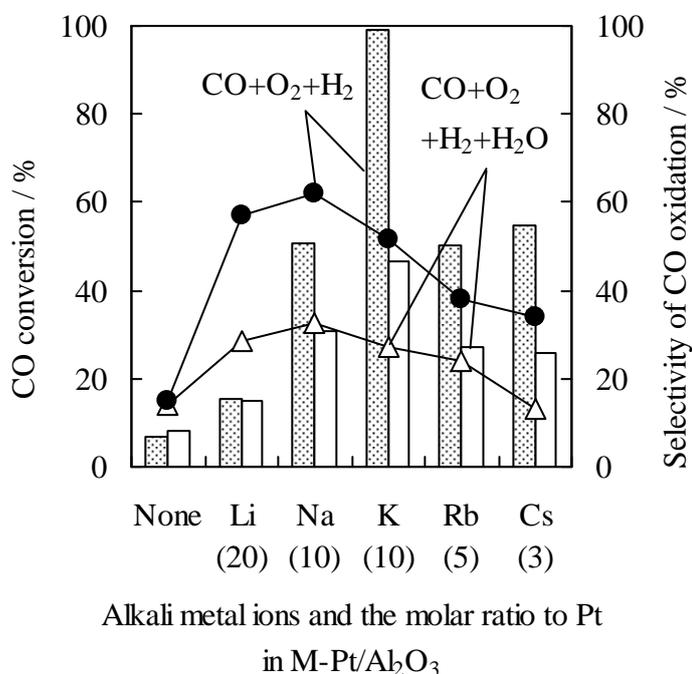# Preferential CO oxidation in hydrogen-rich stream
over Pt catalysts modified with alkali metals : Part I. Catalytic performance

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In preferential CO oxidation in H_2-rich stream (PROX), the additive effect of potassium to Pt/Al_2O_3 was more effective than other alkali metals. The PROX activity of $K-Pt/Al_2O_3$ was much higher than that of Pt/Al_2O_3 under the presence of steam, and the effect of steam addition over $K-Pt/Al_2O_3$ suggests that the active site can be Pt surface modified with potassium ions.

Preferential CO oxidation in hydrogen-rich stream

over Pt catalysts modified with alkali metals : Part Ⅰ. Catalytic performance

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Abstract

In preferential CO oxidation in H_2-rich stream (PROX), the additive effect of potassium on Pt catalysts was more remarkable over Al_2O_3 than over SiO_2, ZrO_2, Nb_2O_5 and TiO_2. The additive effect of potassium to Pt/Al_2O_3 was more effective than other alkali metals. Especially, the presence of H_2 drastically promoted CO oxidation over Pt/Al_2O_3 modified with potassium. On the other hand, the suppressing effect of steam on the PROX was more significant over K-Pt/Al_2O_3 than over Pt/Al_2O_3, although the PROX activity of K-Pt/Al_2O_3 was much higher than that of Pt/Al_2O_3 even under the presence of steam. The different effect of steam addition to the PROX over K-Pt/Al_2O_3

suggests that the active site can be Pt surface modified with potassium ions.

1. Introduction

Preferential CO oxidation in H_2-rich mixtures (PROX) is an important reaction in terms of the purification of the fuel gas when hydrogen is produced by the steam reforming of hydrocarbons and oxygenates [1,2]. This is because the product gases contain CO as an impurity, and this CO is a poison for the anode catalyst of the polymer electrolyte fuel cell [3-5]. Various supported noble metal catalysts such as Pt, Ru and Rh for the preferential CO oxidation in H_2-rich gas have been reported [6-25]. Modification of the noble metal catalysts with various additives enhanced the catalytic performance [15-20]. In particular, the addition of alkali metal to noble metal catalysts is effective to the preferential CO oxidation [23-31]. Our group has recently reported that the activity of the preferential CO oxidation in H_2-rich stream was promoted drastically by the presence of H_2 over the optimized K-Pt/Al_2O_3, and the CO concentration was decreased to be below 10ppm [26-28]. In this article, we evaluated the additive effect of alkali metals (Li, Na, K, Rb and Cs) on the catalytic performance of the PROX reaction over Pt catalysts supported on Al_2O_3 and the other oxides (SiO_2, ZrO_2, Nb_2O_5 and TiO_2).

2. Experimental

2.1. Catalyst preparation

Supported Pt catalysts were prepared by using Al_2O_3 (JRC-ALO-4 from Japan Reference

Catalyst (JRC); BET surface area, 170 m^2/g), SiO_2 (JRC-SIO-7 from JRC; BET surface area, 82 m^2/g), ZrO_2 (RC-100 from Daiichi-Kigenso Co. Ltd.; BET surface area, 49 m^2/g), Nb_2O_5 (prepared by calcining $Nb_2O_5 \cdot H_2O$ from Soekawa Chemicals Co. Ltd. for 1 h at 973 K in air; BET surface area, 45 m^2/g) and TiO_2 (AEROSIL; BET surface area, 39 m^2/g) as support materials. Before the impregnation, Al_2O_3, SiO_2, ZrO_2 and TiO_2 were calcined for 3 h in air at 873, 1173, 873 and 773 K, respectively. Pt/Al_2O_3 catalyst was prepared by impregnating the Al_2O_3 with an aqueous solution of $Pt(NO_2)_2(NH_3)_2$ (Soekawa Chemical Co., Ltd.). After the impregnation, the sample was dried at 383 K for 12 h, and then calcined in air at 773 K for 3 h. The loading amount of Pt was 2 wt%, and the BET surface area of the catalyst was 160 m^2/g. The Pt/Al_2O_3 catalysts modified with alkali metals (M= Li, Na, K, Rb, Cs) were also prepared, and the modification method was as follows: after the impregnation with the aqueous solution of $Pt(NO_2)_2(NH_3)_2$, the sample was dried at 383 K for 12 h. After the further impregnation of the dried sample with an aqueous solution of each alkali nitrate, it was dried again at 383 K for 12 h and calcined at 773 K for 3 h. The loading amount of alkali metals is described in the molar ratio to Pt (M/Pt), and the ratio was in the range of 1-20. The Pt/Al_2O_3 catalysts modified with alkali metals are denoted as $M-Pt/Al_2O_3$ and the molar ratio of M/Pt is shown in parenthesis like $K-Pt/Al_2O_3$ (10). In case of the $K-Pt/Al_2O_3$ (10), the BET surface area of the catalyst was 119 m^2/g. The Pt catalysts supported on the other oxides (SiO_2, ZrO_2, Nb_2O_5, TiO_2) modified with potassium were also prepared in the same way as $K-Pt/Al_2O_3$. The catalysts were reduced with hydrogen at 773 K for 1 h in the reactor before the activity test. Bulk density of the Al_2O_3, SiO_2, ZrO_2, Nb_2O_5, and TiO_2 supported catalysts was 0.50, 0.40, 0.75, 1.0, 0.79 g/cm^3, respectively.

2.2. Activity test of preferential CO oxidation

Preferential CO oxidation in H_2-rich stream (PROX) was carried out in a fixed-bed flow reaction system at atmospheric pressure. In most cases, the feed stream contained 0.2% CO, 0.2% O_2 and 75% H_2, and it was balanced with helium at the total flow rate of 100 cm^3/min (STP). The catalyst weight was 0.10g, and the GHSV was calculated to be 30,000 h^{-1} in the case of alumina supported catalysts. The feed stream containing 1% CO, 1.25% O_2 and 60% H_2 balanced with He at total flow rate of 50 cm^3/min was also used. Activity tests were carried out at every 10 K in the range of 320-450 K. The effluent gas was analyzed using an on-line gas chromatograph (GC) system equipped with a TCD detector. In addition, the concentration of CO at the ppm level in the effluent gas was determined using FID-GC equipped with a methanator. The activity was evaluated by CO and O_2 conversions, which can be calculated on the basis of CO and O_2 concentrations in the reactant and the effluent gases. In addition, the methane concentration in the effluent gas was below the detection limit in all the cases. The selectivity of CO oxidation is estimated by the ratio of O_2 consumption for the CO oxidation to the total O_2 consumption, and it can be calculated by the equation below.

$$\text{Selectivity of CO oxidation} = \frac{\text{CO conversion (\%)} \ \times \ \text{CO partial pressure}}{2 \times \text{O}_2 \text{ conversion (\%)} \ \times \ \text{O}_2 \text{ partial pressure}} \times 100$$

Considering the experimental error, the selectivity was shown when CO conversion was higher than about 5%. The preferential CO oxidation in H_2-rich stream (PROX) is denoted as the $CO+O_2+H_2$ reaction. As a reference, we also carried out the activity test of CO oxidation in the absence of H_2, and this simple CO oxidation is denoted as the $CO+O_2$ reaction. In addition, we investigated the effect of the copresence of steam on the preferential CO oxidation. This reaction is

5

denoted as the $CO+O_2+H_2+H_2O$ reaction. The feeding conditions in the reactions are described in each result. Furthermore, we measured the activity of water gas shift reaction, which is denoted as the $CO + H_2O$ reaction. In all reactions, the activity was observed during 30 min under each reaction condition at least. Since almost no deactivation was observed, the results of the activity test correspond to those under the steady-state condition.

2.3. Catalyst characterization

The catalysts were characterized by the amount of CO adsorption. The amount of the irreversible adsorption of CO (CO/Pt) was measured at room temperature in a vacuum system by the volumetric method [25]. The samples are pretreated in O_2 at 773 K for 1 h, followed by H_2 reduction at 773 K for 1 h at atmospheric pressure. The equilibrium pressure of CO was about 2.7 kPa. Further characterization of the catalysts is described in the following article [32].

3. Results and discussion

3.1. Effect of support materials

Figure 1 shows the dependence of CO conversion and selectivity in the preferential CO oxidation (PROX) in H_2-rich gas (the $CO+O_2+H_2$ reaction) over Pt catalysts supported on various oxides with or without potassium modification at 403 K. In this case, the amount of potassium was K/Pt=3. It is found that the addition of potassium to Pt catalysts enhanced both CO conversion and selectivity of CO oxidation over all the support materials. The K-Pt/Al_2O_3 and K-Pt/SiO_2 exhibited much higher CO conversion and selectivity than K-Pt/ZrO_2, K-Pt/Nb_2O_5 and K-Pt/TiO_2. The high performance

6

of Al_2O_3 and SiO_2 supported catalysts can be related to high BET surface area of the supports, although the details are not investigated at present. As a result, SiO_2 and Al_2O_3 can be promising in the catalyst development for the PROX. Therefore, we investigated the influence of the potassium amount over $K-Pt/Al_2O_3$ and $K-Pt/SiO_2$ catalysts.

Figure 2 shows the reaction temperature dependence of CO conversion and selectivity of CO oxidation in the $CO+O_2+H_2$ reaction over $K-Pt/Al_2O_3$ (0, 3, 10) and $K-Pt/SiO_2$ (0, 3, 10) catalysts. The CO conversion on Pt/SiO_2 was much higher than that on Pt/Al_2O_3, and it approached 100% at 433 K. The addition of potassium to Pt/SiO_2 enhanced the CO conversion at lower reaction temperature and the optimum amount was determined to be K/Pt=3. However, the CO conversion cannot reach almost 100% even at higher reaction temperature. It is concluded that the complete removal of CO seems to be difficult over $K-Pt/SiO_2$. On the other hand, although Pt/Al_2O_3 was not so effective as Pt/SiO_2, the addition of potassium to Pt/Al_2O_3 drastically enhanced the performance in the PROX. In particular, the CO conversion reached almost 100% in the range of 368-428 K over $K-Pt/Al_2O_3$ (10). In addition, the CO concentration in the effluent gas was maintained below 10ppm in the temperature range between 375 K and 410 K over $K-Pt/Al_2O_3$ (10) from the more precise analysis using FID-GC, which is shown in our previous report [26-28]. Based on the comparison among support materials, we investigated the additive effect of various alkali metals over Pt/Al_2O_3 on the catalytic performance in the PROX. In addition, it should be noted that all the catalysts with high activity at lower reaction temperature didn't show high ability for the CO removal when the reaction temperature is higher and the CO conversion is higher. Based on the results, it is better to evaluate the catalytic performance at lower reaction temperature (363 K) for the activity and at higher reaction temperature (403 K) for the CO removal ability.

7

3.2. Additive effect of alkali metals on Pt/Al$_2$O$_3$

Figure 3 shows the effect of molar ratio of Li to Pt (Li/Pt) on CO conversion and selectivity in the PROX over Li-Pt/Al$_2$O$_3$ catalysts at 363 K and 403 K. The Li-Pt/Al$_2$O$_3$ catalysts exhibited lower catalytic activity compared to Pt/Al$_2$O$_3$ modified with other alkali metals, and the dependence of the additive amount of Li on the catalytic performance was almost same at two temperatures. The activity of the PROX increased slightly with increasing Li/Pt at both temperatures. The selectivity of CO oxidation gradually increased.

Figure 4 shows the CO conversion and selectivity of CO oxidation as a function of molar ratio of Na (Na/Pt) over Na-Pt/Al$_2$O$_3$. The addition of Na enhanced the CO conversion and selectivity of CO oxidation dramatically. The additive effect of Na was greatly dependent on the amount of Na added. At 363 K, it seems that the promoting effect of the Na addition was saturated above Na/Pt = 10. On the other hand, at 403 K, the CO conversion was maximum on the catalyst with Na/Pt = 10. As a result, the optimum amount was determined to be Na/Pt=10. The CO conversion was almost 100% at 403 K over Na-Pt/Al$_2$O$_3$ (10).

Figure 5 shows the effect of molar ratio of K (K/Pt) on the CO conversion and selectivity of CO oxidation in the CO+O$_2$+H$_2$ reaction over K-Pt/Al$_2$O$_3$ catalysts. Potassium was the most remarkable additive among alkali metals. It is characteristic that the addition of small amount of potassium enhanced the selectivity of CO oxidation remarkably, and the effect was maintained in higher K/Pt region. In particular, K-Pt/Al$_2$O$_3$ (K/Pt = 5) showed similar CO conversion and selectivity to Na-Pt/Al$_2$O$_3$ (Na/Pt = 10) at 363 K, however, K-Pt/Al$_2$O$_3$ (K/Pt = 5) had much higher ability for CO removal at 403 K than Na/-Pt/Al$_2$O$_3$ (Na/Pt = 5). This comparison demonstrates the superiority of

8

potassium. As shown in Figure 6, the selectivity increased with increasing the additive amount of Rb at 363 K, and the CO conversion was maximum at Rb/Pt = 5. On the other hand at 403 K, the catalyst with Rb/Pt =5 was comparable to that with Rb/Pt = 10. In the case of Cs-Pt/Al$_2$O$_3$, the optimum amount of Cs was determined to be Cs/Pt = 3. Compared to Na and K, the additive effect of Rb and Cs was not so significant. The performance of Rb-Pt/Al$_2$O$_3$ and Cs-Pt/Al$_2$O$_3$ was highest at Rb/Pt=5 and Cs/Pt=3, respectively. Unlike the case of Na and K, the addition of larger amount of Rb and Cs decreased the CO conversion drastically.

3.3. Effect of the presence of H$_2$ on the CO oxidation

Figure 8 shows the comparison in the CO conversion between the CO+O$_2$+H$_2$ and CO+O$_2$ reactions over M-Pt/Al$_2$O$_3$ (M=Li, Na, K, Rb, Cs) catalysts at 363 K and 403 K. We compared the data on the catalysts modified with each alkali metal, which gave highest CO conversion at 363 K based on the results in Figures 3a-7a. The optimum molar ratio of alkali metals tends to decrease from Li to Cs. This tendency can be related to the strength of basicity, which is stronger from Li to Cs [33]. These behaviors indicate that the maximum of promoting effect is obtained by the smaller additive amount of alkali metals with stronger basicity. Another interesting point is that the CO conversion in the CO+O$_2$+H$_2$ reaction was much higher than that in the CO+O$_2$ reaction at 363 K. This represents that the presence of H$_2$ promoted the CO oxidation reaction drastically. The activity of the CO+O$_2$ reaction was also maximum over K-Pt/Al$_2$O$_3$ (10), and at the same time, the promoting effect of the presence of H$_2$ was most remarkable over K-Pt/Al$_2$O$_3$ (10). In particular, the promoting effect of the H$_2$ presence over Pt/Al$_2$O$_3$ without alkali metal was not so remarkable. These results suggest that the additive effect of alkali metals on preferential CO oxidation has two

9

aspects: one is the promotion of the CO+O_2 reaction, and the other is the promotion of the CO oxidation by the H_2 presence.

3.4. Performance of K-Pt/Al$_2$O$_3$ in the PROX

Figure 9 shows the effect of O_2 partial pressure in the PROX over Pt/Al$_2$O$_3$ and over K-Pt/Al$_2$O$_3$ (10) at 363 K and 403 K. Since the partial pressure of CO was 0.2%, the stoichiometric partial pressure of oxygen for CO oxidation was 0.1%. However, under the condition of 0.1% O_2, high CO conversion was not obtained even at high reaction temperature. Therefore, it is necessary to make the partial pressure of oxygen higher than the stoichiometry of CO oxidation. The CO conversion at 363 K over Pt/Al$_2$O$_3$ was very low under all the O_2 partial pressure condition. Even under high temperature like 403 K, Pt/Al$_2$O$_3$ cannot give high CO conversion and selectivity of CO oxidation. At both reaction temperatures, K-Pt/Al$_2$O$_3$ (10) exhibited much higher performance than Pt/Al$_2$O$_3$. The CO conversion increased remarkably with increasing oxygen partial pressure over K-Pt/Al$_2$O$_3$ (10), although the selectivity of CO oxidation decreased gradually. In fact, in the case of K-Pt/Al$_2$O$_3$ (10), the complete removal of CO was impossible under the stoichiometric oxygen partial pressure condition in this reaction temperature range, and this means the demand of higher oxygen partial pressure than the reaction stoichiometry. This demand can be connected to the promoting effect of the H_2 presence on the CO oxidation over K-Pt/Al$_2$O$_3$ (10), and it is suggested that the active species for CO oxidation can be composed of hydrogen species as well as oxygen species, and a part of H_2 is consumed by the formation of the active species and a side reaction (H_2 oxidation to H_2O).

Figure 10 shows the catalytic performance of K-Pt/Al$_2$O$_3$ (10) in the CO+O_2+H_2 reaction under

higher CO pressure (1% CO, 1.25% O_2, 60% H_2, He balance). The CO concentration was below 10ppm in the temperature range of 383-403 K. This result indicates that K-Pt/Al_2O_3 (10) exhibited high catalytic performance in the CO+O_2+H_2 reaction even when CO pressure is high. The temperature dependence of CO conversion and selectivity under higher CO pressure was steeper than that under lower CO pressure (Figure 2a). This behavior can be due to the suppression of CO conversion by higher CO pressure through an increase of the surface coverage of adsorbed CO [34].

3.5. Effect of steam in the CO+O_2+H_2 reaction and discussion on the active site

Figure 11 shows the comparison of CO conversion and selectivity of CO oxidation in the CO+O_2+H_2 and CO+O_2+H_2+H_2O reactions over M-Pt/Al_2O_3 (M=None, Li, Na, K, Rb, Cs). It is characteristic that the additive effect of steam was not so significant over Pt/Al_2O_3 at both reaction temperatures. It is thought that the adsorption of H_2O is rather weak on the active site for the PROX on Pt/Al_2O_3. On Li-Pt/Al_2O_3 (20), the addition of H_2O decreased the selectivity of CO oxidation. On M-Pt/Al_2O_3 (M=Na, K, Rb, Cs), the addition of H_2O decreased both CO conversion and selectivity of CO oxidation. In particular, the decrease in the selectivity was larger than the decrease in the CO conversion at 363 K. The oxidation of H_2 is suppressed by the presence of CO under the PROX condition, but it is interpreted that the suppressing effect of CO on H_2 oxidation becomes weaker by the addition of steam, which is probably due to the decrease of the CO coverage by competitive adsorption between CO and H_2O. An important point is that K-Pt/Al_2O_3 (10) showed the highest activity of CO oxidation even under the presence of steam. The order of the performance in the CO+O_2+H_2+H_2O reaction was almost the same as that in the CO+O_2+H_2 reaction. The suppressing effect of steam addition over M-Pt/Al_2O_3 (M=Na, K, Rb, Cs) suggests

11

that the adsorption of H_2O is strong on the active site on the catalysts. This tendency agrees well with very low catalytic activity of water gas shift reaction on the K-Pt/Al_2O_3 (10) as shown later. In addition, the different behavior in the effect of the steam presence means the difference in the structure of the active site and the reaction mechanism.

Here, the activity of CO oxidation can be compared in terms of the turnover frequency (TOF) on the basis of the amount of CO adsorption. The amount of CO adsorption and the TOF of CO oxidation in the $CO+O_2$, $CO+O_2+H_2$ and $CO+O_2+H_2+H_2O$ reactions are listed in Table 1. The amount of CO adsorption tends to decrease gradually with increasing the additive amount of alkali metals. The amount of CO adsorption on Pt/Al_2O_3 modified with alkali metals was mainly in the range between CO/Pt=0.29 and 0.44, and it is thought that the difference in the number of surface Pt atoms is not so large. We characterized these catalysts by means of the extended X-ray absorption fine structure, transmission electron microscopy, Fourier transform infrared spectroscopy, and so on. The details of these characterization results are described in the next article [32]. Average metal particle size of Pt/Al_2O_3 and K-Pt/Al_2O_3 (10) was determined to be about 0.5 and 2.0 nm, respectively [28]. The TOF of the $CO+O_2$ reaction on Pt/Al_2O_3 modified with an optimal amount of alkali metals was higher than that on Pt/Al_2O_3 (Table 1). This means that the addition of alkali metals enhanced the TOF in the $CO+O_2$ reaction over Pt/Al_2O_3, although the promoting effect was not so remarkable. On the other hand, the enhancement of TOF in the $CO+O_2+H_2$ reaction by the addition of alkali metals was much more remarkable than that in the $CO+O_2$ reaction. This promoting effect of the presence of H_2 on CO oxidation cannot be explained by water gas shift reaction ($CO+H_2O \rightarrow CO_2+H_2$), which is induced by H_2O produced from H_2 oxidation, although this kind of promoting mechanism has been reported in the references [35, 36]. This is because the

activity of the CO + H_2O reaction was much lower than that of CO oxidation on both Pt/Al_2O_3 and

$K-Pt/Al_2O_3$ (10) as shown in Table 1. Similar properties have been reported on Rh catalysts

modified with potassium [23-25]. The decrease of TOF in the $CO+O_2+H_2$ reaction with the steam

addition over $M-Pt/Al_2O_3$ (M=Na, K, Rb and Cs) also indicates that CO_2 is not formed via water

gas shift reaction. As a result, it is found that the presence of H_2 promoted the CO oxidation and the

presence of steam suppressed the PROX reaction more remarkably over $M-Pt/Al_2O_3$ (M=Na, K,

Rb,Cs) compared to Pt/Al_2O_3. Promotion of CO oxidation by the presence of H_2 can be due to the

hydrogen-containing oxidizing species such as hydroxyl group (OH) which can be formed from H_2

and O_2 [10, 28], and it has also been reported that the OH group can promote CO oxidation on Pt

(111) [35, 36]. In fact, the effect of presence of H_2 on CO oxidation over Pt/Al_2O_3 enhanced the

TOF, although it was not so significant (Table 1). In contrast, the promoting effect over Pt/Al_2O_3

modified with alkali metals was much more remarkable. At present, it is thought that the coverage

of the active hydrogen-containing oxidizing species like the OH group can be increased by the

interaction with alkali metal ions, where alkali metal ions are present as carbonate species under

reaction conditions and they are located on the Pt metal particles. The interaction between the active

species on Pt surfaces and alkali metal ion species can be strongly dependent on the strength of the

basicity and the amount of alkali metals. As a result, Pt/Al_2O_3 modified with an optimal amount of

potassium can give the highest performance In addition, the effect of CO_2 coexistence was also

investigated because the fuel gas generally contains CO_2 in the hydrogen production system by the

reforming of hydrocarbons. At 363 K under 0.2% CO+0.2% O_2+75% H_2+24.6% CO_2, the 72% CO

conversion and 56% selectivity over $K-Pt/Al_2O_3$ (K/Pt = 10) were obtained. Despite higher pressure

of CO_2 than H_2O, the suppressing effect of CO_2 presence was much weaker than that of H_2O.

13

Furthermore, the interaction between the active species and alkali metals can be influenced by the presence of steam, and this can explain the suppressing effect of steam addition to the PROX reaction. Structural analysis of Pt/Al_2O_3 modified with alkali metals and the role of alkali metals are described in the following paper [32].

4. Conclusions

1) The addition of potassium over Pt catalysts supported on Al_2O_3, SiO_2, ZrO_2, Nb_2O_5 and TiO_2 enhanced the catalytic performance in the preferential CO oxidation in H_2-rich stream (PROX). Among all these support materials, the most remarkable promoting effect was observed on Pt/Al_2O_3.

2) The additive effect of alkali metals on Pt/Al_2O_3 in the PROX was strongly influenced by the kind of alkali metal and its additive amount. It is concluded that K-Pt/Al_2O_3 with K/Pt = 10 showed highest performance. The tendency of catalytic performance suggests that the addition of the alkali metal can be effective with suitable basicity and amount.

3) From the comparison between the $CO+O_2+H_2$ and $CO+O_2$ reactions, the presence of H_2 promoted the CO oxidation much more remarkably over Pt/Al_2O_3 modified with alkali metals than Pt/Al_2O_3.

4) The remarkable promotion of the CO oxidation by the H_2 presence suggests that the hydrogen-containing oxidizing species such as OH formed by H_2 and O_2 are active and the interaction between the active species and alkali metals is important.

5) The addition of steam to the PROX suppressed the CO oxidation much more significantly over Pt/Al_2O_3 modified with alkali metals than over Pt/Al_2O_3, and it can be explained by the inhibition

with steam of the interaction between the active oxidizing species and the alkali metals.

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Table 1. Adsorption amount of CO and the TOF of CO oxidation in various reactions over M-Pt/Al$_2$O$_3$ (M=None, Li, Na, K, Rb and Cs).

Catalysts	M/Pt	CO/Pt [a]	TOF / $\times 10^{-3}$ s^{-1} [b]			
			CO+O$_2$ [c]	CO+O$_2$+H$_2$ [d]	CO+O$_2$+H$_2$+H$_2$O [e]	CO+H$_2$O [f]
Pt/Al$_2$O$_3$	0	0.52	1.0	1.9	2.3	0.03
Li-Pt/Al$_2$O$_3$	3	0.42		2.2		
	5	0.38		4.8		
	10	0.33		2.9		
	20	0.29	2.2	8.5	11	
Na-Pt/Al$_2$O$_3$	3	0.40		8.7		
	5	0.44		13		
	10	0.36	4.4	20	12	
	15	0.33		19		
K-Pt/Al$_2$O$_3$	3	0.49		13		
	5	0.44		16		
	10	0.40	4.8	32	15	1.0
	15	0.34		30		
	20	0.27		23		
Rb-Pt/Al$_2$O$_3$	1	0.38		7.3		
	3	0.37		12		
	5	0.36	2.4	20	11	
	10	0.29		7.5		
Cs-Pt/Al$_2$O$_3$	1	0.45		5.4		
	3	0.42	2.0	20	9.0	
	5	0.36		14		
	10	0.19		2.9		

a) Irreversible CO adsorption amount at room temperature.

b) TOF of CO oxidation at 363 K is calculated on the basis of CO/Pt.

c) Reaction condition: 0.2% CO and O$_2$ (He balance).

d) Reaction condition: 0.2% CO, O$_2$ and 75% H$_2$ (He balance).

e) Reaction condition: 0.2% CO, O$_2$, 75% H$_2$, 5% H$_2$O (H ebalance).

f) Reaction condition: 0.2% CO, 5% H$_2$O (He balance).
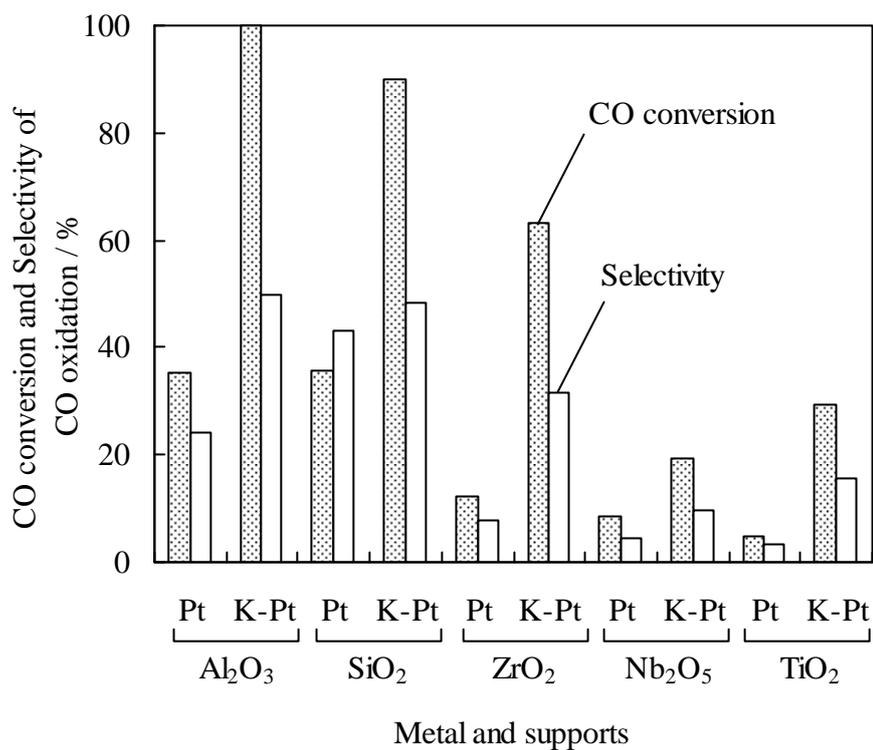
Figure Captions

Fig. 1.   Results of CO conversion and selectivity in the $CO+O_2+H_2$ reaction over Pt catalysts

supported on various oxides with or without potassium modification (K/Pt = 3) at 403 K.

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 2.   Reaction temperature dependence of CO conversion (a) and selectivity of CO oxidation (b)

in the $CO+O_2+H_2$ reaction over K-Pt/Al_2O_3 (K/Pt=0, 3, 10) and K-Pt/SiO_2 (K/Pt=0, 3, 10).

■: Pt/Al_2O_3, ▲:K-Pt/Al_2O_3 (3), ●:K-Pt/Al_2O_3 (10),

□: Pt/SiO_2, △:K-Pt/SiO_2 (3), ○:K-Pt/SiO_2 (10).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 3.   Effect of molar ratio of Li/Pt on CO conversion and selectivity of CO oxidation in the

$CO+O_2+H_2$ reaction over Li-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 4.   Effect of molar ratio of Na/Pt on CO conversion and selectivity of CO oxidation in the

$CO+O_2+H_2$ reaction over Na-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 5.   Effect of molar ratio of K/Pt on CO conversion and selectivity of CO oxidation in the

$CO+O_2+H_2$ reaction over K-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 6. Effect of molar ratio of Rb/Pt on CO conversion and selectivity of CO oxidation in the CO+O_2+H_2 reaction over Rb-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 7. Effect of molar ratio of Cs/Pt on CO conversion and selectivity of CO oxidation in the CO+O_2+H_2 reaction over Cs-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 8. Comparison of CO conversion in the CO+O_2+H_2 and CO+O_2 reactions over M-Pt/Al_2O_3 (M=None, Li, Na, K, Rb, Cs) catalysts at 363 K.

Reaction conditions: CO+O_2+H_2 reaction (0.2% CO, 0.2% O_2 and 75% H_2 balanced with He), CO+O_2 reaction (0.2% CO and 0.2% O_2 balanced with He).

Fig. 9. Effect of O_2 partial pressure on CO conversion and selectivity of CO oxidation in the CO+O_2+H_2 reaction over Pt/Al_2O_3 and K-Pt/Al_2O_3 (10) at 363 K (a) and 403 K (b).

Reaction condition: 0.2% CO, x% O_2 and 75% H_2 balanced with He (x=0.1, 0.15 and 0.2).
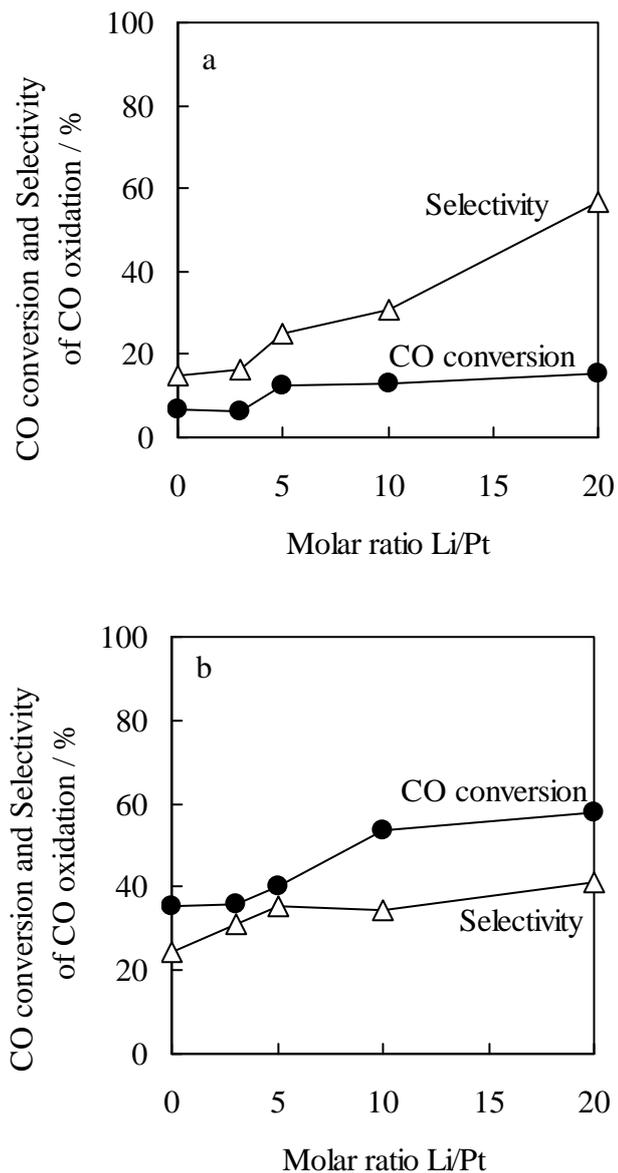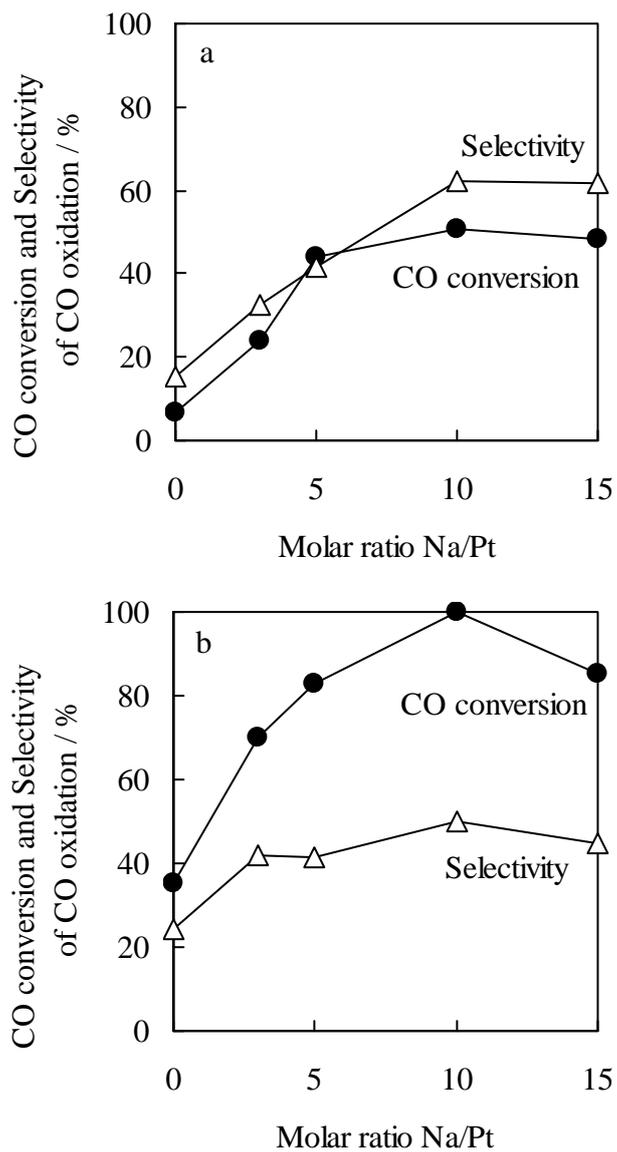
Fig. 10. Reaction temperature dependence of CO conversion, selectivity of CO oxidation and CO concentration in the CO+O_2+H_2 reaction under higher CO pressure over K-Pt/Al_2O_3 (K/Pt =10).

●: CO conversion, △: Selectivity of CO oxidation,

○: CO concentration in the effluent gas.

Reaction condition: 1.0% CO, 1.25% O_2 and 60% H_2 (He balance).

Fig. 11.   Comparison of CO conversion and selectivity of CO oxidation in the $CO+O_2+H_2$ and $CO+O_2+H_2+H_2O$ reactions over M-Pt/Al_2O_3 (M=None, Li, Na, K, Rb, Cs) catalysts at 363 K (a) and 403 K (b).

Reaction conditions: $CO+O_2+H_2$ reaction: 0.2% CO, 0.2% O_2 and 75% H_2 balanced with He, $CO+O_2+H_2+H_2O$ reaction: 0.2% CO, 0.2% O_2, 75% H_2, 5% H_2O balanced with He.

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Reaction condition: 0.2% CO, 0.2% O$_2$ and 75% H$_2$ (He balance).

Fig. 2. Reaction temperature dependence of CO conversion (a) and selectivity of CO oxidation (b) in the $CO+O_2+H_2$ reaction over K-Pt/Al_2O_3 (K/Pt=0, 3, 10) and K-Pt/SiO_2 (K/Pt=0, 3, 10).

■: Pt/Al_2O_3, ▲: K-Pt/Al_2O_3 (3), ●: K-Pt/Al_2O_3 (10),

□: Pt/SiO_2, △: K-Pt/SiO_2 (3), ○: K-Pt/SiO_2 (10).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 3.   Effect of molar ratio of Li/Pt on CO conversion and selectivity of CO oxidation in the $CO+O_2+H_2$ reaction over Li-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

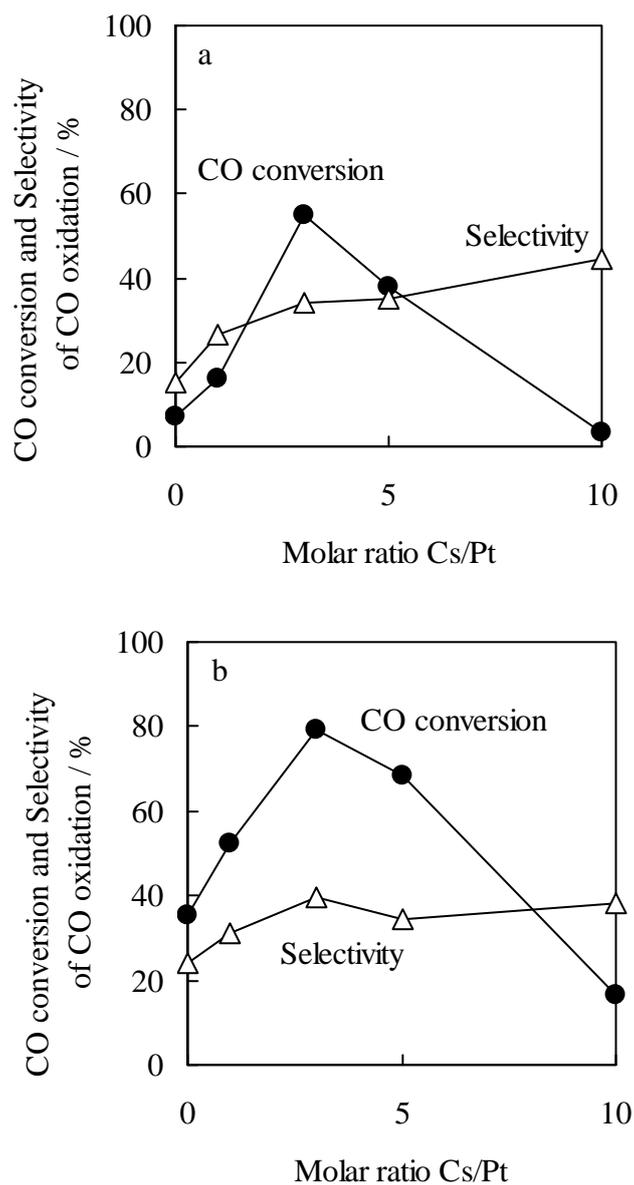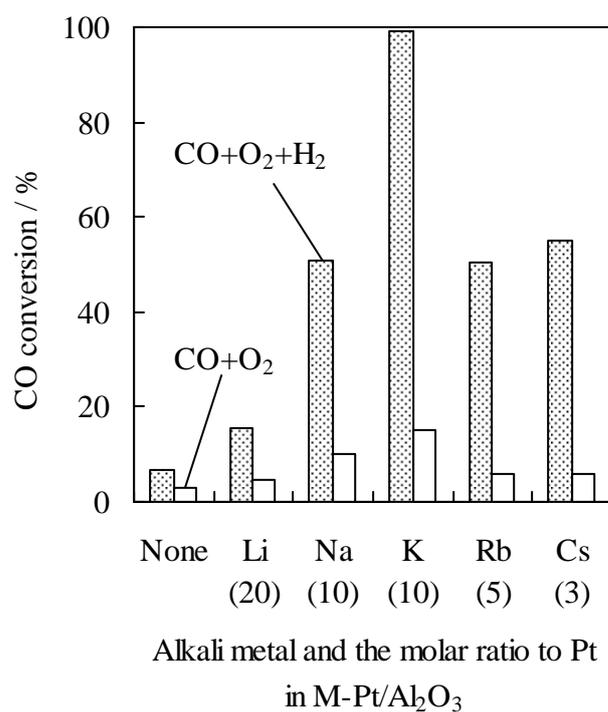Fig. 4.   Effect of molar ratio of Na/Pt on CO conversion and selectivity of CO oxidation in the $CO+O_2+H_2$ reaction over Na-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 5. Effect of molar ratio of K/Pt on CO conversion and selectivity of CO oxidation in the $CO+O_2+H_2$ reaction over K-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).

Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 6. Effect of molar ratio of Rb/Pt on CO conversion and selectivity of CO oxidation in the CO+O_2+H_2 reaction over Rb-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).
Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 7.   Effect of molar ratio of Cs/Pt on CO conversion and selectivity of CO oxidation in the $CO+O_2+H_2$ reaction over Cs-Pt/Al_2O_3 catalysts at 363 K (a) and 403 K (b).
Reaction condition: 0.2% CO, 0.2% O_2 and 75% H_2 (He balance).

Fig. 8.　Comparison of CO conversion in the $CO+O_2+H_2$ and $CO+O_2$ reactions over M-Pt/Al_2O_3 (M=None, Li, Na, K, Rb, Cs) catalysts at 363 K.

Reaction conditions: $CO+O_2+H_2$ reaction (0.2% CO, 0.2% O_2 and 75% H_2 balanced with He), $CO+O_2$ reaction (0.2% CO and 0.2% O_2 balanced with He).

Fig. 9. Effect of O_2 partial pressure on CO conversion and selectivity of CO oxidation in the $CO+O_2+H_2$ reaction over Pt/Al_2O_3 and $K\text{-}Pt/Al_2O_3$ (10) at 363 K (a) and 403 K (b).

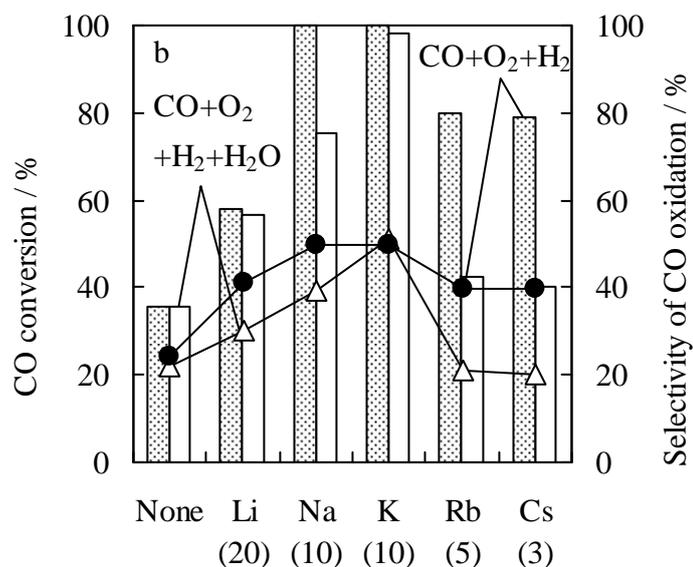Reaction condition: 0.2% CO, x% O_2 and 75% H_2 balanced with He (x=0.1, 0.15 and 0.2).

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