

A new catalyst for selective oxidation of CO in H₂: Part 1, activation by depositing a large amount of FeO_x on Pt/Al₂O₃ and Pt/CeO₂ catalysts

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Received May 30, 2003; accepted 7 November 2003

1% Pt/Al₂O₃ and 1% Pt/CeO₂ are markedly activated by the deposition of a large quantity of FeO_x, about 100 wt% in Fe with respect to the supports. In contrast, the activity of a Ru/Al₂O₃ catalyst was completely suppressed by the deposition of FeO_x, but a Ru-Pt/Al₂O₃ was markedly activated by the FeO_x. The activation depends on the sequence of the deposition, that is, no pronounced activation was observed on the Pt supported on a FeO_x/Al₂O₃ as well as on the Pt codeposited with a small amount of Fe on Al₂O₃, that is, the activity was almost equal to that of the Pt/Al₂O₃. The XPS analysis of the Pt/CeO₂ and FeO_x/Pt/CeO₂ proved that the Pt is effectively covered with the FeO_x. Selectivity for the oxidation of CO in H₂ was also improved on the FeO_x/Pt/Al₂O₃ and FeO_x/Pt/CeO₂ catalysts and it is rather independent of the conversion. In conformity with the feature of the FeO_x/Pt/Al₂O₃ and FeO_x/Pt/CeO₂ catalysts, we deduced that the deposited FeO_x is activated by the Pt and the FeO_x is responsible for the selective oxidation of CO.

KEY WORDS: selective oxidation of CO in H₂; activation of Pt/Al₂O₃ and Pt/CeO₂ catalyst by Fe₂O₃; synergistic effect of Fe₂O₃; activation of Fe₂O₃.

1. Introduction

Anodic oxidation of H₂ on the Pt electrode of the proton exchange membrane (PEM) fuel cell is poisoned by a trace amount of CO of 100 ppm. Therefore, it is imminent to develop a more CO tolerant electrode and an active catalyst for the selective oxidation of small amounts of CO in H₂. It is worthy to note that opposite properties are requested for the electrode and the catalyst. In contrast to a CO-tolerant electrode that demands weakened adsorption of CO, selective oxidation of CO will be attained by stronger adsorption of CO. In fact, Watanabe *et al.* [1] showed that a CO-tolerant electrode of Pt₈₅Fe₁₅ takes up a markedly lower *in situ* CO coverage than a Pt electrode [2]. Therefore, we could speculate that the oxidation of CO in excess H₂ is poorly selective on the Pt₈₅Fe₁₅Pt alloy.

On the other hand, the activity of oxides for the oxidation of CO was studied a long time ago, and the following sequence was reported for activity in CO oxidation: CoO > NiO > MnO₂ >> CuO > FeO_x >

ZnO > TiO₂ > Cr₂O₃ > V₂O₅ [3], and a similar sequence was observed for the oxidation of H₂ [4]. An interesting fact should be pointed out here. The industrial catalyst for the selective oxidation of hydrocarbons has been developed by an entirely different concept in which the contribution of lattice oxygen is indispensable in the catalysis cycle [5]. For example, acrolein produced by the oxidation of propene with ¹⁸O₂ on a MoO₃-Bi₂O₃ catalyst contains a little ¹⁸O in the product [6], that is, acrolein is formed by the reaction of propene with lattice oxygen at a specific site. Taking these facts into account, we could say that the basic concept is entirely different for the oxidation of CO and H₂ and the selective oxidation of hydrocarbons. Oxidation reaction of hydrocarbon gives a variety of products depending on the function of active sites, whereas the oxidation of CO and H₂ yields only CO₂ and H₂O. This might be a reason why such a simple mechanism as the competitive adsorption kinetics has been tacitly accepted for the selective oxidation of CO in H₂.

On the other hand, a contribution of the lattice oxygen was demonstrated in oxidation of CO by the precious metals supported on CeO₂ or CeO₂-ZrO₂. The

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three-way catalyst of Pt–Rh supported on CeO₂ or CeO₂–ZrO₂ [7] is a typical case, in which the redox property of the Rh/Ce_{0.5}Zr_{0.5}O₂ catalyst reflects the mobility of the lattice oxygen of CeO₂ and CeO₂–ZrO₂ during catalysis [8]. On the other hand, lattice oxygen does not attribute to the oxidation of CO on Al₂O₃-supported Pt, Pd, and Rh catalysts. It is known that the oxidation of CO on the precious metal catalysts obeys inverse first order in the CO pressure, that is, the reaction is suppressed by the adsorption of CO on Pt, Pd, and Rh surfaces. Similar negative first-order kinetics was reported for the oxidation of CO on the CeO₂-supported Pt, Pd, and Rh catalysts when the CO pressure was very low [9]. When the CO pressure becomes higher than a certain value, the kinetics is changed from the inverse first order to the zeroth order in CO pressure. The zeroth-order rate was explained by the oxidation of CO with lattice oxygen diffused to the precious metals, that is, the reaction of CO on the precious metals was tacitly assumed when the lattice oxygen contributed to the reaction. If the reaction occurs on metal particles, the oxidation rate of CO at high pressure depends on the density of metal particles on the support, that is, the rate becomes very low when there are no metal particles on the surface. If the reaction would be catalyzed by CeO₂, the activity should be independent of the density of the metal particles. Instead of lowering the activity, unusual activation of Pt/Al₂O₃ by FeO_x was found by Korotkikh and Farrauto [10,11], and they showed that the Pt is partly covered with FeO_x. Taking these facts into account, the activation was explained by the reaction of CO on the activated Pt (electron rich) with the oxygen from the FeO_x. However, it should be pointed out that the time-resolved Diffuse Reflectance IR Fourier-Transform Spectroscopy (DRIFTS) study showed that the dynamics of the adsorbed species on the Pt is very slow compared to the reaction (90% conversion in 0.3 s).

In this paper, we report a new type of activation that was found on the Pt catalyst, mostly covered with a large quantity of FeO_x (100 wt% of Fe with respect to Al₂O₃ or CeO₂). The activity as well as the selectivity for the oxidation of CO in H₂ was markedly improved compared to the Pt catalysts. Taking this fact into account, we could say that the oxidation of CO might occur on the oxides instead of the Pt surface.

2. Experimental

The reaction was carried out by a fixed-bed flow reactor (a glass tube of 14 mm diameter) with 1.5 g catalyst. The flow rate was adjusted to be 100 mL/min in total, where the composition was adjusted by a flow rate of H₂ : CO : O₂ = 20 : 3 : 1.5 mL/min with addition of the balance gas of N₂, and the analysis of gas was performed by an on-line gas chromatography. The

reaction temperature was monitored by a thermocouple placed in the reactor. The conversion ($X_{O_2} = \Delta O_2/a_0$) in this paper represents the total consumption of O₂ by reacting with CO and H₂, and the conversion of CO ($X_{CO} = \Delta CO/b_0$) is the fraction of CO oxidized to CO₂, where a_0 and b_0 are the initial composition of O₂ and CO, and ΔCO and ΔO_2 are the consumed CO and O₂ respectively. The selectivity (S) is the fraction of O₂ consumed by the reaction with CO, which is given by a relation of $S = (1/2)(\Delta CO/\Delta O_2) = (1/2)(b_0 X_{CO})/(a_0 X_{O_2}) = (1/2)(X_{CO}/X_{O_2})(b_0/a_0)$. Therefore, when the initial composition of CO (b_0) and O₂ (a_0) is exactly 2/1, $a_0/b_0 = 1/2$, the selectivity (S) should be equal to the conversion of CO (X_{CO}) at 100% conversion ($X_{O_2} = 1$). Accordingly, the a_0/b_0 ratio is responsible for the slight deviation between the selectivity at 100% conversion and the CO conversion. It should be pointed out that CO remained in gas phase at 100% conversion because the selectivity was less than 100%.

The Al₂O₃ used in the experiment was standard Al₂O₃ of the Catalysis Society of Japan, which was supplied by Sumitomo Chemical Co (AKP GO-15-Al₂O₃; surface 148 m²/g, impurities of Fe 4 ppm, Cu 1 ppm, Mg 1 ppm, Na 2 ppm, and Si 2 ppm), and the CeO₂ was a commercially available Ce(IV) hydroxide (Wako Pure Chemicals Co. 032-01842) baked at 400 °C. Pt/Al₂O₃, Pt/CeO₂, and Ru/Al₂O₃ were prepared by immersing the support oxide in a solution of PtCl₄ or RuCl₄ and were dried for 3 h at 140 °C. The deposited Pt, Ru, and Pt–Ru were about 1 wt% with respect to Al₂O₃ or CeO₂.

- (i) FeO_x/Pt/Al₂O₃, FeO_x/Ru/Al₂O₃, FeO_x/Pt–Ru/Al₂O₃, and FeO_x/Pt/CeO₂: Pt/Al₂O₃, Ru/Al₂O₃, Pt–Ru/Al₂O₃, and Pt/CeO₂ were immersed in a solution of Fe(NO₃)₃, which contained 100 wt% of Fe³⁺ with respect to the Al₂O₃ or CeO₂. Then the solution containing Pt/Al₂O₃, Ru/Al₂O₃, Pt–Ru/Al₂O₃, and Pt/CeO₂ was dried and calcined in air at 400 °C, and these are described as FeO_x/1%-Pt/Al₂O₃, FeO_x/1%-Ru/Al₂O₃, FeO_x/1%-Pt–Ru/Al₂O₃, and FeO_x/1%-Pt/CeO₂. FeO_x takes the color of Fe₂O₃, so the deposited FeO_x is about 143 wt% with respect to Al₂O₃ or CeO₂. The color, however, changes to dark black depending on the ambient reaction gas. In addition, the surface area of small particles of Al₂O₃ or CeO₂ should be changed by deposition of FeO_x. If we assume a flat surface of 148 m²/g, the deposited Fe₂O₃ corresponds to about 3.7×10^{15} of Fe₂O₃ unit per cm². Therefore, we could estimate that the deposition is more than 10 mL of FeO_x on Pt/Al₂O₃.
- (ii) 1%-Pt/FeO_x/Al₂O₃ and 1%-Ru/FeO_x/Al₂O₃: Pt was deposited by immersing FeO_x/Al₂O₃ in a solution of PtCl₃ or RuCl₄ and was dried and calcined in air at 400 °C. The amount of FeO_x deposited on the FeO_x/Al₂O₃ was almost equal to

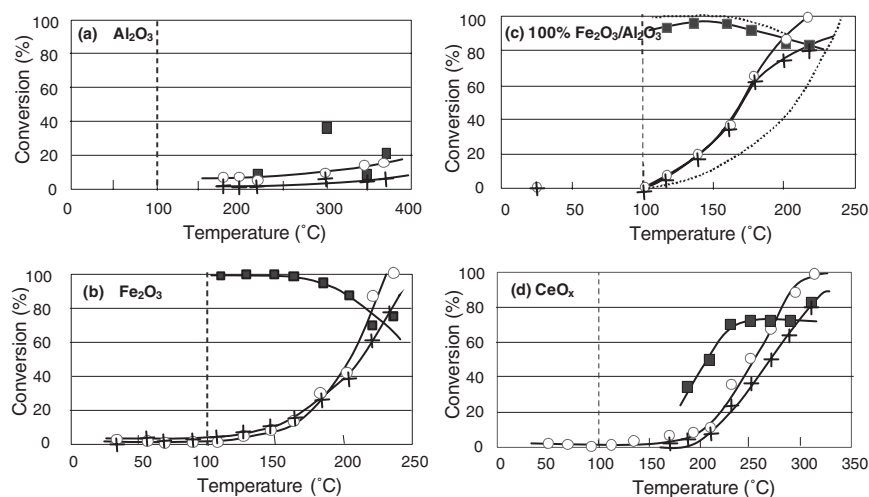


Figure 1. Conversion of CO and O₂ in a flow of CO (3 mL/min), O₂ (1.5 mL/min), H₂ (20 mL/min), and N₂ (75.5 mL/min) on (a) Al₂O₃, (b) Fe₂O₃, (c) Fe₂O₃ on Al₂O₃, and (d) CeO₂. Dotted line in the (c) corresponds to the line of Fe₂O₃ in the (b). (○) Conversion of O₂, (+) Conversion of CO, and (■) selectivity for CO oxidation.

that of FeO_x/Pt/Al₂O₃, that is, the FeO_x is ca. 100 wt% in Fe with respect to Al₂O₃.

The XPS analysis was performed on the Pt/CeO₂ and FeO_x/Pt/CeO₂ catalysts by a Phi-quantum 2000 Scanning ESCA microprobe spectrometer with Al K α (1486.6 eV). The powdered sample was stuck on a carbon tape with conductive glue. The XPS analysis of the Pt/Al₂O₃ and FeO_x/Pt/Al₂O₃ catalyst was also performed, but the Pt(4f) peak overlaps the Al (2p) peak and is difficult to separate (not shown).

3. Results and discussion

1.1. (a) Al₂O₃, (b) FeO_x, (c) FeO_x/Al₂O₃, and (d) CeO₂

It is known that the Al₂O₃ used in this experiment had no detectable activity for the oxidation of CO and H₂ at lower than 300 °C as shown in figure 1(a). On the other hand, Fe₂O₃ had a certain activity for the oxidation of CO in H₂ at higher than about 130 °C. It should be pointed out that the selectivity was very high when the conversion was lower than 40% on the Fe₂O₃ catalyst as shown in figure 1(b). Fe₂O₃-deposited Al₂O₃ (100 wt% in Fe with respect to Al₂O₃) was very similar to the simple Fe₂O₃ as indicated with the dotted lines in figure 1(c), that is, more than 90% selectivity was attained at ca. 60% conversion as shown in figure 1(c). CeO₂ used in this experiment had poor catalytic activity, and no detectable reaction occurs at lower than ca. 200 °C as shown in figure 1(d), which is similar to a reference data [12]. It is a noteworthy fact that the CeO₂ gives about 80% selectivity at 100% conversion at high temperature. These facts prompt us that if we could activate the FeO_x and the CeO₂ by some means and if the reaction occurs at lower temperature, we could get

highly active and highly selective catalyst for the selective oxidation of CO in H₂.

So far, the selectivity in the oxidation of CO in H₂ has been explained by a competitive adsorption mechanism, that is, the stronger the adsorption of CO, the higher the selective oxidation of CO. In this case, the selectivity will be steeply lowered while increasing the conversion in excess H₂, and this is also the case for the metallic catalyst. Therefore, a conversion-independent selectivity, such as that observed on Fe₂O₃ and CeO₂ is an interesting property for the catalyst by which the CO in H₂ can be selectively removed. In this paper, we report an interesting activation of Fe₂O₃ and CeO₂, on which the selective oxidation of CO is attained at low temperature.

1.2. (a) Pt/Al₂O₃, (b) FeO_x/Pt/Al₂O₃, and (c) Pt/FeO_x/Al₂O₃

As the Al₂O₃ has no catalytic activity for the oxidation of CO, the activity of 1 wt% Pt/Al₂O₃ shown in figure 2(a) attributes to the Pt metal. It is known that the selectivity steeply decreases upon increasing the conversion. An EXAFS study [13] suggested that a small amount of Fe (Fe/Pt = 5) improves the dispersion of Pt on Al₂O₃, where the Fe locates at the interface of Pt and Al₂O₃. In contrast, Kоротких and Farrauto [11] characterized a 5%/Al₂O₃ activated by a certain amount of FeO_x by the TEM and DRIFTS, and they concluded that the FeO_x covers a part of Pt surface so that the adsorption of CO and H₂ is suppressed. As they believed the catalysis by Pt, the enhanced activity was explained by the activation of the Pt, that is, the reaction takes place at the uncovered Pt surface by reacting adsorbed CO with oxygen from the oxide. However, it should be pointed out that the IR detectable species are not necessarily the intermediates.

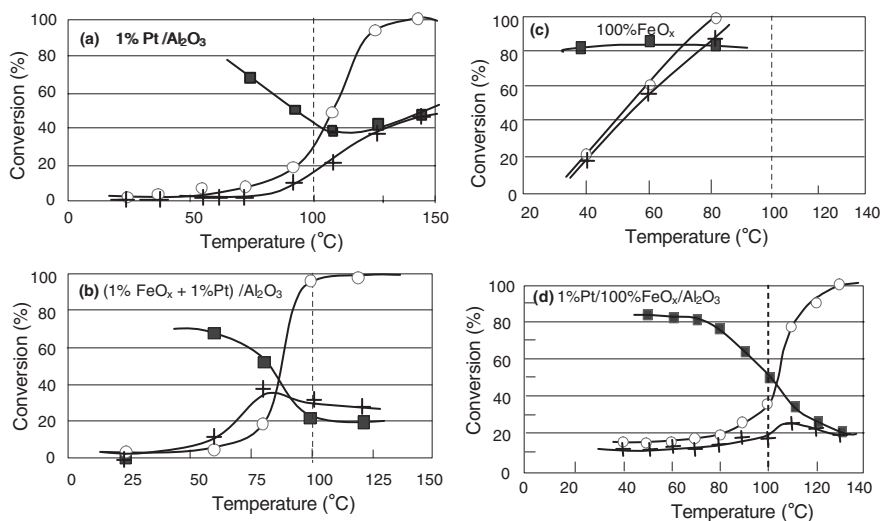


Figure 2. Conversion of CO in a mixture of CO, H₂, and O₂ (1.5:20:3 mL/min). (a) 1% Pt/Al₂O₃, (b) (1%Pt + 1%Fe) on Al₂O₃, (c) 100% FeO_x on a 1% Pt/Al₂O₃, and (d) 1% Pt on a 100% FeO_x/Al₂O₃, (O) Conversion of O₂, (+) Conversion of CO, and (■) selectivity for CO oxidation.

In fact, 90% conversion was attained in a contact time of 0.3 s but the dynamics of the adsorption of CO and CO₂ by the DRIFTS was not so rapid.

Taking these facts into account, we carefully studied the activation mechanism by FeO_x. Addition of a small amount of FeO_x (1 wt% in Fe) influenced little on the activity as shown in figure 2(b). The selectivity decreases sharply with increasing conversion, which is very similar to that of the Pt/Al₂O₃. Contrary to this, we found an unexpected activation of the 1% Pt/Al₂O₃ catalyst when a large quantity of FeO_x (100 wt% in Fe) was deposited on it as shown in figure 2(c). It is known that the selectivity is dramatically improved and ca. 80% selectivity was attained at 100% oxygen conversion, that is, the selectivity is independent of the conversion. It is a reasonable speculation that the Pt is almost covered by the FeO_x. In fact, the XPS analysis of the FeO_x/Pt/CeO₂ gave the Pt peaks lower than the detectable level as it will be shown below. Smearing of the Pt of the FeO_x/Pt/Al₂O₃, however, cannot be shown because the Pt(4f) and Al(2p) peaks overlap. It is an amazing fact that the activity and the selectivity are markedly improved by covering the Pt/Al₂O₃ catalyst with FeO_x. To confirm this curious synergetic effect of FeO_x, the catalysis of the FeO_x/Pt/Al₂O₃ was compared with that of a Pt/FeO_x/Al₂O₃ prepared by depositing 1 wt% of Pt on a FeO_x/Al₂O₃ (100 wt% of Fe with respect to Al₂O₃). One can expect that the Pt locates on the surface of Pt/FeO_x/Al₂O₃, whereas the Pt is embedded by FeO_x on the FeO_x/Pt/Al₂O₃. It is clear that the Pt/FeO_x/Al₂O₃ catalyst (figure 2(b)) is entirely different from the FeO_x/Pt/CeO₂ catalyst (figure 2(c)) but is similar to the (1%Fe + 1%Pt)/Al₂O₃ catalyst (figure 2(d)). It is worthy to note that the selectivity on the Pt/FeO_x/Al₂O₃ catalyst is also steeply decreased

upon increasing conversion, which is similar to that on the Pt/Al₂O₃ catalyst shown in figure 2(a). These results may indicate that the Pt is responsible for the oxidation of CO on the Pt/FeO_x/Al₂O₃ catalyst but this may not be the case on the FeO_x/Pt/Al₂O₃ catalyst.

1.3. (a) Ru/Al₂O₃, (b) Ru/FeO_x/Al₂O₃, (c) FeO_x/Ru/Al₂O₃ and (d) FeO_x/Pt-Ru/Al₂O₃

To confirm such an unusual synergetic effect of FeO_x observed on the FeO_x/Pt/CeO₂ catalyst, the oxidation of CO in excess H₂ was performed on an anticipating metallic catalyst of 1 wt% Ru/Al₂O₃ catalyst. The activity and the selectivity of the Ru/Al₂O₃ catalyst were compared with those of a FeO_x/Ru/Al₂O₃ catalyst, which was prepared by depositing a large amount of FeO_x on the Ru/Al₂O₃ catalyst. As shown in figure 3(a), the catalytic activity of Ru/Al₂O₃ is similar to that of Pt/Al₂O₃ catalyst, that is, the oxidation of CO starts at a similar temperature as shown in figure 2(a). Selectivity of the Ru/Al₂O₃ catalyst is also similar to that of the Pt/Al₂O₃ and (Pt + 1%FeO_x)/Al₂O₃ catalysts, and it is steeply lowered while increasing the conversion. It is known that the activity of Ru/Al₂O₃ is slightly enhanced by adding a small amount of FeO_x (about 1% of Fe with respect to Al₂O₃) as shown in figure 3(b), which is similar to the Pt/Al₂O₃-added 1% FeO_x shown in figure 2(b).

However, the catalytic activity of Ru/Al₂O₃ was effectively suppressed by adding a large amount of FeO_x (100% in Fe to Al₂O₃) as shown in figure 3(c), and the activity becomes almost equal to that of the FeO_x/Al₂O₃ shown in figure 1(c). This result is entirely different from the Pt/Al₂O₃ activated by a large

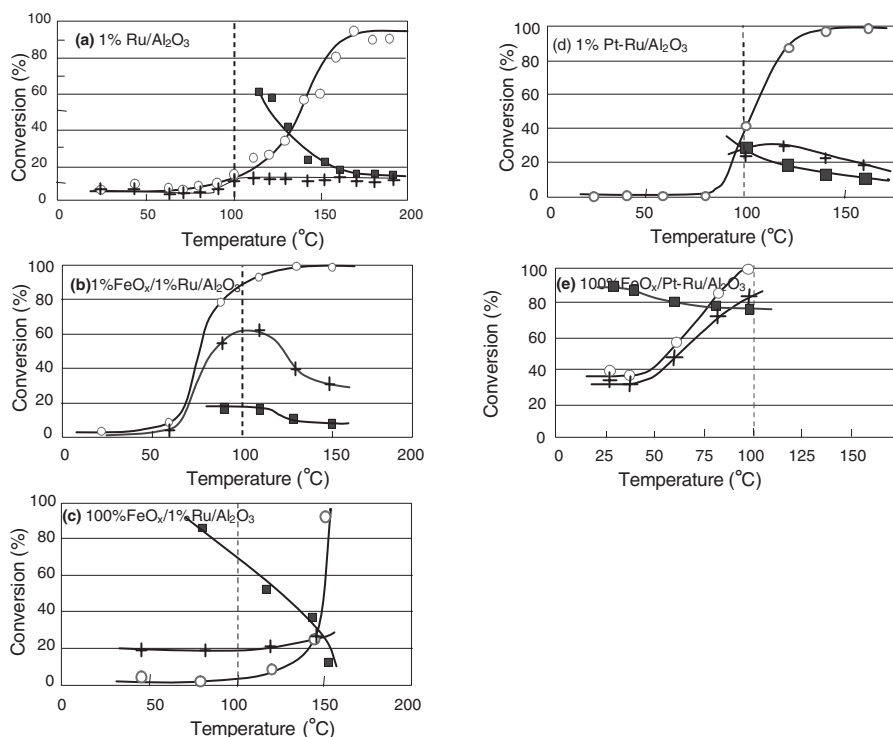


Figure 3. Conversion of CO in a mixture of CO, H₂, and O₂ (1.5:20:3 mL/min). (a) 1% Ru/Al₂O₃, (b) (1% Ru + 1% Fe) on Al₂O₃, (c) 100% FeO_x on a 1% Ru/Al₂O₃, and (d) 1% Ru-Pt/Al₂O₃, (e) 100% FeO_x on a 1% Ru-Pt/Al₂O₃ (○) Conversion of O₂, (+) Conversion of CO, and (■) selectivity for CO oxidation.

quantity of FeO_x. In order to make sure the difference of the synergetic effect of FeO_x on the Ru/Al₂O₃ and the Pt/Al₂O₃ catalysts, the effect of FeO_x on a 1 wt% Pt-Ru/Al₂O₃ bimetallic catalyst (Pt/Ru = 1) was studied. As shown in figure 3(e), the activity and the selectivity of the Pt-Ru/Al₂O₃ were markedly improved by adding a large amount of FeO_x, which are very similar to that of FeO_x/Pt/Al₂O₃ catalyst shown in figure 2(c). It should be pointed out that the selectivity is again independent of the conversion. Accordingly, we can conclude that the FeO_x is activated by Pt but not by Ru.

1.4. (a) CeO₂, FeO_x/CeO₂, (b) Pt/CeO₂ and (c) FeO_x/Pt/CeO₂

CeO₂ shows poor catalytic activity for the oxidation of CO in H₂ as shown in figure 1(d). However, the selectivity of about 70% is independent of the conversion even at the temperature higher than 220 °C. When 1 wt% of Pt was loaded on the CeO₂, the activity was markedly improved as shown in figure 4(a), and the conversion was reversibly changed by raising or lowering the temperature. It should be pointed out that the catalytic activity of the Pt/CeO₂ is much higher than that of the CeO₂, and the selectivity of 70–80% is almost equal to that on CeO₂ shown in figure 1(d). In addition, the selectivity of the Pt/CeO₂ catalyst is independent of the conversion, which is a remarkable contrast to the

Pt/Al₂O₃ catalyst. This fact suggests that the reaction perhaps occurs on the CeO₂ surface instead on the Pt.

So far, the oxidation of CO on CeO₂-supported precious metal catalysts has been studied by many investigators, and it was shown that the lattice oxygen contributes to the oxidation of CO when the CeO₂ is amorphous [14]. Gorte *et al.* compared the oxidation of CO on the CeO₂-supported Pt, Pd, and Rh catalysts with that on the Al₂O₃-supported Pt, Pd, and Rh catalysts [9,15]. The oxidation of CO on the Al₂O₃-supported Pt, Pd, and Rh catalysts obeys negative first order in CO pressure, and the same negative first-order kinetics is attained on the CeO₂-supported Pt, Pd, and Rh catalysts when the CO pressure is lower than a certain value. However, the inverse first-order kinetics on the CeO₂-supported Pt, Pd, and Rh catalysts changes to the zeroth order when the CO pressure becomes higher than a critical value depending on the precious metals. It should be pointed out that when the CO suppresses the reaction rate to an equal rate on the Pt, Pd, and Rh catalysts, the kinetics is changed. This phenomenon was explained by the suppression of oxygen adsorption, that is, a common rate at the zeroth-order kinetics reflects the diffusion rate of oxygen from the CeO₂. If this mechanism is correct, no promotion effect is expected by the oxide and the activity will be enhanced only by increasing the number of metal particles on the CeO₂ surface. It should be pointed out that the selectivity of the Pt/CeO₂ is very

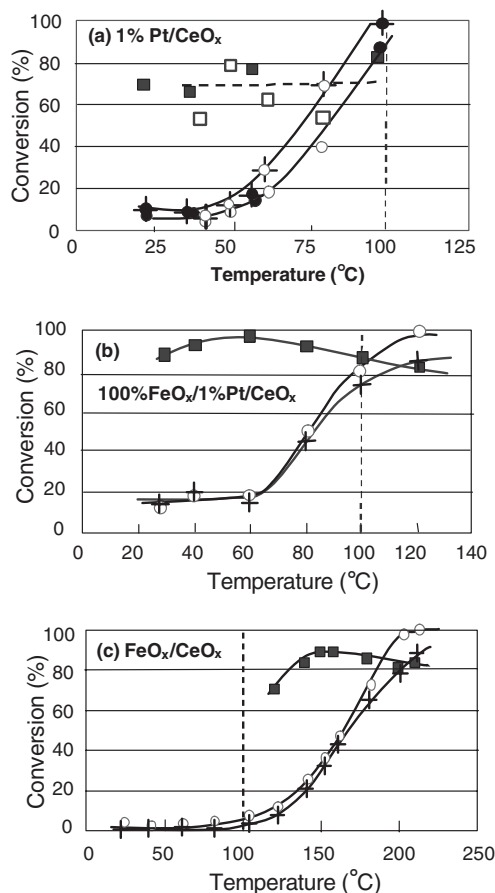


Figure 4. Conversion of CO in a mixture of CO, H₂, and O₂ (1.5:20:3 mL/min). (a) 1% Pt/CeO₂, the solid marks were obtained by temperature raising and the open marks were obtained by temperature-lowering experiments. (b) 100% FeO_x/1% Pt/CeO₂. (c) 100% FeO_x/CeO₂. (□) Conversion of O₂, (+) Conversion of CO, and (●) selectivity for CO oxidation.

similar to that of the CeO₂, although their activities are quite different. How can we explain this fact? On the other hand, the adsorption of CO occurs at the sites with coordinative vacancy on ceria [16] and Fe₂O₃ [17], and the H₂-D₂ hydrogen isotopic exchange and the hydrogen isotopic mixing of ethylene catalyzed by the Fe₂O₃ are poisoned by the adsorption of CO. When a large quantity of FeO_x was deposited on a 1% Pt/CeO₂ catalyst, some Pt was detected by the XPS as shown in figure 5. However, no suppression was observed and the selectivity was improved as shown in figure 4 (a) and (b). It is noteworthy that selectivity of the FeO_x/Pt/CeO₂ catalyst is very similar to that of the FeO_x/CeO₂ catalyst shown in figure 4(c), although the activity of the FeO_x/Pt/CeO₂ is much lower than that of the FeO_x/CeO₂. In addition, it is known that the activity as well as the selectivity of the FeO_x/CeO₂ (figure 4(c)) is very similar to that of the Fe₂O₃ (figure 1(c)) and Fe₂O₃/Al₂O₃ (figure 1(d)). From these facts, we deduced that the FeO_x is responsible for the catalysis of FeO_x/Pt/CeO₂ and FeO_x/Pt/Al₂O₃ catalysts. If this is the case, the FeO_x will be activated by the embedded

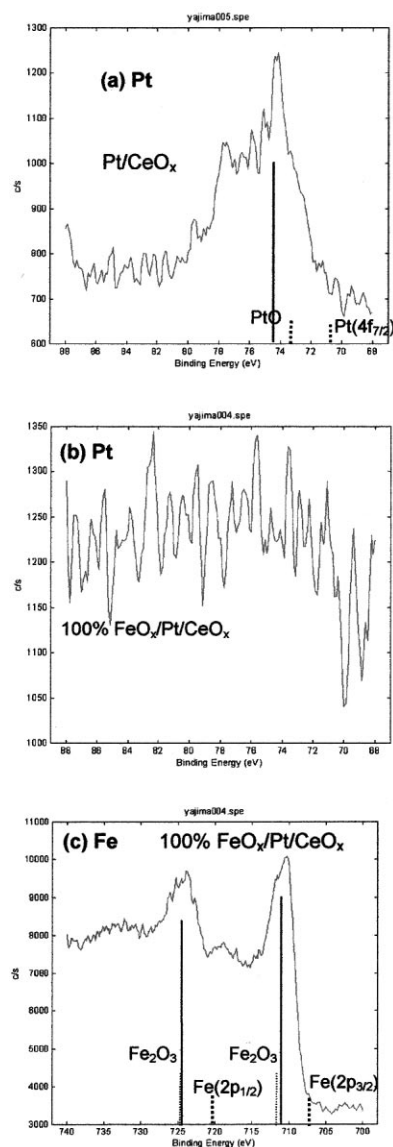


Figure 5. XPS spectra of 1%-Pt/CeO₂ and FeO_x/1%-Pt/CeO₂. (a) Pt spectrum of 1%-Pt/CeO₂, (b) Pt spectrum of FeO_x/1%-Pt/CeO₂, and (c) Fe Spectrum of FeO_x/1%-Pt/CeO₂.

Pt. Another interesting fact is that the support oxides, Al₂O₃ and CeO₂, have little influence on the activity and the selectivity of the FeO_x, but it is entirely different in the presence of embedded Pt, that is, the activation of Fe₂O₃ by the Pt is influenced by the support oxides.

Smearing of the Pt with FeO_x was proved by the XPS analysis. As the Pt(4f) peak overlaps a large Al(2p) peak, it is difficult to show the smearing of the Pt on the FeO_x/Pt/Al₂O₃ catalyst. Therefore, the XPS analysis of the Pt/CeO₂ and FeO_x/Pt/CeO₂ catalysts are shown in this paper. As shown in figure 5(a), XPS spectrum of the Pt/CeO₂ catalyst clearly showed the Pt of a form of PtO. However, no detectable Pt peaks were observed on the FeO_x/Pt/CeO₂ catalyst even if the sensitivity was raised as shown in figure 5(b), that is, the Pt was completely smeared with FeO_x. Accordingly, it is reasonable that

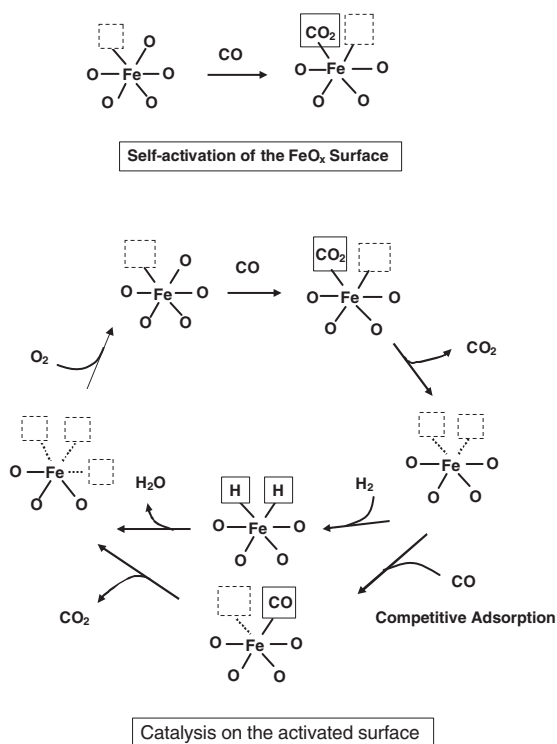


Figure 6. Formation of active site on the FeO_x surface and the catalysis on it.

the Pt is smeared with FeO_x on the FeO_x/Pt/Al₂O₃ catalyst too. If the Pt attributes to the catalysis of the FeO_x/Pt/CeO₂ and FeO_x/Pt/Al₂O₃, Pt should be detected by the XPS because the FeO_x/Pt/CeO₂ and FeO_x/Pt/Al₂O₃ take higher activity than the Pt/CeO₂ and Pt/Al₂O₃ respectively. Accordingly, we deduced that the FeO_x activated by the Pt is responsible for the new catalysts that were developed in this paper. However, the chemical state of the activated FeO_x and the active sites are difficult to identify by the XPS spectrum shown in figure 5(c).

If this mechanism is the case, it is a reasonable phenomenon that the selectivity of the FeO_x/Pt/CeO₂ and the FeO_x/Pt/Al₂O₃ is similar to that of the FeO_x/CeO₂ and the FeO_x/Al₂O₃ although the activity is quite different. Contribution of lattice oxygen may take place at the Fe-sites with coordinative vacancy where CO and/or H₂ undergo adsorption as shown on the evacuated Fe₂O₃ surface [17]. If Pt would contribute to the formation of such an active Fe-site on FeO_x/Pt/Al₂O₃ and FeO_x/Pt/CeO₂ catalysts, we could expect the highly active and highly selective oxidation of CO on the FeO_x/Pt/Al₂O₃ and FeO_x/Pt/CeO₂ catalysts.

Self-activation of the surface under the reaction condition is also important to deduce the role of active sites on which a catalytic cycle is accomplished [18,19]. In the case of catalysis by an isolated site, the selectivity might be less dependent on the conversion if the sites are formed by self-activation [19,20]. A good example is the

hydrogenation of acetylene to ethylene on the sulfur-coated Ni catalyst, where the sites are formed in the presence of acetylene so that the hydrogenation of ethylene is stopped when the acetylene in gas phase is consumed [18]. Figure 6 is a speculative model for the site on the FeO_x surface activated by CO. The Fe site having two vacancies is active for the adsorption of CO as well as for the dissociation of H₂ but the Fe site with one coordinative vacancy can adsorb only the CO molecule. Therefore, the catalytic cycle may promote only the oxidation of CO when the oxygen is in equilibrium with lattice oxygen. Details of this mechanism will be discussed in the following paper.

Acknowledgment

This work was supported by the High-Tech Research Center of Saitama Institute of Technology and was also partly supported by a Grant-in-Aid for Scientific Research [(B) 14,380,238] and [(C) 15510095] of the Ministry of Education, Culture, Sports, Science, and Technology of Japan.

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