Dynamic Characterization of the Intermediates for Low-Temperature PROX Reaction of CO in H₂—Oxidation of CO with OH via HCOO Intermediate

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The preferential oxidation (PROX) reaction of CO ($\text{CO} + \text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$) on a $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ catalyst (~ 140 wt % FeO_x on 1 wt % Pt/TiO_2) was studied at 60 °C by using in situ DRIFT spectroscopy. The PROX reaction of CO occurs via a HCOO intermediate and its oxidation with OH instead of oxygen, which is different from ordinary oxidation of CO with O_2 ($\text{CO} + \frac{1}{2}\text{O}_2 \rightarrow \text{CO}_2$). The mechanism is as follows: (i) $\text{CO(a)} + \text{OH}^- \rightarrow \text{HCOO} + \text{e}^-$, (ii) $\text{O} + \text{e}^- + \text{H}^+ \rightarrow \text{OH}$, and (iii) $\text{HCOO} + \text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$, and step (iii) is the rate-determining step. Providing HCOO intermediates by a reaction of CO(a) with the OH^- anion, step (i), was deduced by combining an electroconductive PROX catalyst (Pt/CNT (carbon nanotube)) with a hydrogen fuel cell. The oxidation of CO enhanced by H_2 and H_2O and the hydrogen isotope effect by H_2/D_2 and $\text{H}_2\text{O}/\text{D}_2\text{O}$ on the $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ catalyst are well explained by this mechanism.

1. Introduction

There has been a great deal of research effort directed toward hydrogen fuel cells as a promising clean energy system with high thermodynamic efficiency. One difficulty associated with hydrogen fuel cells is contamination of the anode by trace amounts of CO in H_2 , i.e., ordinary anodes of Pt or Pt-alloy supported on carbon are contaminated by CO at levels lower than 100 ppm.^{1,2} Therefore, removal of CO with minimal hydrogen consumption is necessary. One of the most straightforward processes to achieve this is the preferential oxidation (PROX) of CO in H_2 . The selective oxidation of CO in excess H_2 is also interesting as basic research with regards to the activity and the selectivity of heterogeneous catalysis. Atalik and Uner³ reported a discrepancy between the specific activity (dispersion insensitive) and the TOF (dispersion sensitive) for the oxidation of CO on Pt. That is, the activity is insensitive to particle size,³ although the oxidation of CO on terraces is preferential to that on the steps or kinks⁴ and the turnover frequency (TOF) for the oxidation of CO is higher on larger Pt particles.^{5–7} Selective oxidation of CO in H_2 has usually been discussed by relating to particle size and the surface composition of bimetals.^{7,8} As will be discussed in this paper, the actual mechanism of the PROX reaction and its activity is difficult to understand by studying phenomenological correlation with particle size. The same is true for Au particles supported on oxides. Although the activity has been discussed in relation to particle size by assuming the competitive reaction of CO and H with O not only on supported metals^{9–12} but also for the role of Au-cations,¹⁰ the effect of calcination temperature,¹¹ and the activation of inactive Au/TiO_2 by covering with TiO_x ¹² but it is difficult to explain them without insight into the reaction mechanism. As shown in this paper, the PROX reaction of CO taking place on the $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ catalyst at low temperature

is different from the ordinary oxidation reaction of CO with O_2 , i.e., the intermediates are completely different.

Several low-temperature PROX catalysts have been reported to date.^{9–17} Among them, Au catalysts^{9,11,12} and a limited number of catalysts^{13,15,17} are active even at room temperature, but the activity is discussed only relating to particle size or dispersion of metals, that is, few provide insight into the reaction mechanism.

This study was performed to determine the reaction mechanism to gain a deeper understanding of the activity and selectivity of the PROX reaction taking place on the $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ catalyst at low temperature. As shown in Figure 1a, the $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ catalyst (~ 140 wt % in Fe_3O_4) is unique, that is, 1 wt % Pt/TiO_2 catalyst has low activity for the PROX reaction of CO at low temperature, but the 1 wt % Pt/TiO_2 loading a large amount of FeO_x (~ 140 wt % in Fe_3O_4) is superior active for the PROX reaction.^{13,16} Similar activation by loading FeO_x was found not only on Pt/TiO_2 but also on $\text{Pt}/\text{Al}_2\text{O}_3$, Pt/CeO_2 ,¹³ and on the poorly active Au/TiO_2 catalyst with large Au particles.¹⁸ Bolinger and Vannice¹² also reported similar activation of inactive Au/TiO_2 by depositing TiO_x , and Ayastuy et al.¹⁹ recently reported activation of $\text{Pt}/\text{Al}_2\text{O}_3$ by loading MnO_x .

It should be pointed out that the low-temperature PROX reaction of CO taking place on the $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ catalyst is caused by the marked enhancement of CO oxidation by H_2 and/or H_2O as shown in Figure 2.¹⁶ In addition, the enhancement of oxidation of CO by H_2/D_2 and $\text{H}_2\text{O}/\text{D}_2\text{O}$ showed a common hydrogen isotope effect.²⁰ These phenomena strongly suggest that the PROX reaction of CO, that is, the oxidation of CO enhanced by H_2 and/or H_2O , is undoubtedly different from ordinary oxidation of CO with oxygen.²¹

2. Experimental Section

The reaction was performed in a flow system with a fixed catalyst bed using a Pyrex glass reactor, and the gas analysis was performed by online gas chromatography. Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was

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Figure 1. Activity of Pt/TiO₂, FeO_x/Pt/TiO₂, Pt/Vulcan-C, and Pt/CNT catalysts for the PROX reaction of CO. TEM images are 1 wt % Pt/TiO₂ and FeO_x/Pt/TiO₂ (ca. 140 wt % in Fe₃O₄). (a) Conversion of CO (□, ■) and O₂ (○, ●), and the selectivity (+) attained in a flow of CO (2 mL/min) + O₂ (1 mL/min) + H₂ (20 mL/min) + N₂ (77 mL/min) on 1 wt % Pt/TiO₂ (1.5 g) (open symbols) and FeO_x/Pt/TiO₂ (1.5 g) (solid symbols). (b) Conversion of CO (□, ■) and O₂ (○, ●) attained in a flow of CO (1.5 mL/min) + O₂ (1.5 mL/min) + H₂ (15.0 mL/min) + N₂ (38.5 mL/min) on 15 wt % Pt/Vulcan-C (0.29 g) and 15 wt % Pt/CNT (0.39 g) catalysts.

applied to a fine powder of the FeO_x/Pt/TiO₂ catalyst (see the preparation in refs 13 and 14) mounted in an IR cell for the reaction. The catalyst was pretreated in a flow of pure N₂ at 350 °C. In situ DRIFT spectra were measured under a stream of 10% CO/N₂ (120 mL/min) + O₂ (6 mL/min) + H₂ (40 mL/min) + N₂ (74 mL/min) (total flow = 240 mL/min, O₂/CO = 1/2) at 60 °C, using a Thermo Nicolet Nexus 670 spectrometer with a mercury–cadmium–telluride (MCT) detector at a resolution of 4 cm⁻¹. Changes of the in situ DRIFT spectra with time taking place by removing CO or H₂ from the stream of (CO + O₂) or (CO + O₂ + H₂) and by adding H₂ to (CO + O₂) were obtained by subtracting the spectrum measured in the stream of (CO + O₂) or (CO + O₂ + H₂) as the background spectrum. Therefore, the positive or negative growth of the IR peaks with time reflects the dynamics of intermediates during catalysis. It is worthy of note that the amount of intermediates during catalysis is given by the dynamic balance of formation and consumption of intermediates at each elementary step. Therefore, intermediates preceding the rate-determining step may be detected, but those after the rate-determining step are difficult to detect.

Figure 2. (a) Oxidation of CO enhanced by H₂ on the FeO_x/Pt/TiO₂ catalyst and (b) by H₂O at 60 °C. Reaction was performed in a flow of 100 mL/min of [CO (3 mL/min) + O₂ (1.5 mL/min) + N₂] and [CO (3 mL/min) + O₂ (1.5 mL/min) + H₂ (15.0 mL/min) + N₂]. H₂O was added by bubbling N₂ through water at room temperature.

3. Results and Discussion

As mentioned above, oxidation of CO enhanced by H₂ and H₂O on the FeO_x/Pt/TiO₂ catalyst shown in Figure 2 is difficult to explain by the traditional reaction mechanism expressed by CO(a) + O(a) → CO₂. That is, the oxidation of CO proceeds via the intermediate Xi(a) containing hydrogen as described by eq 1:

where CO(g) is gas phase CO, and CO(a) and Xi(a) are intermediates. The amounts of CO(a) and Xi(a) are given by the dynamic balance of provision and consumption of the corresponding intermediates in steady-state catalysis. Accordingly, we can deduce the rate-determining step by studying the dynamics of the intermediates.

3.1. Dynamics of Intermediates CO(a) and Xi(a) Depending on CO. As reported previously,²² Pt-sites on 1 wt % Pt/TiO₂ undergo reconstruction by loading FeO_x, i.e., linearly bonded CO is predominant on the Pt/TiO₂ catalyst, but bridge-bonded CO and linearly bonded CO are comparable (IR peak ratio ~1.1) on the FeO_x/Pt/TiO₂ catalyst. If the bridged and linearly bonded CO(a) are real intermediates, their reaction should be enhanced in the presence of H₂. When CO(g) is removed from the stream of (CO + O₂), the amounts of adsorbed CO(a) and Xi(a) will decrease according to the reaction rate of CO(a) → Xi(a) → CO₂ in eq 1. Decreasing CO(a) and Xi(a) intermediates by removing CO in the gas phase reflects the rate-determining step, which is either CO(a) → Xi(a) or Xi(a) → CO₂. When Xi(a) → CO₂ is the rate-determining step, CO(a) and Xi(a) will decrease together. On the other hand, if CO → Xi(a) is the rate-determining step, the amount of Xi(a) will be

Figure 3. Dynamics of the in situ DRIFT spectra on FeO_x/Pt/TiO₂ at 60 °C: (a) (i) spectrum in (CO + O₂) and (ii) the spectrum changing with time in (CO + O₂) - CO. (b) (i) spectrum in (CO + O₂ + H₂) and (ii) the spectrum changing with time in (CO + O₂ + H₂) - CO.

lower than detectable. Similarly, if the adsorption of CO is the slow rate-determining step, neither CO(a) nor Xi(a) could be detected during catalysis. From this viewpoint, the dynamics of the in situ DRIFT spectroscopy of the intermediates were studied.

The IR peaks of the linearly bonded CO(a) and the bridge-bonded CO(a) in a steady stream of (CO + O₂) as well as of (CO + O₂ + H₂) at 60 °C can be seen in Figure 3, panels a and b, where the gas phase CO peaks are subtracted. Large adsorbed CO peaks indicate that the adsorption of CO is sufficiently rapid relative to the subsequent reactions, i.e., the adsorption of CO is not the rate-determining slow step. When the CO is removed from a steady stream of (CO + O₂) and (CO + O₂ + H₂) at 60 °C, linearly bonded CO peaks and the bridge bonded CO peaks decreased as shown in Figure 3a and b. The decreasing rate of CO(a) peaks is quite different in the presence or absence of H₂. As shown in Figure 3a, the decreasing of CO(a) peaks is slow in the absence of H₂, and the linearly bonded as well as the bridge-bonded CO peaks remained after 45 min. If the decreasing rate of the two CO(a) is compared, the decrease of bridge-bonded CO peaks is faster than that of linearly bonded CO. In contrast, when CO was removed from a stream of (CO + O₂ + H₂) at 60 °C, not only the bridge-bonded CO but also the linearly bonded CO peaks disappeared immediately from the catalyst surface, as shown in Figure 3b. This result indicates that the reaction of CO(a) to Xi(a) is quite rapid in the presence of H₂.

Taking these results into account, the dynamics of the intermediate Xi(a) taking place by removing CO from a steady

stream of (CO + O₂) and (CO + O₂ + H₂) at 60 °C were studied. To extract the changes in the Xi(a) peaks with time, the steady-state spectrum in (CO + O₂) or (CO + O₂ + H₂) was subtracted as background. Therefore, increasing of the negative peaks with time reflects the decrease of Xi(a) from the catalyst surface. When CO was removed from the steady stream of (CO + O₂), negative peaks increased at 1836, 1824, 1632, 1396, and 1293 cm⁻¹, as shown in Figure 4a. The peaks at 1836 and 1824 cm⁻¹ were attributed to bridge-bonded CO(a) on Pt-Pt and Pt-Fe sites by a simple calculation. The peaks at 1632 and 1396 cm⁻¹ (and probably 1293 cm⁻¹) were in good agreement with the bicarbonate (CO₂(OH)), on oxides (1615–1630 (ν_{as}), 1400–1500 (ν_s), 1225 (γOH) cm⁻¹),²³ and on Au/Fe₂O₃ (1621, 1414, and 1222 cm⁻¹).²⁴ Therefore, the spectra indicate the decrease of CO(a) and bicarbonates on the catalyst when CO(g) was removed from the stream of (CO + O₂).

Large CO(a) peaks observed during oxidation of CO reflect rapid adsorption of CO(a), as described above, and large CO₂(OH) peaks indicate faster formation than decomposition of CO₂(OH), i.e., step ii in eq 2, CO₂(OH) → CO₂ + OH, is the rate-determining step.

Decomposition of CO₂(OH) by step ii in eq 2 will provide OH on the catalyst. In fact, with decreases in CO₂(OH) species (growing negative peaks), the growth of OH peaks was observed at 3691 and 3697 cm⁻¹, as shown in Figure 4a. Figures 2a, 3b, and 4b indicate that CO(g) in the gas phase as well as adsorbed CO(a) on the catalyst undergo very rapid reaction in the presence of H₂. To elucidate the intermediates Xi(a), the in situ IR changing with time was measured by removing CO in (CO + O₂ + H₂) at 60 °C (333 K), where the steady spectrum in (CO + O₂ + H₂) was subtracted. When CO was removed, large negative peaks grew very rapidly at 1836, 1522(ν_{as}), and 1354 cm⁻¹ (ν_s) (shoulder at 1296 cm⁻¹), as shown in Figure 4b. The peak at 1836 cm⁻¹ was the bridge-bonded CO(a), and the peaks at 1522 cm⁻¹ (ν_{as}) and 1354 cm⁻¹ (ν_s) (shoulder at 1296 cm⁻¹) were classified as surface formates (HCOO). The peaks at 1522 cm⁻¹ (ν_{as}) and 1354 cm⁻¹ (ν_s) with shoulder at 1296 cm⁻¹ are similar to the spectrum observed during oxidation of formaldehyde on a Pt/TiO₂ catalyst²⁵ and adsorption of HCOOH.^{26–30} A density functional theory (DFT) calculation with the MPW1PW91 + Sdd basis set³¹ was applied to a monodentate formate on a Ti-ion, as shown in Figure 4e. Vibration bands appearing at 1533, 1377, and 1334 cm⁻¹ were in good agreement with the peaks at 1524 and 1379 cm⁻¹ of adsorbed HCOOH on the TiO₂(110) surface.²⁶ The asymmetric vibration band (ν_{as}) at 1533 cm⁻¹ was stronger than the symmetric vibration (ν_s) at 1334 cm⁻¹. Large negative formate (HCOO) peaks grown by removing CO from (CO + O₂ + H₂) indicate large amounts of HCOO intermediates existing on the catalyst during steady reaction in (CO + O₂ + H₂), that is, the rate-determining slow step is the reaction of HCOO. To clarify the difference of the spectra obtained by removing CO from (CO + O₂) and (CO + O₂ + H₂), the two results are shown together in Figure 4c. Negative growth of the peaks at 1522 (HCOO), 3350 (OH), and 1632 cm⁻¹ (bicarbonate) is plotted with respect to time in Figure 4d. Not only the IR peaks but the dynamics of the peaks

were also clearly different in $(\text{CO} + \text{O}_2)$ and $(\text{CO} + \text{O}_2 + \text{H}_2)$. Figure 4b shows the concomitant negative growth of HCOO peaks and the broad OH(a) band centered at 3350 cm^{-1} , that is, HCOO (1522 cm^{-1}) and OH (3350 cm^{-1}) are completely erased from the catalyst surface within 1 min at $60\text{ }^\circ\text{C}$ when CO is removed from $(\text{CO} + \text{O}_2 + \text{H}_2)$. On the basis of these results, we conclude that the oxidation of CO in $(\text{CO} + \text{O}_2 + \text{H}_2)$ and that in $(\text{CO} + \text{O}_2)$ are different reactions, because the intermediates and their reaction dynamics are completely different.

It is worth noting that the broad band at $3000\text{--}3600\text{ cm}^{-1}$ may not be adsorbed H_2O molecules on the catalyst, because the characteristic scissor vibration mode of H_2O expected at approximately 1650 cm^{-1} is very weak in the spectra, as observed in Figure 4b. Taking these results into account, we conclude that the rate-determining step in the oxidation of CO is the reaction of HCOO with OH instead of O, step iii in eq 3. To our knowledge, this is the first spectroscopic evidence showing the oxidation of CO via HCOO intermediates with OH instead of O(a).

Calculation of the oxidation of CO with H_2O on the surface of $\text{Pt}_2\text{Mo}(111)$ by density functional theory suggested the

oxidation of CO with OH via HCOO,³² although the mechanism differed from the mechanism deduced on $\text{FeOx}/\text{Pt}/\text{TiO}_2$. The mechanism deduced in this paper explains the oxidation of CO enhanced by H_2 and/or H_2O as well as the hydrogen isotope effect on the oxidation of CO by H_2/D_2 and $\text{H}_2\text{O}/\text{D}_2\text{O}$. However, the adsorption sites described in the reaction scheme are speculative, because adsorption sites as well as the migration of the intermediates among them are difficult to clarify at the present time.

The role of H_2 and provision of HCOO intermediates from CO(a) in the presence of H_2 or H_2O will be discussed in the following.

3.2. Dynamics of CO(a), HCOO, and OH Intermediates Influenced by H_2 . As deduced in the previous section, the oxidation of CO in the presence of H_2 proceeds via HCOO intermediates. Here we discuss the dynamics of the intermediates

Figure 4. DRIFT spectroscopy changing with time when CO was removed during oxidation of CO on $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ catalyst at $60\text{ }^\circ\text{C}$. (a) Decrease of bicarbonate ($\text{CO}_2(\text{OH})$) by removing CO from $(\text{CO} + \text{O}_2)$. (b) Decrease of formate (HCOO) by removing CO from $(\text{CO} + \text{O}_2 + \text{H}_2)$. Simultaneous growth of HCOO, OH ($3000\text{--}3600\text{ cm}^{-1}$), and C–H ($2864, 2929, 2960\text{ cm}^{-1}$) peaks occurs. (c) Spectra shown in panels a and b are displayed together. The peaks given by density functional theory calculations for a surface bicarbonate (1624 and 1360 cm^{-1}) and a surface formate ($1533, 1377$, and 1334 cm^{-1}) are shown with solid bars. (d) Dynamics of intermediate peaks. Removing CO from $(\text{CO} + \text{O}_2 + \text{H}_2)$ induces simultaneous rapid growth of the negative peaks of HCOO (1522 cm^{-1}) and OH (broad band of $\sim 3350\text{ cm}^{-1}$), but the remove of CO from $(\text{CO} + \text{O}_2)$ makes bicarbonate peaks grow slowly (1632 cm^{-1}). (e) Model of monodentate formate on a Ti-ion and a density functional theory (DFT) calculation using the MPW1PW91 + Sdd.

Figure 5. (a) When H₂ is removed from (CO + O₂ + H₂), HCOO on the catalyst undergoes rapid increase (solid spectra) at 60 °C, but rapid decrease of HCOO occurs by adding H₂ to (CO + O₂). (b) Rapid increase of HCOO by removing H₂ from (CO + O₂ + H₂).

CO(a), HCOO(a), and OH(a) when H₂ is removed from a stream of (CO + O₂ + H₂) or added to a stream of (CO + O₂). When H₂ was removed from (CO + O₂ + H₂), very rapid growth of positive HCOO peaks was observed in (CO + O₂) but no CO(a) peak appeared, as shown in Figure 5a (solid spectra). The growth of the HCOO peak (1520 cm⁻¹) with removal of H₂ was very rapid, and was completed within 1 min, as shown in Figure 5b. When the oxidation of HCOO with OH is stopped by removing H₂ from (CO + O₂ + H₂), the amount of HCOO(a) is increased by dynamic balance, because the CO(a) on the catalyst does not change in (CO + O₂) and the provision of HCOO(a) may not stop immediately. As will be shown in the next section, a reaction of CO(a) with OH⁻ anions provides HCOO intermediates, which may not stop instantly by removing H₂ in (CO + O₂ + H₂).

On the other hand, when H₂ was added to a stream of (CO + O₂), rapid growth of tiny negative peaks was observed, which completed within 1 min, as shown in Figure 5a with a dotted spectrum. The tiny peaks are assigned to HCOO and C–H (2964 and 2870 cm⁻¹, respectively). These observations indicate the presence of a trace amount of HCOO species even in the stream of (CO + O₂), i.e., a trace amount of H₂O necessarily exists in the stream of (CO + O₂). The small amount of HCOO is rapidly removed from on the catalyst surface by reacting with OH when H₂ is added to (CO + O₂).

By removing CO from (CO + H₂ + O₂), the gas phase changes to (H₂ + O₂), but no OH species were detected on the catalyst in the stream of (H₂ + O₂). This phenomenon is also well explained by the dynamic balance of the formation and consumption of OH species, i.e., the reaction of OH with H to

Figure 6. Experimental system to test the activity of Pt/CNT catalyst for the PROX reaction of CO in H₂ when it is installed in front of the humidifier or is contacted with the anode of the PEFC.

form H₂O, OH + H → H₂O, is very rapid in the absence of CO; thus, the OH level is below the limit of detection in (H₂ + O₂).

The provision of HCOO intermediates from adsorbed CO(a) is the final problem to be resolved. To address this, we performed a new experiment combining an electroconductive PROX catalyst with a polymer electrolyte hydrogen fuel cell (PEFC).

3.3. Vital Role of OH⁻ Anion in the PROX Reaction of CO. Dynamic characterization of the intermediates on the FeO_x/Pt/TiO₂ catalyst suggested that the PROX reaction of CO proceeds via the oxidation of HCOO intermediates with OH. However, the formation of HCOO from CO(a) in a stream of (CO + O₂ + H₂) has yet to be resolved. To address this problem, a new experiment was performed by combining an electroconductive PROX catalyst with a PEFC. As will be discussed below, the PROX catalyst for this experiment should be electroconductive catalyst. Fortunately, we recently developed an electroconductive PROX catalyst being highly active at room temperature by supporting Pt on a carbon nanotube (CNT),¹⁵ and it was proved that the superior activity of the Pt/CNT catalyst for the low-temperature PROX reaction appeared in the presence of Ni-MgO in the CNT.³³ It should be addressed that the feature of the Pt/CNT catalyst for the PROX reaction is very similar to that of the FeO_x/Pt/TiO₂, that is, the oxidation of CO is markedly enhanced by H₂ and/or H₂O and the oxidation of CO enhanced by H₂/D₂ shows hydrogen isotope effect. A 5 wt % Pt/CNT catalyst was installed in the PEFC in two ways, i.e., with and without contact with the anode, as illustrated in Figure 6.

Figure 7a shows a blank current–voltage (*I*–*V*) profile of the PEFC attained in a stream of H₂ (400 mL/min) containing 25 000 ppm O₂, where 5 wt % Pt/CNT catalyst (~0.8 g) was installed in front of the humidifier of the PEFC. Then, the output voltage at a current of 0.75 A/cm² was monitored by increasing CO in H₂ stepwise from 0 to 1500 ppm at 60-min intervals, and finally to 2000 ppm. As shown in Figure 7b, no retardation effect of CO was observed on the output voltage at 0.75 A/cm² to 1500 ppm, i.e., the CO in the stream of H₂ was completely oxidized by the PROX reaction on the Pt/CNT catalyst installed in front of the humidifier at room temperature. In contrast, when the 5 wt % Pt/CNT catalyst was in contact with the Pt/C anode

Figure 7. (a) A blank current–voltage profile (output) of the PEFC attained by flowing of H_2 containing 25 000 ppm O_2 at 400 mL/min. (b) Output voltage at 0.75 of the PEFC installed 5 wt % Pt/CNT catalyst (0.8 g) in front of the humidifier CO. No voltage drop was confirmed for 60 min by stepwise increasing of CO up to 1500 ppm. (c) A 5 wt % Pt/CNT catalyst was installed in contact with the anode. Output voltage of the PEFC at 0.75 A/cm² dropped immediately by adding 500 ppm of CO in H_2 .

of PEFC, the output voltage at 0.75 A/cm² was dropped markedly with the addition of 500 ppm of CO in H_2 , as shown in Figure 7c. That is, the performance of the Pt/CNT catalyst was diminished by contact with the anode of the PEFC. From this experiment, we postulate that a large amount of H^+ provided by ionization of H_2 on the Pt/C anode ($\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$) disturbed the PROX reaction of CO on the Pt/CNT, i.e., a large amount of H^+ diffused onto the Pt/CNT catalyst may react with OH^- anions on the PROX catalyst as described by eq 4; thus, the reaction of CO(a) with OH^- anion, $\text{CO(a)} + \text{OH}^- \rightarrow \text{HCOO}^-$, stopped. It is worth noting that this elementary reaction is similar to the known formic acid-producing chemical reaction of CO with Ca(OH)_2 or NaOH:

(i) ionization of H_2 on the Pt/C anode and (ii) neutralization of OH^- anion with H^+ on the Pt/CNT catalyst. Taking these processes into account, the total mechanism for the PROX reaction of CO in H_2 is described as follows:

where the bold characters indicate intermediates detected by in situ dynamics of DRIFT IR spectroscopy. According to this

mechanism, H_2O plays a role in positive feedback providing HCOO^- intermediates, which results in selective oxidation of CO in H_2 . That is, H_2O is a molecular catalyst promoting the low-temperature PROX reaction of CO.

Taking account of the mechanism for the low-temperature oxidation of CO via HCOO^- intermediates, we wish to infer the interesting contrast between the catalytic oxidation of CO on $\text{FeO}_x/\text{Pt}/\text{TiO}_2$ enhanced by H_2O and the electrochemical oxidation of CO on the Pt electrode in an aqueous solution. On the Pt(111) electrode, oxidation of OH^- to OH occurs in a potential range of $0.6 \text{ V} < E < 0.9 \text{ V}$ (RHE),³⁴ and the oxidation of methanol with OH in this potential range forms HCOO^- .³⁵ However, HCOO^- has never been detected during electrochemical oxidation of CO on the Pt electrode. The electrochemical oxidation of CH_3OH with OH is analogous to the catalytic oxidation of HCHO with O_2 on a Pt/TiO_2 catalyst²⁵ and the oxidation of HCOO^- with OH at step iii in eq 3. As deduced in this paper, however, HCOO^- (precursor of HCOO) would be provided by the reaction of CO(a) with OH^- anions. If this would be the case on the electrochemical oxidation of CO, HCOO^- intermediates cannot be formed on the electrode in acidic solution. Accordingly, HCOO^- species are formed in the electrochemical oxidation of CH_3OH with OH on the Pt electrode in the potential range of $0.6 \text{ V} < E < 0.9 \text{ V}$ (RHE) but not in electrochemical oxidation of CO.

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