surfaces. This can be well-explained based on electrostatic interactions between oxygen and the surface atoms. From Bader analysis of all the atoms on the surfaces, we estimated the average partial charges of the atoms on the top-most layer, with results shown in Figure 9c. If the Pt and Ru atoms are mixed, Ru atoms become partially positive, while Pt atoms are partially negative. The more positive Ru atoms show stronger electrostatic interactions with the electronegative oxygen atoms of glycerol, and thus exhibit higher binding energies. The highest binding energy is observed for the Pt7Ru3 surface, where the average charge of Ru atoms is the most positive. As can be seen in Figure 10, there seems to exist a volcano-type relation between the theoretically calculated values of glycerol binding energy and the experimentally obtained values of onset potential for glycerol electrooxidation. It has been reported that a volcano-shaped curve generated from the Brønsted-Evans-Polanyi relation is



Figure 10. Relation between glycerol binding energy and onset potential (vs. SHE) for glycerol electrooxidation over PtRu/C catalysts.

obtained when the catalytic activity for a reaction is correlated to the ability of the catalyst surface to form chemical bonds with reactants, reaction intermediates, or products.^[41,42] Considering that the Pt₅Ru₅ surface acts as the most active catalyst (see Table 2 and Figure 5), we suggest that the optimal glycerol binding energy is ~1.75 eV for oxidizing glycerol molecules with mixed metal surfaces. This result highlights the idea that the glycerol molecules on the modified PtRu surface can be efficiently oxidized by controlling the adsorption/desorption properties of glycerol and of the other reaction products.

Conclusions

In this work, the electrooxidation of glycerol was investigated on a series of Ru-modified Pt/C catalysts. The XRD and TEM results indicate that bimetallic PtRu nanoparticles with different atomic ratios (Pt:Ru = 7:3, 5:5, 3:7) are well alloyed and uniformly dispersed on the carbon support, with an average particle size of about 2 nm. XPS and XANES analyses revealed that the Pt electronic structure was significantly modified through the formation of the PtRu alloy. The electrochemical measurements showed more enhanced catalytic activities for the glycerol electrooxidation on the bimetallic PtRu/C catalysts than for the Pt/C catalyst in acidic media. In the electrocatalytic batch reactor, the PtRu/C catalyst produced more oxidized products, such as glycolic acid, at higher glycerol conversion compared to the Pt/C catalyst. DFT calculations revealed that there exists a volcanotype relation between the glycerol binding energy and the catalytic activity for glycerol electrooxidation. This study thus highlights that glycerol molecules on the structurally and electronicallymodified PtRu surface can be efficiently oxidized by controlling the adsorption/desorption properties of glycerol and by breaking more C-C, C-H, and O-H bonds. Further systematic studies including theoretical calculations are required to better and O-H understand the C-C. C-H, bond cleavage/adsorption/desorption during glycerol electrooxidation over PtRu/C catalyst.

Experimental Section

Chemicals

Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, ACS reagent, Sigma-Aldrich), ruthenium(III) chloride hydrate (RuCl₃·xH₂O, 99.98%, Sigma-Aldrich), ethylene glycol (99.8%, Sigma-Aldrich), de-ionized water (DI water, 18 MΩ cm, Millipore), sodium hydroxide solution (NaOH, 50% solution in water, Aldrich), Nafion® ionomer solution (5 wt.%, Sigma-Aldrich), carbon black powder (Vulcan® XC72R, Cabot Corp.), Pt/C (20 wt.%, ETEK), hydrochloric acid (HCl, 37%, Sigma-Aldrich), carbon paper (TGP-H090, Toray), and glycerol (≥99.5%, Sigma-Aldrich) were purchased and used as received without further purification.

Synthesis of carbon-supported PtRu electrocatalysts

Prior to its use as a catalyst support, carbon black powder was pretreated with 6 M HCl solution for 12 h and then washed with Dl water until the solution pH was around 5.5; this was followed by filtering and drying for 5 h in air at 120 °C. For a typical synthesis of 20 wt.% PtRu/C, the precalculated amounts of Pt and Ru salts (atomic ratios of Pt:Ru = 7:3, 5:5, or 3:7) were first dissolved in 50 ml of ethylene glycol. Then, the solution was adjusted to pH 12 by adding NaOH solution; mixture was then aged for 30 min at room temperature. Subsequently, the solution was heated at 160 °C for 3 h with stirring under reflux condition and then cooled to room temperature. The acid pretreated carbon powders were then added to the resulting solution and stirred for 24 h. The final solution was filtered and washed with Dl water and was dried using a vacuum freeze dryer. Finally, the dried PtRu/C catalysts were heat treated under N₂ atmosphere at 100 °C for 2 h.

Materials characterization

The XRD patterns of the as-produced samples were obtained using a Rigaku Rotalflex (RU-200B) X-ray diffractometer equipped with a Cu Ka (λ = 1.5405 Å) source and an Ni filter at 40 mA, 40 kV, and a scan rate of 5° min⁻¹. The TEM analysis was performed with a JEOL JEM-2100EX microscope operating at an accelerating voltage of 200 kV. The XPS (ESCALAB 250, UK) was carried out using a monochromic AI Ka X-ray source (E = 1486.6 eV); the data processing was performed with the XPSPEAK software. The binding energy of the C 1s peak at 284.5 eV was taken as an internal standard and the background was fitted by the Shirley method. The XAS measurement was conducted on the 7D beamline of the Pohang Accelerator Laboratory (PLS-II, 3.0 GeV, Korea) using a Si (111) double crystal monochromator. The spectra were taken at room temperature in transmission mode for the L3-edge of Pt (11,564 eV) under ambient conditions; energy calibration was performed using standard metal foil. The X-ray absorption near edge structure (XANES) spectra were processed and analyzed with the ATHENA program.^[43]

Electrocatalytic activity and stability tests

The catalytic activity toward glycerol electrooxidation was investigated from cyclic voltammetry (CV) results using a half-cell system made up of well-polished glassy carbon (0.196 cm²) as a working electrode (WE), a platinum wire as a counter electrode (CE), and an Ag/AgCl (in sat. KCl) as a reference electrode (RE); all were connected to a Solartron Analytical instrument (AMETEK model 1470E). To prepare the WE, each catalyst was homogeneously suspended in a mixture of DI water and 5 wt.% Nafion® ionomer solution and ultra-sonicated to obtain homogeneous inks. Then, the catalyst ink (2.5 µl contains 6.42 µg of metal) was loaded onto the WE and was dried in an oven at 70 °C for 30 min to prepare a thin film of the catalyst electrode. The CV was carried out in the potential range of

0.2 to 1.0 V (vs. Ag/AgCl) at room temperature with a scan rate of 50 mV s^{-1} in N₂ saturated 2 M glycerol in a 0.5 M H₂SO₄ electrolyte solution. All potentials were referenced to the standard hydrogen electrode (SHE).

Electrocatalytic batch reaction and product analysis

Carbon paper was used as the working electrode for the electrocatalytic glycerol batch reaction. A Pt wire and Ag/AgCl (in sat. KCl) were used as the counter electrode and the reference electrode, respectively. For the catalyst coated carbon paper, the prepared Pt/C and PtRu/C catalysts were suspended in isopropyl alcohol, which contained a 5 wt.% Nafion® ionomer solution; mixture was then sonicated for 3 h. Next, catalyst ink was deposited on the surface of the carbon paper electrodes (with a 2 cm² geometric area and 1 mg cm-2 metal loading) using a spray method; this was followed by drying in an oven at 70 °C for 1 h. Using the chronoamperometry technique, oxidation of glycerol was carried out in a 7 ml mixture consisting of 0.1 M glycerol in a 0.5 M H₂SO₄ solution. The reaction temperature of 60 °C was controlled by directly heating the electrochemical reactor using a temperature regulator. Prior to any electrochemical measurements, the mixture was completely purged with pure N₂ to eliminate the dissolved dioxygen gas. The pH values of the mixture were nearly the same during the reaction and were invariant under all conditions of pH variation of 0.4 - 0.6.

The reaction products formed during glycerol electrooxidation were collected and examined by analyzing each phase of the reaction mixture using high-performance liquid chromatography (HPLC, Waters 2535) with an RI detector and a UV–Vis detector (220 nm). A Biorad Aminex HPX-87H sugar column was used with 0.005 M H₂SO₄ (at a flow rate of 0.3 ml min⁻¹) as the eluent at 60 °C. 1 μ l liquid samples were injected after filtration through a 0.2 μ m filter. The amount of consumed glycerol and the reaction product yields were quantified with an external calibration method.

Computational details

All density functional theory (DFT) computations were carried out with the Vienna ab initio simulation package (VASP).[44,45] We employed the optB86b-vdW density functional^[46,47] because noncovalent interactions between glycerol molecules and the metal surface were reasonably explained with this functional.[48] A Pt (111) surface with four layers was generated from the bulk platinum. To avoid non-physical interactions among atoms in different periodic cells, the surfaces were prepared with a size of 16.3 x 14.1 x 25.9 Å³. Other surfaces were prepared by randomly substituting Pt atoms with Ru atoms on the Pt (111) surface. For all metal surfaces, both the cell parameter and the ionic positions were properly relaxed without any constraints. We also optimized the glycerol molecule to its most probable conformation and then placed the molecule on the metal surfaces in such a way that two oxygen atoms pointed towards the surfaces. We relaxed all atoms of the two top layers: we also relaxed the glycerol molecule while fixing two bottom layers of the surface. The kinetic energy cutoff was set at 400 eV for all DFT calculations. The Brillouin zone was sampled with 3 x 3 x 1 Monkhorst-pack k-point grids. All reported structures were optimized until all forces were smaller than 0.05 eV Å-1. Atomic partial charges were computed based on Bader analysis.^[49,50]

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Entry for the Table of Contents

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The promotional effects of Ru addition to Pt/C catalysts for glycerol electrooxidation in acid media were investigated by reaction product analysis and DFT calculations. The glycerol molecules on the structurally and electronically modified PtRu surfaces can be efficiently oxidized by controlling glycerol binding energy and by breaking more C-C, C-H, and O-H bonds.



Youngmin Kim, Hyun Woo Kim, Seonhwa Lee, Jisu Han, Daewon Lee, Jeong-Rang Kim, Tae-Wan Kim, Chul-Ung Kim, Soon-Yong Jeong, Ho-Jeong Chae, Beom-Sik Kim, Hyunju Chang, Won Bae Kim, Sung Mook Choi, * and Hyung Ju Kim*

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Role of Ru on Carbon-supported PtRu Catalysts for Electro-catalytic Glycerol Oxidation in Acidic Condition