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Catalysis Today 90 (2004) 255–261

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New catalyst for selective oxidation of CO in excess H_2 designing of the active catalyst having different optimum temperature

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Abstract

Highly active and highly selective new catalysts for the selective oxidation of CO in excess H_2 were prepared by depositing large amount of FeO_x on 1 wt.% Pt/Al_2O_3, 1 wt.% Pt/CeO_2, and 1 wt.% Pt/TiO_2 catalysts (100 times in weight of the Pt). Optimum activity of the $FeO_x/Pt/Al_2O_3$ and $FeO_x/Pt/CeO_2$ catalysts was attained at 130–140 °C while that of the $FeO_x/Pt/TiO_2$ catalyst was at 70–100 °C in the space velocity of 15,000 and 36,000 h^{-1}. CO conversion of the $FeO_x/Pt/TiO_2$ catalyst was ca. 70% at 40 °C in a flow of 15,000 h^{-1}. Optimum temperature of the $FeO_x/Pt/Al_2O_3$, $FeO_x/Pt/CeO_2$, and $FeO_x/Pt/TiO_2$ catalysts depends on the support oxides, and the feature of the new catalysts is different from that of such metallic catalyst as Pt/Al_2O_3, Pt/CeO_2, and Pt/TiO_2.

Keywords: FeO_x catalyst; Selective oxidation of CO in H_2; Synergic activation of FeO_x on Pt catalyst; Influence of support oxides on activity; Activation of oxide supported Pt catalyst by a large amount of FeOx; Comparison with Au/α-FeO_x, Pt/Al_2O_3 and Pt/TiO_2

1. Introduction

Anodic oxidation of H_2 in the proton exchange membrane (PEM) fuel cell is seriously suppressed by a trace amount of CO so that the CO in H_2 is required to be lower than 100 ppm. Therefore, the catalyst for selective oxidation of CO in excess H_2 is an imminent subject of the ECO-environmental technology. So far, precious metals such as Pt and Pd have been used as the basic metal for both the catalyst for selective oxidation of CO in H_2 as well as for the CO tolerant electrode although these two systems require the opposite properties for the precious metal. The CO tolerant electrode will be attained by weakening the adsorption of CO where the selective oxidation of H_2 will take place. In contrast, selective oxidation of CO in H_2 will be attained by strong adsorption of CO, that is, the oxidation of H_2 is suppressed by CO. Interesting fact is that one can control such opposite property for the precious metals by adding some promoter or modifier. Igarashi et al. [1] developed a CO tolerant $Pt_{85}Fe_{15}$ electrode, and it was shown that in situ coverage of CO on the $Pt_{85}Fe_{15}$ electrode is apparently lower than that on a Pt electrode [2].

If the adsorption of CO on Pt is weakened by adding some elements, the selectivity will be lowered on it. Therefore, if the selective oxidation of CO could be attained by some other mechanism than the competitive adsorption, it is interesting in the basic study as well as in the practical purpose. In this respect, it is worthy of note that industrial catalysts for the selective oxidation of hydrocarbon have been developed by entirely different concept, where the contribution of lattice oxygen is indispensable [3]. For example, the acrolein produced by the oxidation of propene with $^{18}O_2$ on a MoO_3–Bi_2O_3 catalyst contains little ^{18}O in the product [4], that is, the propene is oxidized with lattice oxygen at a specific site. This mechanism is clearly different from the competitive adsorption mechanism for the selective oxidation of CO in H_2. Why no one doubt the competitive adsorption mechanism for the selective oxidation of CO in H_2? We could say that the oxidation of CO in H_2 gives only simple products such as CO_2 and H_2O while the oxidation of hydrocarbon gives variety compounds.

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doi:10.1016/j.cattod.2004.04.049

However, the contribution of lattice oxygen was shown in the oxidation of CO on the CeO_2 or CeO_2–ZrO_2 supported precious metals. A typical example is the Pt–Rh three way catalyst supported on CeO_2 or CeO_2–ZrO_2 [5], where the role of CeO_2, CeO_2–ZrO_2 and $Ce_{0.5}Zr_{0.5}O_2$ has been explained as an oxygen storage provided that the mobility of lattice oxygen is high [6]. On the other hand, it was shown that the oxidation of CO on the precious metal catalysts such as Pt, Pd, and Rh obeys the inverse first-order in CO pressure, that is, the reaction is suppressed by the adsorption of CO. Similar inverse first-order kinetics was reported on the Pt, Pd, and Rh catalysts supported on CeO_2 at very low CO pressure, but the inverse first-order kinetics was changed to the zeroth-order for the CO pressure at higher than a certain pressure [7]. In this case, the zeroth-order rate was explained by the reaction CO with diffused lattice oxygen at the edge of the precious metals saturated with CO. It should be pointed out that the oxidation reaction is tacitly assumed to be catalyzed by precious metals. However, if the oxidation of CO takes place on the CeO_2 instead on the precious metals, the reaction mechanism will be switched when the catalysis by precious metal is suppressed. If the reaction on CeO_2 will be far more active than that on the precious metal, it is a new catalyst. In previous paper, we reported such a new type catalyst for the selective oxidation of CO in H_2 [8]. In this paper, we prepared the new catalysts by depositing a large amount of FeO_x (100 wt.% in Fe with respect to support oxide) on Pt/Al_2O_3, Pt/CeO_2, and Pt/TiO_2 catalysts and compared their catalytic feature, the activity and the selectivity, with ordinary catalyst in the flow rate (GHSV) of 15,000 and 36,000 h^{-1}.

2. Experimental

Pt was deposited by immersing Al_2O_3, CeO_2, and TiO_2 in a solution of $PtCl_4$. About 1 wt.% of Pt deposited Pt/Al_2O_3, Pt/CeO_2, and Pt/TiO_2 catalysts were dried at 140 °C for 3 h. The Al_2O_3 used in this experiment was a standard alumina of the Catalysis Society of Japan supplied from Sumitomo Chemical Co. (AKP GO-15-Al_2O_3; surface 148 m^2/g, impurities of Fe 4 ppm, Cu 1 ppm, Mg 1 ppm, Na 2 ppm, and Si 2 ppm). The CeO_2 prepared by calcinating a commercially available Ce(IV) hydroxide (Wako Pure Chemicals Co. 032-01842) at 400 °C.

New catalysts, $FeO_x/Pt/CeO_2$, $FeO_x/Pt/Al_2O_3$, and $FeO_x/Pt/TiO_2$, were prepared by loading Fe atoms of about 350 times of the Pt atoms on a 1% Pt/Al_2O_3, a 1% Pt/CeO_2, and a 1% Pt/TiO_2 (FeO_x is ca. 100% in Fe weight with respect to the support oxide). Two experiments were performed, one was the experiment to survey the activity and the selectivity of the composite oxides and of the new oxide catalysts. In this experiment, the reaction was performed by using 1.5 g of the catalyst in a fixed-bed flow reactor (a glass tube of 14 mm of diameter). Flow rate of 100 ml/min was attained by H_2 = 20 ml/min, CO = 3 ml/min, O_2 = 1.5 ml/min and a balanced gas of N_2. The other experiment was performed in high gas hourly space velocity (GHSV) of 15,000 and 36,000 h^{-1}, and the activity and the selectivity of the new catalysts of $FeO_x/Pt/CeO_2$, $FeO_x/Pt/Al_2O_3$, and $FeO_x/Pt/TiO_2$ were compared with ordinary catalysts of a Pt/TiO_2 (rutile), a Pt/Al_2O_3, and a Au/α-Fe_2O_3 (Toyo CCI Co.). Fig. 1 shows the experimental system, where 1.8 ml of catalyst was packed in a Al-reactor of 8 mm inner diameter, and the temperature was monitored by the thermocouples placed at the middle of the catalyst and at the center of the outside of the reactor. Highly pure H_2 (six 9 purity) and $CO/CO_2/O_2/N_2$ = 12/50/7/31 were mixed and were bubbled through water (contained about 3.5% of H_2O). Preceding reduction of the catalyst was carried out at 110–120 °C for more than 1.5 h in advance the experiments. Oxygen conversion ($X_{O_2} = \Delta O_2/a_0$) reflects the total consumption of O_2 by the reaction with CO and H_2, and the conversion of CO ($X_{CO} = \Delta CO/b_0$) is the fraction of CO oxidized to CO_2, where a_0 and b_0 are the initial composition of O_2 and CO and ΔCO and ΔO_2 are the reacted CO and O_2, respectively. The selectivity (S) is given by $S = (1/2)(\Delta CO/\Delta O_2) = (1/2)(b_0X_{CO})/(a_0X_{O_2}) = (1/2)(X_{CO}/X_{O_2})(b_0/a_0)$. Therefore, when the initial composition of CO (b_0) and O_2 (a_0) is exactly $a_0/b_0 = 1/2$, the selectivity (S) is equal to the conversion of CO (X_{CO}) at 100% O_2 conversion ($X_{O_2} = 1$). It should be pointed out that the selectivity is lower than 100% in general, so that CO is remained in the exhaust gas at 100% of the oxygen conversion.

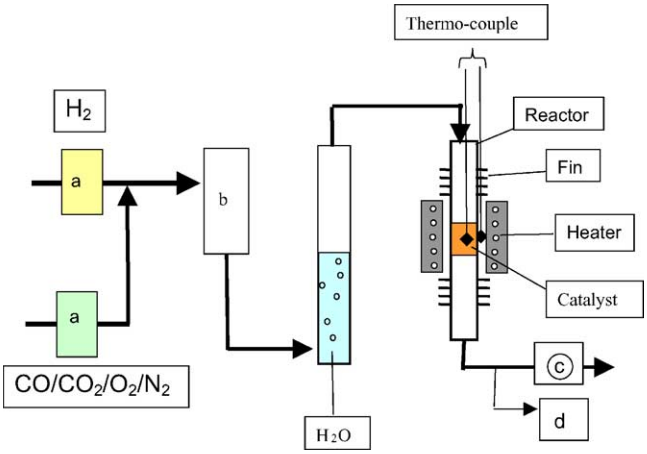


Fig. 1. Flow reactor scheme for activity test at flow rate (GHSV) of 15,000 and 36,000 h^{-1}. (a) Mass flow controller, (b) quarts beads, (c) gas meter, and (d) gas chromatography.

The XPS analysis of the Pt/Al_2O_3, $FeO_x/Pt/Al_2O_3$, Pt/CeO_2, and $FeO_x/Pt/CeO_2$ catalysts was performed by a Phi-quantum 2000 Scanning ESCA microprobe spectrometer with Al Kα (1486.6 eV), where the powdered sample was fixed on a carbon tape by a conductive glue.

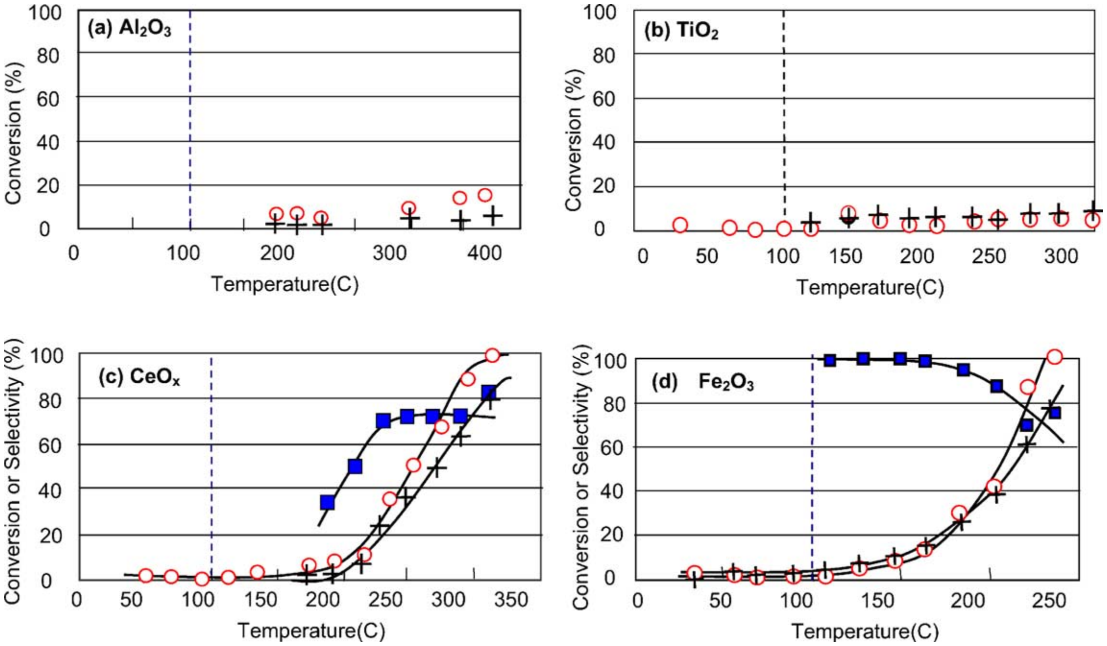


Fig. 2. Activity of (a) Al_2O_3, (b) TiO_2, (c) CeO_2, and (d) FeO_x for the catalytic oxidation of CO in a flow of CO + H_2 + O_2 (CO: 3 ml/min; O_2: 1.5 ml/min; H_2: 20 ml/min; N_2: 75.5 ml/min). (○) O_2 conversion, (+) CO conversion, and (■) selectivity.

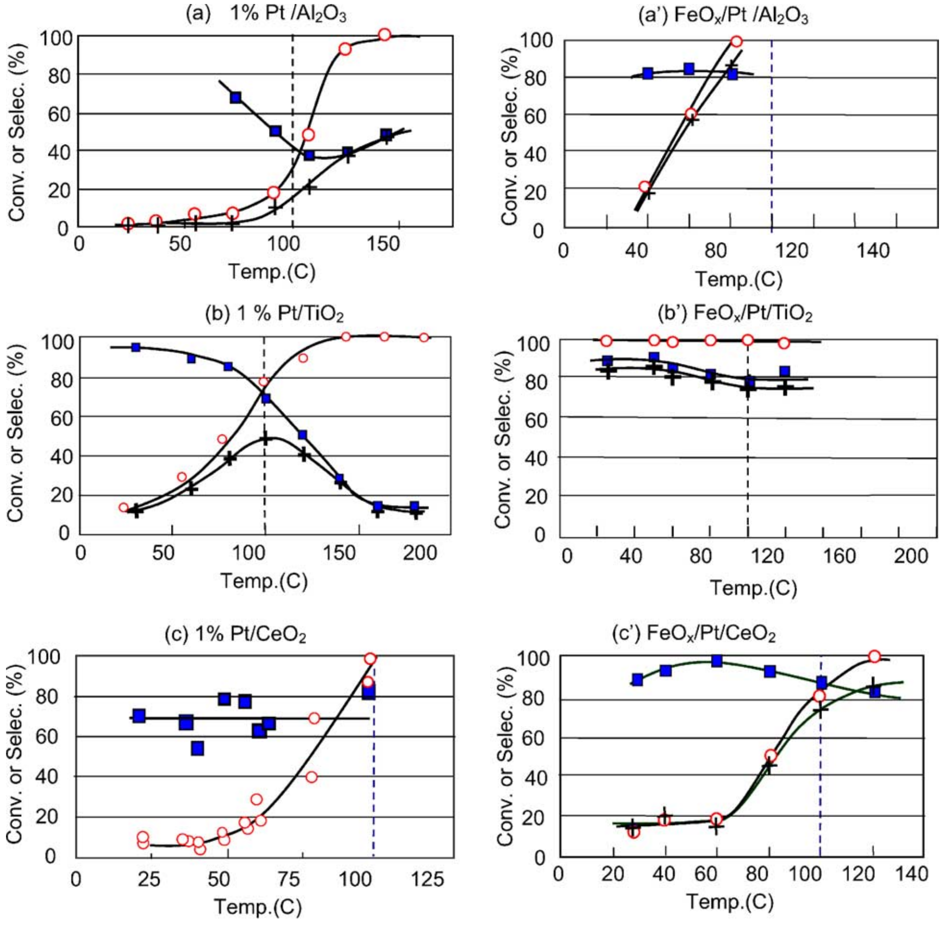


Fig. 3. Enhancement of the activity for the oxidation of CO in H_2 ($CO/H_2 = 3/20$) by loading a large amount of FeO_x. 1 wt.% Pt/Al_2O_3, (a′) 100 wt.% FeO_x/1% Pt/Al_2O_3, (b) 1 wt.% Pt/TiO_2, (b′) 100 wt.% FeO_x/1% Pt/TiO_2, (c) 1 wt.% Pt/CeO_2, and (c′) 100 wt.% FeO_x/1% Pt/CeO_2; (○) O_2 conversion (%), (+) CO conversion (%), and (■) selectivity (%).

3. Results and discussion

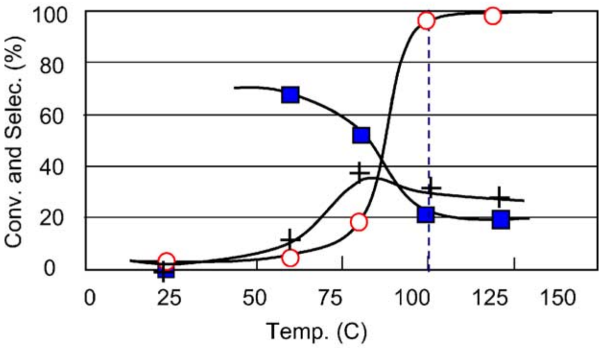
3.1. Reaction on (a) Al_2O_3, (b) TiO_2, (c) CeO_2, and (d) FeO_x

Al_2O_3 and TiO_2 have no appreciable activity for the oxidation of CO and H_2 at temperature lower than 300 °C as shown in Fig. 2a and b, but CeO_2 has activity at temperature higher than 200 °C as reported in a reference data [9]. It is also known that FeO_x becomes active at temperature higher than 150 °C in Fig. 2c and d. It is worthy of note that the selectivity for the oxidation of CO is high on CeO_2 and FeO_x and it is retained at higher conversion. So far the selective oxidation of CO in H_2 is explained by strong adsorption of CO disturbing the dissociation of H_2. Therefore, the reaction by metallic catalyst is the higher the conversion, the lower the selectivity. If the FeO_x and CeO_2 could be activated by some means, which will provide highly active and highly selective catalysts. As reported in this paper, we found a new activation procedure for the FeO_x as will be discussed in the following section.

3.2. Reaction on (a) $FeO_x/Pt/Al_2O_3$, (b) $FeO_x/Pt/TiO_2$, and (c) $FeO_x/Pt/CeO_2$

As described in the experiment, (a) $FeO_x/Pt/Al_2O_3$, (b) $FeO_x/Pt/TiO_2$, and (c) $FeO_x/Pt/CeO_2$ were compared by depositing large amount of FeO_x on Pt/Al_2O_3, Pt/TiO_2, and Pt/CeO_2. As shown in Fig. 3, it is evident that $FeO_x/Pt/Al_2O_3$ and $FeO_x/Pt/TiO_2$ are far more active than Pt/Al_2O_3 and Pt/TiO_2 catalysts, and100% conversion was attained at lower than 100 °C on the new catalysts as shown in Fig. 3a′ and b′. It is worthy of note that the selectivity is rather independent of the conversion on Pt/CeO_2 catalyst as shown in Fig. 3c, which is similar to that of $FeO_x/Pt/CeO_2$ shown in Fig. 3c′. This feature is quite different from the Pt/Al_2O_3 and Pt/TiO_2 catalyst on which the selectivity is steeply lowered as increasing the conversion. The selectivity of Pt/CeO_2 is improved by adding FeO_x, and it is almost equal to that of the $FeO_x/Pt/Al_2O_3$, $FeO_x/Pt/TiO_2$ and $FeO_x/Pt/CeO_2$ catalysts.

An EXAFS study [10] reported that the dispersion of Pt on Al_2O_3 is markedly improved by adding small amount of Fe (Fe/Pt = 5), and the EXAFS data suggested that the Fe is at the interface of Pt and Al_2O_3. Therefore, we studied the effect of small amount of FeO_x on the activity of a Pt/Al_2O_3 catalyst. As shown in Figs. 4a and 3a, addition of small amount of FeO_x (1 wt.% in Fe) to Pt/Al_2O_3 and Pt/TiO_2 enhances the activity of Pt/Al_2O_3 and Pt/TiO_2 (not shown here), which might be similar effect reported on the Pt/Al_2O_3 catalysts by Farrauto and coworkers [11,12] and Sakamoto et al. [13]. It should be emphasized that such promotion of the Pt/Al_2O_3 catalyst by small amount of FeO_x is different from the new catalyst prepared by adding a large amount of FeO_x to the Pt/Al_2O_3, Pt/TiO_2, and Pt/CeO_2. As shown in Fig. 4a, a (Pt + 1% Fe)/Al_2O_3 catalyst is activated by adding small amount of FeO_x, but the selectivity of this catalyst is steeply lowered as increasing the conversion, which is very similar to feature of Pt/Al_2O_3 and Pt/TiO_2 catalysts shown in Fig. 3a and b. If we compare the selectivity on the $FeO_x/Pt/Al_2O_3$ and the $FeO_x/Pt/TiO_2$ catalysts prepared by deposing a large amount of FeO_x, relatively high selectivity is retained up to high conversion as shown in Fig. 3a′–c′.


(a) (1% FeO_x + 1%Pt) /Al_2O_3

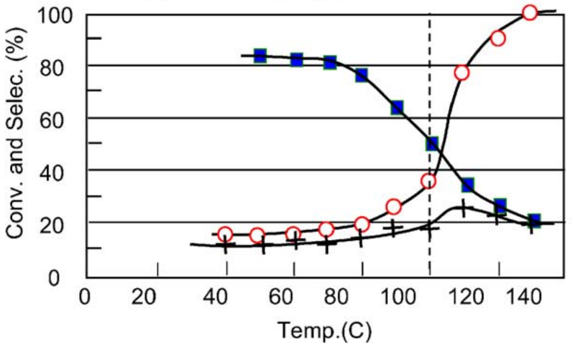

(b) 1%Pt/FeO_x/Al_2O_3

Fig. 4. (a) Effect of 1 wt.% of FeO_x added to a 1 wt.% Pt/Al_2O_3, and (b) the activity of 1 wt.% Pt on a 100 wt.% FeO_x/Al_2O_3; (○) O_2 conversion (%), (+) CO conversion (%), and (■) selectivity (%).

To confirm this unusual synergic effect of FeO_x, Pt was deposited on a FeO_x/Al_2O_3 and its activity and the selectivity was compared with those of the $FeO_x/Pt/Al_2O_3$ catalyst, where the two catalysts contain similar large amount of FeO_x (100 wt.% in Fe). The reaction performed on the $Pt/FeO_x/Al_2O_3$ catalyst is shown in Fig. 4b. It is known that the activity as well as the selectivity is very similar to that of the Pt/Al_2O_3 catalyst shown in Fig 3a. Consequently, we could conclude that large amount of FeO_x deposited on the Pt/Al_2O_3, Pt/TiO_2, and Pt/CeO_2 catalysts is responsible for the unique activity and selectivity of the new catalysts, and that the FeO_x is activated by the embedded Pt. In fact, it was shown that the catalytic activity of Ru/Al_2O_3 is completely suppressed by depositing a large amount of FeO_x whereas the activity of a (Pt + Ru)/Al_2O_3 was markedly enhanced by the deposition of large amount of FeO_x as shown in the previous paper [8]. The XPS spectra of Pt/CeO_2 and $FeO_x/Pt/CeO_2$ also support the

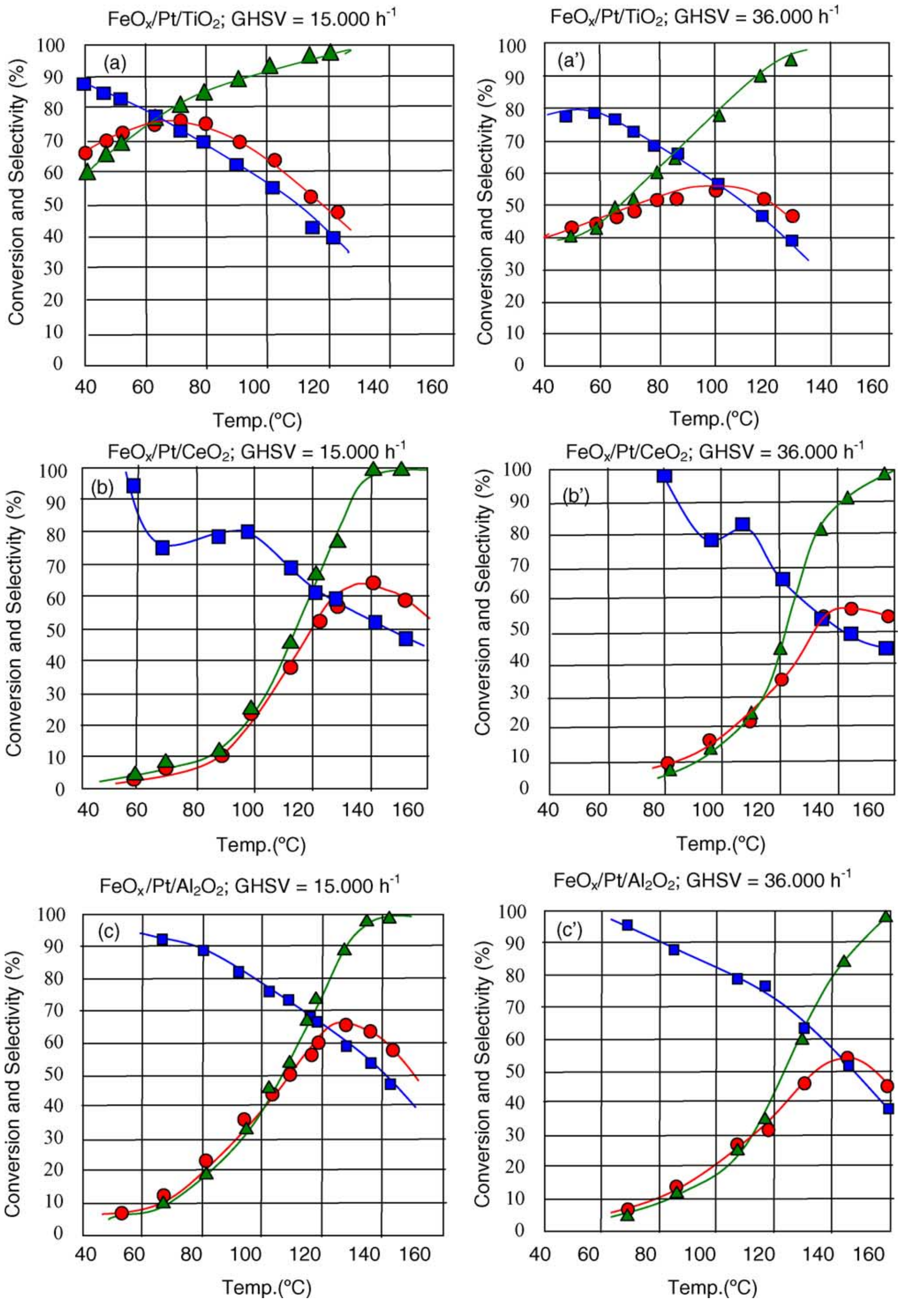


Fig. 5. Activity (%) and selectivity (%) of the new catalysts in the GSHV of 15,000 and 36,000 h^{-1}. (a) Pt/TiO$_2$, (a′) FeOx/Pt/TiO$_2$, (b) Pt/CeO$_x$, (b′) FeOx/Pt/CeO$_x$, (c) Pt/Al$_2$O$_3$, (c′) FeO$_x$/Pt/Al$_2$O$_3$; (■) selectivity, (▲) O$_2$ conversion, and (●) CO conversion.

smearing of Pt by deposited FeO$_x$ [8]. However, we could not show clearly the similar smearing of Pt for Pt/Al$_2$O$_3$ and FeO$_x$/Pt/Al$_2$O$_3$ at the present time because the Pt peaks are too weak. Finally, we compared the new catalysts with the ordinary catalysts in high space velocity of hydrogen.

3.3. Activity and selectivity of new catalysts in large flow rate

The catalyst for the selective oxidation of CO in hydrogen for the fuel cell should work in high space velocity of hydrogen. Therefore, we compared the activity of

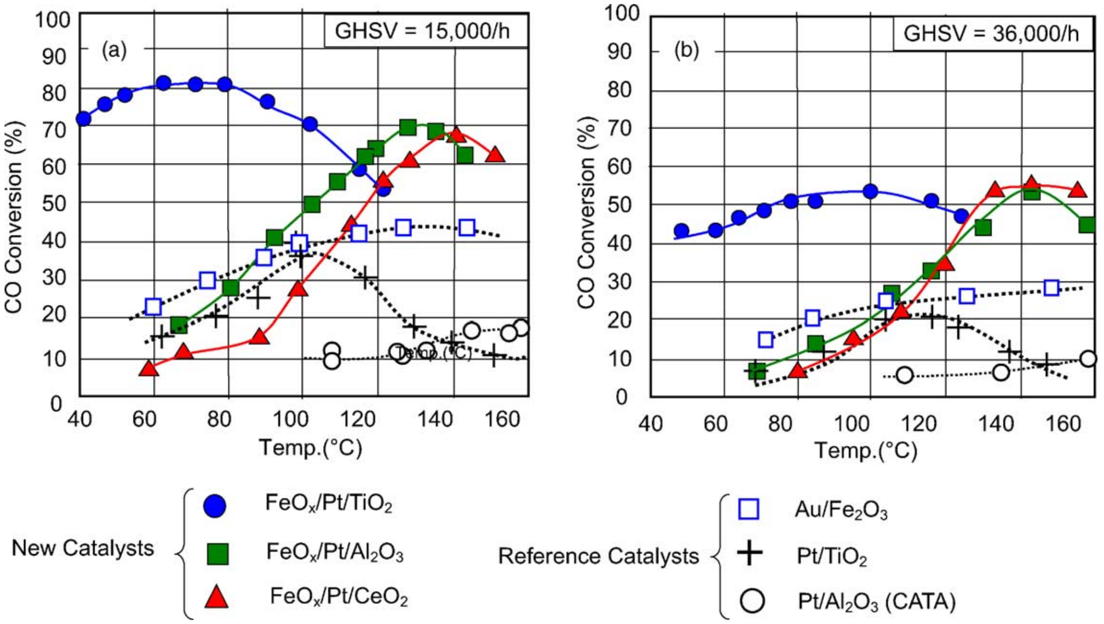


Fig. 6. Activity of the new catalysts and the reference catalysts in the flow of GSHV = 15,000 and 36,000 h^{-1} (▲) FeO$_x$/Pt/TiO$_2$, (●) FeO$_x$/Pt/Al$_2$O$_3$, and (■) FeO$_x$/Pt/CeO$_x$. (□) Au/FeOx, (+) Pt/TiO$_2$, and (○) Pt/Al$_2$O$_3$ (CATA).

the FeO$_x$/Pt/Al$_2$O$_3$, FeO$_x$/Pt/TiO$_2$ and FeO$_x$/Pt/CeO$_2$ catalysts with ordinary catalysts by adopting the space velocity (GHSV) of 15,000 and 36,000 h^{-1}. The flow gas was composed of 75% of H$_2$, 3% of CO, and O$_2$ of a ratio of O$_2$/CO = 0.6, and the balanced gas of N$_2$ contained ca. 3.5% H$_2$O.

The activity and the selectivity of FeO$_x$/Pt/Al$_2$O$_3$, FeO$_x$/Pt/TiO$_2$ and FeO$_x$/Pt/CeO$_2$ catalysts were measured in the space velocity of GHSV = 15,000 and 36,000 h^{-1} and were plotted against the catalyst temperature in Fig. 5a–c′. The activity of the three new catalysts were compared to the ordinary catalysts, Pt/Al$_2$O$_3$, Pt/TiO$_2$ (rutile), and Au/α-Fe$_2$O$_3$ (Toyo CCI Co.) in Fig. 6a and b, where (a) and (b) are the results at the space velocity of GHSV = 15,000 and 36,000 h^{-1}, respectively. Au/α-Fe$_2$O$_3$ catalyst (Toyo CCI Co.) is a commercially available active catalyst for the selective oxidation of CO in H$_2$ working at low temperature. The Pt/Al$_2$O$_3$ and the Pt/TiO$_2$ (rutile) were prepared by depositing Pt on Al$_2$O$_3$ and TiO$_2$ (rutile). It is clear that FeO$_x$/Pt/TiO$_2$ catalyst has extremely high activity at low temperature, that is, about 70% CO conversion was attained at 40 °C in a flow rate of 15,000 h^{-1} and about 40% conversion in a flow of 36,000 h^{-1} as shown in Fig. 6a and b. On the other hand, FeO$_x$/Pt/Al$_2$O$_3$ and FeO$_x$/Pt/CeO$_2$ catalysts are superior at temperature higher than 100 °C. From these results, we can confidently conclude that these new catalysts are superior to ordinary reference catalysts in whole temperature range studied. Selectivity for the oxidation of CO is rather high on the FeO$_x$/Pt/TiO$_2$ catalyst, which is about 90% at 40 °C in 15,000 h^{-1} and about 80% in 36,000 h^{-1} as shown in Fig. 5a and a′, respectively. It is also known that the FeO$_x$/Pt/Al$_2$O$_3$ and FeO$_x$/Pt/CeO$_2$ are more profitable catalyst when the reaction is performed at the temperature higher than100 °C. Consequently, we could say that the catalyst profitable for desired temperature can be designed by changing support oxides.

It is worthy of note that the Au/α-Fe$_2$O$_3$ a catalyst developed for the selective oxidation of CO at low temperature, but our new catalyst of FeO$_x$/Pt/TiO$_2$ is far superior to this catalyst for the selective oxidation of CO at low temperature. The new catalyst of FeO$_x$/Pt/Al$_2$O$_3$ and FeO$_x$/Pt/CeO$_2$ are the most profitable catalyst at higher temperature than 120 °C as shown in Fig. 6, where the CO conversion is about 70% at 130–140 °C. Accordingly, we can conclude that FeO$_x$/Pt/Al$_2$O$_3$, FeO$_x$/Pt/CeO$_2$, and FeO$_x$/Pt/TiO$_2$ are a new type catalyst which selectively promotes the oxidation of CO in excess H$_2$, and the optimum temperature of it can be designed by changing the support oxide.

Acknowledgements

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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