

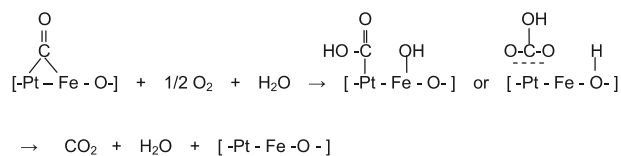
# Significant enhancement of the oxidation of CO by H<sub>2</sub> and/or H<sub>2</sub>O on a FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst

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Oxidation of CO on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst is markedly enhanced by H<sub>2</sub> and/or H<sub>2</sub>O at 60 °C, but no such enhancement is observed on the Pt/TiO<sub>2</sub> catalyst, but shift reaction (CO + H<sub>2</sub>O → H<sub>2</sub> + CO<sub>2</sub>) does not occur on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> 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<sub>x</sub> loaded Pt/TiO<sub>2</sub> catalyst. The *in-situ* DRIFT IR spectra proved that the bridged CO is more reactive than the linearly bonded CO with respect to O<sub>2</sub>, and the reaction of the bridge-bonded CO with O<sub>2</sub> as well as of the linearly bonded CO is markedly enhanced by adding H<sub>2</sub> to a flow of CO + O<sub>2</sub>. From these results, we deduced that the promoting effect of H<sub>2</sub> and/or H<sub>2</sub>O is responsible for the preferential oxidation (PROX) reaction of CO on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> 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<sub>2</sub>O.



**KEY WORDS:** preferential oxidation (PROX) reaction of CO in H<sub>2</sub>; CO oxidation enhanced by H<sub>2</sub>O; CO oxidation enhanced by H<sub>2</sub>; FeO<sub>x</sub> loaded Pt/TiO<sub>2</sub> 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 synergistic 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<sub>x</sub> on the oxide supported Pt catalysts (TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>). A typical example is shown in figure 1, where the activity and the selectivity of 1 wt.% Pt/TiO<sub>2</sub> catalyst are markedly improved by loading a large amount of FeO<sub>x</sub> (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<sub>x</sub> on the Pt/TiO<sub>2</sub> catalyst [8]. The role of FeO<sub>x</sub> 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<sub>2</sub>

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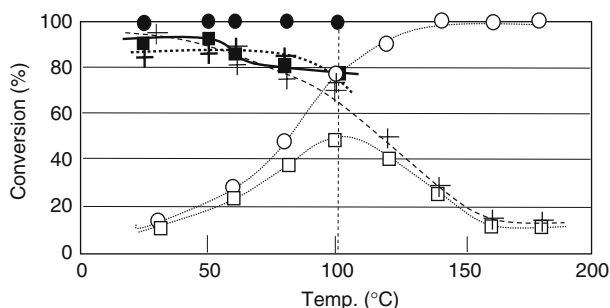


Figure 1. Oxidation of CO in H<sub>2</sub> on 1 wt.% Pt/TiO<sub>2</sub> (open symbols) and 100 wt.% FeO<sub>x</sub> loaded Pt/TiO<sub>2</sub> (solid symbols). CO (3 ml/min) + O<sub>2</sub> (1.5 ml/min) + H<sub>2</sub> (20 ml/min) was adjusted to be 100 ml/min by adding N<sub>2</sub>, and pathed through 1.5 g catalyst. (○, ●) O<sub>2</sub> conversion, (□, ■) CO conversion, (+, +) selectivity to CO.

and/or H<sub>2</sub>O is essentially important for the PROX reaction of CO on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst as discussed in this paper.

## 2. Experiment

FeO<sub>x</sub> was loaded on 1 wt.% Pt/TiO<sub>2</sub> by dipping the Pt/TiO<sub>2</sub> calcined in air at 400 °C in a solution of Fe(NO<sub>3</sub>)<sub>3</sub>. The weight of loaded Fe was almost equal to that of the Pt/TiO<sub>2</sub>, which denotes 100 wt.% FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst (Fe/Pt≈350). After the loading of whole Fe(NO<sub>3</sub>)<sub>3</sub> 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<sub>2</sub> (60 ml/min), O<sub>2</sub> (1.5 ml/min), H<sub>2</sub> (20 ml/min), and a balance gas of N<sub>2</sub> (18.5 ml/min), and the total flow rate was adjusted to be 100 ml/min by N<sub>2</sub> flow. Steady state conversion was obtained by maintaining the flow for more than 30 min at each reaction temperature. The promoting effect of H<sub>2</sub> was measured by adding H<sub>2</sub> (20 ml/min) to a flow of 5% CO/N<sub>2</sub> (60 ml/min) + O<sub>2</sub> (1.5 ml/min) + N<sub>2</sub>. The effect of H<sub>2</sub>O was studied by bubbling N<sub>2</sub> through a water tank at room temperature, where the flow of N<sub>2</sub> was adjusted to be 20 ml/min in the presence of H<sub>2</sub> and 40 ml/min in absence of H<sub>2</sub>. 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<sup>-1</sup> 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<sub>2</sub> (200 ml/min) + O<sub>2</sub> (3 ml/min) + N<sub>2</sub> (40 ml/min), and the spectrum in the presence of H<sub>2</sub> was measured by replacing N<sub>2</sub> (40 ml/min) with a flow of H<sub>2</sub>. As prepared FeO<sub>x</sub>/Pt/TiO<sub>2</sub> had red brown color, but changed to dark brown after the oxidation reaction of CO in H<sub>2</sub>. The XRD

patterns showed that Fe<sub>2</sub>O<sub>3</sub> changed to Fe<sub>3</sub>O<sub>4</sub> during the oxidation of CO in H<sub>2</sub>.

## 3. Results and discussion

Oxidation of CO in excess H<sub>2</sub> on 1 wt.% Pt/TiO<sub>2</sub> catalyst was studied by flowing a mixture of CO (3 ml/min) + O<sub>2</sub> (1.5 ml/min) + H<sub>2</sub> (20 ml/min) + N<sub>2</sub> (75.5 ml/min) through 1.5 g of catalyst. The conversion of CO was about 20% on a Pt/TiO<sub>2</sub> catalyst at 60 °C, but 100% O<sub>2</sub> conversion with about 90% CO conversion (CO/O<sub>2</sub> = 2/1) was attained on the FeO<sub>x</sub> loaded catalyst (FeO<sub>x</sub>/Pt/TiO<sub>2</sub>) even at temperatures lower than 60 °C (figure 1). Interestingly, the CO conversion in the absence of H<sub>2</sub> is only ca. 17% on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst at 60 °C as shown in figure 2(a). The CO conversion in a flow of 3% CO/N<sub>2</sub> (60 ml/min) + O<sub>2</sub> (1.5 ml/min) + N<sub>2</sub> (38.5 ml/min), however, is enhanced to nearly 100% by adding 20 ml/min of H<sub>2</sub>. It should be noted that no such enhancement due to H<sub>2</sub> was observed on the Pt/TiO<sub>2</sub> catalyst. From these results, we deduce that the exceptional high activity of the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> 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<sub>2</sub> is decisively important. A similar role of FeO<sub>x</sub> was also found on a 1 wt.% Au/TiO<sub>2</sub> catalyst [9]. It should be pointed out that if H<sub>2</sub> would participate in the catalytic oxidation of CO, the oxidation of CO necessarily accompanies a constant consumption of H<sub>2</sub>, so it is difficult to attain the preferential oxidation (PROX) reaction of CO.

We found that the oxidation of CO on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst is also significantly promoted by H<sub>2</sub>O. As shown in figure 2(b), the CO conversion was enhanced from ca. 17% to more than 80% at 60 °C by adding H<sub>2</sub>O moisture in a flow of N<sub>2</sub> (38.5 ml/min), where H<sub>2</sub> flow was stopped. When the moisture was removed from the N<sub>2</sub> 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<sub>2</sub>O molecule does not appear in the over-all oxidation reaction of CO, CO + 1/2 O<sub>2</sub> → CO<sub>2</sub> which suggests that a trace amount of H<sub>2</sub>O formed by the oxidation of H<sub>2</sub> may promote the oxidation reaction of CO on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst in the presence of H<sub>2</sub>, where only a limited amount of H<sub>2</sub> is consumed. The role of H<sub>2</sub>O in the oxidation of ethylene to acetaldehyde by PdCl<sub>2</sub> catalyst is analogous, C<sub>2</sub>H<sub>4</sub> + 1/2 O<sub>2</sub> → CH<sub>3</sub>CHO (so called Wacher reaction), in which H<sub>2</sub>O does not appear in the over-all reaction but promotes the reaction [10]. It should be emphasized that no promoting effect of H<sub>2</sub>O was observed on the Pt/TiO<sub>2</sub> catalyst as shown in figure 2(c). Therefore, we could conclude that the unique feature of the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst for the PROX reaction of CO is due to the promotion of the oxidation of CO effect by

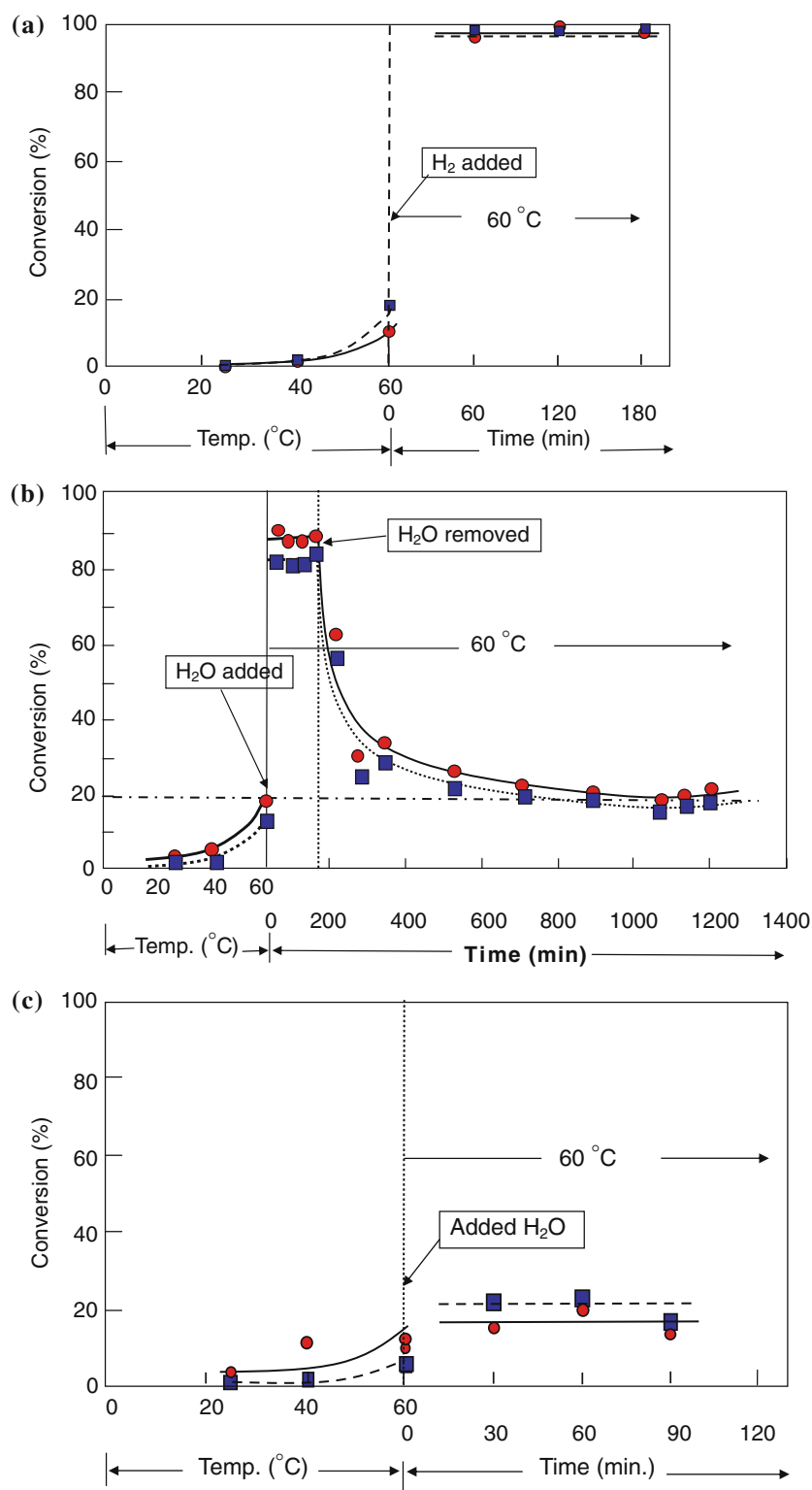


Figure 2. Oxidation of CO enhanced by (a) H<sub>2</sub> and (b) H<sub>2</sub>O on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst. The reaction was performed at a flow rate of 100 ml/min. (a) 5% CO/N<sub>2</sub> (60 ml/min) + O<sub>2</sub> (1.5 ml/min) + N<sub>2</sub> (38.5 ml/min). (b) 5% CO/N<sub>2</sub> (60 ml/min) + O<sub>2</sub> (1.5 ml/min) + H<sub>2</sub> (20 ml/min) + N<sub>2</sub> (18.5 ml/min). (c) No enhancement of oxidation by H<sub>2</sub>O on the Pt/TiO<sub>2</sub> catalyst. (●) O<sub>2</sub> conversion, (○) CO conversion.

H<sub>2</sub>O, which is formed by the oxidation of H<sub>2</sub>. In fact, the oxidation of CO performed in the presence of moisture did not gain any further enhancement by adding H<sub>2</sub> (not shown here).

It is well known that the water gas shift reaction,  $\text{CO} + \text{H}_2\text{O} \rightarrow \text{H}_2 + \text{CO}_2$ , occurs on Fe-oxide at high temperature. However, observed oxidation of CO promoted H<sub>2</sub>O on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst is

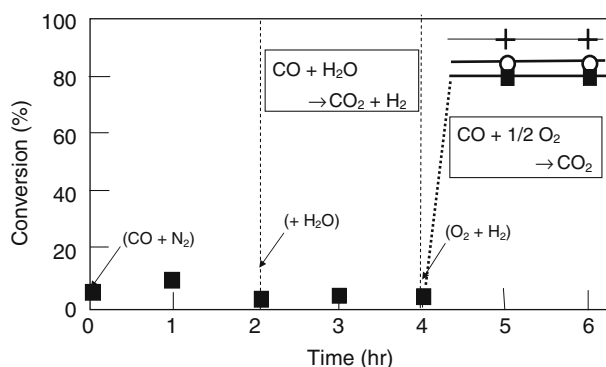


Figure 3. CO (3 ml/min) + N<sub>2</sub> (97 ml/min) was flow on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst for 2 h at 60 °C, and then N<sub>2</sub> was bubbled through water. No shift reaction occurred by adding H<sub>2</sub>O, but the oxidation of CO was markedly enhanced by adding O<sub>2</sub> (1.5 ml/min) and H<sub>2</sub> (20 ml/min) at 4 h. (○) O<sub>2</sub> conversion, (■) CO conversion, (+) selectivity to CO.

presumably not the shift reaction. To confirm this, the reaction of CO with H<sub>2</sub>O was performed on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst. As shown in figure 3, no shift reaction of CO occurs by the addition of H<sub>2</sub>O in absence of O<sub>2</sub> on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst at 60 °C, but the oxidation of CO with O<sub>2</sub> is markedly enhanced by the addition of H<sub>2</sub>. Therefore, we can conclude that the reaction of CO with O<sub>2</sub> is promoted by H<sub>2</sub>O on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst.

As reported in our previous paper [8], Pt-sites on the Pt/TiO<sub>2</sub> catalyst may be reconstructed by loading FeO<sub>x</sub>, and the IR spectra in figure 4 suggest the reconstruction of Pt-sites. The CO peaks at 2073 and 2094 cm<sup>-1</sup> (assignable to linearly adsorbed CO) decrease in intensity and a peak at 1809 cm<sup>-1</sup> of bridged CO is markedly increased on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst. To confirm the effect of H<sub>2</sub> on oxidation of adsorbed CO on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst, the catalyst surface during the oxidation of CO was monitored in the absence and the presence of H<sub>2</sub> by *in-situ* DRIFT spectroscopy. Figure 5(a) and (b) show the IR spectra of the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst obtained in a flow of 3% CO/N<sub>2</sub> (200 ml/min) + O<sub>2</sub> (3 ml/min) + N<sub>2</sub> (40 ml/min), and 3% CO/N<sub>2</sub> (200 ml/min) + O<sub>2</sub> (3 ml/min) + H<sub>2</sub> (40 ml/min) (CO/O<sub>2</sub> = 2/1) at 60 °C. Both linearly bonded CO and bridge bonded CO were detected during the oxidation of CO with O<sub>2</sub> in the absence (a) and presence (b) of H<sub>2</sub>, 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<sub>2</sub>. Figure 5(a) shows the decrease of adsorbed CO by the oxidation with O<sub>2</sub> in the absence of H<sub>2</sub>. It is known that the bridged CO peak at 1809 cm<sup>-1</sup> 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<sub>2</sub>. If the bridged CO observed in the

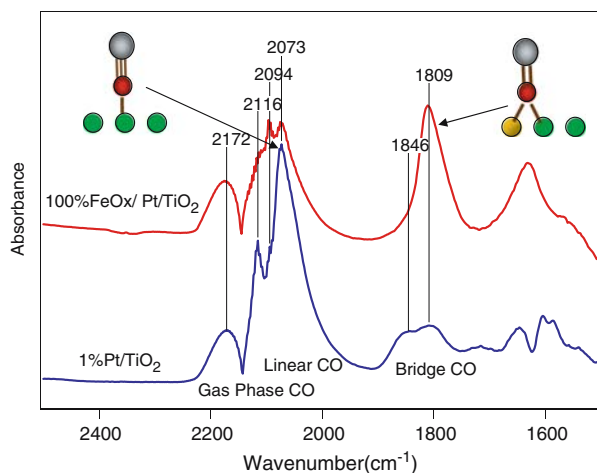


Figure 4. *In-situ* DRIFT IR spectra of Pt/TiO<sub>2</sub> and FeO<sub>x</sub>/Pt/TiO<sub>2</sub> exposed to a flow of 3% CO/N<sub>2</sub> (200 ml/min) + N<sub>2</sub> (40 ml/min) at 40 °C.

spectra is a real intermediate, remove of the bridged CO by reacting with O<sub>2</sub> should be enhanced in the presence of H<sub>2</sub>.

A steady state *in-situ* IR spectrum of the catalyst obtained in a flow of 3% CO/N<sub>2</sub> (200 ml/min) + O<sub>2</sub> (3 ml/min) + H<sub>2</sub> (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<sub>2</sub> compared to that in the absence of H<sub>2</sub>. Adsorption of CO during the catalysis in the presence of H<sub>2</sub> 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<sub>2</sub>. When the CO flow was stopped while retaining the H<sub>2</sub> 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<sub>2</sub>. Taking these results into account, we conclude that the catalytic oxidation reaction of CO is enhanced by H<sub>2</sub>O provided by the oxidation of H<sub>2</sub>, which is a feature of the extraordinarily high activity of the PROX FeO<sub>x</sub>/Pt/TiO<sub>2</sub> 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<sub>2</sub>O on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> 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<sub>2</sub>O molecule plays the role of a molecular catalyst to promote the oxidation of CO with O<sub>2</sub>.

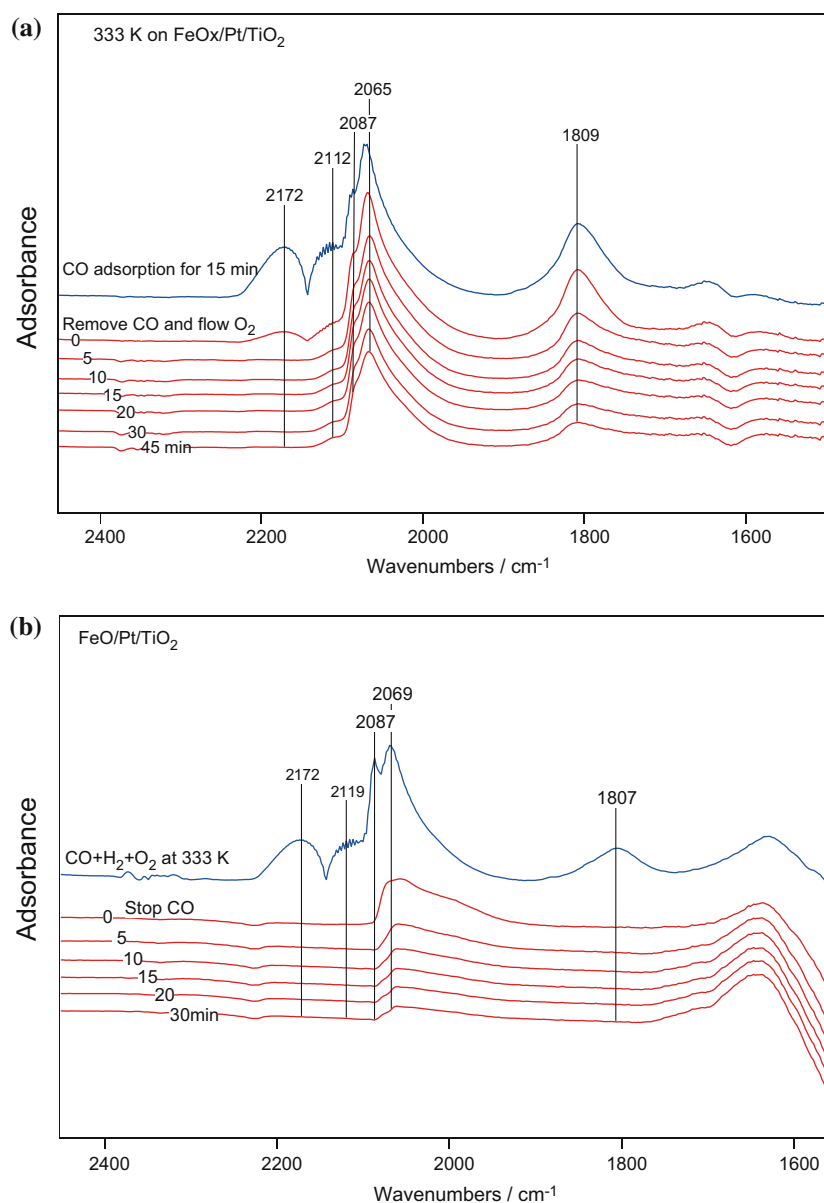


Figure 5. In-situ IR spectra showing the reaction of adsorbed CO with O<sub>2</sub> on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst at 60 °C in absence of H<sub>2</sub>. (a) IR spectra obtained in the absence of H<sub>2</sub>. The catalyst was exposed to a flow of 3% CO/N<sub>2</sub> (200 ml/min) + O<sub>2</sub> (3 ml/min) + N<sub>2</sub> (40 ml/min), and then the flow of CO was stopped. (b) IR spectra obtained in the presence of H<sub>2</sub>. The catalyst was exposed to a flow of 3% CO/N<sub>2</sub> (200 ml/min) + O<sub>2</sub> (3 ml/min) + H<sub>2</sub> (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<sub>2</sub>O and/or H<sub>2</sub> [11–14], which is quite interesting in relation to the reaction on the FeO<sub>x</sub>/Pt/TiO<sub>2</sub> catalyst of this paper. Costello *et al.* [11] reported an isotope effect of 1.4 for H<sub>2</sub>/D<sub>2</sub> but little isotope effect for H<sub>2</sub>O/D<sub>2</sub>O on the oxidation of CO on the Au/Al<sub>2</sub>O<sub>3</sub> catalyst. They explained that the isotope effect is given by a balance of poisoning and recovering of the sites with carbonate (Au–CO<sub>3</sub>) by H<sub>2</sub> and D<sub>2</sub>, which is entirely different from our proposed mechanism for the oxidation reaction of CO promoted by H<sub>2</sub>O as a molecular catalyst. Date *et al.* [15] also reported the oxidation of

CO on the Au/Al<sub>2</sub>O<sub>3</sub> catalyst enhanced by a trace amount of H<sub>2</sub>O 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<sub>2</sub>O 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

This work was supported by the High-Tech Research Center of Saitama Institute of Technology, and by a Grant-in-Aid for Scientific Research [(C) 17550136] of the Ministry of Education and Technology of Japan. One of the authors, K. Tanaka, sincerely thanks Mr. Mitsushi Umino, the president of Astech Co., of his long standing consideration for my research works.

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