Effect of Metal Addition to Ru/Al₂O₃ Catalyst on CO Methanation Removal from Reformed Gas for Polymer Electrolyte Fuel Cell Applications

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The effect of K, V, Mo, and La addition to Ru/Al₂O₃ on its performance in CO methanation removal from simulated hydrocarbon reformed gas was investigated for polymer electrolyte fuel cell (PEFC) applications. The addition of V or Mo enhanced the CO methanation removal activity, while that of K and La did not. CO removal from the simulated reformed gas to levels below 20 ppm was achieved using Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃, while with the use of Ru/Al₂O₃, the lowest achievable level was 100 ppm. However, the addition of V or Mo to Ru/Al₂O₃ increased the methanation activity of not only CO but also CO₂. Therefore, the reaction temperature window, wherein CO removal can be performed with high selectivity for the methanation of CO vs. CO₂, was narrow.

Introduction

Polymer electrolyte fuel cell (PEFC) systems are being actively developed and commercialized for transportation and stationary power source applications. Hydrogen-rich reformed gases derived from hydrocarbons, such as natural gas, are convenient fuels for stationary PEFC systems, especially for residential use, in terms of infrastructure. The natural gas steam reforming process, comprising desulfurization, steam reforming, and CO shift conversion, has already been established for phosphoric acid fuel cell (PAFC) systems (Masuda *et al.*, 1994; Okada and Yokoyama, 2001). Following the CO shift process, the resultant reformed gas contains approximately 0.5 vol% CO. This CO concentration is acceptable for PAFCs, which are operated at approximately 200°C. On the other hand, the anode catalyst of the PEFC, which is operated at 80°C, is poisoned even at CO concentrations as low as 10 ppm (Lemons, 1990). Thus, a CO-tolerant anode catalyst containing Ru in addition to Pt has been developed for the PEFC. Reportedly, the poisoning caused by 100 ppm CO can be averted by the application of a Pt–Ru alloyed anode catalyst (Kawatsu, 1998). However, for the PEFC system, which utilizes a natural gas as the raw fuel, a CO removal process is indispensable in addition to the already established reforming process.

A large number of CO preferential oxidation catalysts and CO selective methanation catalysts have been studied for CO removal. Presently, the CO preferential oxidation removal process has been applied to commercial PEFC sys-

tems for residential use. For example, a Ru catalyst has been used for CO preferential oxidation (Echigo *et al.*, 2010). In the CO preferential oxidation process, a system providing additive air as the oxidant to the reformed gas is required. On the other hand, such a system is not necessary for CO selective methanation. Therefore, by applying CO methanation to the CO removal process, a more cost-effective PEFC system can be obtained because the CO removal system can be simplified (Echigo and Tabata, 2004).

For CO selective methanation removal, Ru and Ni catalysts have predominantly been studied. It has been reported that the maximum CO conversion on 1% Ru/Al₂O₃ is ~97% and that CO in simulated reformed gas could be reduced from 0.54 vol% to below 10 ppm via three-stage CO methanation, whereby the amount of CO₂ converted to CH₄ was 0.27-fold of that of CO (Echigo and Tabata, 2004). Ni/ZrO₂ and Ru/TiO₂ have been reported to decrease CO from 0.5% to 20 ppm in simulated reformed gases with a significantly low conversion of CO₂ to CH₄ (Takenaka *et al.*, 2004). Moreover, several types of catalysts have been studied to improve the CO methanation removal performance. For example, Kimura *et al.* (2010) reported that 1% Ru/NiAl_xO_y reduced the CO concentration from 1% to less than 40 ppm in the temperature range of 200–240°C, with the minimum concentration of 13 ppm being attained at 210°C. Tada *et al.* (2014) studied the effect of metal addition to the Ru/TiO₂ catalyst on selective CO methanation. They reported that the addition of Co and La to Ru/TiO₂ improved both CO and CO₂ methanation, while the addition of Ni enhanced only the CO methanation activity. Additionally, they found that Ru–Ni–La/TiO₂ exhibited the highest CO methanation activity among Ru/TiO₂, Ru–Ni/TiO₂, Ru–Co/TiO₂, Ru–Fe/TiO₂, Ru–La/TiO₂, Ru–K/TiO₂, and Ru–Ni–La/TiO₂, and the temperature window for selective CO methanation,

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wherein CO was reduced from 0.198% to below 100 ppm, was expanded to a lower range of 185–265°C for Ru–Ni–La/TiO₂ compared to the Ru/TiO₂ range (210–285°C).

In this study, the effect of metal addition, namely of K, V, Mo, and La, to Ru/Al₂O₃ on the CO methanation removal performance from a simulated hydrocarbon reformed gas was investigated for PEFC applications. Furthermore, the influence of a side reaction occurring on the catalyst during CO methanation removal is reported.

1. Experimental

The Ru/Al₂O₃ catalyst was prepared employing a previously described impregnation method (Echigo and Tabata, 2004). The precursor was obtained by the impregnation of an aqueous solution of RuCl₃ into γ -Al₂O₃ (2–4 mm ϕ spheres). After washing and drying, the precursor underwent reduction in aq. N₂H₄. Meanwhile, the Ru/M/Al₂O₃ (M = K, V, Mo, and La) catalysts were prepared using a sequential impregnation method. The precursors were obtained by the impregnation of aqueous solutions of KNO₃, (NH₄)₆Mo₇O₂₄·4H₂O, VOCl₃·nH₂O, and La(NO₃)₃·6H₂O into γ -Al₂O₃ (2–4 mm ϕ spheres). The precursors were dried and calcined at 400°C for 4 h in air, followed by impregnation using an aqueous solution of RuCl₃. Next, the precursors were washed and dried, followed by reduction in aq. N₂H₄. **Table 1** shows the Ru and M loadings, the amount of CO adsorption on the catalysts measured employing the pulse method, and the specific surface areas of the catalysts determined employing the BET method using N₂ adsorption.

The catalytic activity was measured in a 17 mm I.D. fixed bed quartz tubular reactor equipped with a 4 mm O.D. protecting tube containing a thermocouple under virtually atmospheric pressure. The catalyst (6 mL) was placed at the center of the reactor. Before measuring the CO methanation activity, the catalyst was reduced at 400°C for 2 h in a flow of N₂ containing 10 vol% H₂ in the fixed bed flow reactor. The test gas, the composition of which was simulated as that of methane steam reforming gas remaining following the CO shift reactor, consisted of 0.47% CO, 18.18% CO₂, 72.25% H₂, and 9.1% H₂O (dry base: 0.52% CO, 20.0% CO₂, and 79.48% H₂). It was fed at a space velocity of 5,000 h^{−1} or 2,500 h^{−1} in dry base. The reaction temperature was measured using a thermocouple located at the center of the catalyst layer. The gas compositions at the inlet and outlet of the reactor at a stationary state were analyzed employing gas chromatography combined with thermal conductivity de-

tector and flame ionization detector. The results for the dry base are shown. For reference, CO concentrations calculated as the equilibrium values of the water–gas shift reaction (WGSR) are shown in bold solid lines in the figures.

CO₂ conversion was determined using the following equation:

$$\text{CO}_2\text{conversion} [\%] = (F_{\text{CO}_2\text{in}} - F_{\text{CO}_2\text{out}}) / F_{\text{CO}_2\text{in}} \times 100$$

Here, $F_{\text{CO}_2\text{in}}$ and $F_{\text{CO}_2\text{out}}$ represent the inlet and outlet flow rates of CO₂ gas, respectively.

2. Results and Discussion

2.1 Effect of K and La addition to Ru/Al₂O₃ on its CO methanation activity

The effect of K and La addition to Ru/Al₂O₃ on CO removal from the simulated reformed gas via methanation was investigated.

Figures 1 and **2** show the catalytic performances of Ru/K/Al₂O₃, Ru/La/Al₂O₃, and Ru/Al₂O₃ for comparison at GHSV = 5,000 h^{−1}. In the case of Ru/Al₂O₃, the CH₄ outlet concentration increased with increasing reaction temperature, and the CO outlet concentration was at a minimum at approximately 240°C, as shown in **Figures 1** and **2**. The CO outlet concentration for Ru/Al₂O₃ was 180 ppm at 238°C. These results are consistent with previously published findings (Echigo and Tabata, 2004). Reportedly, the increase in the CO outlet concentration at higher temperatures is caused by a reverse WGSR (Urasaki *et al.*, 2010; Tada *et al.*, 2014). As shown in **Figure 1**, the activities of Ru/K/Al₂O₃ and Ru/La/Al₂O₃ for CO removal via methanation were slightly lower than that of Ru/Al₂O₃. The CO outlet concentrations for Ru/K/Al₂O₃ and Ru/La/Al₂O₃ were 284 ppm at 237°C and 213 ppm at 238°C, respectively. Thus, the addition of K and La to Ru/Al₂O₃ did not have a positive effect on CO removal via methanation.

Tada *et al.* (2014) reported that CH₄ production followed the order of Ru–K/TiO₂ > Ru–La/TiO₂ > Ru/TiO₂, indicating that La or K addition to Ru/TiO₂ accelerated the CO₂ methanation rate. On the other hand, the CH₄ outlet concentration for Ru/K/Al₂O₃ was comparable to that of Ru/Al₂O₃, while that for Ru/La/Al₂O₃ was slightly lower compared to that of Ru/Al₂O₃ in this test, as shown in **Figure 2**. This can be attributed to the differences in the support, quantity of metal loading, and preparation procedure between the previous report and our study.

Table 1 Characteristics of Ru/M/Al₂O₃ catalysts

Catalyst	Ru loading [wt%]	M loading [wt%]	BET surface area [m ² /g-cat]	CO adsorption [mL/g-cat]
Ru/Al ₂ O ₃	1.3	—	110	0.47
Ru/K/Al ₂ O ₃	1.3	1.4	116	0.46
Ru/V/Al ₂ O ₃	1.2	2.1	108	0.45
Ru/Mo/Al ₂ O ₃	1.4	1.5	131	0.47
Ru/La/Al ₂ O ₃	1.3	2.7	110	0.35

Fig. 1 Comparison of the CO outlet concentrations during methanation on Ru/K/Al₂O₃, Ru/La/Al₂O₃ and Ru/Al₂O₃ at GHSV = 5,000 h⁻¹; (a) logarithmic scale, (b) linear scale

2.2 Effect of V and Mo addition to Ru/Al₂O₃ on its CO methanation activity

The effect of V and Mo addition to Ru/Al₂O₃ on CO removal from simulated reformed gas via methanation was also investigated.

Figures 3 and 4 depict the catalytic performances of Ru/V/Al₂O₃, Ru/Mo/Al₂O₃, and Ru/Al₂O₃ for comparison at GHSV = 5,000 h⁻¹. The CO methanation removal performances of Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ were superior to that of Ru/Al₂O₃, as shown in Figure 3. For example, the CO outlet concentration for Ru/V/Al₂O₃ was 129 ppm at 197°C, and that for Ru/Mo/Al₂O₃ was 55 ppm at 233°C. Thus, the addition of V or Mo to Ru/Al₂O₃ improved the catalytic activity for CO removal via methanation.

As shown in Figure 4, the methanation activities of Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ were higher compared to that of Ru/Al₂O₃. The CH₄ outlet concentrations obtained with Ru/V/Al₂O₃, Ru/Mo/Al₂O₃, and Ru/Al₂O₃ exceeded 0.52% at temperatures above approximately 200, 200, and 220°C, respectively. The reactant gas used in this test contained 0.52% CO in dry base. Therefore, it can be concluded that V or Mo addition to Ru/Al₂O₃ increased the methanation activity in the case of both CO₂ and CO. As shown in Table 1, the BET surface area and the amount of CO adsorbed onto Ru/V/Al₂O₃ were slightly lower than obtained for Ru/Al₂O₃. The amount of adsorbed CO was the same for Ru/Mo/Al₂O₃ and

Fig. 2 Comparison of the CH₄ outlet concentrations during methanation on Ru/K/Al₂O₃, Ru/La/Al₂O₃ and Ru/Al₂O₃ at GHSV = 5,000 h⁻¹; (a) logarithmic scale, (b) linear scale

Ru/Al₂O₃. Although the BET surface area of Ru/Mo/Al₂O₃ was larger than that of Ru/Al₂O₃, the BET surface area of Ru/K/Al₂O₃, the CO methanation activity of which was not higher than that of Ru/Al₂O₃, was also larger than that of Ru/Al₂O₃. Therefore, it is difficult to explain the improvement in the methanation activity based on these characteristics. Considering CO adsorption characteristics, it might be supposed that V and Mo do not directly provide the sites for the active CO adsorption species. As mentioned in the experimental section, the catalysts were prepared via the sequential impregnation method. V and Mo are supported on Al₂O₃ first, followed by Ru. Therefore, there is a possibility that these metal additives may improve the activity of Ru as the underlays. Further analysis is required to clarify the role of V and Mo in improving the methanation activity of Ru/Al₂O₃.

Next, more in-depth evaluation of the effect of V or Mo addition to Ru/Al₂O₃ on its CO removal activity was performed at GHSV = 2,500 h⁻¹. **Figures 5 and 6** show the CO and CH₄ outlet concentrations, respectively. The CO₂ conversion results are provided in **Figure 7**. In this test, the lowest CO content measured on Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ was 13 and 15 ppm at 196°C, respectively. On the other hand, the lowest content on Ru/Al₂O₃ was approximately 100 ppm at ~215°C. Furthermore, in the case of Ru/Al₂O₃, a temperature window within which CO could be removed to below 100 ppm was virtually unattainable, as shown in

Fig. 3 Comparison of outlet CO concentrations during methanation on Ru/V/Al₂O₃, Ru/Mo/Al₂O₃, and Ru/Al₂O₃ at GHSV = 5,000 h⁻¹; (a) logarithmic scale, (b) linear scale

Figure 5. It can be considered that the improvement in the CO hydrogenation activity of Ru/V/Al₂O₃ or Ru/Mo/Al₂O₃ at lower temperatures, where the influence of the reverse WGS appears to be diminished, contributes to achieving such thorough CO removal to below 20 ppm.

As shown in Figure 6, the CH₄ outlet concentrations for Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ were higher than that for Ru/Al₂O₃ at all the reaction temperature ranges in this test. Interestingly, the CH₄ outlet concentration for Ru/V/Al₂O₃ becomes higher than that of Ru/Mo/Al₂O₃ at approximately 175°C. Although the CO removal performance of Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ is superior to that of Ru/Al₂O₃, the addition of V or Mo to Ru/Al₂O₃ enhances the methanation of not only CO but also CO₂, as mentioned above. The CH₄ outlet concentrations for Ru/V/Al₂O₃, Ru/Mo/Al₂O₃, and Ru/Al₂O₃ exceeded 0.52% above ~180, ~180, and ~210°C, respectively. CO₂ conversion on Ru/V/Al₂O₃ or Ru/Mo/Al₂O₃ was higher than that on Ru/Al₂O₃ at temperatures above approximately ~180°C, as shown in Figure 7. Therefore, obtaining a wide reaction temperature window within which the selective methanation of CO vs. CO₂ is achieved proved to be challenging. As shown in Figure 5, CO removal to below 100 ppm using Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ appeared to be feasible in the temperature ranges of ~185–290°C and ~185–270°C, respectively. However, to suppress CO₂ methanation within double of

Fig. 4 Comparison of outlet CH₄ concentrations during methanation on Ru/V/Al₂O₃, Ru/Mo/Al₂O₃, and Ru/Al₂O₃ at GHSV = 5,000 h⁻¹; (a) logarithmic scale, (b) linear scale

CO methanation, we surmised that CO removal should be performed at below ~190°C on Ru/V/Al₂O₃ and below ~195°C on Ru/Mo/Al₂O₃, as shown in Figure 6. Thus, the reaction temperature window within which CO removal to below 100 ppm can be achieved and CO₂ methanation suppressed for Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ was narrow, specifically between ~185 and 190°C, and ~185 and 195°C, respectively. Moreover, although CO removal to below 20 ppm could be achieved at ~196°C, CO₂ methanation was not completely inhibited at this temperature. For practical applications, a wider temperature window of catalyst operation is desired to readily control the reactor. Therefore, for the application of such catalysts to practical CO removal reactors, the system should tolerate CO₂ methanation to some extent. However, there is a risk that CO₂ methanation might continue as a self-catalytic reaction using its own exothermal reaction heat, resulting in an uncontrollable reaction temperature, because the reformed gas after the CO shift reactor typically contains as much as 20 vol% CO₂ (Echigo and Tabata, 2003, 2004). As shown in Eqs. (1) and (2), the exothermal reaction heats of CO and CO₂ methanation are 205.7 kJ/mol and 164.5 kJ/mol, respectively.

Fig. 5 Comparison of outlet CO concentrations during methanation on Ru/V/Al₂O₃, Ru/Mo/Al₂O₃, and Ru/Al₂O₃ at GHSV = 2,500 h⁻¹; (a) logarithmic scale, (b) linear scale

The acceptable range for preventing a thermal runaway depends on design of the CO removal reactor, including its radiation capabilities. For reference, a CO removal reactor using a CO preferential oxidation (PROX) catalyst in a residential PEFC system has been put to practical use (Echigo *et al.*, 2010). It was reported that the designed O₂/CO molar ratio at the CO PROX removal reactor was 1.5 and the designed CO inlet concentration was ca. 0.5 vol% (Echigo *et al.*, 2004). As shown in Eqs. (3) and (4), the exothermal reaction heats of CO oxidation and H₂ oxidation are 283.0 kJ/mol and 241.8 kJ/mol, respectively.

The amount of heat generated from the complete oxidation of a CO-H₂ mixture at a CO:H₂ ratio of 1:2 in the CO PROX removal reactor is equivalent to that from complete methanation of a CO-CO₂ mixture at a CO:CO₂ ratio of 1:3.4. Thus, there is a possibility that the total value of CO and CO₂ methanation of approximately 2.4 vol% (dry base) might be acceptable in terms of the heat value for the conventional CO removal reactor. Although the acceptable range can be widened by utilizing a powerful cooling mechanism, this would significantly increase the cost.

Fig. 6 Comparison of outlet CH₄ concentrations during methanation on Ru/V/Al₂O₃, Ru/Mo/Al₂O₃, and Ru/Al₂O₃ at GHSV = 2,500 h⁻¹; (a) logarithmic scale, (b) linear scale

Fig. 7 Comparison of CO₂ conversion levels via methanation on Ru/V/Al₂O₃, Ru/Mo/Al₂O₃, and Ru/Al₂O₃ at GHSV = 2,500 h⁻¹

2.3 Influence of the Fischer-Tropsch side reaction on CO removal

As shown in Figures 5–7, the decrease in CO cannot be explained by CO methanation and the CO shift (water-gas shift) reaction on Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ at low temperatures of ~170°C. Therefore, the production of C₂ and higher hydrocarbons was investigated.

Figure 8 shows the outlet concentrations of hydrocarbons as products of CO hydrogenation on Ru/V/Al₂O₃, Ru/Mo/Al₂O₃, and Ru/Al₂O₃ at GHSV = 2,500 h⁻¹. Evident-

Fig. 8 Outlet C₂ and higher hydrocarbon concentrations produced from the side reaction of CO methanation removal at GHSV = 2,500 h⁻¹; (a) Ru/V/Al₂O₃, (b) Ru/Mo/Al₂O₃, (c) Ru/Al₂O₃

ly, the order of C₂ and higher hydrocarbon production was Ru/V/Al₂O₃ > Ru/Mo/Al₂O₃ > Ru/Al₂O₃. Thus, the Fischer-Tropsch (FT) activity, as the side reaction of methanation, on Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ also increased compared to that on Ru/Al₂O₃. The outlet concentration of the hydrocarbon products decreased with increasing carbon number in each catalyst. C₅ and higher hydrocarbons were not detected on Ru/Mo/Al₂O₃ and Ru/V/Al₂O₃, while C₄ and higher hydrocarbons were not detected on Ru/Al₂O₃. Panagiotopoulou *et al.* (2009) reported that the main by-products formed below 260°C were C₂H₆, C₂H₄, C₃H₈, and C₃H₆, and the formation of higher hydrocarbons is curtailed above

260°C in the case of selective methanation of CO on 5% Ru/Al₂O₃. In our study, C₂H₄ and C₃H₆ were not detected on either Ru/Al₂O₃, Ru/V/Al₂O₃, or Ru/Mo/Al₂O₃. Moreover, for each catalyst, the outlet concentration of each hydrocarbon increased with increasing reaction temperature until a maximum value and then decreased. As shown in Figure 8(c), the maximum amount of C₂H₆ and C₃H₈ was produced on Ru/Al₂O₃ at ~300°C and ~210°C, respectively. On the other hand, as shown in Figure 8(a) and 8(b), for Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃, the maximum amounts of C₂H₆, C₃H₈, and C₄H₁₀ were produced at ~280–290, ~195, and ~195°C, respectively. Thus, the reaction temperature at which the maximum FT activity occurred on Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ was lower than that on Ru/Al₂O₃. It can be supposed that for Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃, the production of C₂ and higher hydrocarbons contribute to CO removal at low temperatures of approximately 170°C. However, C₂ and higher hydrocarbons were produced in small amounts, and decreased with increasing reaction temperature above the maxima given above. Thus, the influence of the FT synthesis reaction heat on the thermal runaway of the CO removal reactor is likely to be small. On the other hand, it is necessary to investigate the influence of the C₂ and higher hydrocarbons on the anode catalyst of a PEFC if such a catalyst is to be applied for CO removal in a PEFC system.

Conclusion

The performances of Ru/K/Al₂O₃ and Ru/La/Al₂O₃ for CO removal via methanation were slightly inferior to that of Ru/Al₂O₃, while those of Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ were superior. A temperature window wherein CO could be removed to below 100 ppm from simulated reformed gas was virtually non-existent when Ru/Al₂O₃ was used at GHSV = 2,500 h⁻¹. In contrast, CO was removed to below 20 ppm on Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ at GHSV = 2,500 h⁻¹. However, the reaction temperature window within which CO removal can be achieved with high selectivity for the methanation of CO vs. CO₂ was narrow because the addition of V or Mo to Ru/Al₂O₃ increases the methanation of CO₂ as well as CO. In terms of the side reaction occurring during methanation, it was confirmed that the production of C₂ and higher hydrocarbons on Ru/V/Al₂O₃ and Ru/Mo/Al₂O₃ occurred to a higher extent than that on Ru/Al₂O₃.

Literature Cited

- Echigo, M. and T. Tabata; "A Study of CO Removal on an Activated Ru Catalyst for Polymer Electrolyte Fuel Cell Applications," *Appl. Catal. A Gen.*, **251**, 157–166 (2003)
- Echigo, M. and T. Tabata; "CO Removal from Reformed Gas by Catalytic Methanation for Polymer Electrolyte Fuel Cell Applications," *J. Chem. Eng. Japan*, **37**, 75–81 (2004)
- Echigo, M., N. Shinke, S. Takami and T. Tabata; "Performance of a Natural Gas Fuel Processor for Residential PEFC System Using a Novel CO Preferential Oxidation Catalyst," *J. Power Sources*, **132**, 29–35 (2004)

- Echigo, M., N. Shinke, Y. Yasuda, S. Takami and T. Tabata; "Development of a Fuel Reforming Catalysis System for Residential Fuel Cells (in Japanese)," *Shokubai*, **52**, 375–376 (2010)
- Kawatsu, S.; "Advanced PEFC Development for Fuel Cell Powered Vehicles," *J. Power Sources*, **71**, 150–155 (1998)
- Kimura, M., T. Miyao, S. Komori, A. Chen, K. Higashiyama, H. Yamashita and M. Watanabe; "Selective Methanation of CO in Hydrogen-Rich Gases Involving Large Amounts of CO₂ over Ru-modified Ni–Al Mixed Oxide Catalysts," *Appl. Catal. A*, **379**, 182–187 (2010)
- Lemons, L. A.; "Fuel Cells for Transportation," *J. Power Sources*, **29**, 251–264 (1990)
- Masuda, M., O. Okada, S. Takami, S. Nagase, N. Iwasa, T. Ohhama and H. Yamamoto; "Development of an Advanced Steam Reforming System for Phosphoric Acid Fuel Cells," Abstracts of 1994 Fuel Cell Seminar, pp. 380–383, San Diego, U.S.A. (1994)
- Okada, O. and K. Yokoyama; "Development of Polymer Electrolyte Fuel Cell Cogeneration Systems for Residential Applications," *Fuel Cells (Weinh.)*, **1**, 72–77 (2001)
- Panagiotopoulou, P., D. I. Kondarides and X. E. Verykios; "Selective Methanation of CO over Supported Ru Catalysts," *Appl. Catal. B*, **88**, 470–478 (2009)
- Tada, S., R. Kikuchi, A. Takagi, T. Sugawara, S. T. Oyama and S. Satokawa; "Effect of Metal Addition to Ru/TiO₂ Catalyst on Selective CO Methanation," *Catal. Today*, **232**, 16–21 (2014)
- Takenaka, S., T. Shimizu and K. Otsuka; "Complete Removal of Carbon Monoxide in Hydrogen-Rich Gas Stream through Methanation over Supported Metal Catalysts," *Int. J. Hydrogen Energy*, **29**, 1065–1073 (2004)
- Urasaki, K., Y. Tampo, T. Takahiro, J. Christopher, R. Kikuchi, T. Kojima and S. Satokawa; "Selective Methanation of CO in Reformate Gas over Ni/TiO₂ Catalyst," *Chem. Lett.*, **39**, 972–973 (2010)