



Mechanism of highly selective low temperature PROX reaction of CO in H₂: Oxidation of CO via HCOO with OH

Ken-ichi Tanaka^{a,*}, Hong He^b, Masashi Shou^a, Xiaoyan Shi^b

^a Advanced Science Research Laboratory, Saitama Institute of Technology, 1690 Fusaiji, Okabe, Saitama 369-0293, Japan

^b Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, China

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ABSTRACT

Oxidation of CO is markedly enhanced by H₂ and/or H₂O on FeO_x loaded Pt/TiO₂ (FeO_x/Pt/TiO₂) catalyst. Similarly, oxidation of CO on the Pt/CNT and Pt/CNF was enhanced by H₂ and/or H₂O. As a result, highly selective preferential oxidation (PROX) of CO is established at low temperature on these catalysts. The oxidation of CO on these catalysts has a hydrogen isotope effect by H₂O/D₂O and H₂/D₂, which suggests the intermediate at the rate determining step involves hydrogen atom. Dynamics of in situ DRIFT spectroscopy on FeO_x/Pt/TiO₂ suggests that the rate determining step of the PROX reaction of CO is the oxidation of HCOO with OH. TEM image proves that Pt particles are on the outer wall of the CNT but Ni–MgO and FeO_x are localized at the end of CNT and CNF. If Ni–MgO and Fe in CNT and CNF were removed (CNT-p and CNF-p), the Pt lost the activity for low temperature PROX reaction of CO. Characteristic feature of the PROX reaction suggests a dual functional catalysis involving ionic process of CO + OH⁻ → HCOO⁻, which is responsible for the low temperature PROX reaction of CO.

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1. Introduction

Hydrogen fuel cell (HFC) system is a high thermodynamic efficient system to lower the CO₂ in atmosphere. Although people spend a lot of effort to develop CO-tolerant Pt-based anode, the poison of Pt electrode is still one awkward problem of the HFC. To avoid the poisoning of Pt-anode by CO, CO in H₂ is lowered to be less than 10 ppm by preferential oxidation (PROX) reaction of CO in H₂ and the methanation reaction of CO (CO + 3H₂ → CH₄ + H₂O), typically, on Ru/Al₂O₃ catalyst at 150 °C–170 °C. The selective oxidation of CO in H₂ has been explained by the competitive oxidation of adsorbed CO(a) and H(a) with O(a), that is, CO(a) + O(a) → CO₂ and H(a) + O(a) → OH(a). It should be pointed out that the oxidation mechanism of CO is the same in the presence or absence of H₂ and/or H₂O. This traditional concept has been a fetter of insight into the real mechanism of the PROX reaction of CO in H₂. So far, we developed several catalysts for the preferential oxidation (PROX) reaction of CO in H₂ at room temperature [1–6], and a new oxidation mechanism of CO was deduced by studying the dynamics of the intermediates [2].

It is a vogue to explain the activity of metal particles by characteristic structure of metal particles such as the particle size, morphology, local bonding and the number of surrounding atoms,

and interaction with support, instead of the reaction mechanism. For example, superior activity of the Au/TiO₂ catalyst having smaller than 3 nm was explained as active perimeter of Au particles by Haruta [7]. However, Chen and Goodman [8] demonstrated a specific activity of a (1 × 3) bi-layer structure Au atoms arrayed on a monolayer of titanium oxide, and they concluded that particle size of Au does not directly influence on the activity of Au/TiO₂ catalyst. We also found that large Au particles on TiO₂ being inactive for the PROX reaction of CO changes to active catalyst by loading a large amount of FeO_x [1]. Another interesting example is the oxidation of CO on a Pt(1 1 1) surface covered with CeO₂ layers. Adsorption of CeO₂ prevents the adsorption of CO on Pt(1 1 1) and the adsorption of CO becomes zero at about 1.5 monolayer coverage of CeO₂. The oxidation of CO is suppressed as increasing the deposition of CeO₂, but Lambert and his coworkers [9] found that the activity is suddenly improved when the Pt(111) surface is covered more than two mono-layers of CeO₂. Such enhancement of the activity cannot be rationalized by the traditional mechanism of the oxidation of adsorbed CO(a) with O(a). Catalytic activity of Pt/TiO₂ is also markedly improved by loading a large amount of FeO_x (ca. 140 wt.% by calculation as Fe₃O₄) [4,10]. As it will be discussed in this paper, low (room) temperature PROX reaction of CO was catalyzed on the Pt supported by the carbon nanotube (CNT) and carbon nano-fiber (CNF) prepared by using Ni–MgO and ferrocene, and it was proved that the Ni–MgO and Fe localized at the end of CNT and CNF are indispensable for the low temperature PROX reaction of CO on the Pt particles dispersed on the wall. Such characteristic activity of the

* Corresponding author. Tel.: +81 585 6874.

E-mail address: ktanaka@sit.ac.jp (K.-i. Tanaka).

PROX reaction of CO in H₂ is difficult to explain by the structure of Pt particles such as morphology and/or the size.

2. Experimental

FeO_x/Pt/TiO₂ was prepared by dipping 1 wt.% Pt/TiO₂ in an aqueous solution of Fe(NO₃)₃. FeO_x of about equal amount to 1 wt.% Pt/TiO₂ was loaded on it, and the catalyst heated in air at 400 °C was denoted as 100 wt.% FeO_x/Pt/TiO₂ (Fe/Pt ≈ 350). The in situ diffuse reflectance IR-Fourier transform (DRIFT) spectra were measured at 60 °C by using a Nexus 670 (Thermo Nicolet) spectrometer by flowing a mixture of 10% CO/N₂ (120 mL/min) + O₂ (6 mL/min) + H₂ (40 mL/min) + N₂ (74 mL/min) (O₂/CO = 1/2) over the FeO_x/Pt/TiO₂ catalyst (0.4 wt.% Pt with respect to FeO_x/TiO₂) mounted in the in situ IR cell using a Thermo Nicolet Nexus 670 spectrometer with an MCT detector with a resolution of 4 cm⁻¹.

The intermediate of catalysis was deduced by the in situ DRIFT spectroscopy, where the dynamics of the intermediates was measured by stopping the CO or H₂ in a flow of (CO + O₂) or (CO + O₂ + H₂), and by adding H₂ to (CO + O₂). Decrease of the intermediates with time was measured by subtracting the spectrum of a steady reaction from the in situ spectrum attained by removing CO or H₂ from (CO + O₂) or (CO + O₂ + H₂).

Catalytic oxidation of CO was carried out by using 1.5 g of FeO_x/Pt/TiO₂ catalyst mounted in a fixed bed flow reactor. A typical flow rate was 5% CO/N₂ (60 mL/min) + O₂ (1.5 mL/min) + H₂ (20 mL/min) and a balanced N₂ (18.5 mL/min) to make total flow rate in 100 mL/min. The effect of H₂ on the oxidation of CO was studied by adding H₂ (20 mL/min) to a flow of 5% CO/N₂ (60 mL/min) + O₂ (1.5 mL/min) + N₂, and the effect of H₂O was studied by bubbling N₂ through water at room temperature.

15 wt.% Pt/graphite powder and 15 wt.% Pt/Vulcan-C (0.8 g) were not so active for the PROX reaction of CO at room temperature, but the PROX reaction of CO was catalyzed at room temperature when a 5 wt.% Pt/graphite and 15 wt.% Pt/Vulcan-C were doped with 5 wt.% Ni-MgO. The reaction was performed by flowing a stoichiometric mixture of CO and O₂ (i.e., O₂/CO = 1/2), that is, O₂ (1.5 mL/min), CO (3.0 mL/min), H₂ (20 mL/min), and N₂ (75.5 mL/min). The hydrogen isotope on the oxidation of CO was studied by replacing D₂ with H₂ in a flow of (CO + O₂ + D₂).

3. Results and discussion

Conversion of CO and O₂ in a flow of CO (3.0 mL/min) + O₂ (1.5 mL/min) + H₂ (20 mL/min) + N₂ (75.5 mL/min) on 1 wt.% Pt/TiO₂ (0.4 g) was very low at room temperature as shown in Fig. 1(a). The conversion of O₂ and CO was markedly improved (85–90% CO and nearly 100% O₂) on the FeO_x/Pt/TiO₂ catalyst (0.8 g) although Pt content of the FeO_x/Pt/TiO₂ was ca. 0.4 wt.%. One remarkable feature of the oxidation of CO on the FeO_x/Pt/TiO₂ catalyst is enhancement by H₂ as shown in Fig. 1(b), because no such enhancement was observed on the oxidation of CO on Pt/TiO₂ catalyst. Therefore, not the structure or dispersion of Pt particles but the oxidation mechanism of CO in the presence of H₂ may be responsible for the low temperature oxidation of CO on FeO_x/Pt/TiO₂.

In this respect, the work of Alayoglu et al. on Pt-shell/Ru-core particles [11] is interesting. They discuss the hydrogen effect on the oxidation of CO from both the reaction mechanism and the structure. The activity of Pt-shell/Ru-core particles, Pt-Ru alloy particles, and a mixture of Pt and Ru particles for the oxidation of CO in H₂ was studied by a temperature programmed reaction in a flow of H₂ containing 1000 ppm ~1% CO and 0.5% O₂, and the oxidation of CO enhanced by hydrogen was observed on the Pt-shell/Ru-core catalyst. They calculated the adsorption energy and the reaction barrier by assuming several elementary reactions on a Pt-layer/Ru(0001)

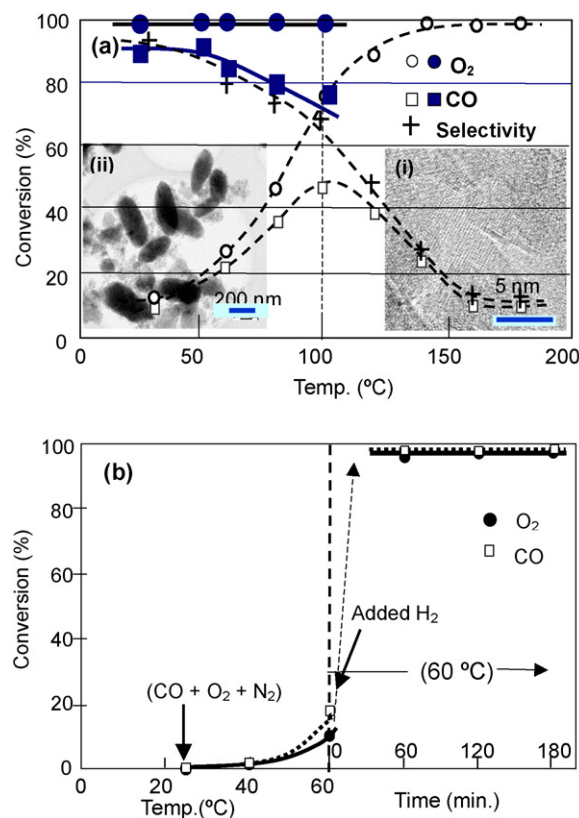


Fig. 1. (a) Conversion of CO and O₂ in a steady reaction of CO (3.0 mL/min) + O₂ (1.5 mL/min) + H₂ (20 mL/min) + N₂ (75.5 mL/min) on 1 wt.% Pt/TiO₂ (0.8 g, open symbol) and FeO_x/Pt/TiO₂ (0.4 wt.% Pt) (0.8 g, solid symbol). Inset TEM images are (i) Pt-TiO₂ and (ii) FeO_x/Pt/TiO₂. (b) Enhancement of a steady oxidation of CO in a flow of CO (1.5 mL/min) + O₂ (3 mL/min) + N₂ (95.5 mL/min) at 60 °C by H₂ (20 mL/min).

surface as a model of Pt-shell/Ru-core particles and compared the calculation on Pt(111) surface as a model of Pt particles, and proposed a suitable reaction mechanism in the premised elementary reactions. One important calculation was H-assisted dissociation of O₂ via hydroperoxy intermediate, H + O₂ → HO₂ → O + OH, and it was concluded that the H-assisted dissociation of O₂ was responsible for the preferential oxidation (PROX) reaction of CO in H₂ on the Pt-shell/Ru-core catalyst. However, they premised the competitive oxidation of CO(a) and H(a) with O(a) for the PROX reaction of CO. If the real mechanism for the PROX reaction of CO would be different from the competitive mechanism, their calculation has little scientific meaning.

The oxidation of CO enhanced by H₂ on FeO_x/Pt-TiO₂ catalyst shows a hydrogen isotope effect by H₂/D₂ and H₂O/D₂O (*r_H* > *r_D*) [6]. Hydrogen isotope effect suggests that the intermediate of the oxidation reaction of CO at the rate determining step involves hydrogen atom(s). In this reason, hydrogen assisted dissociation of O₂ proposed on the Pt-shell/Ru-core catalyst may not be appropriate on the FeO_x/Pt/TiO₂.

We found that the Pt supported on carbon nanotube (Pt/CNT) and on carbon nanofiber (Pt/CNF) takes extremely high catalytic activity for low temperature PROX reaction of CO [12]. Enhancement of the oxidation of CO by H₂ and/or H₂O is responsible for the low temperature PROX reaction of CO, and a hydrogen isotope effect on the oxidation of CO appears by H₂/D₂ as shown in Fig. 4. If Ni-MgO in CNT and Fe in CNF were purified, however, low temperature PROX reaction was markedly suppressed. The role of Ni-MgO is clearly proved on Pt/graphite and Pt/Vulcan-C catalysts as shown in Fig. 2. The kinetic feature of the oxidation of CO on Pt/CNT is very similar to that on FeO_x/Pt/TiO₂ catalyst, that is, the PROX reaction

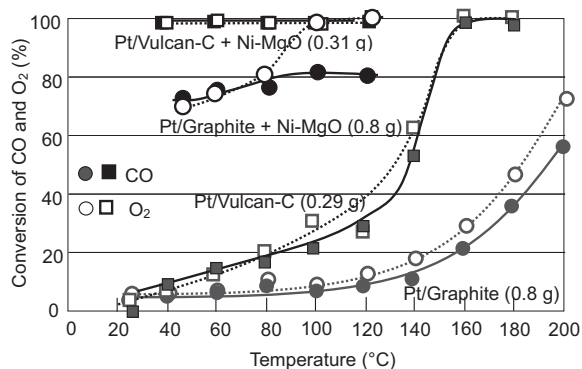


Fig. 2. 15 wt.% Pt/graphite (0.8 g) and 15 wt.% Pt/Vulcan-C (0.29 g) were poorly active for the PROX reaction of CO at room temperature. Doping Ni-MgO (5 wt.%) markedly improves the activity of 5 wt.% Pt/graphite (●,○) and 15 wt.% Pt/Vulcan-C (5 wt.%) (■,□). The reaction was performed in a flow of H₂ (20 mL/min)+CO (3 mL/min)+O₂ (1.5 mL/min)+N₂ (75.5 mL/min) on Pt/Graphite catalyst, and in a flow of CO (1.5 mL/min)+O₂ (1.5 mL/min)+H₂ (15.0 mL/min)+N₂ (38.5 mL/min) (56.5 mL/min in total) on Pt/Vulcan catalyst.

of CO in H₂ is not the competitive oxidation of CO(a) and H(a) with O(a), but a reaction via intermediates X_i as described by Eq. (1):



where (X_i) is the intermediates and (a) represents adsorption states.

As we discussed in our previous paper [2], amount of intermediates in a steady reaction is decided by a dynamic balance of the formation and the consumption of intermediates. As various adsorbed species exist on the catalyst in a steady state of the reaction, we have to extract the real intermediates. One promising way is to extract the adsorbed species changing with time when the reaction is stopped by removing CO or is enhanced by adding H₂. In this case, it should be reminded that the intermediates precede the rate determining step is detectable, but the intermediates after the rate determining step may be lower than the detectable level. Based on this idea, real intermediates were extracted by stopping CO during a steady PROX reaction of CO on the FeO_x/Pt/TiO₂ catalyst. The intermediates rapidly decreased according to the rate at the rate determining step. Fig. 3(a) shows the spectra changing with time when CO was removed from (CO + H₂ + O₂) on FeO_x/Pt/TiO₂. Almost equal amount of bridge-bonded CO and linearly bonded CO were detected on the FeO_x/Pt/TiO₂ catalyst during a steady PROX reaction of CO [3], and the bridge-bonded CO (1836 cm⁻¹) and linearly bonded CO (2073 cm⁻¹) were decreased with time (growth of negative peaks) as shown in Fig. 3. As the amount of CO(a) reflects a dynamic balance of the adsorption of CO(a) and followed reaction, CO(g) → CO(a) → X_i . Therefore, we confidently say that the adsorption or the diffusion of CO is not the rate determining step but the PROX reaction is controlled by a surface reaction.

When CO(g) was removed from (CO + O₂ + H₂), adsorbed CO(a) peaks were rapidly lowered, which reflects rapid reaction of CO(a) → X_i → CO₂. If the oxidation of CO(a) to CO₂ would proceed via intermediate (X_i) as described in Eq. (1), amount of intermediates (X_i) depends on the dynamic balance of CO(a) → (X_i) and (X_i) → CO₂. When the reaction (X_i) → CO₂ is a rate determining step, the amount of (X_i) in a steady reaction would be large. On the other hand, if reaction CO(a) → (X_i) is a rate determining step, the amount of (X_i) will be very lower. Fig. 3(a) shows the spectra of intermediates changing with time on the FeO_x/Pt/TiO₂ when CO is removed from (CO + H₂ + O₂) at 60 °C (333 K). Increase of negative peaks indicates the decrease of intermediates with time, and large negative peak reflects large amount of intermediates existing on the catalyst in a steady reaction of (CO + O₂ + H₂). The peak at 1836 cm⁻¹

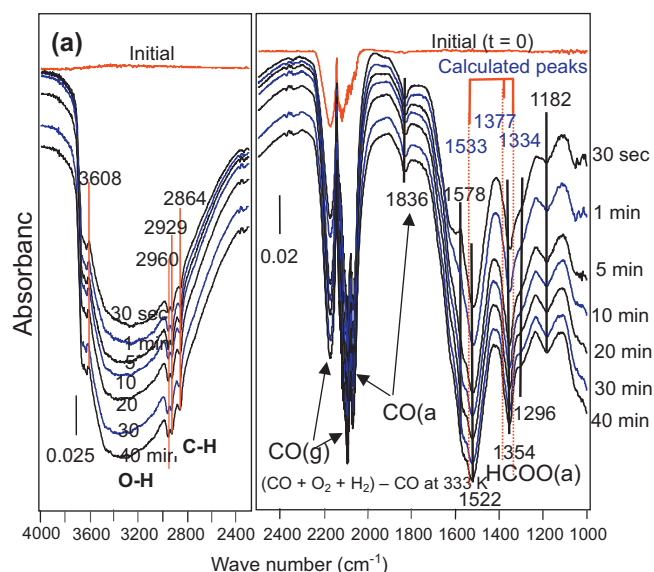
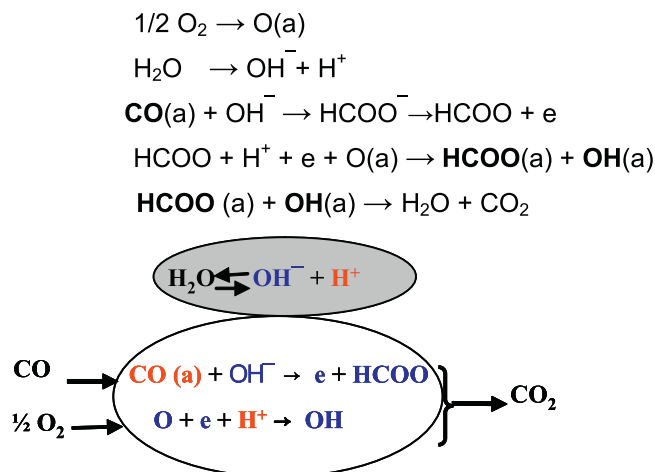


Fig. 3. (a) In situ DRIFT spectra attained on the FeO_x/Pt-TiO₂ catalyst when the CO in a flow (CO + O₂ + H₂) was removed at 60 °C. Negative peaks of HCOO (1522, 1354, 1296 cm⁻¹), OH (3350 cm⁻¹), and C-H (2960–2864 cm⁻¹) with time indicate the decrease of intermediates with time. Bicarbonate (1624 and 1360 cm⁻¹) and formate (1533, 1377, and 1334 cm⁻¹) calculated by the DFT are shown with the solid bar. (b) Growth of corresponding intermediate peaks with time, which reflects decrease of intermediates from the surface by removing gas phase CO.

is a bridge bonded CO(a) and the peaks at 1522 and 1354 cm⁻¹ (with a shoulder at 1296 cm⁻¹) are very close to the HCOO formed on a Pt/TiO₂ catalyst in oxidation of formaldehyde [13] and to adsorbed HCOOH (1524 and 1379 cm⁻¹) on TO₂(1 1 0) surface [14]. A density functional theory (DFT) calculation for a mono-dentate formate on a Ti-ion by the MPW1PW91 + Sdd basis set [15,16] gave the vibration bands at 1533 (ν_{as}), 1377, and 1334 (ν_s) cm⁻¹, in which the asymmetric vibration at 1533 cm⁻¹ was stronger than the symmetric vibration at 1334 cm⁻¹. In contrast, we observed slow growth of negative peak at 1632 cm⁻¹ assignable to bicarbonate on the FeO_x/Pt/TiO₂ catalyst when CO was removed from a flow of (CO + O₂). Growth of negative peaks of HCOO at 1522 cm⁻¹ and bicarbonate at 1632 cm⁻¹ were plotted against the time in Fig. 3(b). It is known that the large amount of HCOO intermediate is completely removed within a 30 s at 60 °C by removing the CO from gas phase, but bicarbonate intermediate ((OH)CO₂) needs more than 60 min to remove it from the surface. This result proves that oxidation mechanism of CO is different from in (CO + O₂ + H₂) and in (CO + O₂) on the FeO_x/Pt/TiO₂ catalyst, and HCOO(a) intermediate is responsible for the rapid oxidation of CO enhanced by H₂.



Scheme 1. PROX reaction of CO in H₂ catalyzed by a dual functional catalysis, in which H₂O plays as a positive feed back molecule recycling the oxidation of CO.

One of the notable changes in Fig. 3(a) is concomitant decrease of broad band (3000–3600 cm⁻¹) and HCOO (1522 cm⁻¹) peaks as shown in Fig. 3(b). We assigned the broad band is OH(a) intermediates instead of adsorbed H₂O(a) because a characteristic scissor vibration mode of adsorbed H₂O usually appears at ca. 1650 cm⁻¹ is very weak. In addition, the broad band and HCOO(a) peaks are simultaneously removed from the catalyst surface when CO is removed from a flow of (CO+O₂+H₂) although H₂ and O₂ exist in gas phase. Therefore, the broad band at 3000–3600 cm⁻¹ is not adsorbed H₂O but a reaction intermediate assignable as OH species. Accordingly, we can conclude that the rate determining step of the PROX reaction of CO in H₂ is the oxidation of HCOO(a) with OH(a) instead of O(a), HCOO(a)+OH(a)→H₂O+CO₂. This mechanism explains well the hydrogen isotope effect observed on the oxidation of CO.

Taking these results into account, the low temperature PROX reaction on the FeO_x/Pt/TiO₂ catalyst may take place by a dual functional catalysis as described below, that is, ionic dissociation of H₂O on FeO_x, and the migration of OH⁻ anion over the surface and reacts with CO to form HCOO⁻ on Pt. At the same time, H⁺ may react with O⁻ (e rapidly reacts with O(a)) to form OH(a) on Pt, and the rate determining step is the reaction of OH(a) with HCOO(a) on Pt as described in Scheme 1:

We found that the Pt supported on a CNT and a CNF gave extremely high catalytic activity for the PROX reaction of CO in H₂ at room temperature [5], where the used CNT was prepared from CH₄ by using Ni–MgO catalyst and CNF was prepared in gas phase by using ferrocene catalyst. If Ni–MgO and Fe being localized at the tail end of CNT and CNF were removed (CNT-p and CNF-p), Pt/CNT-p and Pt/CNF-p lost the activity for low temperature PROX reaction of CO. In contrast, the Pt/CNT-p and Pt/CNF-p recovered the activity by doping Ni–MgO or Fe–Al₂O₃. Such remarked role of Ni–MgO and Fe was confirmed on Pt/graphite and Pt/Vulcan-C (Pt/a-C) in Fig. 2, where Pt/graphite and Pt/Vulcan-C (a-C) are inactive for low temperature PROX reaction of CO but change to active catalyst by doping Ni–MgO and Fe–Al₂O₃ [12]. The TEM image of CNT proves that the Ni–MgO is localized at the tail end of CNT whereas Pt particles are on the outer wall of CNT, that is, Pt-particles are separated from the Ni–MgO and Fe. It should be emphasized that the kinetic feature of the PROX reaction of CO on Pt/CNT catalyst is very similar to that on FeO_x/Pt/TiO₂, that is, the oxidation of CO is markedly enhanced by H₂ and a hydrogen isotope effect appears on the oxi-

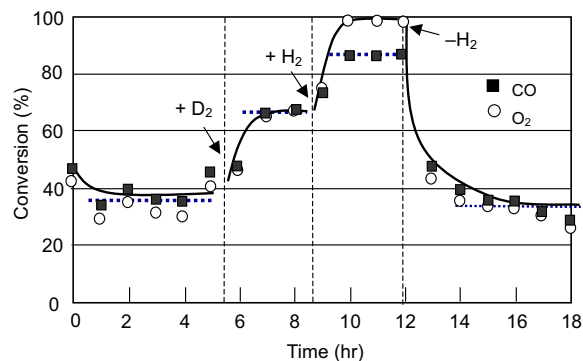


Fig. 4. Oxidation of CO on a 10 wt.% Pt/CNT catalyst is enhanced by hydrogen, and a hydrogen isotope effect is observed by H₂/D₂. Conversion was obtained in a steady state by flowing [CO (3.0 mL/min)+O₂ (1.5 mL/min)+D₂ (20.0 mL/min)+N₂ (95.5 mL/min)] and replaced D₂ with H₂ (20.0 mL/min) or vice versa at 45 °C.

ation of CO by H₂/D₂ as shown in Fig. 4. Taking these results into account, we could conclude that the role of Ni–MgO and Fe–Al₂O₃ on Pt/C catalyst is similar to that of FeO_x of FeO_x/Pt/TiO₂ catalyst, that is, the oxidation of CO may be catalyzed by a dual functional mechanism such as described above. That is, H₂O undergoes dissociation into H⁺ and OH⁻, and the OH⁻ anion reacts with CO to form HCOO⁻, which is similar to a known reaction of CO with Ca(OH)₂. On the other hand, the electron released from HCOO⁻ reacts with adsorbed O(a) and H⁺ to form OH(a) on Pt. These processes would be rapid at room temperature, so that the reaction of HCOO(a) with OH(a) on Pt becomes the rate determining step. However, it is difficult to get spectroscopic evidences of these intermediates on the Pt/CNT catalyst.

4. Conclusion

Ni–MgO in CNT and Fe in CNF are separated from Pt-particles but they are indispensable for low temperature PROX reaction of CO on Pt/CNT and Pt/CNF. Kinetic feature of the low temperature PROX reaction on Pt/CNT is very similar to that on FeO_x/Pt/TiO₂ catalyst. The results suggest a dual functional catalysis involving an ionic process of CO(a)+OH⁻→HCOO⁻ for the low temperature PROX reaction, and the rate determining step is the oxidation of HCOO with OH, OH+HCOO→H₂O+CO₂.

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