A PtAu Nanoparticle Electrocatalyst for Methanol Electro-oxidation in Direct Methanol Fuel Cells

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PtAu alloy nanoparticle catalysts for use in direct methanol fuel cells were synthesized by reduction with $NaBH_4$ and freeze-drying and their electrocatalytic activities were examined for reactions of methanol, formaldehyde, and formic acid. The extent of alloy formation and average particle size were characterized by X-ray diffraction and transmission electron microscopy. X-ray photo-electron spectra confirmed that the surface state of Au in the PtAu alloy was exclusively metallic, while the Ru in the alloy has not only metallic characteristics but is also present in oxidized form. Based on electrochemical measurements, the PtAu catalyst showed a more enhanced activity than pure Pt for the oxidation of methanol, having a lower onset potential and a larger current density. The electrocatalytic activity of the PtAu catalyst was also enhanced in the oxidation of formic acid but not formaldehyde. This provides evidence for differences in the catalytic activity of PtAu in the oxidation of low molecular weight organic compounds. The origin of the enhanced catalytic activity of the PtAu catalysts is discussed from the standpoint of a modified methanol oxidation pathway in which formaldehyde, formic acid, and CO are produced as putative intermediates.
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Direct methanol fuel cells (DMFCs) have attracted considerable interest for use as a power source in portable electronic devices because they have a variety of merits, including low operating temperatures, ease of handling liquid fuel, and the high-energy density of methanol.[1-5] The excellent catalytic activity of Pt for methanol oxidation, especially at low temperatures, makes this metal electrocatalyst attractive for use as an anode in DMFCs. However, pure Pt is readily poisoned by carbon monoxide (CO), an intermediate that is produced during the electro-oxidation of methanol at low temperatures. Based on the bifunctional mechanism, the CO-poisoned Pt can be regenerated via the reaction of surface CO with oxygen species associated with an element such as Ru to yield CO_2. In addition to the applicability range of this mechanism, electronic effects (ligand effects) might also be involved in the enhancement by Ru.[6-16] Other species such as Bi, Os, Rh, W, Sn, Ni, and Mo have been reported to have a positive effect on catalytic activity with respect to methanol oxidation.[17-27] Although Ru and other elements are added to Pt to enhance the oxidation of CO, the rates of methanol oxidation are still too low to guarantee the commercialization of a DMFC. In order to design a new anode catalyst with an acceptable activity, it is essential to clarify the mechanism involved in the oxidation of methanol. Although the formation of various adsorbates, such as $(CH_xOH)_{ad}$, $-(COH)_{ad}$, $(-HCO)_{ad}$, $(-COOH)_{ad}$, linear bonded CO, and bridged CO, have been proposed as reactive intermediates in methanol oxidation from in situ infrared spectroscopy data, it is well known that formic acid (HCOOH) and formaldehyde (HCHO) are formed as intermediates and are dissolved in the solution.[28-33]

The goal of this study was to design Pt-based alloy catalysts containing Au for use in methanol electro-oxidation. Au has long been known as being catalytically less active than other noble metals. Since the discovery of the high catalytic activity of nanosized Au depending on cluster size and types of supports used, many recent studies have focused on the development of Au-based catalysts for use in low-temperature catalytic combustion, the partial oxidation of hydrocarbons, the hydrogenation of unsaturated hydrocarbons, and the reduction of nitrogen oxides.[34-38] It also has been reported that Au-based catalysts are potentially capable of being

effectively employed in fuel cells, such as hydrogen purification and electrochemical oxidation reactions of organic species.[39-42] However, the science of Au catalysis is still quite new and is currently undeveloped.

In this article, PtAu alloy nanoparticle catalysts for enhancing the electro-oxidation of methanol were synthesized by a borohydride reduction method combined with freeze-drying. The structural properties of the alloy catalysts were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and X-ray photoelectron spectroscopy (XPS), and the electrochemical characteristics of the catalysts with respect to methanol oxidation were evaluated. In order to identify the origin of the catalytic activity enhancement by PtAu nanoparticle catalysts in the electro-oxidation of methanol, their catalytic activities were also investigated assuming formaldehyde and formic acid are produced as reaction intermediates.

Experimental

Unsupported Pt-based alloy nanoparticles were synthesized by a conventional borohydride reduction method using $NaBH_4$ (Aldrich Chemical Co.) combined with freeze-drying. $H_2PtCl_6·xH_2O$, $RuCl_3·xH_2O$, and $HAuCl_4·3H_2O$ (all from Aldrich Chemical Co.) in the desired stoichiometry were completely dissolved in Millipore water (18 MΩ cm). After several hours, the solutions were reduced by the addition of 0.2 M $NaBH_4$. A threefold excess of reducing agent over the valences of the metal salts was used, which was sufficient for the complete reduction of the salts to the elemental state. After precipitation, the resulting materials were washed with Millipore water several times and dried by freeze-drying using liquid N_2 without the use of any heat-treatment.

Structural analyses of pure metal and Pt-based alloy catalysts were carried out using a Rigaku X-ray diffractometer equipped with a Cu Kα source. To estimate the extent of alloy formation of the Pt-based alloy catalysts, the (111) peak was fitted using the Lorentzian/Gaussian function. The composition of the alloy catalysts was determined by Vegard's law.[24] The size of the alloy catalysts was investigated by TEM on a JEOL instrument (JEM-2000FXII) at a 200 kV accelerating potential. A specimen was prepared by ultrasonically suspending the particles in deionised water. A drop of the resulting suspension was deposited on a standard Cu grid covered with a carbon film (200 mesh) and allowed to dry before being inserted into the microscope. In order to analyze and
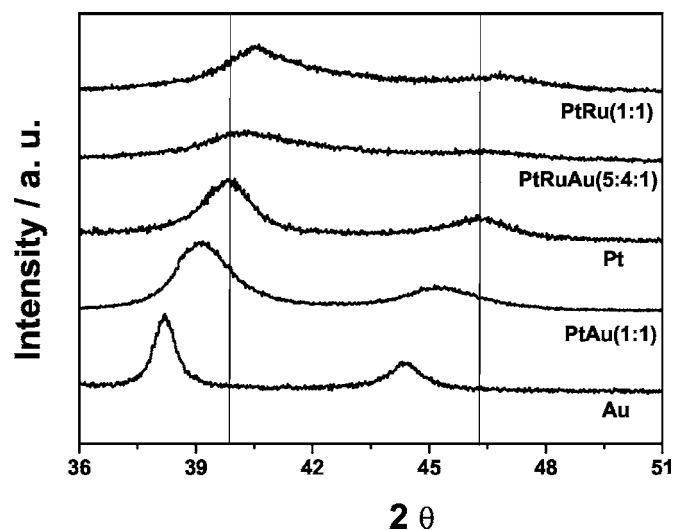
Figure 1. XRD patterns of PtRu (1:1), PtRuAu (5:4:1), pure Pt, PtAu (1:1), and pure Au.

compare the surface chemical states of the samples, XPS was carried out using a VG Scientific (ESCALAB 250) photoelectron spectrometer. The X-ray source was Al Kα with 1486.6 eV operating at 150 kV and 150 W. The base pressure of the system was 2×10^{-9} Torr. The Brunauer, Emmett, and Teller (BET) specific surface areas of the Pt-based alloy catalysts powders were determined using an accelerated surface area and porosimetry system (ASAP) 2010 (Micrometrics Instrument Corporation) at the Korea Basic Science Institute (KBSI), Chonju Branch.

Electrochemical measurements were made using a three-electrode cell. A Pt gauze and Ag/AgCl (in saturated KCl) were used as a counter and a reference electrode, respectively. The electrode potentials in this paper are given with reference to a reversible hydrogen electrode (RHE) in a 0.5 M H_2SO_4 solution. The glassy carbon electrode, working electrode, was polished with 1, 0.3, and 0.05 μm Al_2O_3 paste and then washed in deionized water. The catalyst ink was prepared by ultrasonically dispersing catalyst powders in an appropriate amount of Millipore water, 2-propanol, and 5% Nafion solution (1100 equivalent weight). A 10 μL portion of the catalyst ink was pipetted onto a glassy carbon working electrode. After drying in a vacuum oven, the total catalyst loadings were consistently 3 mg cm^{-2} in which the geometric area of the working electrode was used for the calculation. The solution of 0.5 M H_2SO_4 and 2 M CH_3OH + 0.5 M H_2SO_4 was continuously stirred and purged with nitrogen. In addition, 0.05 M HCHO and 0.05 and 0.5 M HCOOH in 0.5 M H_2SO_4 solutions were also prepared in a manner similar to the intermediates of methanol electro-oxidation. All chemicals used were of analytical grade. Electrochemical experiments were performed using an Eco Chemie AUTOLAB instrument. In order to identify the properties of Pt-based alloy catalysts in sulfuric acid and to measure the catalytic activities for methanol and its reaction intermediates, cyclic voltammetry (CV) was performed in the potential between −0.05 and 1.45 V and chrono-amperometry (CA) measurements were made at 30 min intervals, while a potential of 0.55 V was maintained. For electrochemical CO stripping voltammetry,[43] methanol was chemisorbed in 2 M CH_3OH + 0.5 M H_2SO_4 as the surface CO on alloy catalysts at 0.2 V for 30 min. After rinsing with 0.5 M H_2SO_4, the adsorbed CO was monitored by CV at a scan rate of 20 mV s^{-1}.

Results and Discussion

Structural analysis.— XRD patterns clearly demonstrate all of the Pt-based alloy catalysts have a face-centered cubic (fcc) structure as shown in Fig. 1. The (111) peaks for Pt and Au nanoparticles
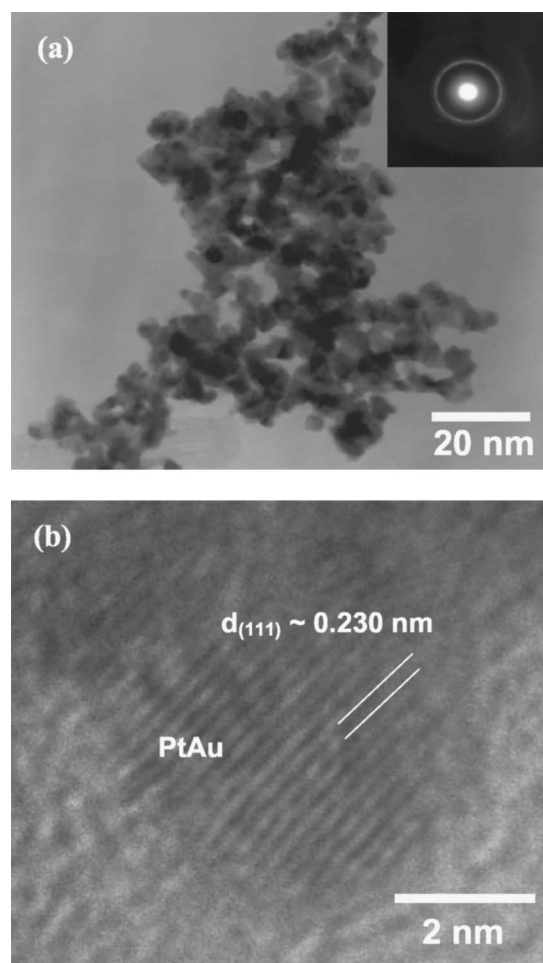

Figure 2. (a) TEM (inset: TED pattern) and (b) high resolution TEM image images of PtAu (1:1).

synthesized by the borohydride reduction method were located at 39.79 and 38.20, respectively, having the original peak positions corresponded to their fcc metallic states. The 2θ of the (111) for PtAu (1:1) and PtRu (1:1) are 39.10 and 40.48, respectively. The (111) peak of PtAu (1:1) was shifted to lower angles while that of PtRu (1:1) was shifted to higher angles compared to the original peak for pure Pt. Assuming alloy formation among Pt, Au, and Ru based on a substitutional solid solution, such a shift can be attributed to the difference in atomic size. For example, a Pt atom is larger than a Ru atom but smaller than a Au atom. Such types of peak shifts indicate good alloy formation between Pt and Au and Ru. PtRu (1:1) is known to alloy well.[44] The (111) peak for PtRuAu (5:4:1) follows this trend depending on the amounts of the second and third metal involved and is located between that of pure Pt and PtRu (1:1). By fitting the (111) peaks, it is clear that the *d* spacings of (111) in the PtRu (1:1), PtRuAu (5:4:1), and PtAu (1:1) alloy catalysts are 0.223, 0.224, and 0.230 nm, whereas those of pure Pt and Au are 0.226 and 0.235 nm. In addition, the intended atomic percent of binary alloy catalysts can also be identified on the basis of Vegard's law.

Figure 2 shows a TEM image of the PtAu (1:1) catalyst, which confirms the presence of a nanosize alloy as evidenced by the ring pattern of transmission electron diffraction (TED) in the insert of Fig. 2a. No major agglomeration was observed in the absence of a carbon support. The particle size of the PtAu (1:1) alloy catalyst is approximately 4–5 nm, in good agreement with XRD data calculated using the Debye–Scherrer equation, and the particles are largely spherical in shape. This size of PtAu (1:1) is slightly larger
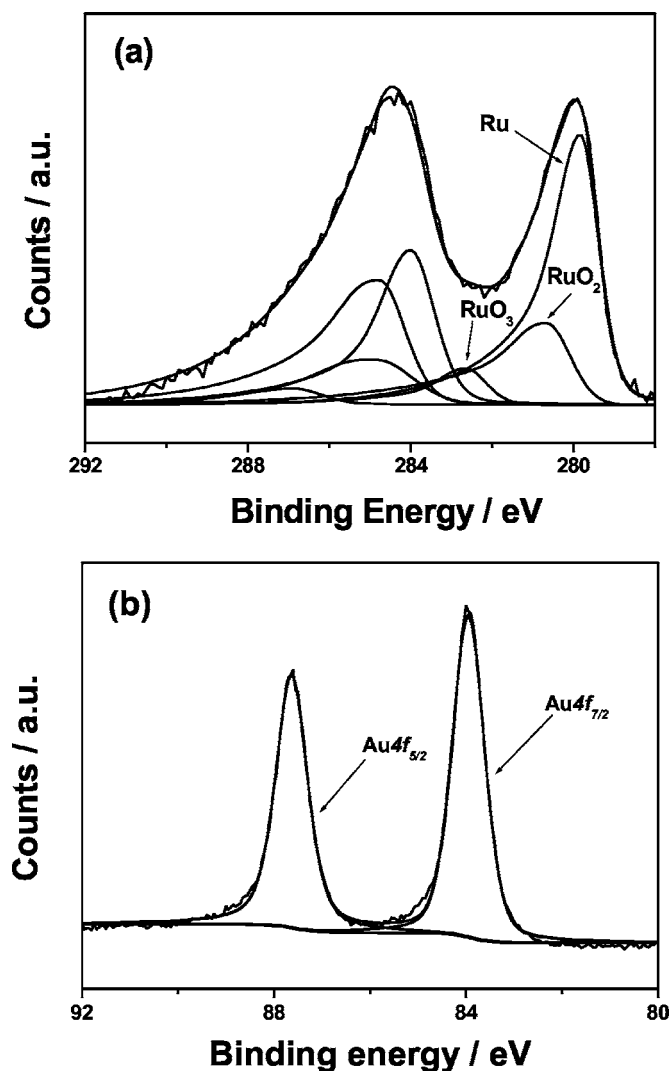
Figure 3. (a) Ru 3d for PtRu (1:1) and (b) Au 4f for PtAu (1:1) X-ray photoelectron spectra.

Figure 4. (a) Potential-current plot for PtAu (1:1) in 0.5 M H_2SO_4, and PtAu (1:1) and pure Pt with respect to methanol oxidation in 2.0 M CH_3OH + 0.5 M H_2SO_4, and (b) time-current plot for PtAu (1:1) and pure Pt in 2.0 M CH_3OH + 0.5 M H_2SO_4 under constant applied potential of 0.55 V (vs RHE).

than that of PtRu (1:1), and this result can also be attributed to the difference in atomic size between them. In the same manner, the BET surface area of the PtAu catalyst was 15–25 m^2/g, while that of PtRu was 65–75 m^2/g. Figure 2b shows a high-resolution TEM lattice image of PtAu (1:1). The interplanar lattice parameter of (111) plane was observed to be 0.230 nm, in good agreement with the results obtained from a *d* spacing calculation using the XRD data. The fact that the interplanar distance of PtAu (1:1) increased compared to that of pure Pt also proves that Au is well alloyed with Pt by interposition. Although the atomic ratios of Pt and Au in the alloy catalysts were found to be varied, ranging from 8:1 to 1:1, alloy formation was good, as evidenced by XRD and TEM data. This indicates that Pt-based binary and ternary alloy catalysts containing Au can be prepared using the borohydride reduction method.

Figure 3 shows Ru 3d in PtRu (1:1) and Au 4f in PtAu (1:1) X-ray photoelectron spectra. Metallic ruthenium appears as a spin-orbit at 279.8 (Ru $3d_{5/2}$) and 284.0 eV (Ru $3d_{3/2}$) with an area ratio of 1.5 and the additional Ru peaks indicate the formation of surface oxides, such as RuO_2 (280.9 and 285.1 eV) and RuO_3 (282.7 and 286.9 eV). According to the bifunctional mechanism, oxophilic Ru sites covered by various ruthenium oxides constitute the source of oxygen required for the removal of surface CO, and as a result, PtRu has excellent catalytic activity compared to Pt. In contrast, Au $4f_{7/2}$ and Au $4f_{5/2}$ lines appear at 84.0 and 87.7 eV, respectively, with a
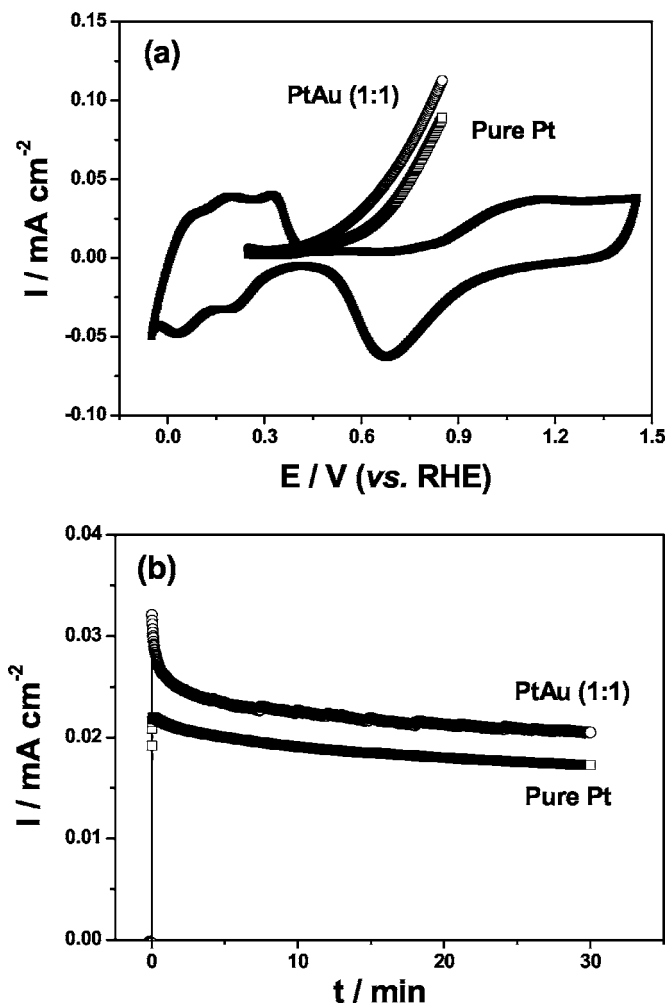
theoretical ratio of 4 to 3, indicating that Au is present only in the metallic state in the alloy without any surface oxide being evident. This property of PtAu catalysts is associated with the catalytic activity for methanol oxidation.

Electro-oxidation of methanol.— The Pt and PtAu (1:1) catalyst were evaluated in 0.5 M H_2SO_4 with and without a 2 M CH_3OH solution using voltammetry and chronoamperometry. All current densities in the voltammograms were normalized to the electrochemically active surface area. This electrochemically active surface area for a pure Pt catalyst could be calculated by utilizing the hydrogen desorption integral on the catalysts in the positive scan because platinum has well separated H desorption and metal oxidation regions and it is well known that the stoichiometry of H to Pt is 1:1.[45-47] The active surface area of PtAu catalyst can be also obtained using the same procedure, assuming that only Pt is active for hydrogen desorption. Assuming that the surface composition of a PtAu alloy is identical in composition to that of the bulk, the Pt density at the surface of the alloy should be only half that for Pt at the surface of pure Pt. Therefore, the electrochemically active surface area calculated from the experimentally measured current for hydrogen desorption on PtAu was multiplied by 2 and used for the normalization of current density to have the same number of Pt active sites for two catalysts. The CV for PtAu (1:1) in 0.5 M
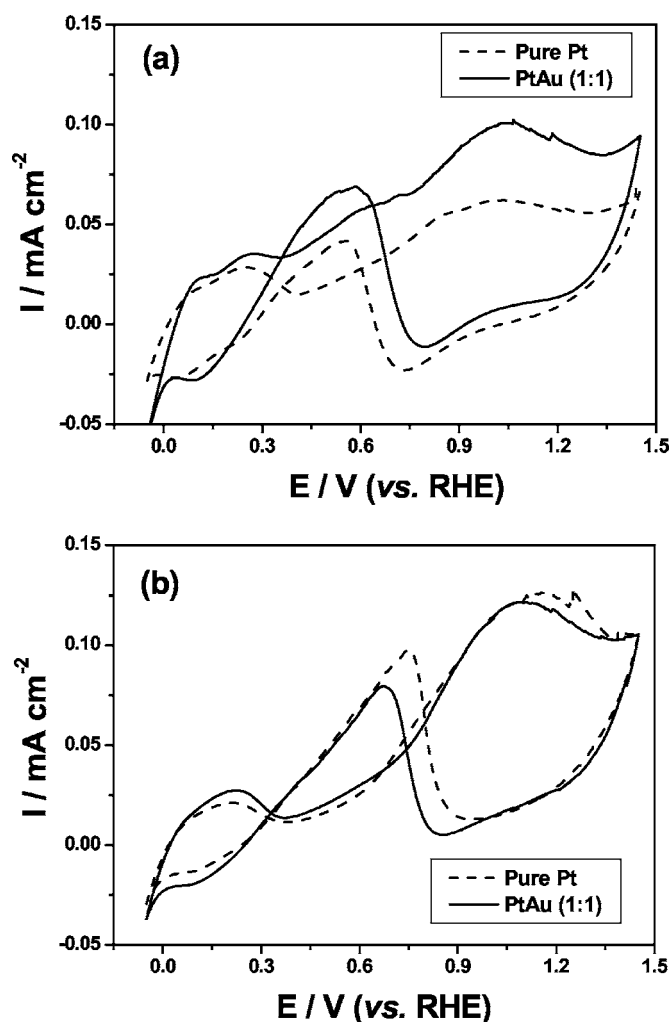
Figure 5. Potential-current plot for PtAu (1:1) and pure Pt (a) in 0.05 M HCOOH + 0.5 M H_2SO_4 and (b) in 0.05 M HCHO + 0.05 M H_2SO_4.

Figure 6. Potential-current plot for PtAu (1:1) and pure Pt in 0.5 M HCOOH + 0.5 M H_2SO_4.

has been reported that Ru is the most promising component in Pt-based binary catalysts for methanol oxidation, by virtue of either a bifunctional mechanism or an electronic effect (ligand effect). In contrast, it is generally understood that the enhanced catalytic activity of PtAu does not follow a bifunctional mechanism because Au does not exist in an oxide form and cannot easily adsorb OH to provide an oxygen source for the removal of adsorbed CO. In order to decipher the origin of the enhanced methanol oxidation, the electro-oxidation of formic acid and formaldehyde, putative reaction intermediates in methanol oxidation, was investigated using the PtAu catalyst.

Electro-oxidation of formic acid and formaldehyde.— In order to investigate the catalytic activity with respect to the above reaction intermediates, 0.05 M HCOOH and 0.05 M HCHO in 0.05 M H_2SO_4 were substituted for methanol. The reason for using such low concentrations, compared to a 2 M CH_3OH solution, is that the reaction kinetics for HCOOH and HCHO are much faster than that of methanol. Figure 5a shows voltammograms of PtAu (1:1) and pure Pt in 0.05 M HCOOH + 0.5 M H_2SO_4 solutions. The findings show that PtAu (1:1) is a superior catalyst for HCOOH oxidation than pure Pt, showing lower onset potentials and larger current densities. The onset potential and current density at 0.45 V for the PtAu (1:1) catalyst are 0.35 V and 41 μA cm⁻², respectively, while those of pure Pt are 0.41 V and 17 μA cm⁻². Unlike HCOOH, there is no distinct difference in the activity for HCHO, as shown in Fig. 5b. This supports the view that both catalysts have similar onset potentials and current densities for HCHO oxidation. In spite of the similar reaction intermediates, PtAu (1:1) shows a difference in catalytic activity for HCOOH and HCHO. In other words, PtAu (1:1) oxidizes HCOOH more readily than HCHO. When the molar concentration of HCOOH was increased, clear differences between the two catalysts were evident. Figure 6 shows voltammograms of PtAu (1:1) and pure Pt in 0.5 M HCOOH + 0.5 M H_2SO_4. Compared to Fig. 5a, the current density values in 0.5 M HCOOH were more than double for both catalysts and the difference in current density was also increased. For example, the current densities of PtAu (1:1) and pure Pt at 0.45 V in 0.5 M HCOOH are 94 and 27 μA cm⁻², respectively, while those in 0.05 M HCOOH are 41 and 17 μA cm⁻². Summarizing the above results, PtAu (1:1) is superior to pure Pt for the electro-oxidation of HCOOH but not HCHO. The reason for this is that electro-oxidation of HCOOH produces CO_2, a final product, and is not required to adsorb oxygen species such as OH compared to HCHO oxidation.[30,49-53] It was also proved that Au adsorbs OH groups in water with great difficulty, based on a voltammogram

H_2SO_4 is represented in Fig. 4a as a thick, solid line. Peaks corresponding to hydrogen adsorption and desorption and a preoxidation peak on the catalyst surface can clearly be seen in Fig. 4a, indicating the characteristics of Pt in nanoparticles, and are consistent with literature involved.[24,48] An alloying effect by Au in the presence of methanol shows a lower onset potential and a larger current density compared to pure Pt. For example, the current densities at 0.45 V for PtAu (1:1) and pure Pt are 9.7 and 5.5 μA cm⁻², respectively. The lower onset potential indicates that methanol oxidation starts at a lower potential on PtAu (1:1) than on pure Pt. In addition to the PtAu (1:1) catalyst, we investigated other PtAu alloy catalysts containing different compositions of Pt and Au from 8:1 to 1:1 for methanol oxidation (not shown here). As a result, only one catalyst, PtAu (8:1), showed almost similar catalytic activity with pure Pt and the others were even better than pure Pt. This indicates that alloying with a second metal, such as Au, enhances the electrocatalytic activity for methanol oxidation. Using these catalysts, chronoamperometry data were measured in 2 M CH_3OH + 0.5 M H_2SO_4 at 0.55 V for 30 min. Figure 4b shows a plot of the oxidation current density vs time. As expected from the voltammetry results, the current density of PtAu (1:1) for the oxidation of methanol is larger than that of pure Pt over all time intervals measured, indicating that a better activity for methanol oxidation is maintained over time. By combining voltammetry and CA, we conclude that the activity of PtAu (1:1) for methanol oxidation is superior to that of pure Pt. It
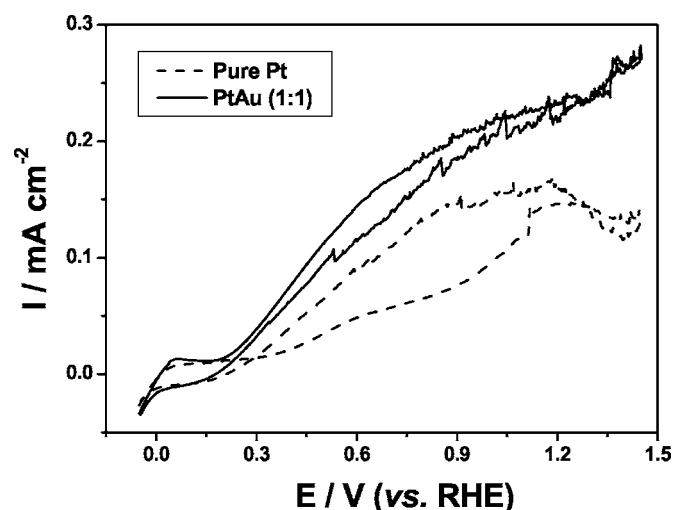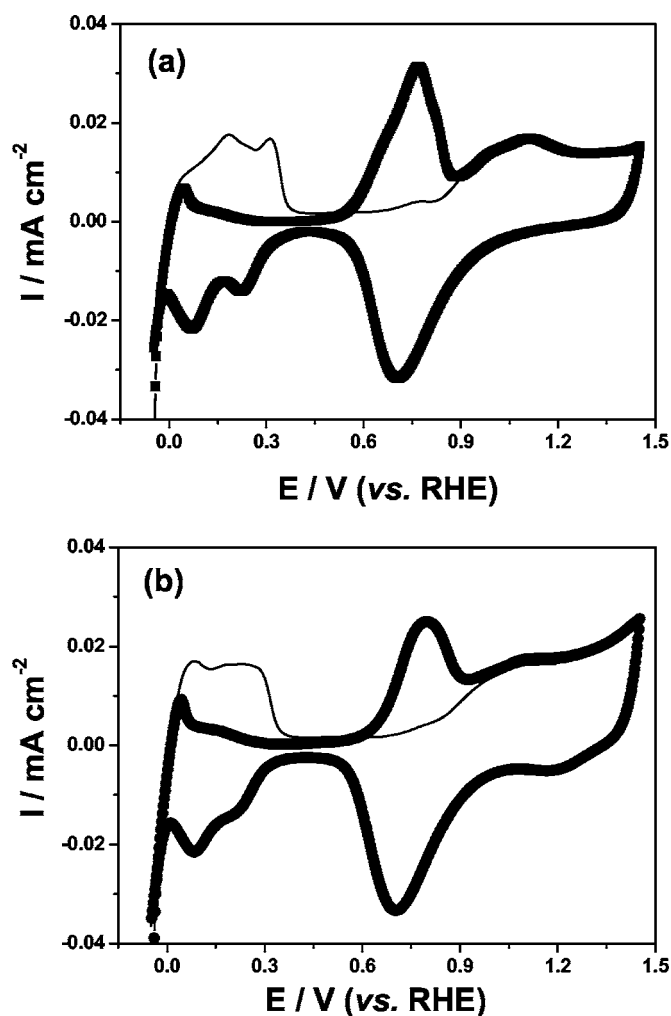
Figure 7. CO stripping voltammetry for (a) pure Pt and (b) PtAu (1:1) in 0.5 M H_2SO_4 at a scan rate of 20 mV s^{-1}. Methanol was adsorbed in 2.0 M CH_3OH + 0.5 M H_2SO_4 at 0.2 V (vs RHE) for a period of 30 min.

Figure 8. Pt 4f X-ray photoelectron spectra for PtRu (1:1) and PtAu (1:1).

obtained in a 0.5 M H_2SO_4 solution. Although Au is known to oxidize HCOOH, but not CH_3OH and HCHO, the main oxidation reaction of HCOOH on a Au electrode could occur, particularly in the potential region of Au oxide formation [>1.2 V vs normal hydrogen electrode (NHE)] and the direct oxidation of HCOOH in the double-layer region was very small compared to pure Pt.[54,55] As a result, it does not appear plausible that the increased activity of the PtAu alloy might simply be due to an increased amount of Au in the catalyst. Combining the results for the electro-oxidation of HCOOH and HCHO, we found that one possibility for the enhancement in catalytic activity for methanol electro-oxidation by alloying Pt with Au is the accelerated rate of HCOOH electro-oxidation. This indicates that Au in PtAu alloy aids in increasing the probability of inducing a major reaction pathway for methanol oxidation to avoid the formation of adsorbed CO. This conclusion is supported by the CO stripping voltammetry results shown in Fig. 7. As described, CO was not adsorbed from CO-containing gas but was produced by being adsorbed from CH_3OH. The most obvious feature in Fig. 7 is the slight positive shift in the stripping peak potential for PtAu at ~0.80 V compared to pure Pt at ~0.76 V. This indicates that the reason for the enhanced methanol oxidation by PtAu is not due to the effective removal of adsorbed CO, unlike PtRu. In addition, the CO coverage of the PtAu catalyst, calculated from the difference in hydrogen desorption integral between the first and second scan,[10] was decreased by as much as 10%, from 0.87 to 0.78, compared to
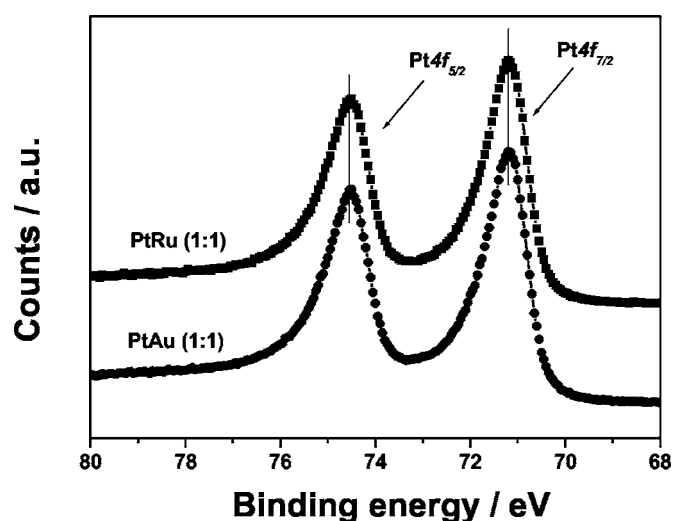
pure Pt. This indicates that less CO is adsorbed to PtAu catalyst surfaces after oxidizing more methanol than for pure Pt. These phenomena were definitely different from those by PtRu catalysts. In order to examine the possibility of an electronic effect by Au, the Pt 4f spectra for PtAu and PtRu are shown in Fig. 8. No shift in the binding energy of Pt 4f in the PtAu (1:1) alloy nanoparticles is evident in spite of the suggestion by Shubina et al. and Hammer et al. that, indeed, an electronic interaction occurs between Pt and Au.[56,57] This indicates that the enhanced activity of PtAu for methanol oxidation is not related to either the modification of the electronic structure or to a bifunctional mechanism.

In summary, we propose that there is another effect for catalytic enhancement by a second element, such as Au, for methanol oxidation. A PtAu catalyst is able to oxidize more methanol than pure Pt and, at the same time, less CO accumulates on the PtAu catalyst surfaces compared to pure Pt. In addition, the findings indicate that the PtAu catalyst was preferable for formic acid oxidation but not for formaldehyde oxidation. Therefore, the overall reaction might be explained by the alteration of the major methanol oxidation pathway by alloying Au with Pt. Thus, PtAu could open an alternative route for methanol oxidation and solve the CO poisoning problem by suppressing the formation of CO, which is distinctly different from the PtRu catalyst. More fundamental studies will be required to verify this hypothesis by analyzing reaction products using in situ infrared spectroscopy and chromatography techniques.

Conclusions

The catalytic activities with respect to methanol oxidation for unsupported Pt alloy nanoparticle catalysts containing Au, synthesized by reduction of the metal salts with $NaBH_4$ and freeze-drying, were investigated using 0.5 M H_2SO_4 + 2 M CH_3OH solutions. The catalytic activity of PtAu (1:1) was found to be superior to that of pure Pt, showing a lower onset potential and large current density. The enhanced activity of the PtAu catalyst for methanol oxidation was investigated using formaldehyde and formic acid, known intermediates in the methanol oxidation pathway. PtAu (1:1) shows a better catalytic activity for the oxidation of formic acid, but not formaldehyde, compared to pure Pt. In addition, it was found that Au, when added to Pt, formed a metallic phase that was similar to Pt based on XPS data and the CO coverage on the PtAu surface after methanol oxidation was decreased compared to that for pure Pt. Given the present results, we propose that the alteration in the major reaction pathway by Au may contribute to the enhanced methanol oxidation, that is, the methanol oxidation pathway is modified when Au is present and the major route is the formation of formic acid and

the production of CO_2 and not CO. Although it was not possible to provide more sufficient supporting evidence for this effect, we believe that the findings herein will be helpful in attempts to understand methanol oxidation mechanism. Furthermore, we also confirm the possibility that formic acid could be used as a fuel in conjunction with PtAu catalysts, which is a topic for a future study.

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