

The cleanup of CO in hydrogen for PEMFC applications using Pt, Ru, Co, and Fe in PROX reaction

Chih-Yung Huang^a, Yan-Yi Chen^a, Chin-Chia Su^{a,*}, Chuan-Fu Hsu^b

^a Department of Mechanical Engineering, National Taiwan University, No. 1, Sec. 4, Roosevelt Road, Taipei 10617, Taiwan

^b LYDS Technology Co., Ltd., No. 12, 882 Lane, Kao Shi Road, Yangmei Cheng, Taoyuan 32668, Taiwan

Received 26 July 2007; received in revised form 11 September 2007; accepted 11 September 2007

Available online 15 September 2007

Abstract

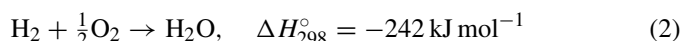
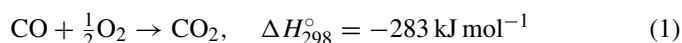
An experimental investigation is performed into the cleanup of CO in hydrogen for proton exchange membrane fuel cell (PEMFC) using Pt/Al₂O₃ and Ru/Al₂O₃ catalysts. Additionally, the effects of adding the transition metals Co and Fe to a Ru/Al₂O₃ catalyst are examined. The results show that as the level of Pt addition is increased, the maximum CO conversion rate is achieved at a lower temperature. With Ru/Al₂O₃ catalysts, the CO conversion rate increases significantly with increasing Ru addition at temperatures lower than 80 °C. For both catalysts, the methane yield increases with increasing temperature and increasing noble metal addition. At temperatures in the range of 100–140 °C, the CO conversion rate and methane yield of the Pt- and Ru-based preferential oxidation (PROX) reactions are both insensitive to the density of the honeycomb carrier. The CO conversion rate is significantly improved by the addition of Fe at temperatures lower than 160 °C and by the addition of Co at temperatures higher than 200 °C. Of the two metals, Fe results in a greater reduction of the methane yield at high temperatures. Finally, both catalysts achieve a stable cleanup performance over the course of a 12-h stability test and suppress the CO concentration to an acceptable level for PEMFC applications. © 2007 Elsevier B.V. All rights reserved.

Keywords: Proton exchange membrane fuel cell (PEMFC); Reformer; Preferential oxidation (PROX); Catalyst; CO conversion rate; Methane yield

1. Introduction

Three processes are available for generating hydrogen fuel for proton exchange membrane fuel cell (PEMFC) from methanol: (i) steam reforming of methanol (SRM), (ii) partial oxidation of methanol (POM) and (iii) combined reforming of methanol (CRM). Among these three reaction processes, the steam reforming of methanol (SRM) reaction is highly developed and is possible to yield a product gas containing up to 75% hydrogen [1]. However, the methanol-reforming process produces not only hydrogen (H₂), but also carbon monoxide (CO), which poisons the membrane and cathode of the PEMFC. Therefore, following the reforming process, a cleanup operation is required to reduce the CO concentration in the reformat to a level of less than 20 ppm [2,3]. This is generally achieved using a preferential oxidation (PROX) process [4]. The main reactions

within the PROX reactor are as follows [5]:



The preferential oxidation of CO was first investigated by Brown and Green [6]. The authors reported that the maximum CO conversion rate was obtained at temperatures between 122 °C and 162 °C when using a 0.5% Ru/Al₂O₃ catalyst. In a more recent study, Oh and Sinkevitch [7] showed that the use of a 0.5% Ru/Al₂O₃ catalyst yielded a 100% CO conversion rate over a temperature range of 102–302 °C. Mariño et al. [8] investigated the CO cleanup properties of various transition metals, including Co, Cr, Cu, Ni and Zn and found that a Cu-CeO₂ catalyst yielded the highest CO conversion rate. Specifically, this catalyst reduced the concentration of CO from 20,000 ppm to 325 ppm at a temperature of 157 °C. Various researchers have investigated the feasibility of adding the transition metals Fe or Co to Pt-based catalysts in order to improve CO cleanup efficiency. For example, in [9–11], the authors demonstrated that the addition of 0.5% Fe to a 5% Pt/Al₂O₃ catalyst yielded a

* Corresponding author. Tel.: +886 2 33662703; fax: +886 2 33662703.
E-mail address: chinchiasu@ntu.edu.tw (C.-C. Su).

Nomenclature

G	methane yield (ppm)
L	length of catalyst carrier (mm)
\dot{m}	methanol feed rate (mol min ⁻¹)
M_{in}	CO concentration at inlet of PROX reactor (ppm)
M_{out}	CO concentration at outlet of PROX reactor (ppm)
	honeycomb cell density (cell in ⁻²)
SV	space velocity (h ⁻¹)
T_1	temperature of methanol steam-reforming catalyst (°C)
T_2	temperature of PROX catalyst (°C)
Y	hydrogen yield rate (mol min ⁻¹)

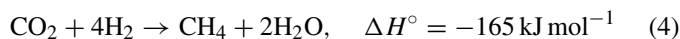
Greek symbols

α	steam-to-methanol ratio (mol mol ⁻¹)
β_{CO}	CO conversion rate (%)
β_{m}	methanol conversion rate (%)

significant improvement in the CO conversion rate. Similarly, Suh and co-workers [12–16] showed that the addition of Co to a Pt/Al₂O₃ catalyst not only enabled the noble metal content of the catalyst to be reduced, but also allowed the cleanup operation to be performed at a lower temperature. Kahlich et al. [17] showed that when the cleanup process was performed using a 0.5% Pt/Al₂O₃ catalyst, the CO conversion rate reduced significantly at temperatures greater than 200 °C. Korotkikh and Farrauto [18] showed that the addition of base metal oxides to Pt/Al₂O₃ catalysts promoted an improvement in the CO conversion rate. Son et al. [19] and Hey et al. [20] used a unique water pre-treatment method to produce nanoscale Pt pellets (i.e. 1–5 nm) in order to enhance the catalyst activity. Besides Pt-based catalysts, the use of Ru in the PROX cleanup process has also been extensively investigated. Han et al. [21,22] demonstrated an increase in both the CO oxidation rate and the level of CO₂ methanation when using a 5% Ru/Al₂O₃ catalyst at temperatures higher than 150 °C with a space velocity of 82.19 h⁻¹ and an O₂/CO ratio of 1. Echigo and Tabata [23] used a pre-treatment method to improve the activity and selectivity of an Ru catalyst over a wide range of temperatures, from 85 °C to 170 °C. Xu and Zhang [24] reported that when performing the PROX process using a 0.5% Ru/Al₂O₃ catalyst with a space velocity of 4250 h⁻¹ and an O₂/CO ratio of 2, the maximum CO conversion rate was obtained at temperatures in the range of 110–170 °C. Chin et al. [25] showed that CO concentrations of less than 30 ppm could be obtained in PROX processes performed with a space velocity of 120,000 h⁻¹ and an O₂/CO ratio of 1 at temperatures of 120–170 °C using a Ru/SiO₂ catalyst, or at temperatures of 180–200 °C using a Ru/Al₂O₃ catalyst. Additionally, the effect of non-noble metal catalysts of CoO [26] and CuO-CeO₂ [27–29] on the selective oxidation of CO was also reported.

During the PROX process, the carbon monoxide and carbon dioxide (CO₂) in the reformat may react with the hydrogen to produce methane and water [30]. The corresponding methana-

tion reactions are given by:



Eqs. (3) and (4) are both exothermic reactions and result in the consumption of hydrogen. Consequently, even though methanation reduces the CO content of the reformat, it also results in a significant loss of hydrogen and therefore reduces the energy value of the reformat gas. Consequently, the methane yield should be carefully controlled during the PROX process. In the 1920s, Fischer et al. [31] demonstrated that a decreasing intensity of methanation activity was observed when using catalysts based on Ru, Ir, Rh, Ni, Co, Os, Pt, Fe, Mo, Pd and Ag, respectively.

As indicated above, previous studies have considered the use of either Pt or Ru catalysts in the CO PROX process. The objective of the current study is to compare and contrast the PROX characteristics of these two noble metals in terms of the CO conversion rate and methane yield. The experimental investigations focus specifically on the relative effects of the type and quantity of the noble metal, the temperature, and the cell density of the honeycomb catalyst carrier. The effects on the CO conversion rate and methane yield of adding the transition metals Fe or Co to the Ru-based catalysts are then examined.

The O₂/CO ratio is also an important factor in the cleanup of hydrogen gas. It was reported [32] that when the O₂/CO ratio is doubled from its stoichiometric value, the maximum conversion rate of CO increases from 51% to 98%, while the selectivity decreases from 55% to 50%. Additionally, the CO conversion rate may be further enhanced if the PROX reaction is performed using O₂/CO ratios higher than 3 [6,27,32–35]. Therefore, the experiment in this work are conducted using an O₂/CO ratio of 4 and a space velocity of 20.93 h⁻¹. Note that the CO selectivity decreases with increasing O₂/CO ratio [16,19,23,24,32–34,36–41]. The generation of methane will thus be reported. Finally, the effect of H₂O and CO₂ on PROX reaction will be studied in the further.

2. Experimentation

In this study, the effectiveness of the PROX cleanup operation is evaluated using the CO conversion rate, β_{CO} :

$$\beta_{\text{CO}} (\%) = \frac{M_{\text{in}} - M_{\text{out}}}{M_{\text{in}}} \times 100 \quad (5)$$

Fig. 1 presents a schematic illustration of the current experimental setup. As shown, the system is comprised of two major parts, namely the methanol steam-reforming (SR) system used to generate the reformat, and the PROX system used to reduce its CO concentration. In accordance with the experimental findings presented in [42,43], the current methanol steaming-reforming process was conducted using a CuO-ZnO-Al₂O₃ catalyst prepared by a commercial supplier. Under test conditions of $\alpha = 1.18$, $N = 400$ cells per square inch (CPSI), $L = 40$ mm, $T_1 = 280$ °C, $SV = 20.93$ h⁻¹, and $\dot{m} = 0.03$ mol min⁻¹, the methanol conversion rate was

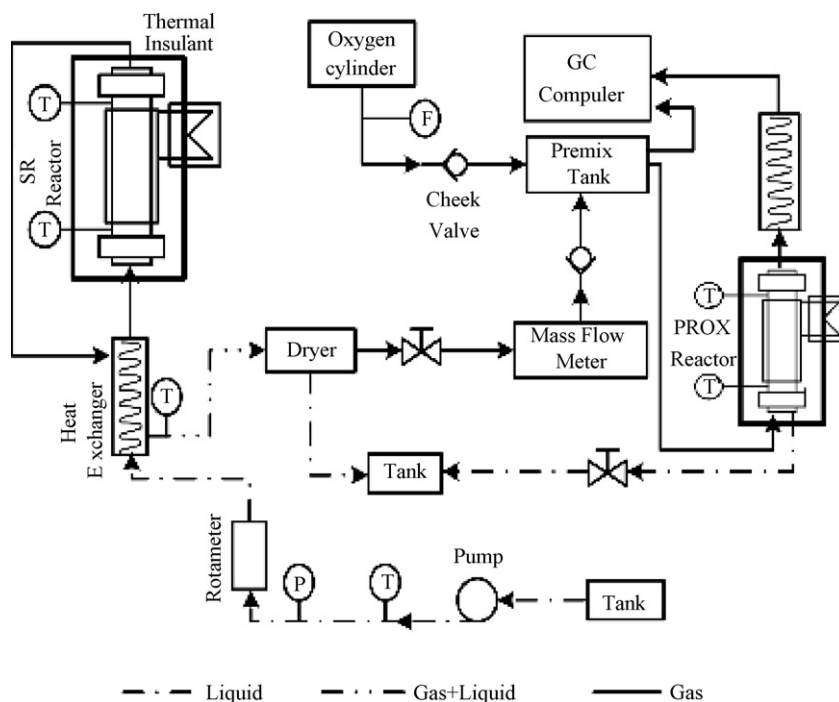


Fig. 1. Schematic illustration of experimental test system.

found to be approximately 89.5% and the hydrogen yield rate was of the order of $0.072 \text{ (mol min}^{-1}\text{)}$. The composition of the reformat was determined to be 70.43% H_2 , 29% CO_2 , 0.53% CO , and the remainder O_2 . Note that the actual composition of the gases feeding into the PROX reaction was 69% H_2 , 28.5% CO_2 , 0.5% CO , and 2% O_2 . The differences were induced by the addition of O_2 for maintaining required O_2/CO ratio.

The PROX system basically comprised of two check valves, a premix tank, an oxygen cylinder, an oxygen flow meter, a PROX reactor unit with an integral electric heater (300 W), a heat exchanger, and a gas chromatograph (GC). The shell of the reactor unit was fabricated from SCM21 alloy steel and had an internal diameter and length of 26 mm and 100 mm, respectively. The reactor unit consisted of two G-type nuts, two T-type channels, two O rings, a turbulence inducer, a circlip, a honeycomb catalyst carrier, a tube-shaped heater, a temperature controller, and two J-type thermocouples. According to the literature [42,43], the use of a turbulence inducer in a methanol steam-reforming reaction increases the methanol conversion rate and hydrogen yield rate by 33–66% and 20–62%, respectively. Accordingly, a turbulence inducer was deliberately incorporated within the current PROX reactor unit to stimulate the reaction process. The honeycomb catalyst carrier in the reactor unit had a diameter and length of 23.4 mm and 40 mm, respectively. The present experiments were performed using catalyst carriers with two different cell densities, namely 300 CPSI and 400 CPSI, respectively. The specific surface area and the particle size of all catalysts were $110 \text{ m}^2 \text{ g}^{-1}$ and 3–5 μm , respectively. The catalysts were incorporated within the carriers using an impregnation method, in which the carriers were first immersed in an aqueous solution of the catalyst of interest, then dried in an oven at $105 \text{ }^\circ\text{C}$ for 24 h and then calcined in air in a sintering furnace at $450 \text{ }^\circ\text{C}$

for 4 h. Finally, the carriers were coated with aluminum oxide to increase the adherence of the catalyst material to the honeycomb structure. As the catalysts were prepared under air flow, the metals are used in oxidized state. The compositional details of the various catalysts employed in the current experiments are summarized in Table 1.

Following the methanol steam-reforming process, the reformat gas was passed into the premix tank where it was mixed with a precise amount of oxygen to achieve an O_2/CO ratio equal to 4. The total flow rate of the reactant was $0.87 \text{ mol min}^{-1}$, which was fixed by the upstream steam-reforming process and O_2 addition. The tests were performed at the temperature range between $60 \text{ }^\circ\text{C}$ and $240 \text{ }^\circ\text{C}$, which was commonly used in the PROX reaction [13–17,24,38]. All the reaction runs were conducted around atmospheric pressure.

As shown in Fig. 1, two check valves were installed between both the premix tank and the oxygen cylinder, and mass flow

Table 1
Compositional details of catalysts

Catalyst type	Metal loading (wt%)	CPSI (lb in^{-2})
Pt/r- Al_2O_3	1	300
Pt/r- Al_2O_3	5	300
Pt/r- Al_2O_3	1	400
Ru/r- Al_2O_3	1	300
Ru/r- Al_2O_3	5	300
Ru/r- Al_2O_3	1	400
Ru/r- Al_2O_3	3	300
Ru/r- Al_2O_3	0.5	300
Ru/r- Al_2O_3	0.1	300
Ru-Fe/r- Al_2O_3	1Ru-1Fe	300
Ru-Co/r- Al_2O_3	1Ru-1Co	300

meter, respectively, to prevent a backflow of the premix tank gases. The mixed gas was then passed into the PROX reactor unit in order to carry out the CO cleanup operation. During the PROX process, the reaction of H₂ and O₂ produces H₂O (see Eq. (2)). To prevent this water from draining back into the premix tank, a run-off pipe was installed at the entrance of the PROX reactor unit. After the system had been operating for a long time, a valve was opened to allow the water to drain away and into a collector tank. The temperature of the PROX catalyst reaction was controlled using an automatic electric heater regulated by two J-type thermocouples installed immediately upstream and downstream of the reactor unit, respectively. To avoid heat losses during the reaction process, the reactor unit was clad in ceramic fiber. The PROX reaction is exothermic and thus the temperature of the reaction products leaving the reactor unit is very high. Hence, the exit gas was cooled using a heat exchanger before being passed to a gas chromatograph for compositional analysis.

The analysis of the effluent gas was carried out by gas chromatograph system equipped with a TCD detector. The calibration gases were H₂, O₂, N₂, CO, CO₂, and CH₄. Through linear regression the regression coefficient, R^2 , of the calibration was above 0.999.

3. Results and discussions

The experiments performed in the current study investigated the effects of the following variables on the CO conversion rate and methane yield during the CO PROX process: temperature, catalyst type and quantity, and honeycomb cell density.

3.1. Effect of Pt catalyst on CO conversion rate and methane yield

Fig. 2 shows that when the PROX process is performed using a 1% Pt/Al₂O₃ catalyst, the maximum CO conversion rate is obtained at a temperature of 140 °C. However, when the Pt content is increased to 5%, the maximum CO conversion rate is obtained at temperatures ranging from 60 °C to 100 °C. From inspection, it can be determined that the corresponding CO con-

centration levels are less than 30 ppm in both cases. According to a previous study [16], catalysts with 1% and 5% Pt addition achieve a maximum CO conversion rate at temperatures of approximately 200 °C and 180 °C, respectively. In other words, both the current results and those presented in [16] indicate that the temperature at which the maximum CO conversion rate is obtained reduces as the Pt content increases. Furthermore, for a given catalyst, the conversion rate falls rapidly once the temperature is increased beyond its optimal value. There are thought to be two reasons for this. First, at high temperature, Pt catalyst was desorbed to adsorption on catalysts' surface of CO [7,17]. Second, Eqs. (1) and (2) are unfavorable reactions at high temperature, and therefore CO is generated via the following reverse water gas shift reaction (RWGS) [23]:



In [16], the O₂/CO ratio was just 1.8. Comparing the two sets of results in Fig. 2, it can be inferred that the temperature at which the maximum CO conversion rate is obtained reduces as the O₂/CO ratio increases. However, while a higher O₂/CO ratio is beneficial in terms of enhancing the CO conversion rate, O₂ reacts with H₂ during the PROX process: thereby reducing the hydrogen yield. Accordingly, in practice, the value of the O₂/CO ratio should be specified such that a satisfactory compromise is obtained between the level of CO cleanup and the hydrogen yield.

Fig. 2 also illustrates the effect of the level of Pt addition on the methane yield during the PROX reaction. In general, it can be seen that the methane yield increases with both increasing temperature and increasing Pt addition. From inspection, it is found that the maximum methane yields generated under the current experimental temperature conditions are 707 ppm when using the 1% Pt/Al₂O₃ catalyst and 1921 ppm when using the 5% Pt/Al₂O₃ catalyst. However, overall the results indicate that the level of methanation activity prompted by the Pt-based catalysts is quite low. Consequently the effects of methanation and the corresponding loss of H₂ can essentially be ignored when performing CO cleanup using Pt/Al₂O₃ catalysts.

3.2. Effect of Ru catalysts on CO conversion rate and methane yield

Fig. 3 illustrates the variations in the CO conversion rate with respect to temperature when the PROX reaction is performed using Ru/Al₂O₃ catalysts with Ru contents ranging from 0.1% to 5%. At low temperatures, e.g., less than 100 °C, it is apparent that the CO conversion rate is highly dependent upon the level of Ru addition. For example, at a temperature of 80 °C, the CO conversion rate obtained using the 5% Ru/Al₂O₃ catalyst is approximately three times that obtained from the 0.1% Ru/Al₂O₃ catalyst. Broadly speaking, the maximum CO conversion rate is obtained at temperatures ranging from 100 °C to 140 °C for all of the catalysts. However, from inspection, it can be seen that the best cleanup results are obtained from the catalysts with 1–5% Ru added. As the temperature is increased from 140 °C to 180 °C, the CO conversion rates of the cata-

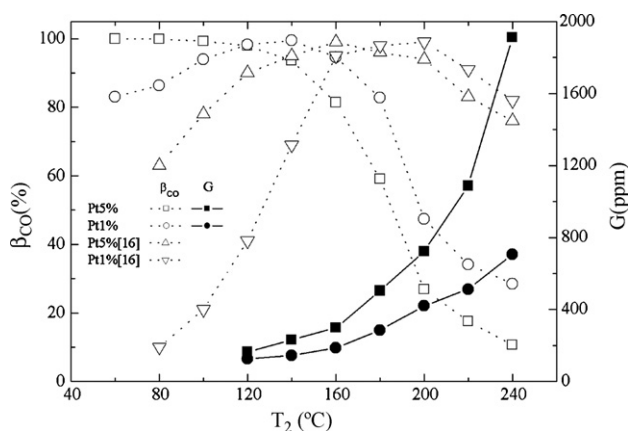


Fig. 2. Variation of CO conversion rate and methane yield with temperature for Pt catalyst. Gas composition: 1.1% CO, 20% CO₂, 67% H₂, 9% H₂O, N₂ as balance [16].

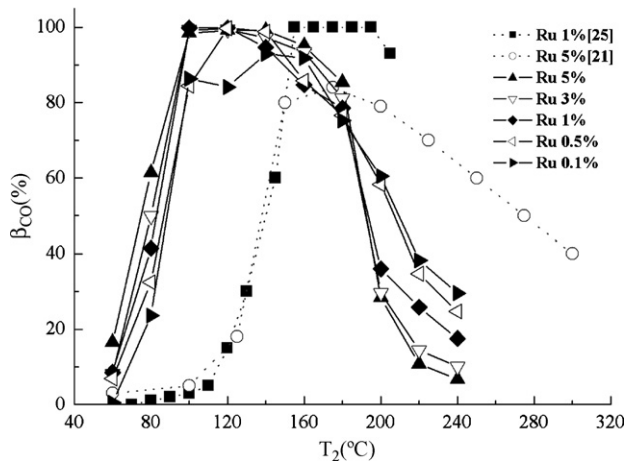


Fig. 3. Variation of CO conversion rate with temperature for Ru catalyst. Gas composition: 1% CO, 1% O₂, 75% H₂, N₂ as balance [21]. Gas composition: 0.5% CO, 0.5% O₂, 45% H₂, 15% CO₂, N₂ as balance [25].

lysts with 0.5%, 1%, 3%, and 5% Ru addition, respectively, gradually reduce. However, when the temperature is increased beyond this point, the conversion rates of these catalysts drop extremely rapidly. Significantly, the rate at which the CO conversion rate reduces is inversely related to the level of Ru addition. Examining the cleanup characteristics of the catalyst with the lowest level of Ru addition (i.e., 0.1%) it is observed that the CO conversion rate has a local peak of approximately 85% at a temperature of 100 °C, but then reduces slightly with increasing temperature before achieving a constant cleanup rate of approximately 92% over the range 140–160 °C. As with the other catalysts, the CO conversion rate then reduces as the temperature is increased beyond this point. However, as implied above, the CO conversion rate reduces more slowly than that of the catalysts with a higher Ru content and hence the 0.1% Ru/Al₂O₃ catalyst achieves the highest CO conversion rate of the current catalysts at the maximum experimental temperature of 240 °C.

From inspection, it is found that the catalysts with 0.5% and 1% Ru addition yield CO concentrations lower than 20 ppm at temperatures of 120 °C and 100–120 °C, respectively. Meanwhile, for catalysts with 3% and 5% Ru addition, CO concentrations lower than 40 ppm are obtained at temperatures of 100–120 °C and 120–140 °C, respectively. From a practical point of view, the 0.1% Ru/Al₂O₃ catalyst can be discounted as a PROX agent since at temperatures lower than 200 °C, its cleanup performance is significantly poorer than that of the other Ru catalysts. Overall, the results suggest that the catalysts with 0.5–5% Ru addition are all suitable PROX reaction agents. However, the optimal catalyst is arguably that with 1% Ru addition since it achieves the highest CO conversion rate of the current catalysts at the lowest temperature (100 °C).

As stated previously, the current PROX experiments were performed using an O₂/CO ratio of 4. However, the results reproduced in Fig. 3 from [21,25] are based on a 1:1 mixture of O₂ and CO. Comparing the current experimental results with those presented in [21,25], it can be inferred that the temperature at which the optimal CO conversion rate is obtained reduces as

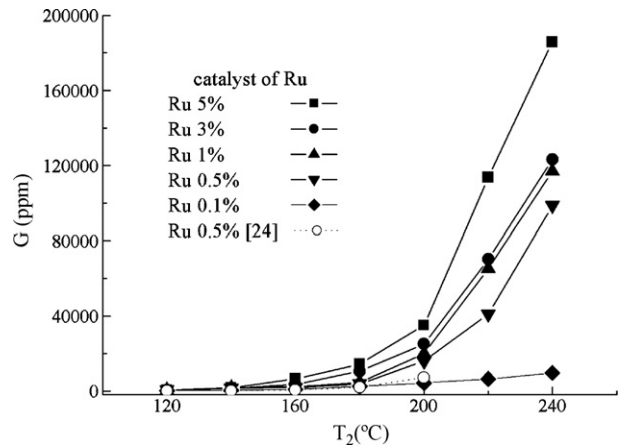


Fig. 4. Variation of methane yield with temperature for Ru catalyst. Gas composition: 1% CO, 29.1% CO₂, 69.4% H₂, 0.5% O₂ [24].

the amount of O₂ is increased (i.e. as observed also with the Pt-based catalyst, see Fig. 2).

Fig. 4 illustrates the variation of the methane yield with the temperature as a function of the Ru content of the Ru/Al₂O₃ catalysts. As with the Pt-based catalysts, it can be seen that the methane yield increases with increasing temperature and increasing Ru content. It is apparent that the methane yield is particularly sensitive to the Ru content at temperatures greater than 160 °C. For example, at a temperature of 180 °C, the methane yield of the catalyst with 3% Ru addition is 10,510 ppm, while that of the catalyst with 5% Ru is 14,347 ppm, respectively. It is also observed that for a given temperature, the methane yield obtained in the current experiments using a 0.5% Ru/Al₂O₃ catalyst and an O₂/CO ratio of 4 is higher than that obtained using an O₂/CO ratio of 1 [24]. In other words, it can be concluded that the methanation activity increases as the level of O₂ in the reactor unit increases. Comparing Figs. 2 and 4, it is apparent that the level of methanation activity induced by the Ru-based catalysts is considerably more intense than that generated by the Pt-based catalysts. As indicated in Eqs. (3) and (4), the methanation process results in a loss of H₂ since for each methane product generated, 3–4 mol of hydrogen are consumed. Accordingly, the current results confirm that the effects of methanation must be carefully considered when performing the PROX process using a Ru-based catalyst [21,22,44].

3.3. Effect of honeycomb catalyst carrier cell density on CO conversion rate and methane yield

Fig. 5 illustrates the variation of the CO conversion rate and the methane yield with the temperature as a function of the honeycomb catalyst carrier cell density when performing the PROX process using a 1% Pt/Al₂O₃ catalyst. At lower temperatures, the CO conversion rate increases slightly with a reducing cell density. At temperatures higher than 180 °C, the conversion rates obtained using both carriers reduce rapidly. However, in contrast to the low-temperature regime, it is found that the carrier with the higher cell density achieves an improved CO cleanup performance. The results presented in Fig. 5 also show that the methane

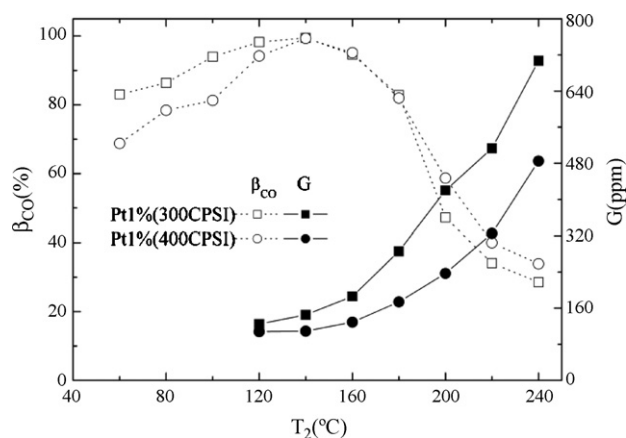


Fig. 5. Variation of CO conversion rate and methane yield with temperature as function of honeycomb cell density for Pt catalyst.

yield produced by the Pt catalyst increases with a decreasing cell density.

Similar tendency of variation in CO conversion rate and methane yield can be found from the test results using a 1% Ru/Al₂O₃ catalyst as shown in Fig. 6. At lower temperatures, the CO conversion rate increases with increasing cell density. The effect of the cell density is particularly apparent at the lowest temperature of 60 °C, at which the CO conversion rate achieved using the carrier with a cell density of 400 CPSI is approximately twice that achieved using the carrier with a more open honeycomb structure. At temperatures higher than 140 °C, the conversion rates achieved using both carriers reduce significantly. In contrast to the low-temperature regime, it is found that the carrier with a less dense cell density has an improved CO cleanup performance. However, as the temperature increases to the maximum value considered in the current experiments, i.e. 240 °C, the cell density effect becomes less profound and both carriers achieve a similar cleanup performance.

Comparing Figs. 5 and 6, it can be seen that the effect of the Pt and Ru catalyst carrier cell densities on the CO conversion rate in the low- and high-temperature regimes are the reverse of those produced. Furthermore, the results confirm that the 1% Pt/Al₂O₃ catalyst provides a significantly better

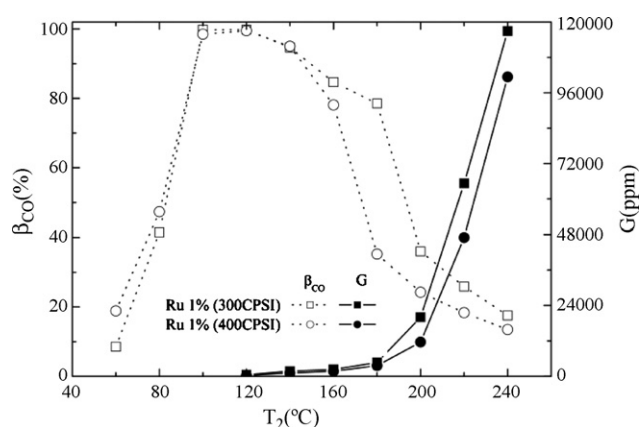


Fig. 6. Variation of CO conversion rate and methane yield with temperature as function of honeycomb cell density for Ru catalyst.

CO cleanup effect than the 1% Ru/Al₂O₃ catalyst at temperatures lower than 80 °C and higher than 220 °C. Conversely, the 1% Ru/Al₂O₃ catalyst achieves a higher CO conversion rate at temperatures in the range of 100–140 °C. Consequently, it can be inferred that the Pt-based catalyst is more suitable for low- and high-temperature PROX reactions, whereas the Ru-based catalyst is a better choice for medium-temperature cleanup operations.

From Fig. 6, it can be seen that almost no methane is generated during the PROX process conducted using a 1% Ru/Al₂O₃ catalyst at temperatures lower than 120 °C. However, as the temperature is increased, significant methanation occurs. At temperatures between 120 °C and 180 °C, the methane yield rises gradually and is insensitive to the cell density. From inspection, the methane yield in this temperature range is found to be less than 5000 ppm in both cases. However, at higher temperatures, the methane yield increases rapidly and it is observed that the more open honeycomb structure results in a higher methane yield. For example, at a temperature of 200 °C, the methane yields generated during the PROX process are found to be 20,000 ppm when using a catalyst carrier with a cell density of 300 CPSI, but 11,500 ppm when using a carrier with a cell density of 400 CPSI. As discussed previously, the generation of methane during the PROX reaction is beneficial in reducing the CO content of the reformat gas, but also consumes H₂. As a result, the temperature conditions under which the PROX reaction is performed should be carefully controlled to achieve a suitable compromise between the CO cleanup effect and the loss of hydrogen. In practice, the PROX process is typically conducted at temperatures in the range of 100–140 °C. From Fig. 6, it is apparent that both cell carriers generate a low methane yield at temperatures in this range, and hence both are suitable candidates for use in the PROX reactor unit.

3.4. Effect of transition metals Co and Fe on CO conversion rate and methane yield of Ru/Al₂O₃ catalysts

Experiments were performed to examine the effects on the CO conversion rate and methane yield of adding the transition metals Co and Fe to the 1% Ru/Al₂O₃ catalyst. (Note that the effects of Co and Fe addition to Pt-based catalysts are reported in [9–16] and are therefore not considered here. However, the PROX characteristics of the current 1% Pt/Al₂O₃ catalyst are presented for comparison purposes.) In general, Fig. 7 shows that at temperatures lower than 80 °C, the 1% Pt/Al₂O₃ catalyst achieves a higher CO conversion rate than any of the Ru-based catalysts. Furthermore, it can be seen that the CO cleanup performance of the original 1% Ru/Al₂O₃ catalyst is improved by the addition of Fe, but is degraded by the addition of Co. However, at temperatures in the range of 120–160 °C, the addition of either Co or Fe improves the CO cleanup performance of the original 1% Ru/Al₂O₃ catalyst and achieves a higher CO conversion rate than that achieved using the 1% Pt/Al₂O₃ catalyst. At temperatures higher than 160 °C, the CO conversion rate decreases rapidly irrespective of the catalyst used in the reaction process.

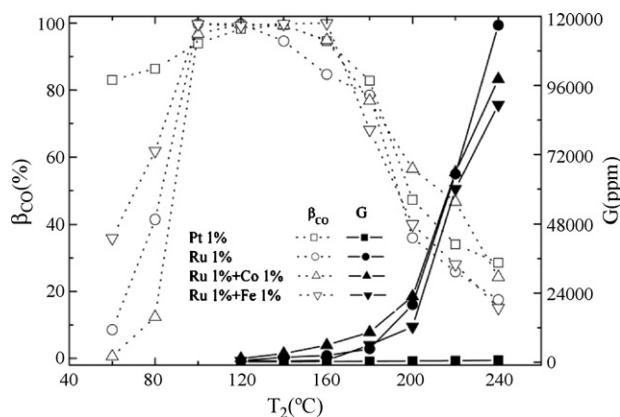


Fig. 7. Variation of CO conversion rate and methane yield with temperature for Pt and Ru noble metal catalysts and Ru catalysts with transition metals Co and Fe.

As discussed above, the 1% Pt/Al₂O₃ catalyst provides optimal cleanup results at temperatures lower than 80 °C. However, Fig. 7 shows that this catalyst also has the best cleanup performance at temperatures of 180 °C and 240 °C, respectively. In other words, the results suggest that Pt is a suitable catalyst for PROX reactions performed under either very low or very high temperature conditions. The results also show that the addition of Co to the 1% Ru/Al₂O₃ catalyst reduces its cleanup performance at temperatures lower than 120 °C, but improves the CO conversion rate marginally over the temperature range of 120–160 °C. At a temperature of 180 °C, the 1% Ru/Al₂O₃ catalyst and the 1% Ru-1% Co/Al₂O₃ catalyst have very similar levels of performance. However, at temperatures in the range of 200–220 °C, the addition of Co to the catalyst yields a significant improvement in the CO conversion rate. Although the improvement obtained in the cleanup rate by the Co addition is slightly reduced at the highest experimental temperature condition of 240 °C, the CO conversion rate is only marginally lower than that using the 1% Pt/Al₂O₃ catalyst. Regarding the addition of Fe to the original 1% Ru/Al₂O₃ catalyst, Fig. 7 shows that the addition of this transition metal yields a significant improvement in the CO conversion rate at temperatures lower than 80 °C. However, the Fe addition still fails to improve the cleanup performance of the Ru-based catalyst to the same level as that achieved using the 1% Pt/Al₂O₃ catalyst. At temperatures in the range of 100–120 °C, the performances of the 1% Ru/Al₂O₃ catalyst and the 1% Ru-1% Fe/Al₂O₃ catalyst are virtually the same. However, as the temperature is increased to 160 °C, it can be seen that the catalyst with Fe addition maintains a very high conversion rate (CO concentration: 30 ppm). However, at higher temperatures, the performance improvement provided by the Fe transition metal reduces with the result that at 180 °C, the original 1% Ru/Al₂O₃ catalyst outperforms the modified catalyst. At temperatures in the range 200–220 °C, the 1% Ru-1% Fe/Al₂O₃ achieves a slightly improved CO conversion rate. However, at the highest temperature of 240 °C, the original catalyst provides a marginally better cleanup performance. Overall, the results presented in Fig. 7 indicate that the addition of Fe to the 1% Ru/Al₂O₃ catalyst is particularly beneficial when the PROX process is conducted at temperatures ranging from 60 °C to 160 °C,

while the addition of Co is advantageous at temperatures in the range of 200–240 °C.

As mentioned above, the effects of adding the transition metals Co and Fe to Pt catalysts are documented in the literature and are therefore not discussed explicitly here [9–16]. In [9,11], it was reported that the addition of Fe to Pt catalysts increased the number of positions available for O₂ absorption [9–11]. The current experiments were performed with a higher O₂/CO ratio than that employed in the literature (i.e. O₂/CO = 4 and O₂/CO = 1, respectively). Therefore, the obvious improvement in the CO cleanup performance of the 1% Ru-1% Fe/Al₂O₃ catalyst compared to the original 1% Ru/Al₂O₃ catalyst at temperatures up to 160 °C. It may be the result of more oxygen being adsorbed by the Fe positions and then used CO with O₂ reaction was increased. Meanwhile, according to the literature [12–16], the characteristics of Co can be produced by resident CoO_x on the catalysts' surface, which results in an increased oxidation of CO [12–16]. Consequently, the respective addition of Co and Fe could be increased the high CO conversion rate region.

Fig. 7 shows that no methane is generated when the PROX reaction is conducted at temperatures lower than 120 °C. However, as the temperature is increased from 120 °C to 180 °C, the methane yield generated by the three Ru-based catalysts increases gradually. In this temperature range, the methane yields of the original 1% Ru/Al₂O₃ catalyst and the 1% Ru-1% Fe/Al₂O₃ catalyst, respectively, are very similar. However, it is observed that the addition of Co to the catalysts yields a significant increase in the methane yield. At temperatures in the range of 200–240 °C, the methane yields generated by all three catalysts increase rapidly. However, it can be seen that the addition of transition metals to the catalyst suppresses the methanation activity to a certain extent; particularly at the highest temperature of 240 °C. Comparing the two transition metals, it is evident that Fe yields a more effective reduction in the methane yield. Finally, Fig. 8 demonstrates that compared to the Ru-based catalysts, the 1% Pt/Al₂O₃ catalyst produces an insignificant amount of methane during the PROX process under the current experimental temperature conditions.

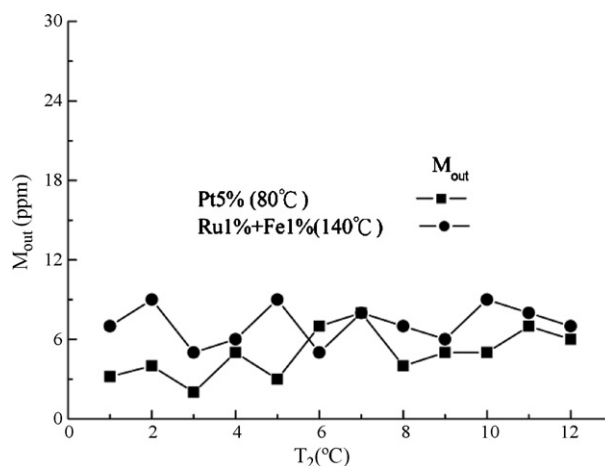


Fig. 8. Stability testing of 5% Pt and 1% Ru/1% Fe catalysts.

3.5. Stability of 5% Pt/Al₂O₃ catalyst and 1% Ru-1% Fe/Al₂O₃ catalyst

To assess the time-dependent stabilities of the 5% Pt/Al₂O₃ and 1% Ru-1% Fe/Al₂O₃ catalysts, stability tests were performed in accordance with the method described in [19,26]. Fig. 8 illustrates the variation of the measured CO concentration following PROX reaction processes conducted over a period of 12 h at temperatures of 80 °C and 140 °C using 5% Pt/Al₂O₃ and 1% Ru-1% Fe/Al₂O₃ catalysts, respectively. The results show that the both catalysts remain stable over the entire 12 h of the test.

4. Conclusions

When performing the PROX process using Pt/Al₂O₃ catalysts, the temperature at which the maximum CO conversion rate is obtained reduces as the level of noble metal increases. Significantly, the Pt catalysts are characterized by an extremely low methane yield in the temperature range of 60–240 °C. The CO conversion rate of Ru/Al₂O₃ catalysts is highly sensitive to variations in the noble metal content at temperatures lower than 100 °C. Compared to the Pt/Al₂O₃ catalysts, the Ru/Al₂O₃ catalysts generate a significant methane yield during the PROX process. The methane yield is directly related to the level of noble metal addition, and increases significantly at temperatures greater than 160 °C.

Comparing the current results to those presented in the literature, it can be inferred that a higher O₂/CO ratio reduces the temperature at which the maximum CO conversion rate can be achieved, but increases the methane yield. In the temperature range of 100–140 °C used in most CO cleanup operations, the CO conversion rate and the methane yield are insensitive to the cell density of the honeycomb catalyst carrier for both catalysts.

The addition of the transition metal Fe to the Ru/Al₂O₃ catalysts improves the CO conversion rate at temperatures in the range 60–160 °C, whereas the addition of Co enhances the CO cleanup performance at temperatures greater than 200 °C. Both Fe and Co suppress the methane yield of the original Ru/Al₂O₃ catalysts at high temperature. However, the suppression effect of Fe is greater than that of Co; particularly at the highest experimental temperature of 240 °C. Finally, the 5% Pt/Al₂O₃ and 1% Ru-1% Fe/Al₂O₃ catalysts provide a stable cleanup performance over the course of a 12-h stability test.

Acknowledgement

The financial support of this study by the National Science Council of Taiwan under Grant number NSC94-2218-E-002-012 is gratefully acknowledged.

References

- [1] B. Lindström, L.J. Pettersson, J. Power Sources 118 (2003) 71–78.
- [2] M.G. Poirier, C. Sapundzhiev, Int. J. Hydrogen Energy 22 (1997) 429–433.
- [3] K. Otsuka, Y. Shigeta, S. Takenaka, Int. J. Hydrogen Energy 27 (2002) 11–18.
- [4] L.P.L. Carrette, K.A. Friedrich, M. Huber, U. Stimming, Phys. Chem. Chem. Phys. 3 (2001) 320–324.
- [5] Y. Choi, H.G. Stenger, J. Power Sources 129 (2004) 246–254.
- [6] M.L. Brown, A.W. Green, Ind. Eng. Chem. Res. 52 (1960) 841–844.
- [7] S.H. Oh, R.M. Sinkevitch, J. Catal. 142 (1993) 254–262.
- [8] F. Mariño, C. Descorme, D. Duprez, Appl. Catal. B: Environ. 58 (2005) 175–183.
- [9] G.W. Roberts, P. Chin, X. Sun, J.J. Spivey, Appl. Catal. B: Environ. 46 (2003) 601–611.
- [10] A. Sirijaruphan, J.G. Goodwin Jr., R.W. Rice, J. Catal. 224 (2004) 304–313.
- [11] M. Kotobuki, A. Watanabe, H. Uchida, H. Yamashita, M. Watanabe, J. Catal. 236 (2005) 262–269.
- [12] D.J. Suh, C. Kwak, J.H. Kim, S.M. Kwon, T.J. Park, J. Power Sources 142 (2005) 70–74.
- [13] C. Kwak, T.J. Park, D.J. Suh, Appl. Catal. A: Gen. 278 (2005) 181–186.
- [14] C. Kwak, T.J. Park, D.J. Suh, Chem. Eng. Sci. 60 (2005) 1211–1217.
- [15] C.B. Wang, H.K. Lin, J.L. Bi, S.J. Gau, J. C.C.I.T. 33 (2004) 1.
- [16] Y. Jing, M.J. Xin, Z. Wei, Acta Chim. Sin. 62 (2004) 2143–2149.
- [17] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 171 (1997) 93–105.
- [18] O. Korotkikh, R. Farrauto, Catal. Today 62 (2000) 249–254.
- [19] I.H. Son, M. Shamsuzzoha, A.M. Lane, J. Catal. 210 (2002) 460–465.
- [20] K.L. Hey, J. Roes, R. Wolters, J. Power Sources 86 (2000) 556–561.
- [21] Y.F. Han, M. Kinne, R.J. Behm, Appl. Catal. B: Environ. 52 (2004) 123–134.
- [22] Y.F. Han, M.J. Kahlich, R.J. Behm, Catal. Appl. B: Environ. 50 (2004) 209–218.
- [23] M. Echigo, T. Tabata, Catal. Today 90 (2004) 269–275.
- [24] G. Xu, Z.G. Zhang, J. Power Sources 157 (2005) 64–77.
- [25] S.Y. Chin, O.S. Alexeev, M.D. Amiridis, Appl. Catal. A: Gen. 286 (2005) 157–166.
- [26] Y. Teng, H. Sakurai, A. Ueda, T. Kobayashi, Int. J. Hydrogen Energy 24 (1999) 355–358.
- [27] H. Igarashi, H. Uchida, M. Suzuki, Y. Sasaki, M. Watanabe, Appl. Catal. A: Gen. 159 (1997) 159–169.
- [28] G. Avgouropoulos, T. Ioannodes, H.K. Matralis, J. Batista, S. Hocevar, Catal. Lett. 73 (1) (2001) 33–40.
- [29] G. Avgouropoulos, T. Ioannodes, Ch. Papadopoulou, J. Batista, S. Hocevar, H.K. Matralis, Catal. Today 75 (2002) 157–167.
- [30] I.H. Son, A.M. Lane, D.T. Johnson, J. Power Sources 124 (2003) 415–419.
- [31] F. Fischer, H. Tropsch, P. Dilthey, Brennstoff-Chemie 6 (1925) 265.
- [32] A. Manasilp, E. Gulari, Appl. Catal. B: Environ. 37 (2002) 17–25.
- [33] C.D. Dudfield, R. Chen, P.L. Adcock, J. Power Sources 85 (2000) 237–244.
- [34] S.H. Lee, J. Han, K.Y. Lee, J. Power Sources 109 (2002) 394–402.
- [35] A. Wörner, C. Friedrich, R. Tamm, Appl. Catal. A: Gen. 245 (2003) 1–14.
- [36] D.H. Kim, M.S. Lim, Appl. Catal. A: Gen. 224 (2002) 27–38.
- [37] G. Chen, Q. Yuan, H. Li, S. Li, Chem. Eng. J. 101 (2004) 101–106.
- [38] A. Wootsch, C. Descorme, D. Duprez, J. Catal. 225 (2004) 259–266.
- [39] S. Zhou, Z. Yuan, S. Wang, Int. J. Hydrogen Energy 31 (2006) 924–933.
- [40] O. Pozdnyakova, D. Teschner, A. Wootsch, J. Kröhnert, B. Steinhauer, H. Sauer, L. Toth, F.C. Jentoft, A. Knop-Gericke, Z. Paál, R. Schlögl, J. Catal. 237 (2006) 17–28.
- [41] I.H. Son, J. Power Sources 159 (2006) 1237–1266.
- [42] C.Y. Huang, Y.M. Sun, C.Y. Chou, C.C. Su, J. Power Sources 166 (2007) 450–457.
- [43] C.Y. Huang, J.H. Lin, C.Y. Chou, C.C. Su, 4th International Conference on Fuel Cell Science, Engineering and Technology, Irvine, CA, USA, June 19–21, 2006 (Paper No. FUELCELL2006-97045).
- [44] M.V. Twigg, Catalyst Handbook, second ed., Wolfe Publishing Ltd., London, UK, 1989.