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# The Mechanism for the Selective Oxidation of CO Enhanced by $H_2O$ on a Novel PROC Catalyst

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**Abstract** Preferential oxidation (PROX) reaction of CO in $H_2$ catalyzed by a new catalyst of $FeO_x/Pt/TiO_2$ (Fe: Pt: $TiO_2$ = 100: 1: 100) was studied by dynamic in-situ DRIFT-IR spectroscopy. The oxidation of CO is markedly enhanced by $H_2$ and $H_2O$, and the enhancement by $H_2/D_2$ and $H_2O/D_2O$ takes a common hydrogen isotope. Dynamics of DRIFT-IR spectroscopy suggests that the oxidation of CO with $O_2$ in the absence of $H_2$ proceeds via bicarbonate intermediate. In contrast, rapid oxidation of CO in the presence of $H_2$ proceeds via HCOO intermediate and the subsequent oxidation of HCOO by the reaction with OH, that is, CO + OH→ HCOO and HCOO + OH → $CO_2$ + $H_2O$. The latter reaction is a rate determining step being responsible for a common hydrogen isotope effect by $H_2/D_2$ and $H_2O/D_2O$.

**Keywords** Mechanism of CO oxidation reaction · Novel PROX catalyst · $FeO_x/Pt/TiO_2$ · Dynamics of in-situ IR spectroscopy · $H_2O$ promoted oxidation of CO · Intermediates, formate and bicarbonate · Rate determining step · Hydrogen isotope effect

## 1 Introduction

Preferential oxidation (PROX) of CO in $H_2$ is an important process to produce CO free hydrogen gas for hydrogen fuel cell. On the other hand, highly selective oxidation of CO in excess $H_2$ is undoubtedly a curious phenomenon if we consider the selectivity by traditional kinetics, because CO adsorbs stronger than $H_2$ on metallic catalysts and the oxidation of $H_2$ is far more rapid than that of CO. Therefore, the mechanism of the PROX reaction will make clear a valuable insight into the selectivity behind the heterogeneous catalysis. It is known that Ru and Au supported on oxide are a high performance PROX catalyst, but it is not obvious whether this is intrinsic property of Ru and Au or a kinetic phenomenon. In addition, when the oxidation of CO is enhanced by $H_2O$, the reaction is often discussed by relating to the shift reaction CO + $H_2O$ → $H_2$ + $CO_2$ [1]. The mechanism shift reaction has been explained by nucleophilic attack of $H_2O$ to coordinated CO and the oxidation is catalyzed by a redox cycle of central metal ion with the reduction of $H^+$ to $H_2$ [2]. In previous paper, we developed a new PROX catalyst, $FeO_x/Pt/TiO_2$, on which the oxidation of CO is markedly accelerated by adding $H_2$ and/or $H_2O$ at 60 °C, but no water gas shift reaction occurs even at 80 °C.

It should be mentioned that the activity and the selectivity for the oxidation of CO in $H_2$ on a 1 wt% Pt loaded on a $FeO_x/TiO_2$ ($FeO_x$ is ca. 100 wt% in Fe) are similar to that on the Pt catalysts supported on $TiO_2$, $Al_2O_3$ and $CeO_2$. However, when a 1 wt% $Pt/TiO_2$ is covered with 130–140 wt% $FeO_x$ (ca. 100 wt% in Fe), the activity and the selectivity for the PROX reaction of CO are dramatically improved as referred the reaction at 60 °C in Fig. 1(a) and (b) [3]. Therefore, we could say the $FeO_x/Pt/TiO_2$ is a new PROX catalyst being active at low temperature. It is evident that the enhancement by $H_2$ and/or $H_2O$ is responsible for high performance of this new PROX catalyst, that is, ca. 18–20% conversion of CO in absence of $H_2$ is elevated to ca. 90–100% by adding $H_2$ or $H_2O$ at 60 °C

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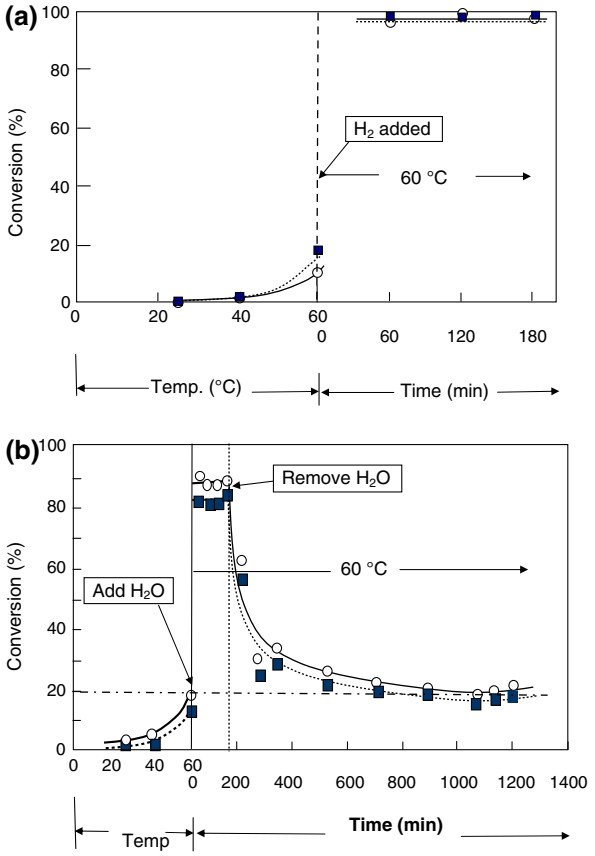



**Fig. 1** Oxidation of CO on the $FeO_x/Pt/TiO_2$ catalyst (1.5 g) enhanced by $H_2$ **(a)** (20 ml/min) and $H_2O$ **(b)**. Total flow rate of 100 ml/min was attained by a mixture of **(a)** 5% $CO/N_2$ (60 ml/min) + $O_2$ (1.5 ml/min) + $N_2$ (38.5 ml/min), and **(b)** 5% $CO/N_2$ (60 ml/min) + $O_2$ (1.5 ml/min) + $H_2$ (20 ml/min) + $N_2$ (18.5 ml/min). ■ CO conversion, ◯ $O_2$ conversion

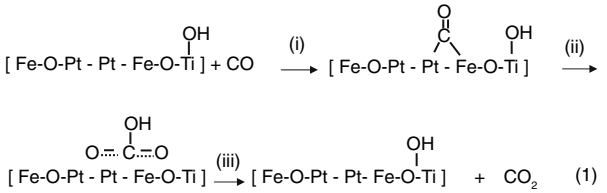
[4]. We also found that the enhancement of CO conversion by $H_2/D_2$ and $H_2O/D_2O$ takes a common hydrogen isotope effect of ca. 1.4 at 60 °C [5]. These results strongly suggest that $H_2O$ molecule contributes to the oxidation reaction of CO and hydrogen is involved at the rate determining step on the $FeO_x/Pt/TiO_2$ catalyst. It should be pointed out once again that no shift reaction, $CO + H_2O \rightarrow CO_2 + H_2$, occurs on this catalyst at 80 °C. Taking these facts into account, the reaction mechanism was deduced from the dynamic spectroscopy of intermediates taking place by adding or removing CO and/or $H_2$.

## 2 Experimental

The spectra were measured using a Nexus 670 (Thermo Nicolet) in-situ diffuse reflection chamber with a high sensitivity MCT detector by a resolution of 4 $cm^{-1}$. After pretreatment of the catalyst ($FeO_x/Pt/TiO_2$) at 350 °C in pure nitrogen, a steady state DRIFT IR spectrum was obtained by exposing the catalyst to the flow of a desired mixture of reactant gases at 60 °C. A total flow rate of 240 ml/min of $(CO + O_2 + H_2 + N_2)$ was composed 120 ml/min of 10% CO in $N_2$, 6 ml/min of $O_2$, and 40 ml/min of $H_2$ with a balanced gas of $N_2$ (74 ml/min), and that of $(CO + O_2 + N_2)$ was composed of 120 ml/min of 10% CO in $N_2$, 6 ml/min of $O_2$, and 114 ml/min of a balanced $N_2$. The dynamics of intermediates were deduced by the in-situ IR spectrum obtained by stopping the CO flow of $(CO + O_2 + N_2)$ or $(CO + O_2 + H_2 + N_2)$. The enhancement effect of the reaction by $H_2$ was studied by adding $H_2$ to $(CO + O_2 + N_2)$ or by removing $H_2$ from $(CO + O_2 + H_2 + N_2)$. Subtraction of the steady-state DRIFT spectrum from the flow of $(CO + O_2 + N_2)$ or $(CO + O_2 + H_2 + N_2)$ yielded the dynamic change of the surface species in response to the addition or removal of CO in the presence or absence of $H_2$.

## 3 Results and Discussion

If IR detectable species are the intermediate of the oxidation of CO, their intensity should be decreased by stopping the CO in a flow of either $(CO + O_2 + N_2)$ or $(CO + O_2 + H_2 + N_2)$. Figure 2(a) shows the change of the DRIFT-IR spectrum by stopping CO at 60 °C in the absence of $H_2$. When the CO of $(CO + O_2 + N_2)$ was stopped, negative peaks were grown at 1,836 $cm^{-1}$, 1,824 $cm^{-1}$, 1,632 $cm^{-1}$, 1,396 $cm^{-1}$, and 1,292 $cm^{-1}$. These peaks reflect the decrease of adsorbed species by removing CO from the gas phase. Negative bands at 1,836 $cm^{-1}$ and 1,824 $cm^{-1}$ are the decrease of bridge-adsorbed CO by the reaction with $O_2$, where the two bands may be the CO on Pt–Pt and Pt–Fe sites, respectively [6]. The other three peaks at 1,632 $cm^{-1}$, 1,396 $cm^{-1}$ and 1,293 $cm^{-1}$ are temporarily assigned as a bicarbonate intermediate according to references [7–9]. It is an interesting fact that the negative growth of the bicarbonate peaks accompanies with the positive growth of the OH peaks at 3,691 $cm^{-1}$ and 3,697 $cm^{-1}$. The surface may have a constant amount of OH species even in the absence of $H_2$. Therefore, if a part of these OH species steadily contribute to the formation of bicarbonate species during the oxidation of CO with $O_2$, decrease of the bicarbonate species by stopping CO will make increase surface OH species according to **step (iii)** in Eq. 1.



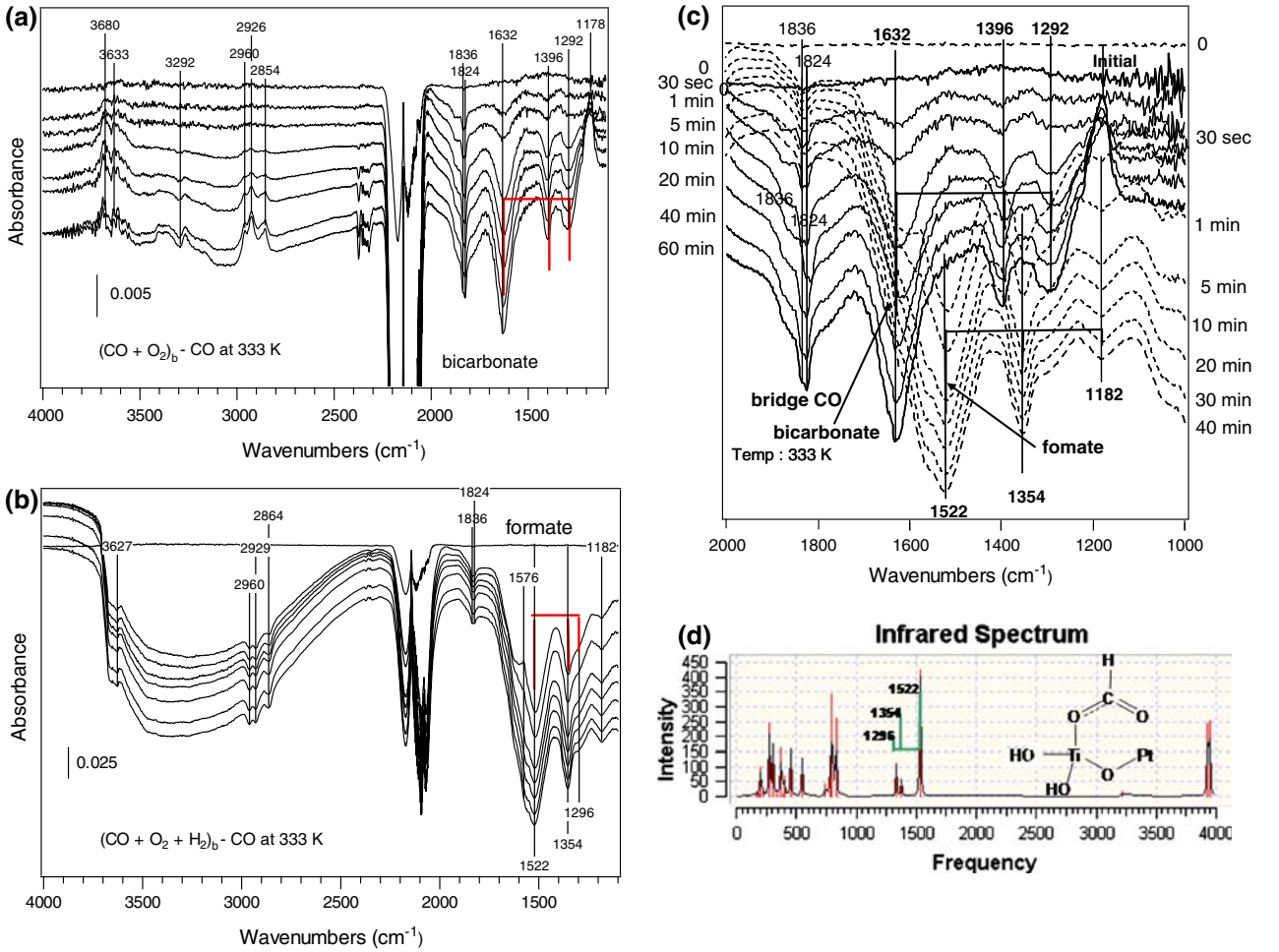



**Fig. 2** (**a**) Dynamics of the in-situ DRIFT-IR spectrum of a $FeO_x$/Pt/$TiO_2$ catalyst at 60 °C when the CO in a flow of (CO + $O_2$) was stopped. Negative growth of the spectrum assignable to bicarbonate was recorded at 0 (initial), 30 sec, 1, 5, 10, 20, 40, 60 min after the stop of CO. (**b**) Dynamics of the in-situ DRIFT-IR spectrum of a $FeO_x$/Pt/$TiO_2$ catalyst at 60 °C when the CO in the flow of (CO + $O_2$ + $H_2$) was stopped**.** Negative growth of the spectrum assignable to formate was recorded at 0 (initial), 30 sec, 1, 5, 10, 20, 30, 40 min after the stop of CO. (**c**) Spectra **a** of bicarbonate and **b** of fomate were put on together. (**d**) Calculation of formate was performed for a model using B3LYP + LANL2DZ method

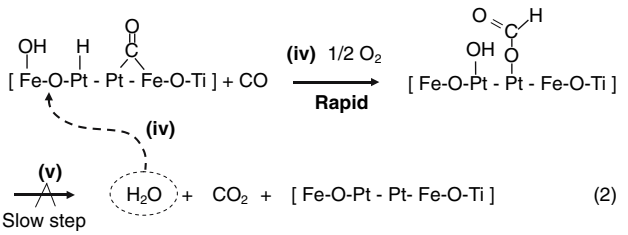
In contrast, when the CO in a flow of (CO + $O_2$ + $H_2$) was stopped, negatively grown bands were different from the bicarbonate peaks as shown in Fig. 2(b). That is, the bridge-adsorbed CO peaks at 1,836 $cm^{-1}$ and 1,824 $cm^{-1}$ are the same, but the peaks at 1,522 $cm^{-1}$, 1,354 $cm^{-1}$ and 1,296 $cm^{-1}$ (shoulder) are undoubtedly different from the bicarbonate peaks. In addition, the decreasing rate of these peaks is very rapid to accomplish within 1 min. These bands observed in the presence of $H_2$ are very similar to the formate spectrum observed during the oxidation of formaldehyde ($H_2CO$) at 1,522 $cm^{-1}$ ($\upsilon_{as}$) and 1,354 $cm^{-1}$ ($\upsilon_s$) on the Pt/$TiO_2$ catalyst (the same $TiO_2$ used in here) [10] and the peaks given by the adsorption of HCOOH on a Pt/$TiO_2$ [9]. By putting spectrum (a) to spectrum (b) in Fig. 2(c), it is evident that the oxidation of CO proceeds via different intermediates in the presence of $H_2$. That is, the bridge-adsorbed CO rapidly changes to HCOO in the presence of $H_2$ or $H_2O$, and is followed by a rapid decomposition as discussed below.

The peaks of formate depend on its conformation on metal or oxide, but the characteristics peaks of mono- or bi-dentate are similar on various systems [11–13]. We performed a simple calculation for a model shown in Fig. 2(d) by using B3LYP + LANL2DZ method [14]. The calculation gives characteristic peaks at 1,300 ($\upsilon_s$), 1,369 and 1,485 $cm^{-1}$($\upsilon_{as}$), which may correspond to the experimental peaks at 1,354 $cm^{-1}$ ($\upsilon_s$) and 1,522 $cm^{-1}$ ($\upsilon_{as}$), but their agreement is not so good. One impressive result of the dynamic in-situ IR spectroscopy is that the negative growth of formate peaks accompanies negative growth of broad OH bands at 3,000–3,600 $cm^{-1}$ and C–H vibration bands at 2,870–2,960 $cm^{-1}$ as shown in Fig. 2(b). This fact

indicates that the OH species contribute to the decomposition of HCOO intermediates into $CO_2$ and $H_2O$. The amount of intermediate species detected during catalysis depends on the dynamic balance of the formation of intermediate and its forward reaction. When the CO is removed from a steady flow of ($CO + O_2 + H_2$), the bridge-adsorbed CO completely disappeared within a 30 s as shown in Fig. 2(b). In contrast, the negative growth of the bridge-adsorbed CO as well as of the bicarbonate in the absence of $H_2$ are slow as shown in Fig. 2(a), which takes more than 10 min. Very rapid decrease of the adsorbed CO may be schematically described by step (iv) in Eq. 2, that is, the bridge-adsorbed CO reacts very rapidly with $Fe–OH^-$ and the produced HCOO subsequently reacts with Pt–OH to decompose into $CO_2$ and $H_2O$ according to step (v). It is known that formic acid is formed by the reaction of CO with $Ca(OH)_2$ or NaOH. Therefore, we could say that the step (v) is a thermodynamically feasible reaction.

The dynamics of the spectroscopy taking place by stopping gas phase CO shown in Fig. 2(b) represents the simultaneous decrease of the broad band at 3,000–3,600 $cm^{-1}$ and the HCOO bands with time. This fact reveals that the HCOO undergoes oxidative decomposition by the reaction with OH on Pt surface as is described by the **step (v)**, which is the rate determining slow step being responsible for the hydrogen isotope effect. In addition, an interesting point is that the local hydrophilic property is directly influenced by the interaction with adsorbed species.

Accordingly, we could say that $H_2O$ molecule promotes the reaction as a molecular catalyst, where a small amount of $H_2O$ is steadily provided by the oxidation of $H_2$ In other words, highly selective oxidation of CO is attained by repeated formation of HCOO according to Eq. 2.




As indicated above, the amount of HCOO depends on the dynamic balance of the formation and decomposition of HCOO intermediate. Therefore, the amount of HCOO should be influenced not only by CO but also by $H_2$ (or $H_2O$). In a flow of ($CO + O_2$), a trace amount of $H_2O$ is hard to remove so that a small amount of HCOO necessarily exists on the catalyst during reaction. When $H_2$ is added to a flow of ($CO + O_2$), a small amount of HCOO on the surface is quickly decomposed within 1 min as shown by the dotted spectrum (a) in Fig. 3 by reacting with OH formed on the Pt, because the formation of $HCOO^-$ is behind by the slow increase of $Fe–OH^-$. In contrast, when $H_2$ is removed from a flow of ($CO + O_2 + H_2$), the decomposition of HCOO (vi) is suppressed, but the reaction of CO with $Fe–OH^-$ does not stop immediately because enough amount of $Fe–OH^-$ exists on the surface. As a result, the HCOO is increased instead of decreased as shown in Fig. 3(b).

## 4 Conclusion

One important conclusion is that we cannot gain insight into the activity and selectivity without clarifying the reaction mechanism, although the catalytic activity and/or the selectivity of supported metal catalysts are so often

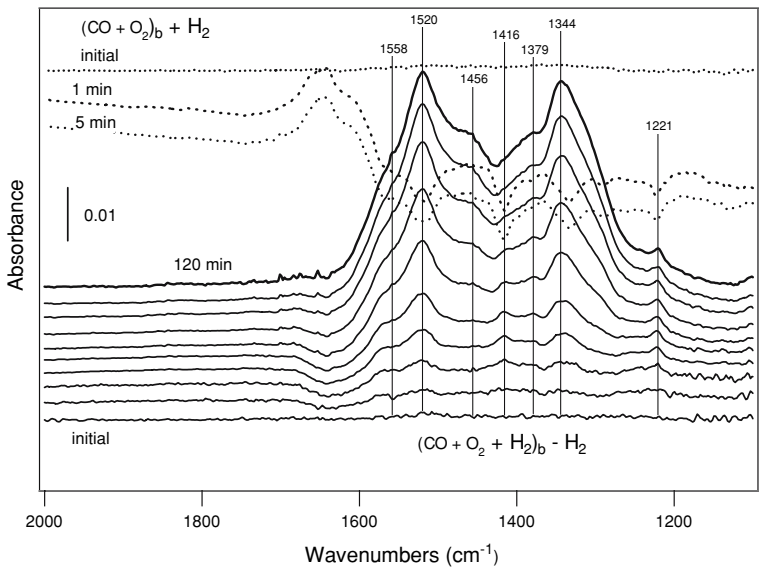



**Fig. 3** Dynamics of the in-situ DRIFT-IR spectrum taking place by the addition of $H_2$ to a flow of ($CO + O_2$) or by the remove of $H_2$ form a flow of ($CO + H_2 + O_2$) at 60 °C

discussed in relation to the particle size. The oxidation of CO via HCOO intermediate is responsible for the PROX reaction of CO on the $FeO_x$/Pt/$TiO_2$ catalyst, but it is undoubtedly different form the shift reaction. It is also shown that the subsequent oxidative decomposition of HCOO with OH is the rate determining step, so that $H_2/D_2$ and $H_2O/D_2O$ give a common hydrogen isotope effect. The role of $FeO_x$ is still unsolved big puzzle, but I could say that one vital role of $FeO_x$ is the formation of bridged CO adsorption sites, which may be Pt–Fe sites. Similar role was observed on a Au/$TiO_2$ by loading a large amount of $FeO_x$, where a poorly active Au/$TiO_2$ catalyst with large Au particles changes to a superior active catalyst by loading a large amount of $FeO_x$, and the adsorption of bridge-adsorbed CO on Au–Fe sites was confirmed by in-situ IR spectroscopy [15]. Such unexpected restructuring or new site formation by $FeO_x$ was supported quite recently by the calculation for the $FeO_x$–Pt–$TiO_2$ system [16]. Finally, it should be pointed out that the collision of reactant molecules from gas phase to Pt or Au particles should be markedly lowered by loading with a large amount of $FeO_x$, but the reaction rate is markedly enhanced. We could say that this is a typical common feature of heterogeneous system observed on the crystal habit, enzyme reaction, sticking probability, and heterogeneous reaction, that is, it is caused by the efficient delivery of molecules or atoms by rapid migration over the inactive surface area to active sites. This important ignored problem will be discussed in a next paper.

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