

Effect of Particle Size and Composition on CO-Tolerance at Pt–Ru/C Catalysts Analyzed by In Situ Attenuated Total Reflection FTIR Spectroscopy

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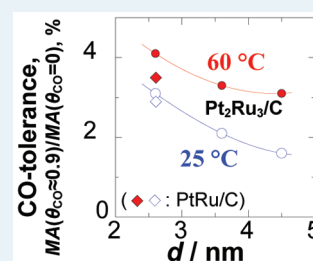
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Supporting Information

ABSTRACT: The particle size dependence of activities for the hydrogen oxidation reaction (HOR) on monodisperse Pt₂Ru₃ ($d = 2.6, 3.6,$ and 4.5 nm) supported on carbon black prepared by the nanocapsule method (Pt₂Ru₃/C) was investigated by in situ attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy in 1% CO (H₂-balance)-saturated 0.1 M HClO₄. The highest CO-tolerant HOR activity at both 25 and 60 °C was observed for the smallest Pt₂Ru₃ particle ($d = 2.6$ nm), with a Pt-rich top surface and an Ru-rich core. At 25 °C, the suppression of the adsorption of CO on Ru sites was a dominant factor to maintain the electronic modification effect that weakens the bond strength of CO_{ad}. The adsorption of CO on Ru at all catalysts was found to decrease markedly by increasing the temperature to 60 °C, probably because of a decrease in the bond strength of CO_{ad} on Ru sites.

At 60 °C, the coverage of bridged CO, $\theta[\text{CO}_B]$, on Pt sites was found to be lowest on the smallest Pt₂Ru₃ particle. Because CO_B blocks two active sites for the HOR, the largest number of HOR active sites can be available at the smallest particle. The effect of chemical composition on the CO-tolerance was also analyzed on Pt₂Ru₃/C and PtRu/C with the identical particle size $d = 2.6$ nm. While both catalysts exhibited nearly comparable CO-tolerance at 25 °C, Pt₂Ru₃/C showed higher CO-tolerance at 60 °C, which is ascribed to the lower $\theta[\text{CO}_B]$, probably because of an electronic effect of the Ru-rich core.

KEYWORDS: Pt–Ru, anode catalyst, CO-tolerance, CO adsorption, fuel cell, FTIR



1. INTRODUCTION

Polymer electrolyte fuel cells (PEFCs) have been developed intensively for applications in residential cogeneration systems and electric vehicles. The commercialization of a 1 kW-class residential PEFC (ENE-FARM) system started in 2009 in Japan. With a subsidy from the government, the number of systems installed or going to be installed was 5,030 in FY 2009, 4,985 in FY 2010, and 8,000 until July in FY2011. Hydrogen-rich gas (reformate) is produced in a fuel processing system (FPS) by the steam-reforming of raw fuels (CH₄, C₃H₈, or kerosene), followed by the water gas shift reaction. To maintain a practical rate for the hydrogen oxidation reaction (HOR) at a commercially available Pt–Ru alloy anode catalyst (Pt₂Ru₃ nanoparticles supported on high-surface area carbon black, c-Pt₂Ru₃/C), the reformate is purified further by a preferential oxidation (PROX) of CO, which reduces the CO concentration to ≤ 10 ppm. This is because the CO-tolerance of the state-of-the-art c-Pt₂Ru₃/C is not sufficient; CO molecules strongly adsorb on the active sites, blocking the HOR.^{1–3} For the further cost reduction of the system, toward larger scale commercialization, it is effective to exclude PROX with noble metal catalysts (Ru or Pt) from the FPS. In such a case, the CO concentration is estimated to be 500 ppm. Hence, it is very important to develop anode catalysts with higher CO-tolerance.

To design highly CO-tolerant catalysts, however, we encounter several questions. What kinds of alloys, and what composition should we choose? What size of such catalyst particles should we prepare to obtain the best performance? Unfortunately, there have been large discrepancies among such issues. One of the possible reasons could be nonuniform chemical composition within given batches of alloy nanoparticles, as well as nonuniform sizes. For example, so far, the particle size was controlled by changing the heat treatment temperature (or time) and/or the metal loading levels on the support. However, this conventional technique has resulted in large standard deviations for both particle sizes and compositions. Recently, we have succeeded in preparing monodisperse Pt and Pt–M (M = Ru, Co) alloy nanoparticles supported on carbon black (Pt/C, Pt₂Ru₃/C, Pt₃Co/C) by the nanocapsule method,⁴ and to control the particle size simply by changing the molar ratio of metal precursor(s) to surfactant (M/S) in the preparation, with the other conditions being identical.⁵ To establish a clear strategy for CO-tolerant catalysts, we have examined the adsorption/oxidation of CO and the HOR in the presence of adsorbed CO (CO_{ad}) on Pt

Received: October 31, 2011

Revised: January 17, 2012

Published: February 22, 2012

and Pt-based alloy catalysts (both bulk and nanoparticle forms) systematically by using various techniques, whose results can complement each other.^{6–22}

In our previous research,²⁰ we investigated the CO-tolerance mechanism on monodisperse Pt₂Ru₃ ($d = 3.6$ nm) nanoparticles supported on high surface area carbon black, which were prepared by the nanocapsule method,⁵ by use of in situ attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy in 1% CO (H₂ balance)-saturated 0.1 M HClO₄ at 25 and 60 °C. It was found that the CO-tolerance on the Pt₂Ru₃/C was greatly improved by a heat treatment in 5% H₂ at 200 °C and was superior to a commercial Pt₂Ru₃/C catalyst at an apparent coverage of CO (θ_{CO} , calculated based on the decrease in the hydrogen desorption charge) of 0.95.

In the present research, we first focus on the particle size dependence of HOR activities in the presence of CO on Pt₂Ru₃/C ($d = 2.6, 3.6,$ and 4.5 nm, heat-treated in H₂ at 200 °C). It was found that the CO-tolerance (HOR mass activity at $\theta_{\text{CO}} \approx 0.9$) increased with decreasing particle size. At the identical particle size of 2.6 nm, the CO-tolerance of Pt₂Ru₃/C was found to be higher than that of PtRu/C (1:1 atomic ratio), even though the initial HOR activity at $\theta_{\text{CO}} = 0$ on PtRu/C was higher than that on Pt₂Ru₃/C.

2. EXPERIMENTAL SECTION

The catalysts employed were Pt₂Ru₃/C (atomic ratio of Ru to Pt = 1.5, with three different particle sizes) and PtRu/C (atomic ratio of Ru to Pt = 1) prepared by the nanocapsule method.⁵ These catalysts were treated in 5% H₂ (N₂-balance) at 200 °C for 5 h.²⁰ Pt₂Ru₃/C and PtRu/C catalysts were characterized by use of scanning transmission electron microscopy (STEM, Hitachi HD-2300C) with an energy dispersive X-ray analysis (EDX, EDAX Genesis) system. Figure 1 shows STEM images and particle size distribution histograms of H₂-treated Pt₂Ru₃/C and PtRu/C. The average particle sizes d and chemical compositions, as well as their standard deviations, are summarized in Table 1. The values of d determined among 500 particles in several STEM images were $2.6 \pm 0.3, 3.6 \pm 0.3,$ and 4.5 ± 0.5 nm. The amounts of metal loaded were close to the projected values (50 wt %) and nearly independent of d . The average chemical composition C_{EDX} evaluated by EDX spot analysis was nearly identical to the target value, irrespective of d (very close to Pt₂Ru₃ or PtRu), and the standard deviations for both d and C (σ_d and σ_C) for all Pt₂Ru₃/C and PtRu/C catalysts were very narrow. Thus, we have confirmed that all Pt₂Ru₃ and PtRu alloy nanoparticles were monodisperse with uniform alloy composition.

These catalysts were dispersed uniformly on the Au film deposited on an Si ATR prism at a loading of $17.8 \mu\text{g}_{\text{metal}} \text{cm}^{-2}$ for Pt₂Ru₃/C and $15.2 \mu\text{g}_{\text{metal}} \text{cm}^{-2}$ for PtRu/C in a similar manner to that described in a previous paper.²⁰ The amount of Pt loaded for all samples corresponds to $10 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$. The catalyst layer was dried in air with ethanol vapor at room temperature. Then, an aliquot of Nafion solution was measured out onto the catalyst layer to yield an average film thickness of $0.013 \mu\text{m}$. The Nafion-coated working electrode was dried under ethanol vapor at room temperature. Finally the working electrode was heated at 130 °C for 30 min in air.

A rubber O-ring, Valflon made from perfluoro-elastomers, was used to fit the prism to the spectro-electrochemical cell. The geometrical surface area of the working electrode, defined by the O-ring (inner diameter = 14.8 mm), was 1.72cm^2 . The electrolyte solution of 0.1 M HClO₄ was prepared from

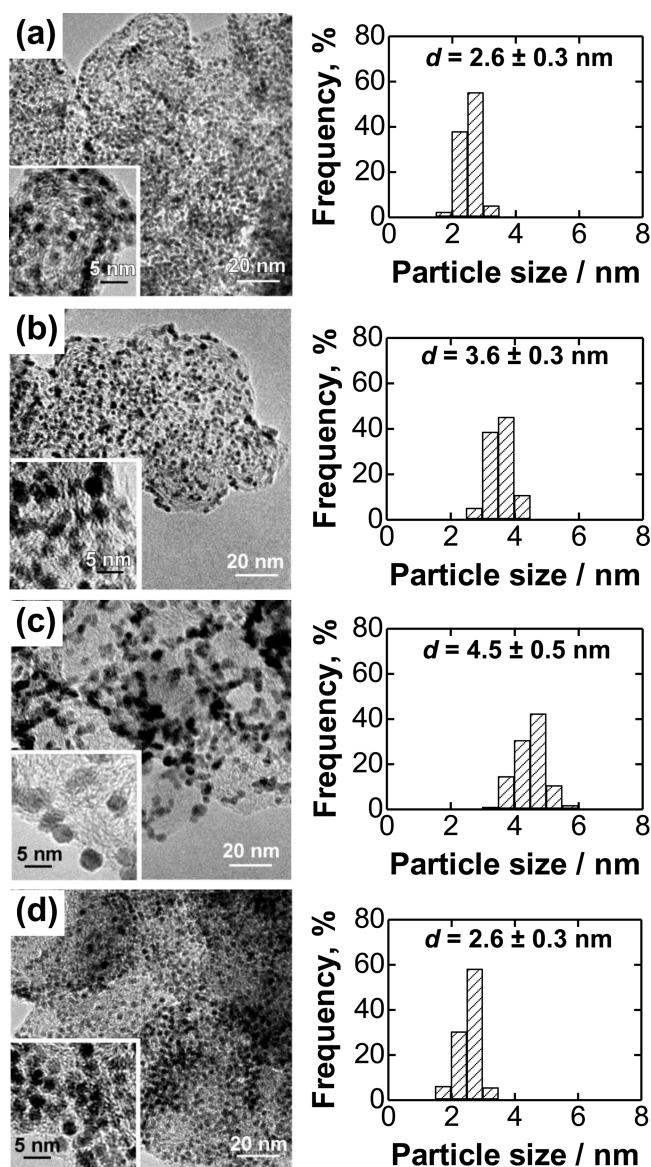


Figure 1. STEM images and particle size distribution histograms of (a, b, c) Pt₂Ru₃/C and (d) PtRu/C prepared by the nanocapsule method after H₂-treatment (5% H₂/N₂-balance at 200 °C for 5 h).

Table 1. Typical Properties of Pt₂Ru₃/C and PtRu/C Catalysts^a

catalyst	d^b /nm	loaded (wt %) ^c	composition ^d	
			Pt (atom %)	Ru (atom %)
Pt ₂ Ru ₃ /C	2.6 ± 0.3	47.4	41.0 ± 2.2	59.0 ± 2.2
	3.6 ± 0.3	46.4	40.3 ± 3.1	59.7 ± 3.1
	4.5 ± 0.5	48.6	40.2 ± 2.2	59.8 ± 2.2
PtRu/C	2.6 ± 0.3	47.1	51.6 ± 2.3	48.4 ± 2.3

^aProjected value of metal-loading level (wt %) of all catalysts was 50 wt %. ^bAverage particle size and standard deviations (σ_d) based on the STEM observation. ^cMetal weight percent in the catalysts analyzed by weight loss using thermogravimetry (TG). ^dAverage composition and standard deviations (σ_C) of the Pt₂Ru₃ particles analyzed by spot-analysis with EDX of 20 randomly selected particles.

suprapur-grade chemicals (Merck) and Milli-Q water (Milli-Pore Japan Co., Ltd.) and purified in advance by conventional pre-electrolysis methods.²³

A platinum mesh covered with platinum black and a reversible hydrogen electrode (RHE) were used as the counter and reference electrodes, respectively. For the stable RHE with a sufficient triple phase zone, about 2/3 portion of Pt mesh covered with Pt black was immersed in the electrolyte solution, exposing the rest of it to pure H₂ gas phase. We checked the zero point of the RHE for every measurement, that is, $E(\text{RHE}) = 0$ at zero current. All of the potentials will be referenced to the RHE in this paper. A potentiostat (ALS 600A, BAS, Inc.) was used for the electrochemical measurements. All measurements were conducted in a class 1000 clean room with a constant temperature of 25 °C and humidity of 40% RH. A silicone-rubber heater, thermocouple, and PID-controller were used to control the cell temperature at 25 and 60 °C.

Prior to the measurements, the working electrode surface was cleaned by repeated potential sweeping between 0.05 and 0.80 V in 0.1 M HClO₄. To determine the electrochemically active area S_H of the working electrode, the cyclic voltammogram was measured in N₂ (UHP-grade, 99.9999%)-purged 0.1 M HClO₄ solution at the sweep rate of 0.05 V s⁻¹. The S_H of the CO-free surface was estimated from the hydrogen desorption charge sQ_H in the positive-going scan, assuming $\Delta Q_H^\circ = 210 \mu\text{C cm}^{-2}$, the value adopted conventionally for smooth polycrystalline Pt.²⁴

The ATR-FTIR measurements were controlled by a spectrometer (FTS7000, Digilab) with an MCT detector using unpolarized infrared radiation. The spectral resolution, the angle of incidence, and interferometer scan were set at 4 cm⁻¹, 70°, and 40 kHz, respectively. First, a reference spectrum was collected at 0.02 V vs RHE in H₂ (UHP grade)-saturated 0.1 M HClO₄ solution by averaging 500 interferograms. All IR spectra in this research will be shown in absorbance units, defined as $-\log(I/I_0)$, where I and I_0 are the spectral intensities of the sample and reference state, respectively. Then, IR spectra were measured every 10 s (one spectrum by averaging for 10 s), while the HOR current was continuously monitored together with the CO adsorption at 0.02 V after changing the bubbling gas from pure H₂ (UHP) to 1% CO (H₂-balance) at a constant flow rate of 10 mL min⁻¹. The mass activity (MA) for the HOR was defined as the current per mass of alloy loaded on the prism surface ($A \text{ g}_{\text{metal}}^{-1}$). To evaluate the CO coverage θ_{CO} after the ATR-FTIR measurement, first, the dissolved CO in the electrolyte solution was removed by N₂ gas bubbling for 1 h. The CO-stripping voltammogram was then measured between 0.05 and 0.80 V at 5 mV s⁻¹ in CO-free 0.1 M HClO₄ solution. We defined θ_{CO} as the site occupation by the following equation, regardless of the type of adsorbed CO (CO_{ad}), e.g., linear (on-top), bridged, or other variants.

$$\theta_{\text{CO}} = 1 - (\text{CO}Q_H/sQ_H) \quad (1)$$

where $\text{CO}Q_H$ and sQ_H are the hydrogen desorption charges with and without CO_{ad}, respectively.

We performed two or three measurements by using, at least, two different batches of each sample catalysts, and confirmed good reproducibility.

3. RESULTS AND DISCUSSION

3.1. Particle Size Dependencies of HOR Activities at High θ_{CO} . Figure 2 shows in situ FTIR spectra of CO adsorbed on Pt₂Ru₃/C with $d = 2.6, 3.6,$ and 4.5 nm at 0.02 V after CO adsorption in 1% CO saturated 0.1 M HClO₄ for 120 min at 25 and 60 °C. The band around 2035–1980 cm⁻¹ was assigned to

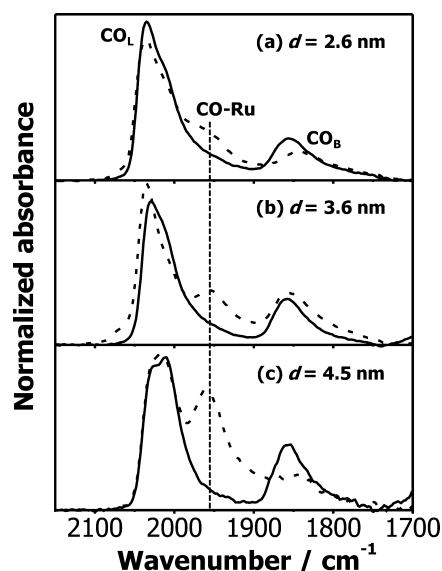


Figure 2. Changes in FTIR spectra of Pt₂Ru₃/C electrodes observed at 0.02 V in 1% CO (H₂ balance)-saturated 0.1 M HClO₄ solution at 25 °C (dashed line) and 60 °C (solid line) after 120 min of CO adsorption. The spectra were normalized with respect to the value of $I[\text{CO}_L]$; (a) $d = 2.6$ nm, (b) 3.6 nm, and (c) 4.5 nm.

linear CO (CO_L, adsorbed atop of Pt atom), while the band at 1850–1800 cm⁻¹ was assigned to bridged CO (CO_B, adsorbed on Pt–Pt pair sites). The broad band around 1950–1900 cm⁻¹ was assigned to bridged CO adsorbed on Ru sites, CO–Ru (CO_B adsorbed on Ru–Ru sites and Ru–Pt sites).^{20,25–32} These spectra were normalized with respect to the integrated band intensity $I[\text{CO}_L]$.³³

The values of CO coverage θ_{CO} became nearly constant (ca. 0.90) for all of the catalysts after bubbling 1% CO for 120 min at 25 and 60 °C. Changes in FTIR spectra during CO adsorption on these catalysts are shown in Supporting Information, Figure S1. For such changes in the spectra during CO adsorption, we have found that each band (CO_L, CO–Ru, and CO_B) consisted of multiple components, suggesting that slightly different adsorption sites can be available,^{17,20} even if the type (or configuration) of CO_{ad} is identical. Then, to determine the integrated intensity of each band, we deconvoluted these bands in each spectrum into several symmetric Gaussian peaks with a linear background by using GRAMS/AI ver. 8.0 software.²⁰ Curve fitting was performed for all spectra with the full width at half-maximum (fwhm) maintained as a constant while allowing the peak wavenumbers and areas to vary. Typical examples with fitting parameters are shown in Supporting Information, Figure S2. Hereafter, the band intensities of $I[\text{CO}_L]$, $I[\text{CO-Ru}]$, and $I[\text{CO}_B]$ will be presented as a sum of each component.

Figure 3 shows changes in $I[\text{CO}_L]$, $I[\text{CO-Ru}]$, and $I[\text{CO}_B]$, together with the mass activity (MA) for the HOR at 0.02 V on each Pt₂Ru₃/C catalyst observed at 25 and 60 °C. Because the kinetically controlled area-specific activities (current density per active area under the infinite supplying rate of dissolved H₂) for the HOR at supported catalysts of $d = 3$ nm (Pt/C, Pt₃Co/C, and PtRu/C) were found to agree well with those of corresponding bulk electrodes in the temperature range from 30 to 90 °C,¹⁹ we could expect that the value of $MA(\theta_{\text{CO}} = 0)$ increases with decreasing d (inversely proportional to d for the spherical particles). However, the values of $MA(\theta_{\text{CO}} = 0)$ at t_{ad}

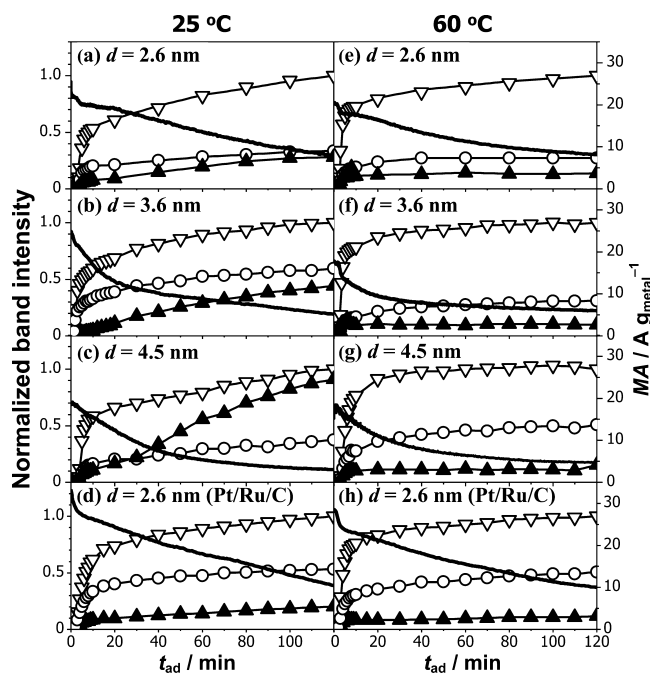


Figure 3. Changes in (∇) $I[CO_L]$, (\circ) $I[CO_B]$, (\blacktriangle) $I[CO-Ru]$, and (solid black lines) HOR mass activity on (a, b, c, e, f, g) Pt_2Ru_3/C and (d, h) $PtRu/C$ at 0.02 V during CO adsorption in 0.1 M $HClO_4$ with bubbling 1% CO at a constant flow rate of 10 mL min^{-1} . Temperatures were (a, b, c, d) 25 °C and (e, f, g, h) 60 °C. The values of $I[CO_L]$, $I[CO_B]$, and $I[CO-Ru]$ were normalized with respect to the value of $I[CO_L]$ at $t_{ad} = 120$ min (see notes in ref 33).

= 0 in Figure 3 and in Supporting Information, Table S1 did not show such clear behavior. This is probably because the current observed in the present experiments was not controlled simply by the kinetic process, but by a mixed process, including both kinetics and H_2 diffusion to the nanocatalyst surface at the relatively high overpotential of 0.02 V in HOR, that is, no forced H_2 supply, which was unavoidable because of a limitation of the present in situ ATR-FTIR cell. We judged, however, that the value of $MA(\theta_{CO} = 0)$ measured under such conditions is still sufficiently valid as a base case to monitor the poisoning process by CO adsorption.

Therefore, we have calculated $MA(\theta_{CO \approx 0.9})/MA(\theta_{CO} = 0)$ to clarify the particle size effect on the CO-tolerance. Because the amount of Pt_2Ru_3 loaded on the electrode was unchanged during CO adsorption, the value of $MA(\theta_{CO \approx 0.9})/MA(\theta_{CO} = 0)$ corresponds to the ratio of the area-specific current densities $j_s(\theta_{CO \approx 0.9})/j_s(\theta_{CO} = 0)$ for each catalyst. It was found in Figure 4 that the values of $MA(\theta_{CO \approx 0.9})/MA(\theta_{CO} = 0)$ increased in the order, 4.5 nm < 3.6 nm < 2.6 nm at both temperatures (25 and 60 °C). As shown in Figures 3 and 4, it is clear during the CO adsorption process, especially at the lower temperature of 25 °C, that the MA decreased steeply with increasing $I[CO-Ru]$ and that $I[CO-Ru]$ increased with increasing d . In our previous work,¹⁴ we found that the bond strength of Pt–CO decreased by alloying Pt with Ru because of the electronic modification effect by Ru. It was also found that the adsorption of CO on Ru sites led to decreased HOR activity, because the CO–Ru interaction caused the electronic modification of Ru to weaken.²⁰ A Pt-rich top-surface with underlying Pt–Ru alloy, which was formed by the heat treatment in H_2 atmosphere, was found to be effective to maintain the electronic modification effect by Ru. Then, the

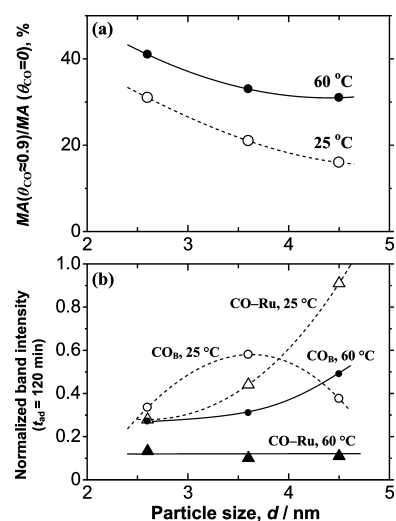


Figure 4. Particle size dependencies of (a) CO-tolerance parameter $MA(\theta_{CO \approx 0.9})/MA(\theta_{CO} = 0)$ and (b) band intensities of (\circ , \bullet) $I[CO_B]$ and (\triangle , \blacktriangle) $I[CO-Ru]$ at 25 °C (dashed line) and 60 °C (solid line) after $t_{ad} = 120$ min.

chemical compositions of the top-surface and the remaining core-part of each catalyst were estimated based on the hydrogen adsorption charge for the CO-free surface in the voltammogram measured in N_2 -purged solution at 25 °C (Supporting Information, Figure S3). The fraction of top-surface atoms was calculated assuming that the particles have an ideal cubooctahedral shape,^{34,35} as described in Supporting Information. The calculated values are summarized in Table 2 and Supporting Information, Figure S4.

Table 2. Chemical Compositions of the Top-Surface and the Remaining Core of Pt_2Ru_3/C and $PtRu/C$ Catalysts^a

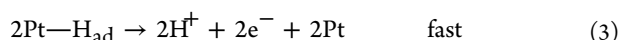
catalyst	d/nm	composition	
		top-surface	core
		Pt/Ru (atom %)	Pt/Ru (atom %)
Pt_2Ru_3/C	2.6	82/18	12/88
	3.6	71/29	27/73
	4.5	44/56	35/65
$PtRu/C$	2.6	95/5	20/80

^aSee Supporting Information.

It was found that, with decreasing d , the atomic ratio of Pt to Ru (Pt/Ru) on the top-surface layer increased, while the core became Ru-rich in composition. Such an exchange of Pt and Ru atoms between the top-surface and the core was caused by the H_2 -treatment, probably because of a stronger affinity of Pt to hydrogen than that of Ru. It is also suggested that the surface metal atoms are more mobile with decreasing particle size, while the chemical compositions of the top-surface and the remaining core of the largest 4.5 nm catalyst got closer to the bulk composition (Pt 40 atom %, Ru 60 atom %, see Supporting Information, Figure S4). Thus, the formation of a Pt-rich top-surface with an underlying Ru-rich core was found to be essential to preserve HOR active sites. The electronic modification effect of Ru can weaken the bond strength of Pt–CO (or increasing the mobility of CO_{ad}).

At the higher temperature of 60 °C, the value of $MA(\theta_{CO \approx 0.9})/MA(\theta_{CO} = 0)$ also increased with decreasing

d. As shown in Figures 3 and 4, however, $I[\text{CO-Ru}]$ at all catalysts decreased significantly and became nearly identical. Such a decrease in $I[\text{CO-Ru}]$ is certainly because the adsorption of CO on Ru sites became weak at 60 °C. It is noted that the MA at larger particles ($d = 4.5$ or 3.6 nm) decreased rapidly at the initial stage ($t_{\text{ad}} < \text{ca. } 30$ min), followed by a gradual decrease, whereas the initial decrease in the MA at the 2.6 nm catalyst was much slower, and the decrease rate gradually slowed down with t_{ad} . Here, we compare the $I[\text{CO}_B]$ among these catalysts at 60 °C. It was found that the $I[\text{CO}_B]$ at the 4.5 nm catalyst increased gradually and reached nearly twice the value compared with that of the 2.6 nm catalyst at $t_{\text{ad}} = 120$ min. According to the conventional electrochemical analysis for the HOR,^{19,36} a dissociative adsorption step of H_2 is generally accepted as the rate-determining step (*rds*).



It has been reported that the HOR activities at Pt/C catalysts and bulk Pt electrodes decreased steeply for $\theta_{\text{CO}} > 0.6$ and reached zero at $\theta_{\text{CO}} > 0.9$.^{2,13,19} Because one CO_B blocks a Pt-Pt pair site, the dissociative adsorption of hydrogen, eq 2 (*rds* of the HOR), is certainly suppressed at larger catalyst particles with larger $I[\text{CO}_B]$. Therefore, the smallest catalyst, $d = 2.6$ nm, with the largest number of Pt-Pt free sites, exhibited the highest CO-tolerance at 60 °C, at which $I[\text{CO-Ru}]$ was nearly identical for all of the catalysts. Such an advantage of small $I[\text{CO}_B]$ at the 2.6 nm catalyst was also seen at 25 °C, in addition to the reduction of $I[\text{CO-Ru}]$. The value of $I[\text{CO}_B]$ was also small on the 4.5 nm catalyst at 25 °C. This was probably due to the largest Ru atom % at the top-surface (ca. 2 times larger than that of the 3.6 nm catalyst), leading to an increase in CO-Ru (bridged CO at both Ru-Ru sites and Ru-Pt sites) and a decrease in CO_B adsorbed on Pt-Pt pair sites.

3.2. Effect of Alloy Composition on CO-Tolerance. As discussed above, the formation of a Pt-rich top-surface with an underlying Ru-rich core is one of the possible explanations why the coverage of CO_B was suppressed at the smallest Pt_2Ru_3 catalyst. For Pt_2Ru_3 particles with different sizes, however, one may claim differences in the geometrical factor (long-range order of terrace and/or ratio of terrace to step/edge) besides the change in the composition of the core, which is closely related to the electronic effect. Then, we focused on the effect of the alloy composition on the CO-tolerance by using the identical particle size catalysts. Both $\text{Pt}_2\text{Ru}_3/\text{C}$ (59.1 atom % Ru, $d = 2.6 \pm 0.3$ nm) and PtRu/C (48.4 atom % Ru, $d = 2.6 \pm 0.3$ nm) catalysts were prepared by the nanocapsule method, followed by H_2 -treatment. The calculated values of Pt/Ru of the top-surface and the core are summarized in Table 2. It was found that the Pt atom % at the top-surface of PtRu/C was larger than that of $\text{Pt}_2\text{Ru}_3/\text{C}$, whereas the Ru atom % in the core of PtRu/C was smaller than that of $\text{Pt}_2\text{Ru}_3/\text{C}$.

Figure 5 shows in situ FTIR spectra on PtRu/C ($d = 2.6$ nm) and $\text{Pt}_2\text{Ru}_3/\text{C}$ ($d = 2.6$ nm) electrodes observed at 0.02 V in 1% CO (H_2 -balance) saturated 0.1 M HClO_4 solution at 25 and 60 °C. These spectra were normalized with respect to the value of $I[\text{CO}_L]$ at $t_{\text{ad}} = 120$ min. The values of θ_{CO} became nearly constant (ca. 0.9) for both catalysts after 120 min at 25 and 60 °C. At both temperatures, the $I[\text{CO-Ru}]$ on PtRu/C was smaller than that on $\text{Pt}_2\text{Ru}_3/\text{C}$, whereas $I[\text{CO}_B]$ on PtRu/C was larger than that on $\text{Pt}_2\text{Ru}_3/\text{C}$.

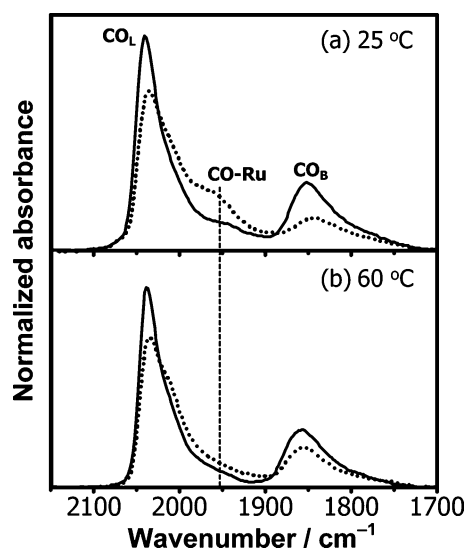


Figure 5. Comparison of FTIR spectra of PtRu/C (solid line) and $\text{Pt}_2\text{Ru}_3/\text{C}$ (dotted line) electrodes observed at 0.02 V in 1% CO (H_2 balance)-saturated 0.1 M HClO_4 solution at (a) 25 °C and (b) 60 °C after 120 min of CO adsorption. The spectra were normalized with respect to the value of $I[\text{CO}_L]$.

The time courses of $I[\text{CO}_L]$, $I[\text{CO}_B]$, $I[\text{CO-Ru}]$, and the MA for the HOR on the PtRu/C electrode are shown in Figures 3d and h. The values of MA at $\theta_{\text{CO}} = 0$ (CO-free) on PtRu/C were larger than those of $\text{Pt}_2\text{Ru}_3/\text{C}$ at 25 and 60 °C. This is probably ascribed to a large Pt atom % of the top-surface for PtRu/C (see Table 2), because pure Pt was found to exhibit the largest HOR rate constant in CO-free electrolyte solution.¹⁹ However, the value of $\text{MA}(\theta_{\text{CO}} \approx 0.9)/\text{MA}(\theta_{\text{CO}} = 0)$ on PtRu/C was nearly comparable to that on $\text{Pt}_2\text{Ru}_3/\text{C}$ at 25 °C, and the MA on PtRu/C decreased with t_{ad} somewhat steeper than that on $\text{Pt}_2\text{Ru}_3/\text{C}$. These results suggest that the advantage of the reduction of $I[\text{CO-Ru}]$ at PtRu/C having a Pt-rich top-surface was canceled by the increase in $I[\text{CO}_B]$, as shown in Figure 5a. At the higher temperature of 60 °C, $\text{Pt}_2\text{Ru}_3/\text{C}$ exhibited a larger value of $\text{MA}(\theta_{\text{CO}} \approx 0.9)/\text{MA}(\theta_{\text{CO}} = 0) = 41\%$ than that on PtRu/C (35%, see Supporting Information, Table S1). It is also seen in Figures 3e and h that the MA on $\text{Pt}_2\text{Ru}_3/\text{C}$ decreased with t_{ad} more gently than that on PtRu/C at 60 °C. Thus, $\text{Pt}_2\text{Ru}_3/\text{C}$ exhibited higher CO-tolerance. For both catalysts at 60 °C, $I[\text{CO-Ru}]$ decreased markedly and became nearly identically low. At both temperatures, $I[\text{CO}_B]$ on $\text{Pt}_2\text{Ru}_3/\text{C}$ was smaller than that on PtRu/C . Thus, $\text{Pt}_2\text{Ru}_3/\text{C}$ exhibited higher CO-tolerance at 60 °C, because the suppression of CO_B is essential to maintain active Pt-Pt pair sites for the HOR, as well as the increase in the mobility of CO_{ad} by the electronic modification effect of Ru, as discussed in the previous section.

Taking these results into account, we have clarified the important factors to enhance the CO-tolerance. First is the suppression of adsorption of CO on Ru sites to maintain the electronic modification effect, especially at low temperature (around 25 °C). The H_2 -treatment of small particles is very effective to prepare a Pt-rich top surface. The second important one is the mitigation of the blocking effect of CO_B on the HOR active sites. It is clear that a Ru-rich core is effective to suppress CO_B adsorption. Hence, the $\text{Pt}_2\text{Ru}_3/\text{C}$ with the smallest particle size is the best choice as a CO-tolerant anode catalyst

for PEFCs, although we still need to examine the durability for long-term operation.

CONCLUSIONS

The effects of particle size and alloy composition for Pt–Ru alloy nanocatalysts on the CO-tolerance were investigated by in situ ATR-FTIR spectroscopy in 1% CO (H₂-balance)-saturated 0.1 M HClO₄ at 25 and 60 °C. The highest CO-tolerant HOR activity at both temperatures was observed for the smallest Pt₂Ru₃ particle (*d* = 2.6 nm) with a Pt-rich top surface and Ru-rich core. We have clarified important strategies for improving the HOR activities in the presence of CO_{ad}. The Pt-rich surface is effective to suppress the adsorption of CO on Ru sites, especially at the low temperature of 25 °C. This can maintain the electronic modification effect that weakens the bond strength of Pt–CO¹⁴ or increase the mobility of CO on the surface. High temperature operation is very effective, because the $\theta[\text{CO–Ru}]$ decreased markedly because of a decrease in the bond strength of CO_{ad} on Ru sites, resulting in an increased HOR activity. To maintain the active sites for the HOR at 60 °C, the suppression of adsorption of bridged CO (CO_B) on Pt sites is important, because one CO_B blocks Pt–Pt pair active sites. The electronic modification effect by the underlying Ru-rich core is essential to decrease $\theta[\text{CO}_B]$. The present research provides a clear clue for designing CO-tolerant anode catalysts for PEFCs.

ASSOCIATED CONTENT

Supporting Information

Changes in FTIR spectra of Pt₂Ru₃/C (*d* = 2.6, 3.6, and 4.5 nm) during CO adsorption, deconvolution of FTIR spectra of CO_{ad} on Pt₂Ru₃/C, cyclic voltammograms of H₂-treated Pt₂Ru₃/C and PtRu/C, calculation method for the chemical compositions of the top-surface and the remaining core-part of each catalyst, all data of MA for the HOR at 0.02 V on these catalysts with $\theta_{\text{CO}} = 0$ and about 0.9. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Funding

This work was supported by funds for the “Highly CO-Tolerant Anode Catalysts for Residential PEFCs Project” from the New Energy and Industrial Technology Development Organization (NEDO) of Japan.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Prof. Donald A. Tryk (Fuel Cell Nanomaterials Center, University of Yamanashi) for his kind advice.

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