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Development of novel Ru catalyst of preferential CO oxidation for residential polymer electrolyte fuel cell systems☆

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Abstract

CO preferential oxidation on a novel Ru catalyst greatly improved in activity and selectivity over a wide temperature range by the pre-treatment of H_2 reduction was characterized. The high performance was obtained by increasing the population of surface Ru(0) which improved O_2 activation at low temperatures. Methanation of CO on the catalyst can also contribute to the final CO clean-up from ca. 100 to <1 ppm at low temperatures where the influence of CO_2 methanation can be ignored.

Keywords: Ru/Al_2O_3 catalyst; ESCA; CO preferential oxidation; Methanation; PEFC; Residential use

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1. Introduction

Polymer electrolyte fuel cell (PEFC) systems have increasingly been developed for vehicle and residential use. From a feasibility study for residential energy demand in Japan, 0.5–1 kW class PEFC cogeneration systems have been mainly developed for residential use. An AC power generation efficiency of not less than 31.5% (HHV) and durability for 10 years' operation are required for these systems.

A hydrogen-rich reformed gas from hydrocarbons like natural gas is a convenient fuel for residential use, in terms of infrastructure. The natural gas reforming process, comprising a desulfurizer, a steam reformer and a CO shift converter, has already been established for the phosphoric acid fuel cell (PAFC) system [1–3]. The reformed gas after the CO shift converter contains about 0.5 vol.% CO. For PEFC systems, a CO removal process is required in addition to the reforming process established for the PAFC because the anode catalyst is poisoned by only 10 ppm of CO [4–6]. Although CO-tolerant anode catalysts containing Ru in addition to Pt have been developed for PEFC [7–9], the acceptable CO concentration of the CO tolerant anode catalyst appears to be about 10 ppm considering long-term durability.

Generally, a CO preferential oxidation (PROX) process using Pt-based catalysts has been used for the CO removal process because of its high activity. It was reported that CO was reduced to ca. 100 ppm on a Pt/Al_2O_3 catalyst with the addition of excess air corresponding to $[O_2]/[CO] = 2$ [4]. It has also been reported that the additive air corresponding to $[O_2]/[CO] \geq 3$ was needed to remove CO completely on the conventional Pt/Al_2O_3 catalyst at single stage [10]. The excess O_2 consumes H_2 in the reformed gas by combustion, which causes a decrease in the power generation efficiency of the PEFC system. Therefore, multi-stage CO PROX has usually been adopted in the actual reactors [11–21] because the total amount of additive air can be reduced by optimizing the additive air at each stage. It has been reported that CO was reduced to less than 10 ppm by a two-stage reactor with a total additive air corresponding to $[O_2]/[CO] = 1.5$ [21]. However, complex hardware is required to control temperatures and oxidant injections along the multi-stage catalytic layer.

On the other hand, although several kinds of the Pt-based catalysts have been studied to improve the CO PROX activity [10,22–29], those performances in an actual reactor under practical reaction conditions have not been confirmed. Meanwhile, there were several reports that Ru/Al_2O_3 catalysts showed higher CO removal performance than conventional Pt/Al_2O_3 catalysts [7,9,30]. Generally, a Ru catalyst also possesses considerable methanation activity [31]. Because temperature control is quite difficult in actual

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reformate due to self-catalytic endothermic CO_2 methanation, a Ru catalyst is seldom used solely except for using in the second stage of the two-stage CO PROX process.

In a previous work [32], we reported that the novel Ru catalyst, which is further reduced by H_2/N_2 after aqueous reduction, has extremely high practical CO removal performance even in a shingle-stage reactor for residential PEFC applications. On the catalyst, CO can be reduced from 0.5 vol.% to < 10 ppm between 358 and 443 K, and < 1 ppm between 373 and 393 K at $[O_2]/[CO] = 1.5$ in a reactant gas containing CO_2 and H_2O. The novel Ru catalyst has already been applied practically [33], and its durability has been demonstrated over 10,000 h on an actual 1 kW-class natural gas fuel processor adopting a single-stage CO PROX reactor. Moreover, its expected life of over 90,000 h has been confirmed by the accelerated deactivation method [33]. In this paper, the reaction on the novel Ru catalyst was characterized to clarify the reasons that this catalyst shows higher performance than the conventional Ru catalyst.

2. Experimental

The Ru/Al_2O_3 catalyst was prepared by impregnating $RuCl_3$ into Al_2O_3 followed by aqueous phase reduction by hydrazine [32]. Ru loading on the catalyst was 1.01 wt.%. The amount of CO adsorption on the catalyst was 1.35 N ml/g-cat, and the specific surface area of the catalyst was 174 m^2/g-cat by BET one point method using N_2 adsorption. For the activated Ru catalyst (the novel Ru catalyst), the Ru/Al_2O_3 was further reduced in N_2 containing 9.5 vol.% H_2 flow for 2 h at 523 K as a pre-treatment for activation [32]. For the non-activated Ru catalyst, Ru/Al_2O_3 was used without the pre-treatment. As a reference, a conventional Pt/Al_2O_3 catalyst was prepared by the impregnation method. Pt loading on the catalyst was 1.00 wt.%, and the amount of CO adsorption and BET surface area were 0.38 N ml/g-cat and 165 m^2/g-cat, respectively.

Catalytic activity was measured in a fixed bed flow reactor made of stainless steel tubing (16.4 mm i.d.) under almost atmospheric pressure. Eight milliliter (5.6 g) of the Ru/Al_2O_3 catalyst was placed at the center of the reactor. To measure the CO preferential oxidation activity, the temperature of the reactor was increased to the test temperature under an N_2 flow. The test gas, generated from standard gas by mass flow controllers, was fed at a flow rate of 1000 ml/min, corresponding to GHSV = 7500 h^{-1}. The GHSV value was shown in dry base. In some tests, water was added to the test gas by a pump through a vaporizer before the reactor. Reaction temperatures were measured by a thermocouple located along the centerline of the reactor. The maximum temperature of the catalyst layer, which was always at the top of the layer, is shown in the table and figures as the reaction temperature.

The gas compositions at the inlet and the outlet of the reactor at a stationary state were analyzed with a gas chromatograph equipped with TCD and FID. The results are shown in dry base. The detection limit of both CO and CH_4 was 1 ppm, while the detection limit of O_2 was 20 ppm. Concentrations below the detection limit are plotted as 0 ppm on the linear plot and 1 ppm on the log plot in the figures.

The ratio of Ru(0) to total Ru atoms on the surface of the catalyst was measured by using ESCA. All ESCA spectra were taken on a PHI 5700 ESCA System with a PC-ACCESS data analysis system (Physical Electronics Inc.). The ratio of Ru(0) to total Ru atoms on the surface of the catalyst was calculated by separation of the Ru 3d spectra [34].

3. Results

3.1. Comparison of CO PROX activities of Pt and Ru catalysts

Fig. 1 shows the CO PROX activities of Pt and Ru catalysts at $[O_2]/[CO] = 1.5$. The reactant gas containing CO_2 and H_2O simulated an outlet gas of a CO shift converter in the natural gas steam reforming process. In the case of the Pt catalyst and the non-activated Ru catalyst, CO was not removed to below 10 ppm under the condition. In contrast, in the case of the activated Ru catalyst, CO was removed to below 10 ppm between 358 and 443 K and to below 1 ppm (the detection limit) between 373 and 393 K at $[O_2]/[CO] = 1.5$.

Fig. 2 shows the outlet O_2 and CH_4 concentrations of the non-activated Ru and the activated Ru catalysts under CO PROX at $[O_2]/[CO] = 1.5$. As shown in Fig. 2a, O_2 was completely consumed at over 373 K on the activated Ru catalyst, but at over 443 K on the non-activated Ru catalyst. Thus, the active temperature range of the oxidation by O_2 on the activated Ru catalyst was shifted to about 60 K lower compared to that on the non-activated Ru catalyst. Regarding methanation as a side reaction, methanation occurred much

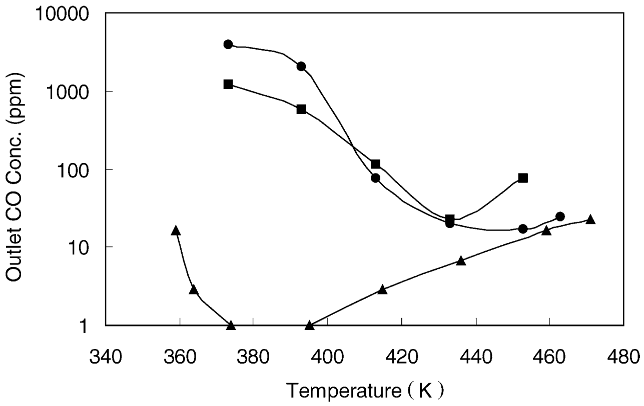

Fig. 1. Comparison of CO PROX activities on Pt and Ru catalysts at $[O_2]/[CO] = 1.5$. Reaction conditions: 0.5 vol.% CO, 20 vol.% CO_2, 0.75 vol.% O_2, 3 vol.% N_2, H_2 balance (dry base), 11 vol.% H_2O (wet base), GHSV = 7500 (dry base); (■) Pt catalyst, (●) non-activated Ru catalyst, (▲) activated Ru catalyst.

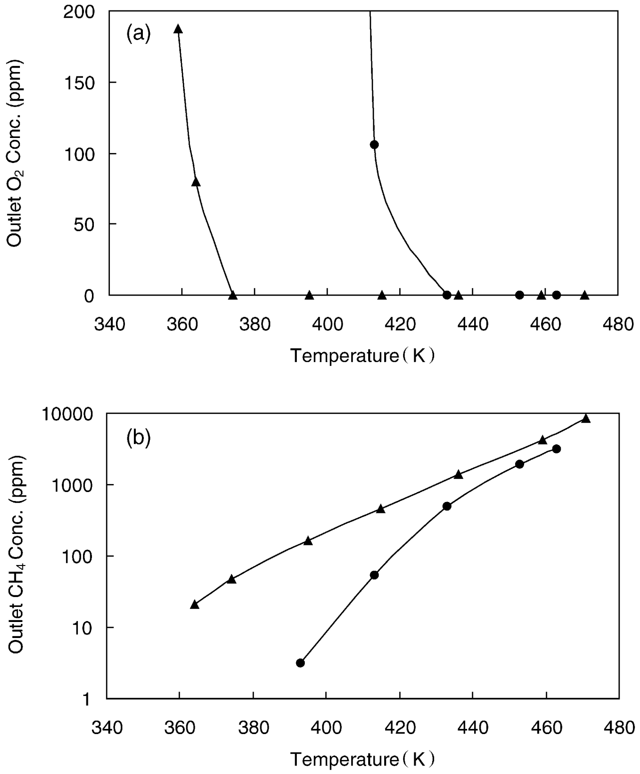

Fig. 2. Comparison of the outlet O_2 and CH_4 concentration on the non-activated Ru and the activated Ru catalysts under CO PROX at $[O_2]/[CO] = 1.5$: (a) the outlet O_2 concentration and (b) the outlet CH_4 concentration. Reaction conditions: 0.5 vol.% CO, 20 vol.% CO_2, 0.75 vol.% O_2, 3 vol.% N_2, H_2 balance (dry base), 11 vol.% H_2O (wet base), GHSV = 7500 (dry base); (●) non-activated Ru catalyst, (▲) activated Ru catalyst.

more on the activated Ru catalyst than on the non-activated Ru catalyst, especially at low temperatures, as shown in Fig. 2b.

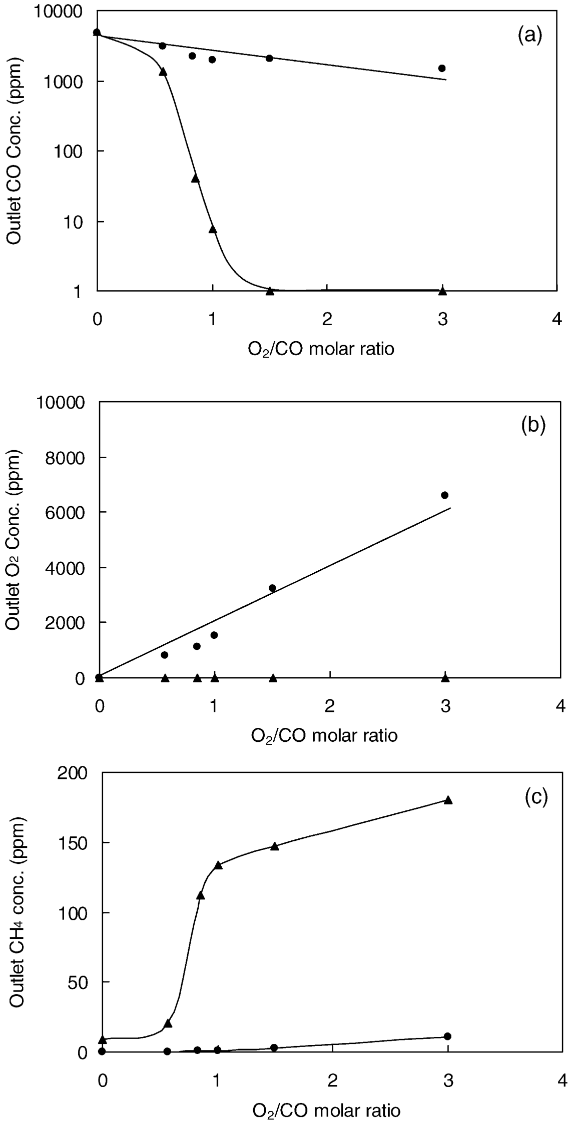

Fig. 3. Dependence of CO PROX activities on O_2/CO molar ratio at 393 K: (a) the outlet CO concentration; (b) the outlet O_2 concentration and (c) the outlet CH_4 concentration. Reaction conditions: 0.5 vol.% CO, 20 vol.% CO_2, 0–1.5 vol.% O_2, 0–6 vol.% N_2, H_2 balance (dry base), 11 vol.% H_2O (wet base), Temperature = 393 K, GHSV = 7500 (dry base); (●) non-activated Ru catalyst, (▲) activated Ru catalyst.

Fig. 3 shows the dependence of CO PROX activities of the non-activated Ru and the activated Ru catalysts on the O_2/CO molar ratio at 393 K. As shown in Fig. 3a, outlet CO concentrations decreased as the O_2/CO molar ratio increased in both catalysts. However, CO cannot be removed to less than 1000 ppm even at $[O_2]/[CO] = 3.0$ on the non-activated Ru catalyst at this temperature. In contrast, CO was removed to less than 8 ppm at $[O_2]/[CO] = 1.0$ and less than 1 ppm at $[O_2]/[CO] \geq 1.5$ on the activated Ru catalyst. As shown in Fig. 3b, the outlet O_2, which failed to react at 393 K, increased on the non-activated Ru catalyst as the O_2/CO molar ratio increased. Thus, the amount of O_2 used for CO oxidation was limited on the non-activated Ru catalyst at low temperatures where high selectivity for CO oxidation is expected. In contrast, additive O_2 was completely consumed at all the O_2/CO molar ratios on the activated Ru catalyst even at the low temperature. As for the methanation shown in Fig. 3c, in the case of the non-activated Ru catalyst, outlet CH_4 was not detected at O_2/CO molar ratios between 0 and 0.6, and the outlet CH_4 concentration slightly increased to 11 ppm as the O_2/CO molar ratio increased to 3.0. On the other hand, in the case of the activated Ru catalyst, 9.2 ppm CH_4 was generated on the activated Ru catalyst at an O_2/CO molar ratio of 0, and the outlet CH_4 concentration increased as the O_2/CO molar ratio increased. In particular, as the O_2/CO molar ratio increased from 0.6 to 1.0, the outlet CH_4 concentration remarkably increased from 21 to 133 ppm on the activated Ru catalyst.

3.2. Methanation activities of the Ru catalyst at both low CO concentration and temperature

In order to investigate the remarkable increase in the outlet CH_4 concentration of the activated Ru catalyst at the O_2/CO molar ratio from 0.6 to 1.0, the methanation activ-

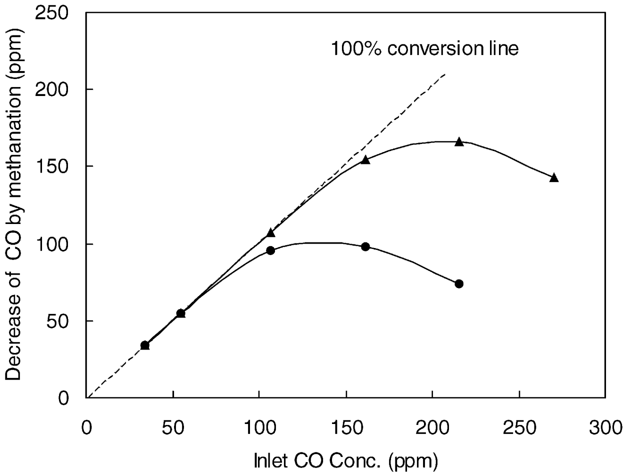

Fig. 4. Dependence of methanation activity in the absence of CO_2 on inlet CO concentration at 393 K. Reaction conditions: 34–270 ppm CO, H_2 balance (dry base), 11 vol.% H_2O (wet base), Temperature = 393 K, GHSV = 7500 (dry base); (●) non-activated Ru catalyst, (▲) activated Ru catalyst.

ities of the catalyst were measured in the absence of CO_2. Fig. 4 shows the dependence of methanation activities of the non-activated Ru and the activated Ru catalysts on the inlet CO concentration at 393 K. In the case of the activated Ru catalyst, CO methanation conversion was 100% at an inlet CO concentration of ca. 110 ppm, however, it remarkably decreased as inlet CO concentration increased over ca. 160 ppm. In the case of the non-activated Ru catalyst, CO methanation conversion was 100% up to an inlet CO concentration of ca. 60 ppm, and it also decreased as inlet CO concentration increased over 60 ppm.

3.3. *Difference between methanations of CO and CO_2 under CO PROX conditions*

In order to investigate the occurrence of CO_2 methanation under CO PROX condition, the methanation activities of the activated Ru catalyst were measured in the reactant gas with CO_2 and without CO_2. Fig. 5 shows the comparison of the outlet CH_4 concentration of the catalyst in the absence and the presence of CO_2, under the CO PROX at $[O_2]/[CO] = 1.0$. The outlet CH_4 concentrations at 373 K were 45ppm in the presence of CO_2 and 34 ppm in the absence of CO_2, respectively. The difference in the outlet CH_4 concentrations between those two conditions was only ca. 100 ppm at 433 K, and widened as reaction temperature increased. The CH_4 concentration in the presence of CO_2 was rapidly increased due to the methanation of CO_2, as the reaction temperature was increased above 453 K.

3.4. *Correlation between surface Ru(0) on the catalyst and CO PROX activity*

In order to investigate the reason the activation improved the CO PROX activity, the oxidation state of the Ru on the catalyst surface was studied by using ESCA. On the activated catalyst, 77% of surface Ru atoms was reduced to metal, while 8% was reduced on the non-activated catalyst [34]. Thus, there was big difference between those two catalysts in the population of metal Ru on the surface. In order to investigate the effect of surface Ru(0), CO PROX activities of

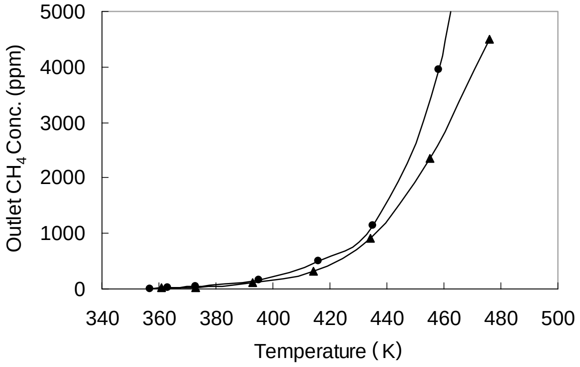

Fig. 5. Comparison of the outlet CH_4 concentration of the activated Ru catalyst in the absence of CO_2 and in the presence of CO_2. Reaction conditions: 0.5 vol.% CO, 20 vol.% CO_2, 0.5 vol.% O_2, 2 vol.% N_2, H_2 balance (dry base), 11 vol.% H_2O (wet base), GHSV = 7500 (dry base); (●) with CO_2, (▲) without CO_2.

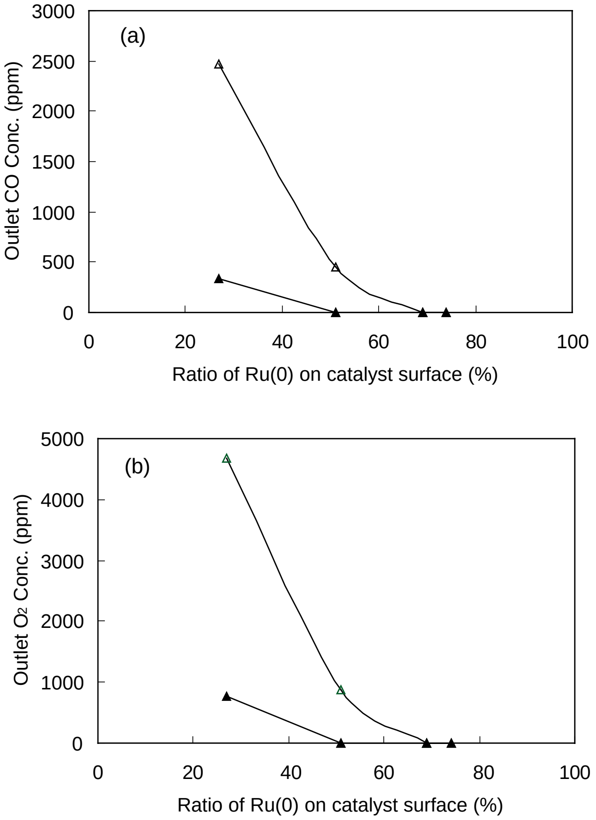

Fig. 6. Dependence of CO PROX activity on the ratio of surface Ru(0) at $[O_2]/[CO] = 1.5$: (a) the outlet CO concentration and (b) the outlet O_2 concentration. Reaction conditions: 0.5 vol.% CO, 20 vol.% CO_2, 0.75 vol.% O_2, 3 vol.% N_2, H_2 balance (dry condition), GHSV = 7500 (dry base); (△) Temperature = 373 K, (▲) Temperatures = 393 K.

various Ru catalysts having different Ru(0) populations were measured. A 0.98 wt.% Ru/Al_2O_3 obtained by the above aqueous phase reduction was used for the test. The Ru/Al_2O_3 was further reduced by heating in the H_2/N_2 mixed gas for 1.5 h at 343, 373, 453 and 493 K as pre-treatment. Consequently, the ratio of Ru(0) on the surface of the catalyst was increased to 27, 51, 69 and 72% by those pre-treatments, respectively. Fig. 6 shows the dependence of CO PROX activity of the Ru catalyst on the surface Ru(0) population of the catalyst at 373 and 393 K. As shown in Fig. 6a, the outlet CO concentration decreased as the surface Ru(0) increased. Also, outlet O_2 concentration decreased as the surface Ru(0) increased, as shown in Fig. 6b.

4. Discussion

As shown in Fig. 1, at $[O_2]/[CO] = 1.5$, there was no temperature window where CO was reduced to below 10 ppm on Pt/Al_2O_3 and non-activated Ru/Al_2O_3, while a wide window appeared on activated Ru/Al_2O_3. Comparing Fig. 2a with Fig. 1, the temperature at which unreacted oxygen disappeared almost corresponded to the lower edge of the temperature window, and the temperature was greatly lowered by the activation. Therefore, it can be considered that the high CO conversion of the activated Ru catalyst at low temperatures is derived from the improvement in the activity of CO oxidation by O_2. On the other hand, the higher edge of the window seems to be determined by methanation of CO_2 or a reverse water–gas shift reaction. As shown in Fig. 2b, the temperature region where evolved CH_4 exceeded several thousand ppm was not so different between the two catalysts, and CO_2 methanation could occur above this temperature range. There is a possibility that the CO is generated as a by-product of CO_2 methanation. It was reported that CO was an intermediate of CO_2 methanation on Ni catalysts [35,36]. Further investigations are required to clarify which determines the higher edge of the window.

Methanation of CO_2 does not contribute to CO removal but wastes H_2 as fuel. Furthermore, there is a risk in practical use that CO_2 methanation is accelerated as a self-catalytic reaction by its own exothermal reaction heat and that the reaction temperature may become uncontrollable, because the reformed gas after the CO shift converter typically contains as much as 20 vol.% CO_2. Therefore, CO_2 methanation should be avoided in the CO removal process. As shown in Fig. 5, it was found that the amount of the CH_4 generation derived from CO_2 was sufficiently low below 433 K on the activated Ru catalyst. In the activated Ru catalyst, a wide temperature window exists at low temperatures where little methanation of CO_2 occurs. Therefore, in spite of using Ru, the activated Ru catalyst can be used without the risk of CO_2 methanation.

On the other hand, methanation of CO contributes to CO removal. Moreover, CH_4 generated by the methanation during the CO removal process can finally be used as the fuel of the reformer burner through the cell stack in the steam reforming process. Therefore, CO methanation is acceptable to some extent in the CO removal process for residential PEFC systems adopting the steam reforming process [37]. As shown in Fig. 2b, the outlet CH_4 concentration of the activated Ru catalyst was higher than that of the non-activated Ru catalyst, especially at low temperatures. There is a possibility that CO methanation contributed to the high CO conversion of the activated Ru catalyst. As shown in Fig. 3c, when the O_2/CO molar ratio was increased from 0.6 to 1.0, the outlet CH_4 concentration remarkably increased from 21 to 133 ppm and the outlet CO concentration decreased from 1350 ppm to below 10 ppm on the activated Ru catalyst at 393 K. The slope of the increase in the outlet CH_4 concentration between $[O_2]/[CO]$ of 0.6 and 1.0 was steeper than those between 0 and 0.6 or between 1.0 and 3.0. On the other hand, CO was completely methanated up to ca. 110 ppm on the activated Ru catalyst at 393 K, as shown in Fig. 4. From these results, it is considered that residual CO of around 100 ppm, which cannot be removed by simple oxidation, can be reduced to less than 1 ppm by methanation on the activated Ru catalyst. Such final clean-up by CO methanation is only effective when CO PROX proceeds at low temperatures where the influence of CO_2 methanation can be ignored.

On the other hand, CO methanation conversion remarkably decreased over an inlet CO concentration of ca. 160 ppm on the activated Ru catalyst and over an inlet CO concentration of ca. 60 ppm on the non-activated Ru catalyst, as shown in Fig. 4. The negative slope at such inlet CO concentrations in Fig. 4 means the self-poisoning of CO, and as a result, CO methanation is greatly suppressed. Therefore, at 393 K, CO methanation was negligible on the activated Ru catalyst at O_2/CO molar ratios below 0.6, because CO was decreased only to ca. 1300 ppm by oxidation as shown in Fig. 3a. In the case of the non-activated Ru catalyst at 393 K, CO was decreased only to ca. 1500 ppm even at $[O_2]/[CO] = 3.0$ due to low CO oxidation activity by O_2, as shown in Figs. 3a and 3b). Therefore, methanation of CO hardly occurred at that temperature on the non-activated Ru catalyst even at the high O_2/CO molar ratio.

At the same time, there is a possibility that the water–gas shift reaction also contributes to CO removal. The equilibrium constants of the water–gas shift reaction are calculated to be 1.3×10^3 at 393 K, 4.0×10^2 at 443 K, respectively [31]. If the water–gas shift reaction reaches equilibrium in the outlet of CO PROX, the outlet CO concentration (dry base) under the conditions of $S/C = 2.5$ and $[O_2]/[CO] = 1.5$ can be calculated to be ca. 0.086 vol.% at 393 K and ca. 0.28 vol.% at 443 K. From these calculations, the water–gas shift reaction may assist the CO removal although CO cannot be reduced to below 10 ppm by the reaction. However, Fig. 3a shows that the water–gas shift reaction did not occur on either the activated or the non-activated Ru catalysts at 393 K in the reactant gas corresponding to $[O_2]/[CO] = 0$. Although further investigations are required to clarify the contribution of the water–gas shift reaction to CO removal, it is considered that the water–gas shift reaction does not play an important role in the activation.

The ratio of Ru(0) on the surface of the activated Ru catalyst, which showed high CO PROX activity at low temperatures, was estimated to be 77%, while that of the non-activated Ru catalyst was estimated to be 8% by ESCA analysis. This agrees with the previous result that the Ru/Al_2O_3 catalyst, in which the Ru having a significantly more metallic character, showed better CO PROX performance [38]. As shown in Fig. 6, as the ratio of Ru(0) on the catalyst surface was increased, both the CO conversion and the O_2 consumption increased at low temperatures such as 373 and 393 K. The O_2 slip exactly corresponded to the CO slip at these low temperatures. As mentioned above, the CO conversion of the Ru catalyst at low temperature can be increased by improving the activity of CO oxidation by O_2. Therefore, it can be considered that O_2 activation on Ru(0) is a key step for the CO PROX on the Ru catalyst at low temperatures. Moreover, the activated Ru catalyst showed higher CO methanation activity than the non-activated Ru catalyst under higher inlet CO concentration conditions at 393 K, as shown in Fig. 4. Therefore, it is expected that the effect of the final CO clean-up by methanation at low temperatures is enhanced on the catalyst having more surface Ru(0) at lower $[O_2]/[CO]$ PROX conditions. However, the difference in CO methanation between the activated and the non-activated catalysts is limited, and so, the main reason of the improvement in the CO conversion at low temperatures is considered to be derived from the improvement in the O_2 activation.

Thus, on the activated Ru catalyst, the active temperature range is expanded to lower temperatures, where high selectivity for CO oxidation can be expected, by increasing surface Ru(0) population through the increase in CO oxidation activity by O_2 at low temperatures. Consequently, this catalyst offers extremely high practical performance: high activity, high selectivity and a wide temperature range without the risk of CO_2 methanation.

5. Conclusion

CO PROX on the novel Ru catalyst greatly improved in activity and selectivity over a wide temperature range by the activation of H_2 reduction was characterized. The CO conversion of the Ru catalyst at low temperatures can be increased by improving the activity of CO oxidation by O_2. As the ratio of Ru(0) on the catalyst surface was increased, the CO oxidation activity by O_2 increased at low temperatures. The effect of H_2 reduction is a dramatic improvement in O_2 activation at low temperatures by the increase of surface Ru(0). As a result, the active temperature range of the Ru catalyst is greatly shifted to low temperatures, where high selectivity for CO oxidation can be expected, by this activation. Moreover, methanation activity of the catalyst was high for a low CO concentration below ca. 100 ppm at low temperatures. Consequently, it is suggested that both the high activity and the high selectivity of the catalyst are achieved by PROX of CO from 0.5 vol.% to ca. 100 ppm followed by methanation of the residual CO from ca. 100 ppm to less than 1 ppm at low temperatures where the influence of CO_2 methanation is ignored.

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