# Significant enhancement of the oxidation of CO by H_2 and/or H_2O on a FeO_x/Pt/TiO_2 catalyst

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Oxidation of CO on the FeO_x/Pt/TiO_2 catalyst is markedly enhanced by H_2 and/or H_2O at 60 °C, but no such enhancement is observed on the Pt/TiO_2 catalyst, but shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) does not occur on the FeO_x/Pt/TiO_2 catalyst at 60 °C. DRIFT-IR spectroscopy reveals that the fraction of bridge bonded CO increases while that of linearly bonded CO decreases on the FeO_x loaded Pt/TiO_2 catalyst. The *in-situ* DRIFT IR spectra proved that the bridged CO is more reactive than the linearly bonded CO with respect to O_2, and the reaction of the bridge-bonded CO with O_2 as well as of the linearly bonded CO is markedly enhanced by adding H_2 to a flow of $CO + O_2$. From these results, we deduced that the promoting effect of H_2 and/or H_2O is responsible for the preferential oxidation (PROX) reaction of CO on the FeO_x/Pt/TiO_2 catalyst, and a following new mechanism via the hydroxyl carbonyl or bicarbonate intermediate is proposed for the oxidation of CO in the presence of H_2O.
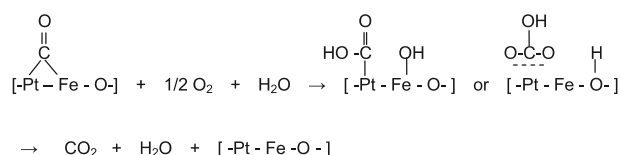
KEY WORDS: preferential oxidation (PROX) reaction of CO in H_2; CO oxidation enhanced by H_2O; CO oxidation enhanced by H_2; FeO_x loaded Pt/TiO_2 catalyst; *In-situ* DRIFT IR; hydroxyl carbonyl intermediate; bi-carbonate intermediate.

1. Introduction

It is well known that the catalytic activity of precious metals supported on oxides depends some times critically on the oxides, but the role of the oxides is still a puzzle of heterogeneous catalysis. So far, improvement of activity has been explained by such factors as size, thickness, crystal planes, lattice strain of metallic particles on the oxide, and also so often by the distinctive electronic state of the particles or by the name of synergetic effect of support. Such a change in the wording, however, does not lead to scientific sufficient understanding of the activity. The activity of Au catalyst supported on oxides is a typical case. It has been accepted that the activity for the oxidation of CO of supported Au catalyst depends on the size of Au particle [1,2], but Chen and Goodman [3] have claimed that the activity depends on the array of Au atoms and the size and the perimeter of Au are not important. These facts indicate that the activity is still controversial in relating to the site and kinetics [1,4].

From a view point of chemical kinetics, the activity (per site) will vary by changing the rate determining step (rate constant) or by opening a new reaction route. It has been tacitly assumed that the reaction between adsorbed CO and adsorbed O atom is the slow step of oxidation of CO on the supported metal catalyst, where the adsorbed CO and O atoms are provided from the gas phase onto metal particles. However, the reaction is not so simple as visualized by such mechanism, because the molecules are transported to active sites via precursor state formed the support. Therefore, the surface diffusion of precursor molecules or intermediates is critically important to understand the activity. In fact, when the migration of precursor molecule is improved by water molecule, the catalytic activity is markedly enhanced [5,6]. In our previous paper [7], the unique improvement of the activity was found by loading a large amount of FeO_x on the oxide supported Pt catalysts (TiO_2, Al_2O_3, and CeO_2). A typical example is shown in figure 1, where the activity and the selectivity of 1 wt.% Pt/TiO_2 catalyst are markedly improved by loading a large amount of FeO_x (ca. 100 wt.% in Fe atom). The IR spectrum of this catalyst showed that the fraction of linearly bonded CO is decreased while that of bridged CO is increased by loading FeO_x on the Pt/TiO_2 catalyst [8]. The role of FeO_x is not only limited to such the modification of Pt-sites as observed by the adsorption of CO but the kinetic enhancement in the presence of H_2

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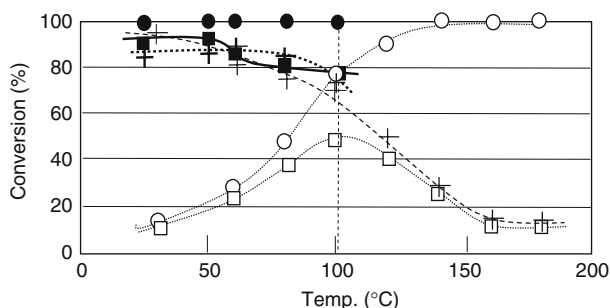E-mail: ktanaka@sit.ac.jp

Figure 1. Oxidation of CO in H_2 on 1 wt.% Pt/TiO_2 (open symbols) and 100 wt.% FeO_x loaded Pt/TiO_2 (solid symbols). CO (3 ml/min) + O_2 (1.5 ml/min) + H_2 (20 ml/min) was adjusted to be 100 ml/min by adding N_2, and pathed through 1.5 g catalyst. ($\bigcirc$, $\bullet$) O_2 conversion, ($\square$, $\blacksquare$) CO conversion, (+, +) selectivity to CO.

and/or H_2O is essentially important for the PROX reaction of CO on the $FeO_x/Pt/TiO_2$ catalyst as discussed in this paper.

2. Experiment

FeO_x was loaded on 1 wt.% Pt/TiO_2 by dipping the Pt/TiO_2 calcined in air at 400 °C in a solution of $Fe(NO_3)_3$. The weight of loaded Fe was almost equal to that of the Pt/TiO_2, which denotes 100 wt.% $FeO_x/Pt/TiO_2$ catalyst ($Fe/Pt \simeq 350$). After the loading of whole $Fe(NO_3)_3$ on the catalyst, it was again calcined at 400 °C in air. The oxidation of CO was carried out by a fixed-bed flow reactor with 1.5 g of catalyst, where a typical flow was 5% CO/N_2 (60 ml/min), O_2 (1.5 ml/min), H_2 (20 ml/min), and a balance gas of N_2 (18.5 ml/min), and the total flow rate was adjusted to be 100 ml/min by N_2 flow. Steady state conversion was obtained by maintaining the flow for more than 30 min at each reaction temperature. The promoting effect of H_2 was measured by adding H_2 (20 ml/min) to a flow of 5% CO/N_2 (60 ml/min) + O_2 (1.5 ml/min) + N_2. The effect of H_2O was studied by bubbling N_2 through a water tank at room temperature, where the flow of N_2 was adjusted to be 20 ml/min in the presence of H_2 and 40 ml/min in absence of H_2. The DRIFT-IR (Diffuse Reflectance IR-Fourier Transform) spectra were measured by a Nexus 670 (Thermo Nicolet) *in-situ* DRIFTS spectrometer with *in-situ* diffuse reflection chamber and a high sensitivity MCT detector. The spectrum was measured with a resolution of 4 cm^{-1} by using 0.06 g catalyst at 40 °C (unless another temperature is indicated). The *in-situ* IR was measured in a flow of a mixture of 3% CO/N_2 (200 ml/min) + O_2 (3ml/min) + N_2 (40 ml/min), and the spectrum in the presence of H_2 was measured by replacing N_2 (40 ml/min) with a flow of H_2. As prepared $FeO_x/Pt/TiO_2$ had red brown color, but changed to dark brown after the oxidation reaction of CO in H_2. The XRD

patterns showed that Fe_2O_3 changed to Fe_3O_4 during the oxidation of CO in H_2.

3. Results and discussion

Oxidation of CO in excess H_2 on 1 wt.% Pt/TiO_2 catalyst was studied by flowing a mixture of CO (3 ml/min) + O_2 (1.5 ml/min) + H_2 (20 ml/min) + N_2 (75.5 ml/min) through 1.5 g of catalyst. The conversion of CO was about 20% on a Pt/TiO_2 catalyst at 60 °C, but 100% O_2 conversion with about 90% CO conversion ($CO/O_2 = 2/1$) was attained on the FeO_x loaded catalyst ($FeO_x/Pt/TiO_2$) even at temperatures lower than 60 °C (figure 1). Interestingly, the CO conversion in the absence of H_2 is only ca. 17% on the $FeO_x/Pt/TiO_2$ catalyst at 60 °C as shown in figure 2(a). The CO conversion in a flow of 3% CO/N_2 (60 ml/min) + O_2 (1.5 ml/min) + N_2 (38.5 ml/min), however, is enhanced to nearly 100% by adding 20 ml/min of H_2. It should be noted that no such enhancement due to H_2 was observed on the Pt/TiO_2 catalyst. From these results, we deduce that the exceptional high activity of the $FeO_x/Pt/TiO_2$ catalyst is not only due to the bridged CO on the Pt-sites but the kinetic promotion of the oxidation of CO in the presence of H_2 is decisively important. A similar role of FeO_x was also found on a 1 wt.% Au/TiO_2 catalyst [9]. It should be pointed out that if H_2 would participate in the catalytic oxidation of CO, the oxidation of CO necessarily accompanies a constant consumption of H_2, so it is difficult to attain the preferential oxidation (PROX) reaction of CO.

We found that the oxidation of CO on the $FeO_x/Pt/TiO_2$ catalyst is also significantly promoted by H_2O. As shown in figure 2(b), the CO conversion was enhanced from ca. 17% to more than 80% at 60 °C by adding H_2O moisture in a flow of N_2 (38.5 ml/min), where H_2 flow was stopped. When the moisture was removed from the N_2 flow, the CO conversion was went down steeply and reached the initial value after about 15 h. It should be pointed out that the H_2O molecule does not appear in the over-all oxidation reaction of CO, CO + 1/2 O_2 → CO_2 which suggests that a trace amount of H_2O formed by the oxidation of H_2 may promote the oxidation reaction of CO on the $FeO_x/Pt/TiO_2$ catalyst in the presence of H_2, where only a limited amount of H_2 is consumed. The role of H_2O in the oxidation of ethylene to acetaldehyde by $PdCl_2$ catalyst is analogous, C_2H_4 + 1/2 O_2 → CH_3CHO (so called Wacher reaction), in which H_2O does not appear in the over-all reaction but promotes the reaction [10]. It should be emphasized that no promoting effect of H_2O was observed on the Pt/TiO_2 catalyst as shown in figure 2(c). Therefore, we could conclude that the unique feature of the $FeO_x/Pt/TiO_2$ catalyst for the PROX reaction of CO is due to the promotion of the oxidation of CO effect by
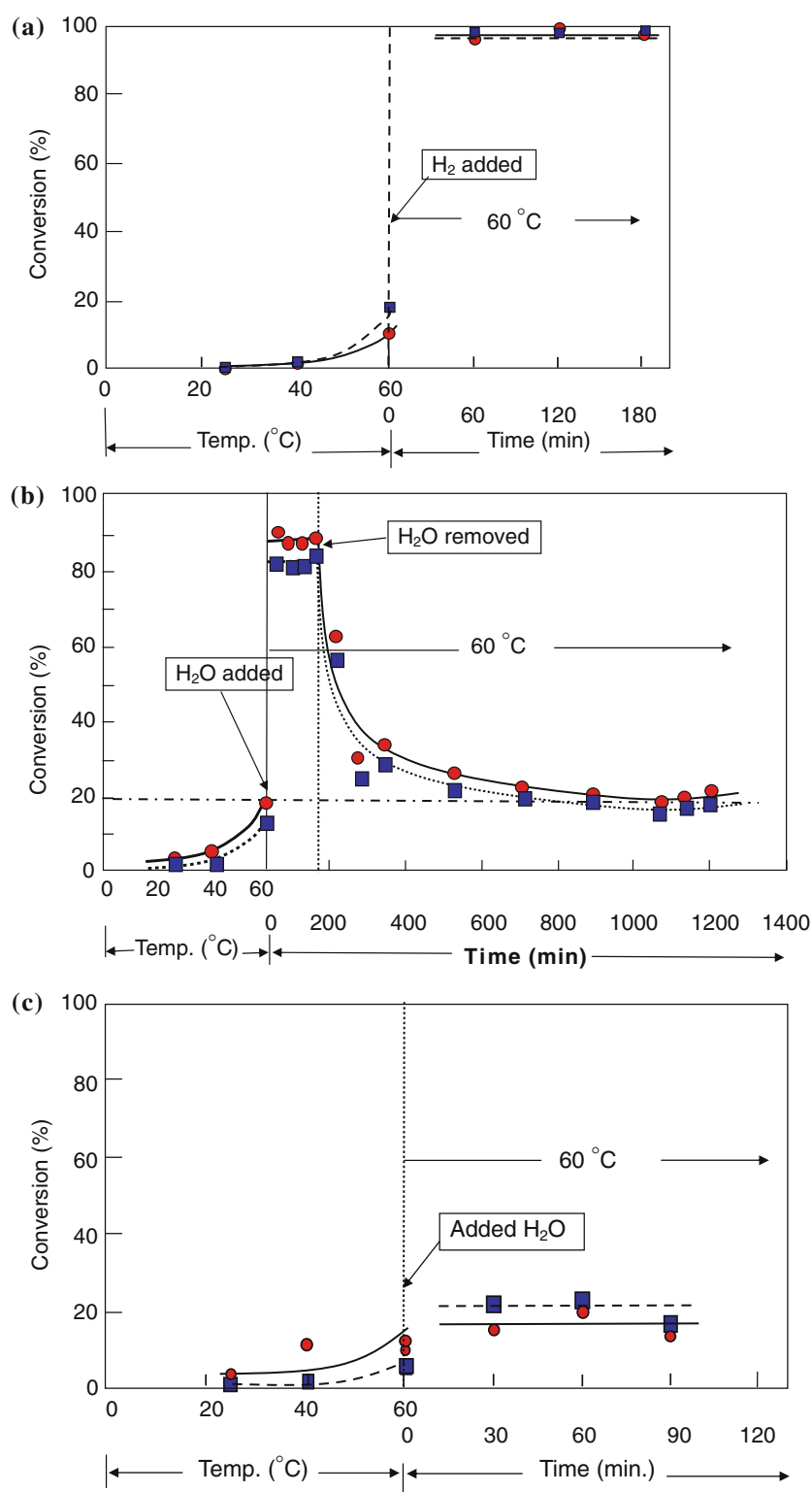
Figure 2. Oxidation of CO enhanced by (a) H_2 and (b) H_2O on the $FeO_x/Pt/TiO_2$ catalyst. The reaction was performed at a flow rate of 100 ml/min. (a) 5% CO/N_2 (60 ml/min) + O_2 (1.5 ml/min) + N_2 (38.5 ml/min). (b) 5% CO/N_2 (60 ml/min) + O_2 (1.5 ml/min) + H_2 (20 ml/min) + N_2 (18.5 ml/min). (c) No enhancement of oxidation by H_2O on the Pt/TiO_2 catalyst. (●) O_2 conversion, (○) CO conversion.

H_2O, which is formed by the oxidation of H_2. In fact, the oxidation of CO performed in the presence of moisture did not gain any further enhancement by adding H_2 (not shown here).

It is well known that the water gas shift reaction, $CO + H_2O \rightarrow H_2 + CO_2$, occurs on Fe-oxide at high temperature. However, observed oxidation of CO promoted H_2O on the $FeO_x/Pt/TiO_2$ catalyst is
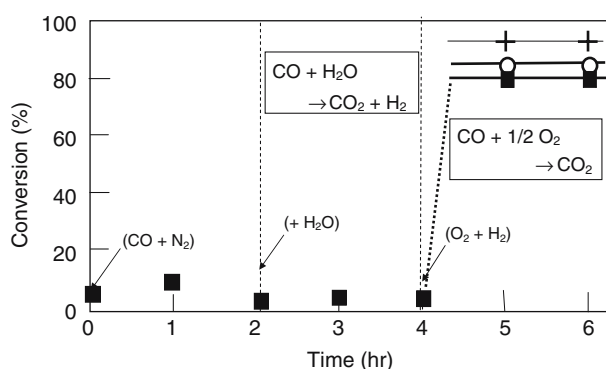
Figure 3. CO (3 ml/min) + N_2 (97 ml/min) was flow on the FeO_x/Pt/ TiO_2 catalyst for 2 h at 60 °C, and then N_2 was bubbled through water. No shift reaction occurred by adding H_2O, but the oxidation of CO was markedly enhanced by adding O_2 (1.5 ml/min) and H_2 (20 ml/ min) at 4 h. (○) O_2 conversion, (■) CO conversion, (+) selectivity to CO.

Figure 4. *In-situ* DRIFT IR spectra of Pt/TiO_2 and FeO_x/Pt/TiO_2 exposed to a flow of 3% CO/N_2 (200 ml/min) + N_2 (40 ml/min) at 40 °C.

presumably not the shift reaction. To confirm this, the reaction of CO with H_2O was performed on the FeO_x/ Pt/TiO_2 catalyst. As shown in figure 3, no shift reaction of CO occurs by the addition of H_2O in absence of O_2 on the FeO_x/Pt/TiO_2 catalyst at 60 °C, but the oxidation of CO with O_2 is markedly enhanced by the addition of H_2. Therefore, we can conclude that the reaction of CO with O_2 is promoted by H_2O on the FeO_x/Pt/TiO_2 catalyst.

As reported in our previous paper [8], Pt-sites on the Pt/TiO_2 catalyst may be reconstructed by loading FeO_x, and the IR spectra in figure 4 suggest the reconstruction of Pt-sites. The CO peaks at 2073 and 2094 cm^{-1} (assignable to linearly adsorbed CO) decrease in intensity and a peak at 1809 cm^{-1} of bridged CO is markedly increased on the FeO_x/Pt/TiO_2 catalyst. To confirm the effect of H_2 on oxidation of adsorbed CO on the FeO_x/ Pt/TiO_2 catalyst, the catalyst surface during the oxidation of CO was monitored in the absence and the presence of H_2 by *in-situ* DRIFT spectroscopy. Figure 5(a) and (b) show the IR spectra of the FeO_x/Pt/TiO_2 catalyst obtained in a flow of 3% CO/N_2 (200 ml/ min) + O_2 (3 ml/min) + N_2 (40 ml/min), and 3% CO/ N_2 (200 ml/min) + O_2 (3 ml/min) + H_2 (40 ml/min) (CO/O_2 = 2/1) at 60 °C. Both linearly bonded CO and bridge bonded CO were detected during the oxidation of CO with O_2 in the absence (a) and presence (b) of H_2, that is the adsorption of CO is rapid enough during the oxidation of CO, which is not the rate determining step. When the CO flow is stopped, the adsorbed CO on the catalyst is removed by the reaction with O_2. Figure 5(a) shows the decrease of adsorbed CO by the oxidation with O_2 in the absence of H_2. It is known that the bridged CO peak at 1809 cm^{-1} decreases more rapidly than those of the linearly bonded CO, implying that the bridged CO is more reactive than the linearly bonded CO with respect to O_2. If the bridged CO observed in the
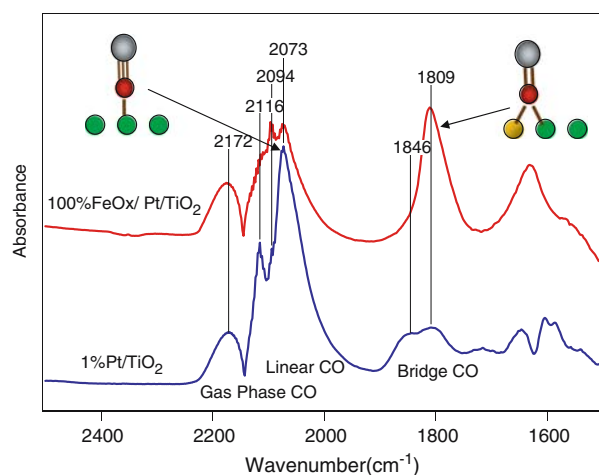
spectra is a real intermediate, remove of the bridged CO by reacting with O_2 should be enhanced in the presence of H_2.

A steady state *in-situ* IR spectrum of the catalyst obtained in a flow of 3% CO/N_2 (200 ml/min) + O_2 (3 ml/min) + H_2 (40 ml/min) at 60 °C is shown in figure 5(b). The oxidation of CO proceeds far more rapidly in the presence of H_2 compared to that in the absence of H_2. Adsorption of CO during the catalysis in the presence of H_2 occurs sufficiently fast to be nearly adsorption equilibrium, so that both linearly bonded CO and bridged CO are detected in the *in-situ* spectra. However, the ratio of intensity of bridged CO to linear CO is slightly lower in the presence of H_2. When the CO flow was stopped while retaining the H_2 flow, not only the bridged CO but also the linear CO disappeared rapidly. In particular, the bridged CO peak was completely eliminated within 2 min as shown in figure 5(b). These observations suggest that the adsorbed CO detected by IR is a real intermediate for the oxidation of CO in the presence of H_2. Taking these results into account, we conclude that the catalytic oxidation reaction of CO is enhanced by H_2O provided by the oxidation of H_2, which is a feature of the extraordinarily high activity of the PROX FeO_x/Pt/TiO_2 catalyst.

As it is mentioned above, improvement of the activity per site is attained by either the enhancement of the rate determining step or by opening a new reaction path. The enhancement of the oxidation of CO by H_2O on the FeO_x/Pt/TiO_2 catalyst is a case of catalysis via a new reaction path. A proposed new mechanism is schematically described in Scheme 1(II), where the oxidation of CO occurs via hydroxyl carbonyl or bicarbonate intermediates and H_2O molecule plays the role of a molecular catalyst to promote the oxidation of CO with O_2.
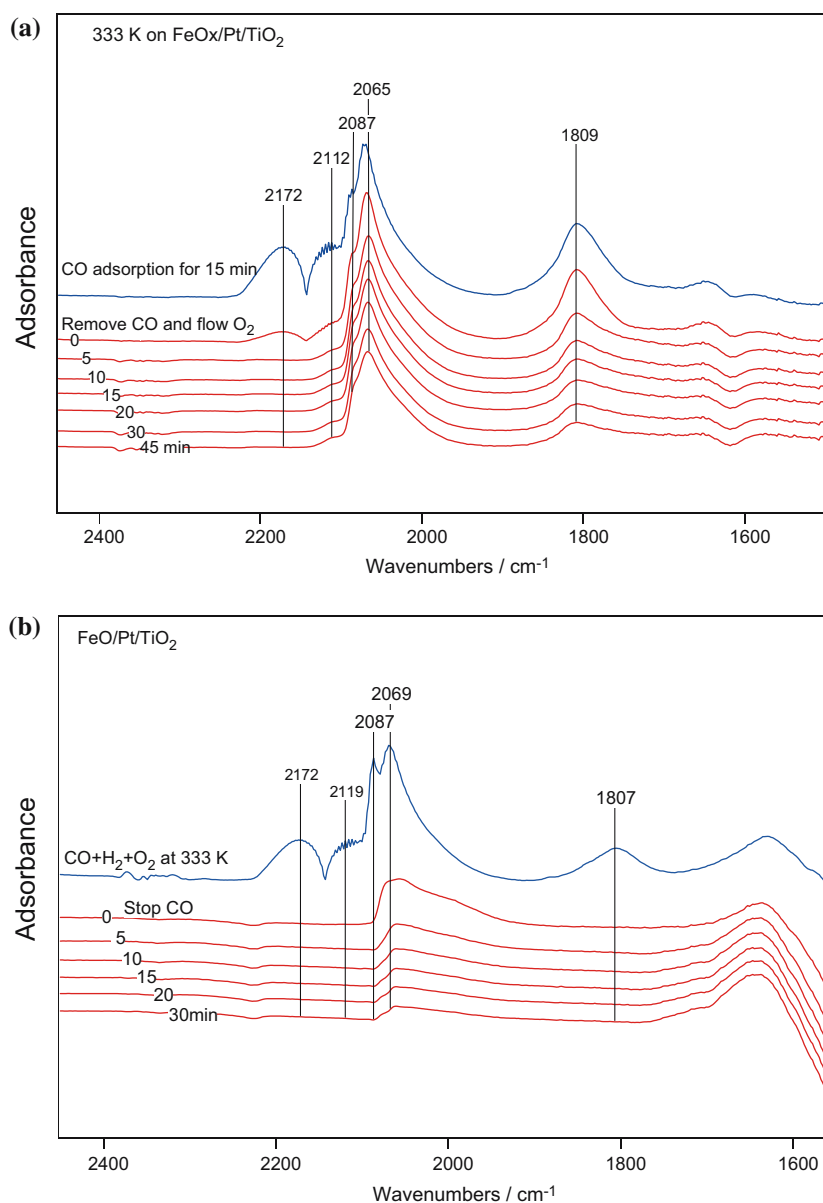
Figure 5. In-situ IR spectra showing the reaction of adsorbed CO with O_2 on the $FeO_x/Pt/TiO_2$ catalyst at 60 °C in absence of H_2. (a) IR spectra obtained in the absence of H_2. The catalyst was exposed to a flow of 3% CO/N_2 (200 ml/min) + O_2 (3 ml/min) + N_2 (40 ml/min), and then the flow of CO was stopped. (b) IR spectra obtained in the presence of H_2. The catalyst was exposed to a flow of 3% CO/N_2 (200 ml/min) + O_2 (3 ml/min) + H_2 (40 ml/min), and then the flow of CO was stopped.

It has been reported that the oxidation of CO on Au catalyst is also enhanced by H_2O and/or H_2 [11–14], which is quite interesting in relation to the reaction on the $FeO_x/Pt/TiO_2$ catalyst of this paper. Costello et al. [11] reported an isotope effect of 1.4 for H_2/D_2 but little isotope effect for H_2O/D_2O on the oxidation of CO on the Au/Al_2O_3 catalyst. They explained that the isotope effect is given by a balance of poisoning and recovering of the sites with carbonate ($Au–CO_3$) by H_2 and D_2, which is entirely different from our proposed mechanism for the oxidation reaction of CO promoted by H_2O as a molecular catalyst. Date et al. [15] also reported the oxidation of CO on the Au/Al_2O_3 catalyst enhanced by a trace amount of H_2O but the effect was explained by the electronic conductivity of the support. Finally, we should be pointed out that the effective transportation of molecules and/or intermediates to active sites improve the activity, which is decisively controlled by the support oxide and some times by moisture or H_2O molecule. If this is the case, the physical meaning of the sticking probability as well as the turn-over frequency in catalysis is not so simple as their definition. So far the activity of supported metallic catalyst has been discussed by the size, crystal shape, perimeter, specific electronic structure etc., but we should be

more careful about the surface transportation of molecules and the reaction mechanism influenced by the properties of support.

Acknowledgments

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