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Preferential CO oxidation over supported noble metal catalysts

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ABSTRACT

We conducted a comparative study for the preferential CO oxidation (PROX) over supported noble metal catalysts. The CO chemisorption in the absence and presence of H_2, the O_2 chemisorption, the temperature-programmed oxidation (TPO), the temperature-programmed reduction (TPR) after O_2 chemisorption and the transmission electron microscopy (TEM) were conducted to characterize the catalysts. Commercial catalysts such as 1 wt.% Pt/γ-Al_2O_3, 0.5 wt.% Ru/γ-Al_2O_3, 0.5 wt.% Rh/γ-Al_2O_3, 5 wt.% Pt/γ-Al_2O_3, 5 wt.% Ru/γ-Al_2O_3, and 5 wt.% Rh/γ-Al_2O_3 were utilized. Among them, 5 wt.% Ru/γ-Al_2O_3 showed the highest PROX activity. This catalyst can be considered to be promising because it can reduce the high inlet CO concentration to be less than 10 ppm at low temperatures where the reverse water–gas shift reaction can be minimized. No detectable amount of chemisorbed O_2 was measured at 373 K over 1 wt.% Pt/γ-Al_2O_3, 0.5 wt.% Rh/γ-Al_2O_3 and 5 wt.% Pt/γ-Al_2O_3. The moderate degree of CO and O_2 chemisorption at reaction temperatures appeared to be essential for the optimum PROX activity. Although 0.5 wt.% Ru/γ-Al_2O_3 and 5 wt.% Ru/γ-Al_2O_3 have the similar particle size distribution based on TEM analysis, the latter catalyst with smaller amount of chemisorbed CO and O_2 per Ru metal showed much better PROX activity. Based on TPO and TPR result, 0.5 wt.% Ru/γ-Al_2O_3 can be oxidized at lower temperatures but can be reduced at higher temperatures compared with 5 wt.% Ru/γ-Al_2O_3. Therefore, the easily reducible Ru species can give us the better PROX activity over a wide reaction temperature for Ru catalysts.

1. Introduction

The polymer electrolyte membrane fuel cell (PEMFC), in which H_2 is utilized as a fuel to produce H_2O as an end product, has recently attracted much attention as a small-scale power generation system [1]. The H_2 production is currently carried out in a fuel processor in which various hydrocarbons can be converted into H_2 and CO_2 via steam reforming and water–gas shift reaction. Because the latter reaction is thermodynamically limited, a small amount of CO can be present in the H_2 stream and this can cause the degradation of electrochemical performance of Pt-based anode of PEMFC. Therefore, the further purification process is in need to meet the purity of hydrogen for this PEMFC. Until now, several methods including the membrane separation as well as the catalytic removal have been disclosed [2]. Among them, the preferential CO oxidation (PROX) in which CO can be selectively oxidized with O_2 in the presence of H_2, has been intensively studied [2]. Although this PROX system had already been introduced into H_2 purification for the ammonia synthesis, the comparison work among various commercial catalysts for the PROX conducted by Oh and Sinkevitch can be regarded as the pioneering work for the application to the fuel cell system [3]. They proposed Ru/Al_2O_3 and Rh/Al_2O_3 catalysts as the promising candidates. However, they performed the screening experiment under rather mild condition such as 0.85% H_2, 900 ppm CO and 800 ppm O_2 in N_2. As expected, the catalytic performance can be affected by the reactant composition. Interestingly, little works have been conducted to compare commercial noble metal catalysts in a realistic condition [4,5]. On the other hand, lots of works on different catalyst systems such as metal oxides including CuO-CeO_2, supported gold catalysts, supported noble metal catalysts including Pt-based and Ru-based catalysts have been reported separately [2]. In this work, we examined the PROX activity over commercial noble metal catalysts under severe reaction condition.

In general, the following 5 different reactions can occur in a different degree over catalysts:

$$CO(g) + \tfrac{1}{2}O_2(g) \rightarrow CO_2(g), \quad \Delta H^0_{298} = -282,984\,\mathrm{J/mol} \qquad (1)$$

$$H_2(g) + \tfrac{1}{2}O_2(g) \rightarrow H_2O(g), \quad \Delta H^0_{298} = -241,818\,\mathrm{J/mol} \qquad (2)$$

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$$CO(g) + 3H_2(g) \rightarrow CH_4(g) + H_2O(g), \quad \Delta H^0_{298} = -205{,}813\,\text{J/mol} \qquad (3)$$

$$CO_2(g) + 4H_2(g) \rightarrow CH_4(g) + 2H_2O(g), \quad \Delta H^0_{298} = -164{,}647\,\text{J/mol} \qquad (4)$$

$$CO(g) + H_2O(g) \rightarrow CO_2(g) + H_2(g), \quad \Delta H^0_{298} = -41{,}166\,\text{J/mol} \qquad (5)$$

The most plausible catalysts should be preferentially active for the reaction (1). The additional CO removal can be accomplished via the reaction (3) although the extra H_2 should be consumed for this reaction. During the PROX reaction, the undesired reactions such as (2) and (4) should be minimized. During an unsteady-state operation, the low-space velocity can be encountered, which might cause the reverse water–gas shift reaction in the presence of H_2 and CO_2 especially at high temperatures such as above 420 K to produce the extra CO. Therefore, the PROX catalysts operating at low temperatures are quite desirable. For the practical view point, the PROX activity in the presence of H_2O and CO_2 should be reported and the exit CO concentration in ppm level can be important data to evaluate the PROX catalysts. Until now, several Pt-based [3–63] and Ru-based [64–73] catalysts have been examined. In the case of Ru-based catalysts, the CO methanation has been frequently reported to occur with the PROX [67,73]. In this work, we have found that 5% Ru/γ-Al_2O_3 can decrease 1 vol.% CO to be less than 10 ppm at low temperatures even in the presence of H_2O and CO_2.

2. Experimental

All the catalysts were purchased from Aldrich. The metal content in each catalyst and its BET surface area are displayed in Table 1.

The CO chemisorption was conducted over 0.2 g sample in a He (or H_2) stream at 300 K by a pulsed injection of 50 μl of CO after samples were pretreated with H_2 at 573 K for 1 h.

The O_2 chemisorption was conducted over 0.2 g sample in a He stream at 373 K by a pulsed injection of 50 μl of O_2 after samples were pretreated with H_2 at 573 K for 1 h.

Temperature-programmed reduction (TPR) was conducted after O_2 chemisorption at 373 K over Ru catalysts in a 10 vol.% H_2/Ar stream from 313 to 573 K at a heating rate 10 K/min monitoring TCD signals. The amounts of Ru catalysts were adjusted to contain the same amounts of Ru in the sample.

Temperature-programmed oxidation (TPO) was conducted after reduction at 573 K over Ru catalysts in a 10 vol.% O_2/He stream from 313 to 573 K at a heating rate 10 K/min monitoring TCD signals. The amounts of Ru catalysts were adjusted to contain the same amounts of Ru in the sample.

Bright-field images of transmission electron microscopy (TEM) were obtained using a Technai G^2 TEM (FEI) operated at 200 kV and used to determine the particle size of Ru metal. Samples were ground in a mortar to fine particles and then dispersed ultrasonically in methanol. The sample was deposited on a Cu grid covered by a holey carbon film.

Table 1
Characteristics of catalyst samples used.

Catalyst	Metal loading (wt.%)	BET surface area (m^2/g)
1% Pt/γ-Al_2O_3	1	94.0
5% Pt/γ-Al_2O_3	5	110.2
0.5% Ru/γ-Al_2O_3	0.5	94.5
5% Ru/γ-Al_2O_3	5	87.1
0.5% Rh/γ-Al_2O_3	0.5	105.4
5% Rh/γ-Al_2O_3	5	115.0

The catalytic activity was carried out in a small fixed bed reactor with catalysts that had been retained between 45 and 80 mesh sieves. For screening tests, a standard gas of 1 vol.% CO, 1 vol.% O_2 and 50 vol.% H_2 balanced with He was fed to the reactor, in which 0.10 g of catalyst without diluents was contacted with a reactant gas at a flow rate of 100 ml/min, at an atmospheric pressure. The catalytic activity was measured with a ramping rate 1 K/min. To obtain the kinetic data at 333 K, the O_2 conversion was controlled to be less than 10 % by adjusting the amount of Ru-based catalysts at the same feed composition and the total flow rate. The similar O_2 conversions with those over 0.5% Ru/γ-Al_2O_3 could be achieved over 5% Ru/γ-Al_2O_3 by diluting the catalyst with an inert γ-Al_2O_3. Two separate experiments were also conducted to find out the catalytic activity for the water–gas shift reaction or CO methanation reaction over 5% Ru/γ-Al_2O_3 catalyst at the same experiment condition except the feed composition. The standard gas of 1 vol.% CO and 10 vol.% H_2O in He and the standard gas of 1 vol.% CO and 50 vol.% H_2 in He were utilized for the water–gas shift reaction and CO methanation reaction, respectively. The effluent from the reactor was analyzed by gas chromatograph (HP5890A, molecular sieve 5A column) to determine CO conversion, O_2 conversion, CO_2 selectivity, and CH_4 yield. The detection limit of CO was 10 ppm. The CO conversion, O_2 conversion, CO_2 selectivity, and the CH_4 yield were calculated using the following formulas:

$$\text{CO conversion}(\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} \times 100;$$

$$O_2\ \text{conversion}(\%) = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} \times 100;$$

$$CO_2\ \text{selectivity}(\%) = 0.5 \times \frac{([CO]_{in} - [CO]_{out} - [CH_4]_{out})}{[O_2]_{in} - [O_2]_{out}} \times 100;$$

$$CH_4\ \text{yield}(\%) = \frac{[CH_4]_{out}}{[CO]_{in}} \times 100.$$

For 5% Ru/γ-Al_2O_3 catalyst, a realistic gas flow condition of 0.9 vol.% CO, 0.9 vol.% O_2, 17.4 vol.% CO_2, 64.6 vol.% H_2, and 13 vol.% H_2O in balanced N_2 for PROX was adopted to confirm the catalytic performance. In this case, 1.0 g of catalyst without diluents was contacted with a reactant gas at a flow rate of 345 ml/min at an atmospheric pressure. The dry effluent gas composition was determined on an online gas analyzer (NGA2000, MLT4, Rosemount Analyzer System from Emerson Process Management) of each gas components (CO at ppm level, CO_2, H_2, CH_4 at % level). In this case, the exit CO concentration less than 10 ppm can be detected and measured. The water trap was installed before an online gas analyzer to remove all water vapor present in a feed and formed by reactions as mentioned earlier.

3. Results and discussion

The PROX activity was examined over γ-Al_2O_3-supported noble metal catalysts, in which the metal content was 5 wt.%, at different reaction temperatures as shown in Fig. 1. In the absence of H_2O and CO_2, 100% CO conversion can be achieved over 5% Ru/γ-Al_2O_3 over wide reaction temperatures from 333 to 473 K. At the same reaction temperatures, 100% O_2 conversion was also obtained. From 353 K, CH_4 was formed over this catalyst and its formation increased with increasing reaction temperature. Therefore, the CO_2 selectivity decreased from 50% at 333 K to be less than 50% with increasing reaction temperature. Based on the separate experiment for the water–gas shift reaction at the same reaction condition with the PROX except the feed composition, it was proved that the water–gas shift reaction did not occur in the presence of 1 vol.% CO and 10 vol.% H_2O in He over 5% Ru/γ-Al_2O_3 at the same temperature range. The CO methanation appeared to

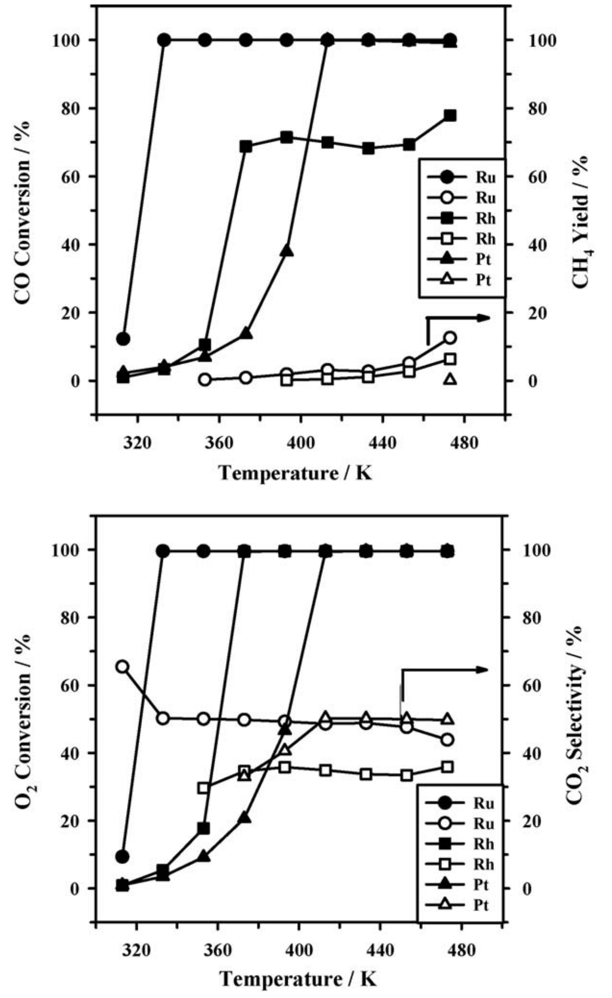

Fig. 1. CO conversion, CH_4 yield, O_2 conversion and CO_2 selectivity for the PROX over 5% noble metal catalysts supported on γ-Al_2O_3 with increasing temperature. All the catalysts were reduced in H_2 at 573 K before a reaction. F/W = 1000 ml/(min g_{cat}). Reaction conditions: 1 vol.% CO + 1 vol.% O_2 and 50 vol.% H_2 in He.

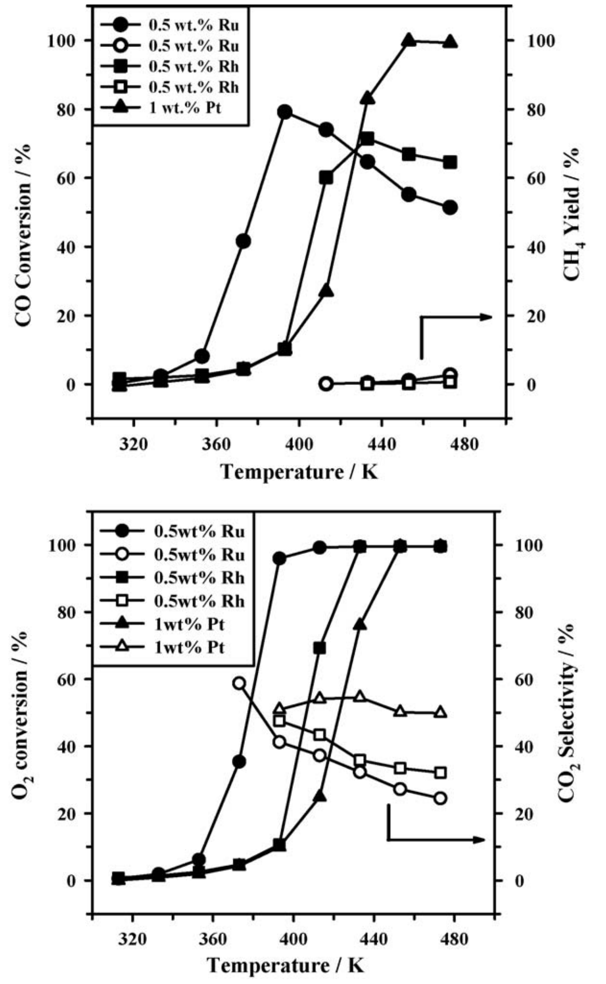

Fig. 2. CO conversion, CH_4 yield, O_2 conversion and CO_2 selectivity for the PROX over γ-Al_2O_3-supported noble metal catalysts with increasing temperatures. All the catalysts were reduced in H_2 at 573 K before a reaction. F/W = 1000 ml/(min g_{cat}). Reaction conditions: 1 vol.% CO + 1 vol.% O_2 and 50 vol.% H_2 in He.

occur over 5% Ru/γ-Al_2O_3 with a feed composition of 1 vol.% CO and 50 vol.% H_2 in He only when the reaction temperature was above 423 K. Therefore, the CO conversion observed over 5% Ru/γ-Al_2O_3 especially at low temperatures must be due to the preferential CO oxidation. 5% Rh/γ-Al_2O_3 showed the highest PROX activity at low temperatures next to 5% Ru/γ-Al_2O_3. 5% Rh/γ-Al_2O_3 appeared to be active for CO methanation above 393 K. 5% Rh/γ-Al_2O_3 showed the much less selectivity for CO oxidation than 5% Ru/γ-Al_2O_3. 5% Pt/γ-Al_2O_3 exhibited the least PROX activity at low temperatures among three catalysts. However, 100% CO conversion can be achieved at 413 K. The CO_2 selectivity increased, showed the maximum value such as 50%, and then decreased with increasing reaction temperature. The small amounts of CH_4 formation can be observed at 473 K over this catalyst. Based on this screening test, 5% Ru/γ-Al_2O_3 can be regarded as the best PROX catalyst whereas 5% Rh/γ-Al_2O_3 exhibited the worst PROX activity. The PROX activity was also examined over γ-Al_2O_3-supported noble metal catalysts containing the small amounts of metals at different reaction temperatures as shown in Fig. 2. Although 0.5% Ru/γ-Al_2O_3 showed the low-temperature PROX activity, the high CO conversion cannot be accomplished. Instead, 1% Pt/γ-Al_2O_3 showed the highest CO_2 selectivity among three catalysts at 100% O_2 conversion. The comparison between Figs. 1 and 2 can reveal the effect of metal contents on the PROX activity. The little effect of metal content was observed over supported Pt catalysts. However, the noticeable change in the PROX activity can be found over supported Ru catalysts. To remove the possibility that the higher catalytic activity can be caused by the larger amounts of Ru over supported Ru catalysts, the PROX activity at much lower space velocity was measured over 0.5% Ru/γ-Al_2O_3 as shown in Fig. 3. The low-temperature activity was increased as expected. However, the wide temperature window showing 100% CO conversion observed over 5% Ru/γ-Al_2O_3 cannot be obtained over 0.5% Ru/γ-Al_2O_3 even at the same contact time normalized by the amount of Ru metal. The higher CO conversion over 5% Ru/γ-Al_2O_3 cannot be due to the additional CO methanation because the similar CH_4 yields were obtained over both Ru catalysts irrespective of Ru contents. This implies that there must be additional factors working on these Ru catalysts. Based on them, 5 wt.% Ru/γ-Al_2O_3 can be chosen as the optimum PROX catalyst.

CO and O_2 chemisorptions were carried out to quantify the amounts of active sites as shown in Table 2. The CO chemisorptions data measured in He condition showed that the amounts of chemisorbed CO per metal decreased in the order: Rh > Pt > Ru. In the case of Pt and Ru catalysts, the higher amounts of CO were chemisorbed per metal over catalysts with smaller amounts of metal than those of catalysts with larger amounts of metal. However, the dispersion determined from CO chemisorption increased with the metal content in the catalyst for supported Rh catalysts. The CO chemisorption in the presence of H_2 was also

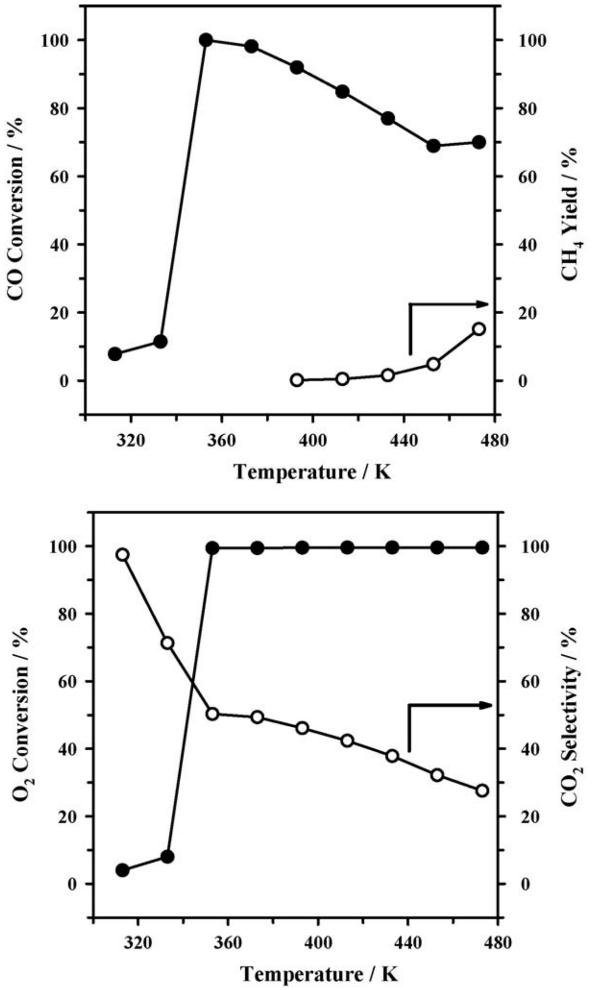

Fig. 3. CO conversion, CH_4 yield, O_2 conversion and CO_2 selectivity for the PROX over 0.5% Ru/γ-Al_2O_3 catalysts with increasing reaction temperatures. All the catalysts were reduced in H_2 at 573 K before a reaction. F/W = 100 ml/(min g_{cat}). Reaction conditions: 1 vol.% CO + 1 vol.% O_2 and 50 vol.% H_2 in He.

carried out because CO can compete with H_2 in the PROX condition. There was no noticeable effect of H_2 on the CO chemisorption except in the case of 5% Pt/γ-Al_2O_3. About half of CO can be chemisorbed on Pt in the presence of H_2 compared with the case in the absence of H_2. In the case of the O_2 chemisorption, the highest amounts of O_2 can be chemisorbed over Rh catalyst. No O_2 chemisorption can be measured at 373 K over 5% Pt/γ-Al_2O_3. The larger amounts of chemisorbed O_2 per metal were obtained over 0.5% Ru/γ-Al_2O_3 than that of 5% Ru/γ-Al_2O_3. This implies that the most active PROX catalyst can adsorb the smallest amount of CO but the moderate amounts of O_2.

As presented in Fig. 4, TEM analysis showed that there was no noticeable difference in the particle size distribution between them. The average particle sizes of Ru metal in 0.5% Ru/γ-Al_2O_3 and 5% Ru/γ-Al_2O_3 were determined to be 5.2 ± 1.5 and 4.9 ± 1.5 nm, respectively.

To differentiate the catalytic activity of Ru-based catalysts, the kinetic data were obtained at 333 K and listed in Table 3. To compare the CO_2 selectivity at similar O_2 conversions, different contact times were chosen for 0.5% Ru/γ-Al_2O_3 and 5% Ru/γ-Al_2O_3. 5% Ru/γ-Al_2O_3 showed the far superior CO_2 selectivity to 0.5% Ru/γ-Al_2O_3 at 333 K under the similar O_2 conversions. The Ru dispersions for 0.5% Ru/γ-Al_2O_3 and 5% Ru/γ-Al_2O_3 were estimated from the average particle size of Ru particles determined through TEM analysis. The hemispherical Ru metal particle was assumed. The amount of exposed surface atoms in the Ru catalyst was estimated based on the assumption that the (0 0 1), (1 0 0), and (1 0 1) planes participates equally (an average area of 8.17 Å^2/surface atom) [74]. Finally, the turnover frequency can be calculated based on Ru dispersion calculated from TEM results. Two catalysts showed the similar turnover frequencies for O_2 consumption at 333 K. On the other hand, the turnover frequency for CO oxidation of 5% Ru/γ-Al_2O_3 appeared to be higher than that of 0.5% Ru/γ-Al_2O_3 at 333 K by 3 times. The turnover frequency for CO oxidation can also be calculated based on Ru dispersion calculated from CO chemisorption data. In this case, the turnover frequency for CO oxidation of 5% Ru/γ-Al_2O_3 appeared to be higher than that of 0.5% Ru/γ-Al_2O_3 at 333 K by about 8 times. Therefore, 5% Ru/γ-Al_2O_3 can be considered to be more plausible for PROX compared with 0.5% Ru/γ-Al_2O_3.

TPR pattern was obtained over supported Ru catalysts after O_2 chemisorption at 373 K as shown in Fig. 5. The rather narrow TPR peak was obtained over 5% Ru/γ-Al_2O_3 with a peak maximum at 345 K and a shoulder around 370 K. No noticeable reduction peak can be observed above 400 K. On the other hand, the broad TPR peak from 340 to 500 K was displayed over 0.5% Ru/γ-Al_2O_3 with peak maxima at 390 and 440 K. This implies that there exists much stronger interaction between chemisorbed oxygen and Ru in 0.5% Ru/γ-Al_2O_3 than in 5% Ru/γ-Al_2O_3. The larger TPR peak area in 0.5% Ru/γ-Al_2O_3 than that in 5% Ru/γ-Al_2O_3 based on the same Ru content in samples is consistent with the O_2 chemisorption data in which the larger amount of chemisorbed O_2 per metal was observed in 0.5% Ru/γ-Al_2O_3 than in 5% Ru/γ-Al_2O_3.

TPO pattern was obtained over supported Ru catalysts after reduction at 573 K as shown in Fig. 6. O_2 chemisorption can occur at lower temperature in 0.5% Ru/γ-Al_2O_3 than in 5% Ru/γ-Al_2O_3. The larger amounts of O_2 can be chemisorbed in 0.5% Ru/γ-Al_2O_3 than in 5% Ru/γ-Al_2O_3. Therefore, 0.5% Ru/γ-Al_2O_3 can chemisorb O_2 easily at low temperatures but the oxidized Ru species cannot be reduced easily compared with 5% Ru/γ-Al_2O_3.

The performance of 5% Ru/γ-Al_2O_3 in the realistic PROX condition was examined as shown in Fig. 7. Less than 10 ppm exit CO concentration can be obtained from 385 to 423 K, in which no noticeable reverse water–gas shift reaction can be occurred even at the low-space velocity. However, the undesired methanation reaction occurs simultaneously above 410 K, which resulted in the rapid formation of CH_4 instead of large consumption of H_2. This implies that the plausible operating temperature window over 5% Ru/γ-Al_2O_3 should be between 385 and 410 K.

The PROX activity observed over Pt/γ-Al_2O_3 in this work is consistent with the previous works in which the conventional monometallic Pt catalyst has the noticeable PROX activity above 150 °C [4,6–9]. This is not plausible because the complete CO oxidation cannot be achieved at a low-space velocity often encountered in the cyclic operation due to the reverse water–gas shift reaction. This absence of PROX activity at low temperatures might be due to its inability to activate O_2, which was revealed from O_2 chemisorption data in this work. Until now, several efforts have been made to improve this low-temperature PROX activity over Pt-based catalysts. Kinds of support [10–23], pretreatment methods [24], and the presence of 2nd metals [25–63] have been reported to affect the PROX activity at low temperatures in a different degree by facilitating the O_2 activation.

The supported Ru catalyst has been reported to be affected noticeably by the preparation parameters such as Ru precursors, reducing agents, and pretreatment conditions [64–68]. In this work, we cannot mention the effect of the preparation methods on the PROX activity because we utilized the commercial Ru catalysts. However, we have found that there was clear difference in the oxidation state of Ru species between in 0.5% Ru/γ-Al_2O_3 and 5% Ru/γ-Al_2O_3 even though they have similar particle size distribution

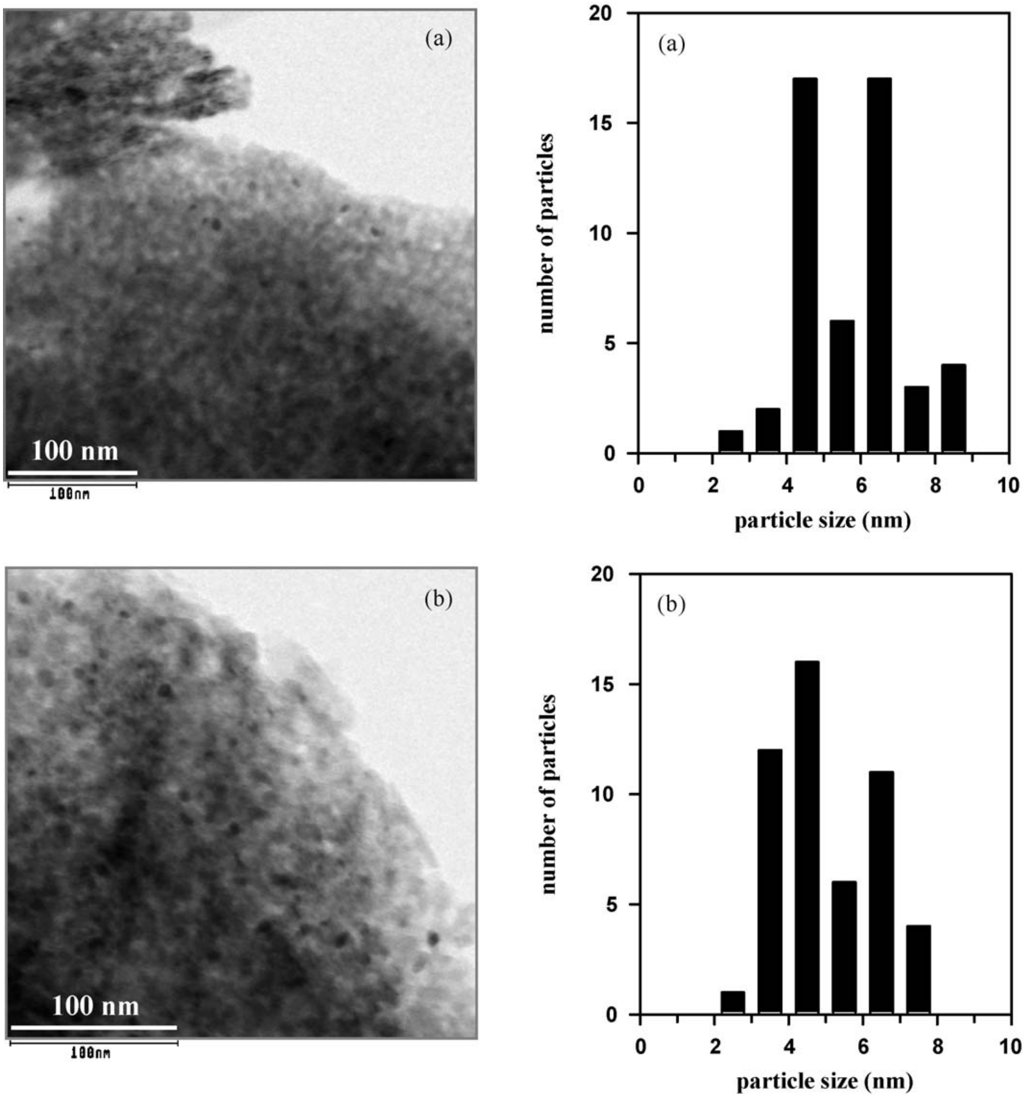

Fig. 4. The bright-field TEM images and the particle size distribution of (a) 0.5 wt.% Ru/γ-Al_2O_3 and (b) 5 wt.% Ru/γ-Al_2O_3.

of Ru metals. The Ru species in 0.5% Ru/γ-Al_2O_3 can chemisorb the larger amounts of CO and O_2 per Ru metal and can be oxidized easily at lower temperatures but cannot be reduced easily compared with the Ru species in 5% Ru/γ-Al_2O_3. This implies that the easily reducible Ru species can be essential for the optimum PROX activity. The close relation between the low-temperature PROX activity and the ratio of Ru(0) was revealed by XPS study [66]. Until now, this Ru/Al_2O_3 catalyst can be considered to be the most promising based on the real operation data [69–72]. However, there have been few reports that the acceptable CO removal can be achieved with the high inlet CO concentration such as around 1 vol.% in the real gas composition. In this work, it has been found that 5% Ru/γ-Al_2O_3 can decrease the CO concentration from 0.9 vol.% to be less than 10 ppm in a realistic condition over wide reaction temperatures. In the previous works, supported Ru catalysts have been reported to provide the extended temperature range to achieve the acceptable CO removal because both oxidation and hydrogenation can be accomplished at once [67,73]. These

Table 2
CO and O_2 chemisorptions of supported noble metal catalysts.

Catalyst	Amount of chemisorbed CO[a] (μmol/g_{cat})	[CO]/[M][a]	Amount of chemisorbed CO[b] (μmol/g_{cat})	[CO]/[M][b]	Amount of chemisorbed O_2 [c] (μmol/g_{cat})	[O_2]/[M][c]
1% Pt/γ-Al_2O_3	26.36	0.51	N.D.	N.D.	~0	~0
5% Pt/γ-Al_2O_3	76.28	0.3	39.21	0.15	~0	~0
0.5% Ru/γ-Al_2O_3	18.16	0.37	15.67	0.32	6.15	0.12
5% Ru/γ-Al_2O_3	65.87	0.13	67.76	0.14	34.49	0.07
0.5% Rh/γ-Al_2O_3	28.94	0.59	N.D.	N.D.	~0	~0
5% Rh/γ-Al_2O_3	421.32	0.86	350.89	0.73	183.7	0.38

N.D.: not determined.
[a] CO chemisorptions at 300 K measured in He.
[b] CO chemisorptions at 300 K measured in H_2.
[c] O_2 chemisorptions at 373 K measured in He.

Table 3
Turnover frequencies for the O_2 consumption and the CO oxidation during the preferential CO oxidation over 5% Ru/γ-Al_2O_3 and 0.5% Ru/γ-Al_2O_3.

Catalyst	Dispersion (%)[a]	O_2 conversion (%)	CO conversion (%)	CO_2 selectivity	TOF[b] (O_2) (s^{-1})	TOF[c] (CO) (s^{-1})	TOF[d] (CO) (s^{-1})
0.5% Ru/γ-Al_2O_3 [e]	19.1	8.5	2.7	15.9	6.6×10^{-2}	2.1×10^{-2}	1.1×10^{-2}
5% Ru/γ-Al_2O_3 [f]	20.3	6.8	8.3	61.0	5.0×10^{-2}	6.1×10^{-2}	8.9×10^{-2}

Feed composition: 1 vol.% CO + 1 vol.% O_2 + 50 vol.% H_2 balanced with He.
[a] The dispersion was calculated based on the average particle size of Ru particles determined from TEM analysis.
[b] Turnover frequencies for the O_2 consumption based on Ru dispersion calculated from TEM results.
[c] Turnover frequencies for the CO oxidation based on Ru dispersion calculated from TEM results.
[d] Turnover frequencies for the CO oxidation based on Ru dispersion calculated from CO chemisorptions data.
[e] F/W = 1000 ml/(min g_{cat}).
[f] F/W = 10,000 ml/(min g_{cat}).

simultaneous reactions were also observed over Ru catalysts in this work. However, it cannot be said that the only CO methanation can provide 100% CO conversion at high temperatures because 0.5% Ru/γ-Al_2O_3 could not give us 100% CO conversion even with the similar CH_4 yield with that of 5% Ru/γ-Al_2O_3. Therefore, it can be said that the presence of optimum Ru species for the PROX is essential to provide the wide temperature range to achieve the acceptable CO removal. The presence of simultaneous methanation reaction over Ru catalysts also tell us the importance of temperature control during a reaction not to consume most of hydrogen fuel via CO_2 methanation reaction observed over 5% Ru/γ-Al_2O_3 above 410 K in this work. The further work on the catalyst design is required not to cause this undesired reaction while maintaining the high PROX activity over wide reaction temperatures.

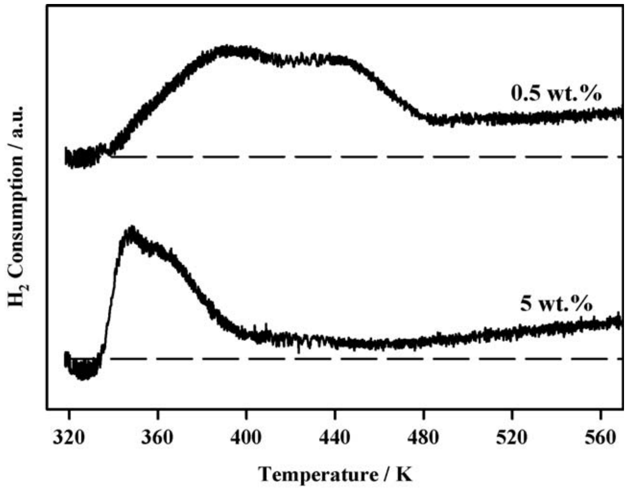

Fig. 5. TPR patterns of Ru/γ-Al_2O_3 catalysts after O_2 chemisorption at 373 K.

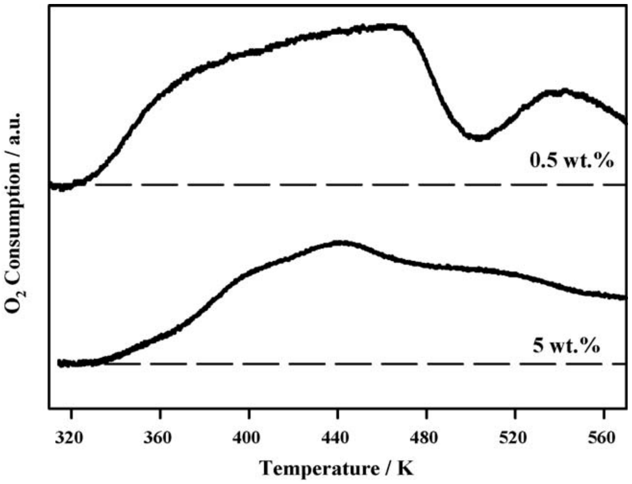

Fig. 6. TPO patterns of Ru/γ-Al_2O_3 catalysts after reduction at 573 K.

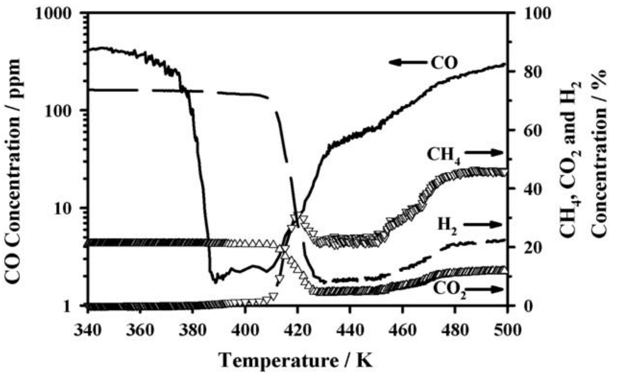

Fig. 7. CO, CH_4, CO_2 and H_2 concentration based on the dry basis for the PROX over supported 5 wt.% Ru/γ-Al_2O_3 at different reaction temperatures. F/W = 345 ml/(min g_{cat}). Reaction conditions: 0.9 vol.% CO + 0.9 vol.% O_2 + 63.6 vol.% H_2 + 17.4 vol.% CO_2 and 13.0 vol.% H_2O with balanced N_2.

4. Conclusion

A comparative study for the PROX over commercial noble metal catalysts such as 1 wt.% Pt/γ-Al_2O_3, 0.5 wt.% Ru/γ-Al_2O_3, 0.5 wt.% Rh/γ-Al_2O_3, 5 wt.% Pt/γ-Al_2O_3, 5 wt.% Ru/γ-Al_2O_3, and 5 wt.% Rh/γ-Al_2O_3 was conducted under the more realistic condition than that done by Oh and Sinkevitch [3]. Among them, 5 wt.% Ru/γ-Al_2O_3 showed the highest PROX activity. This catalyst can be considered to be promising because it can reduce the high inlet CO concentration such as ~1 vol.% to be less than 10 ppm at low temperatures where the reverse water–gas shift reaction can be minimized. No detectable amount of chemisorbed O_2 was measured at 373 K over 1 wt.% Pt/γ-Al_2O_3, 0.5 wt.% Rh/γ-Al_2O_3 and 5 wt.% Pt/γ-Al_2O_3. The moderate degree of CO and O_2 chemisorption at reaction temperatures appeared to be essential for the optimum PROX activity. Although 0.5 wt.% Ru/γ-Al_2O_3 and 5 wt.% Ru/γ-Al_2O_3 have the similar particle size distribution based on TEM analysis, the latter catalyst with smaller amount of chemisorbed CO and O_2 per Ru metal showed much better PROX activity. Based on TPO and TPR result, 0.5 wt.% Ru/γ-Al_2O_3 can be oxidized at lower temperatures but can be reduced at higher temperatures compared with 5 wt.% Ru/γ-Al_2O_3. Therefore, the easily reducible Ru species can give us the better PROX activity over a wide reaction temperature for Ru catalysts.

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