

Lowest O₂/CO mole ratio for preferential oxidation of CO in hydrogen-rich stream over Pt/Al₂O₃ catalysts

Cheng-Chun Chen^{*a,b}, Chih-Hsing Leu^b, Yu-Li Lin^b, Shun-Chih King^b, and Shu-Yii Wu^a

^aDepartment of Chemical Engineering, Feng Chia University

^bGreen Energy and Environment Research Laboratories, Industrial Technology Research Institute

*Email: charliechen@itri.org.tw

Abstract

The preferential oxidation of carbon monoxide in a hydrogen-rich stream is an important reaction in fuel cell technology. The CO concentration of hydrogen-rich stream must be controlled below 10 ppm for proton exchange membrane fuel cells (PEMFCs). In this paper the design and experimental work concerning a small reformer for the preferential oxidation of carbon monoxide in hydrogen-rich stream. The activity of Pt/Al₂O₃-based catalyst during preferential CO oxidation in hydrogen-rich stream was studied in a small methanol processor. The lowest O₂/CO ratio is expected for CO oxidation under hydrogen-rich stream. The operating conditions that can reduce CO concentration to 10 ppm while minimizing parasitic loss of H₂ in the hydrogen-rich stream. This study prepared the highest activity of Pt/Al₂O₃ catalysts that can work at room temperature and reduce 1 % CO to below 10 ppm under the hydrogen-rich stream condition. The preferential oxidation unit can reduce the CO from up to 1% to less than 10 ppm and is suitable for a PEM fuel cell.

Keywords: proton exchange membrane fuel cell (PEMFC), preferential CO oxidation (PROX), hydrogen rich stream, CO/O₂ ratio.

BOE Project No. : BOE 101-D0211

1 Introduction

Fuel cells are becoming increasingly attractive for the environmentally compatible supply of electric energy. Recently, the research and development of the proton exchange membrane fuel cells (PEMFCs) has been increasing for transportation, portable and stationary applications. Reforming of hydrocarbons and

methanol has been studied for on-board production of H₂ for the PEMFCs [1,2]. However, the reformed gases from a fuel reformer typically contains 40-75 vol% H₂, 20-25 vol% CO₂, 0.5-2 vol% CO, 10-20 vol% H₂O and N₂ [3]. Carbon monoxide is an undesirable product of methanol steam reforming because it poisons the Pt catalyst in PEMFCs. Typical PEMFCs can only tolerate 10 ppm CO [4]. Therefore, the fuel processor must be equipped with a CO removal system.

There are four typical methods of CO removal: pressure swing adsorption (PSA), methanation, Pd/Pd-alloy membranes separation and preferential oxidation (PROX) reactions, also known as selective CO oxidation reactions [1]. The CO removal of PSA requires expensive compressors. Methanation includes CO hydrogenation that consumes three moles of hydrogen for every mole of CO. The membranes separation of palladium and its alloy can effectively remove CO from the reforming stream, which is the output of fuel reformers operating at large pressure drops and high temperatures, but this reduces the system efficiency. The CO removal of the PROX reaction takes place at low temperatures and atmospheric pressure and is relatively inexpensive and easy to apply in small-scale systems.

The possible reactions in a PROX reactor are as follows [5]:

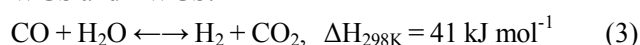
CO oxidation:



H₂ oxidation:



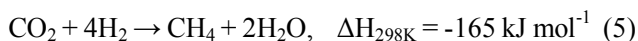
WGS and RWGS:



CO methanation:



CO₂ methanation:



The main reactions to be considered are the PROX of CO (Eq. (1)), which is the desired reaction and several side reaction (Eqs. (2)-(5)). During the PROX reaction, the undesired reactions such as Eq. (2) and Eq. (5) should be minimized. While the WGS reaction (Eq. (3)) is beneficial in its forward direct, methanation reactions are always detrimental and should be avoided. The selectivity is crucial considering the competing H₂ oxidation that may lead to a decrease in the overall PEMFC efficiency. Generally, a PROX reaction using Pt-based catalysts has been used for the CO removal process because of its high activity.

However, these are less selective catalysts for the oxidation of CO and require more than 2% O₂ addition to oxidize 1% CO in hydrogen-rich stream, although it should take only 0.5% O₂ to oxidize 1% CO stoichiometrically. The remainder of O₂ added causes H₂ combustion leading to the energy loss [6]. They has been reported that additive O₂ corresponding to [O₂]/[CO] > 3 was need to remove CO completely on the conventional Pt/Al₂O₃ catalyst [6]. The excess O₂ consumes H₂ in the hydrogen-rich stream by combustion, which causes a decrease in the power generation efficiency of the PEMFC. Since power generation efficiency is the most important requirement for the PEMFC, a low [O₂]/[CO] operation is necessary for the PROX system [7]. There were several reports that Ru/Al₂O₃ catalysts showed higher CO removal performance than Pt/Al₂O₃ catalysts [6, 7]. Generally, a Ru/Al₂O₃ catalyst also possesses considerable methanation activity. Pt is known to be a poor catalyst for methanation reactions if compared to Ru or Ni.

This study prepared the highest activity of Pt/Al₂O₃ catalysts that can work at room temperature and reduce 1 % CO to below 10 ppm under the hydrogen-rich stream condition by two stages of catalyst beds. The PROX unit can reduce the CO from up to 1% to less than 10 ppm and is suitable for a PEM fuel cell.

2 Experiments

2.1 Catalyst preparation

For the experiments in this study, a commercial catalyst and several in house prepared catalysts have been test. A Pt(NH₃)₂(NO₃)₂ solution was impregnated into alumina pellets (207 m² g⁻¹, 2 mm diameter), and then the impregnated balls were dried at 100 °C and calcined for one hour at 400 °C [2]. The 3 wt. % Pt/Al₂O₃ catalysts were prepared for PROX catalysts (C18, C25 and C41) [1]. The commercial catalyst used the PROX catalyst manufactured by TANAKA (Ru/Al₂O₃, TSSA-5). The PROX catalyst is a 1-3 mm sized pellet catalyst composed of 0.4 wt.% Ru on a γ-alumina support.

2.2 Catalytic activity

PROX reaction was initially investigated using a fixed-bed reactor system under atmospheric pressure. The PROX reactor was made with 316 stainless steel wit 16 mm i.d. and 100 mm long. Reaction temperature was controlled using a thermocouple inserted into the center of the catalyst bed. The reaction temperature was measured in the reactor with three thermocouples, which were located on 2.5 cm, 5.0 cm, 7.5 cm, respectively [1]. The composition of the simulated reformat was 1 vol.% CO, 24 vol.% CO₂ and 75% H₂, and air added additionally as the oxidant. The test was performed over the temperature range 25-130°C at various flow rates of inlet air. Gas hourly space velocity (GHSV) is defined as the ratio of the volumetric flow rate of the feed steam at standard temperature and pressure (STP) to the volume of the catalyst bed. Calculation of the CO conversion was based on the formation of CO. The CO selectivity was defined as the ratio of O₂ consumption for the CO oxidation over the total O₂ consumption. Selectivity is defined as the ratio between the O₂ involved in the CO oxidation and the total amount of reacted O₂ (for oxidising CO and H₂).

2.3 Produced gas analysis

The total flow rate of product gas was measured by a flow meter and the produced gases were analyzed using a gas chromatograph (GC) (Agilent 6890N) with a

thermal conductivity detector (TCD) and a flame ionization detector (FID). Helium was used as a carrier gas and the GC was equipped with a Carboxen 1000 column (60/80 mesh, 1/8 in SS \times 3.5 ft length) that could separate H₂, CO, CH₄, CO₂. For the purpose of accurate determination of CO at the ppm level, the effluent of the Agilent 6890N was passed through a methanizer and the GC was equipped with a flame ionization detector (FID). The CO detection limit of the methanizer and GC-FID assembly was well below 1 ppm. A non-dispersive infrared (NDIR) NGA-2000 (Rosemount) analyzer connected to a personal computer was used to analyze the CO, H₂, CH₄ and CO₂ outlet concentrations continuously [1,2]. The lowest detection limit of CO was 0.1 ppm. The computerized data acquisition system consisted of two SISC (Scientific Information Service Corporation, Taiwan) data acquisition cards and a data acquisition program.

3 Results and discussions

3.1 CO oxidation activity of catalyst

The comparison of catalyst activities for CO preferential oxidation is shown in Fig. 1. Fig. 1 shows the amount of O₂ required to oxidize 1% CO completely on various catalysts in the hydrogen-rich stream. Pt/Al₂O₃ catalysts (C18, C25 and C41) needed more than 0.75% O₂ to remove CO and Ru/Al₂O₃ catalyst needed more than 1% O₂. The overall activity of CO oxidation decreases in the order of C41 > C25 > C18 > Ru. Pt/Al₂O₃ catalysts exhibits higher activity of CO removal than Ru/Al₂O₃ in the temperature range 25-130°C.

A feasible PROX catalyst for low temperature CO oxidation in hydrogen-rich streams means the catalyst has both high activity and high selectivity to CO₂ production; the H₂ oxidation must be minimized, as well as, methanation and RWGS reactions. Selectivity is a critical parameter since O₂ is in excess (O₂/CO = 1) in relation to stoichiometry of CO oxidation (O₂/CO = 0.5).

The final CO cleanup was accomplished in the PROX systems, to which the hydrogen-rich stream and a small flow of air (oxygen) were fed, with the target of reducing CO concentration to less than 10 ppm. The

critical issue in the design of the PROX system is to achieve a high level of CO conversion while minimizing H₂ loss. These results are in agreement with literature data, reporting CH₄ formation on Ru-based catalysts above 150°C.

3.2 Effect of mole ratio of O₂ to CO

When we evaluate PROX activity of catalysts, the O₂/CO molar ratio is one of the most important factors, because excess O₂ causes undesired H₂ consumption by the oxidation. The effect of O₂/CO mole ratio on the preferential CO oxidation over the Pt/Al₂O₃ catalyst (C18, C25 and C41) is shown in Fig. 1. Fig. 1 is given simply to illustrate that with increasing O₂ amount the residual concentration of CO decreased for all catalysts. Thus, with all catalysts minimum CO elimination from the simulated reformed gas was achieved with an O/CO ratio of 1. Raising the amount of O₂ inevitably led to an increase in H₂ loss.

It is known that H₂ oxidation is strongly inhibited by the presence of CO due to the stronger CO chemisorption on the Pt surfaces as compared to the H₂ and O₂ chemisorption. Further raising the amount of O₂ inevitably led to a H₂ loss since the PROX reaction selective toward H₂ combustion. Igarashi et al. has been reported that 0.5% O₂ is necessary for stoichiometric oxidation of 1% CO, but CO still remained in the outlet gas the 3% O₂ addition on conventional Pt/Al₂O₃ catalyst [6]. Due to injected air dilution, the volumetric concentration of H₂ decreases as the O₂/CO molar ratio increases and thus both H₂O and N₂ concentration in the reactor outlet gas increase. Generally, the catalytic activity for CO conversion increases with the O₂/CO molar ratio. It is very important, however, to keep the O₂/CO molar ratio as low as possible to improve the processor efficiency.

3.3 Effect of reaction temperature

The effect of temperature on the PROX reaction in the reactor is shown in Fig. 2 and Fig. 3. Fig. 2 shows the CO PROX activities of Pt/Al₂O₃ (C41) catalyst at [O₂]/[CO] = 1 (1%CO, 1% O₂, (λ = 2.0)). The Pt/Al₂O₃ catalyst space velocity (GHSV) is 3,150 h⁻¹ and O₂/CO = 1.0. Increasing the temperature from 68 to 125 °C, the

outlet concentration of CO increases and it remains below 10 ppm in the temperature below 80 °C.

Thus, it is desirable to carry out the PROX reaction in the 100-110 °C range, in which the outlet CO concentration can be reduced to less than 80 ppm, particularly in the 65-85 °C range, since it decreases to values than 10 ppm target. Lowering of the CO conversion at temperatures above 95°C is ascribed to higher consumption of O₂ for H₂ oxidation. This may arise from the lowered CO coverage on Pt sites at higher temperatures and a preferential H₂ oxidation at bare Pt surface site thus generated.

The PROX reaction chemistry is complicated, involving not only catalytic oxidation of both CO and H₂ but also methanation and WGS reaction. It is known that CO is generated by the RWGS, as expressed in Eq. (3), which occurs in the CO PROX. The WGS reaction is favored by the high O₂/CO molar ratio. The effect can be simply explained by the fact that the higher the O₂ concentration, the faster the H₂ oxidation. As a result, more water is formed and RWGS is strongly favored. Therefore, the PROX catalysts operating at low temperatures are quite desirable. Our results are consistent with those reported [9, 10]. Traces of CH₄ produced above 150°C do not affect the outlet concentration of CO significantly. Therefore, it is practically impossible to achieve both low H₂ consumption and high CO conversion without using a multi-staged reactor system.

Fig. 3 shows a plot of CO concentration at various O₂/O ratios as a function of reaction temperature for the PROX catalyst. As the O₂/CO molar ratio was increased, the outlet CO concentration was decreased. However, CO cannot be removed less than 4000 ppm even at O₂/CO molar ratio 0.5. Moreover, the outlet CO concentration was less than 10 ppm at O₂/CO ≥ 1.0. The additive O₂ was completely consumed at all the O₂/CO molar ratios.

4 Conclusions

The amount of O₂ required to oxidize 1% CO completely on various catalysts in the hydrogen-rich stream. Pt/Al₂O₃ catalysts (C18, C25 and C41) needed

more than 0.75% O₂ to remove CO and Ru/Al₂O₃ catalyst needed more than 1% O₂. It could minimize the O₂ addition to oxidize CO completely in large excess of H₂ by using the PROX reactor. The overall activity of CO oxidation decreases in the order of C41 > C25 > C18 > Ru. Pt/Al₂O₃ catalysts exhibits higher activity of CO removal than Ru/Al₂O₃ in the temperature range 25-130°C. The Pt/Al₂O₃ catalyst was able to meet the 10 ppm target of CO concentration, even at low O₂/CO ratios and high space velocities.

Acknowledgments

The authors gratefully acknowledge funding from the Bureau of Energy, Ministry of Economic Affairs, Taiwan, Republic of China, and thanks Feng Chia University for supporting this work.

References

- [1] C.C. Chen, M.S. Jeng, C.H. Leu, C.C. Yang, Y.L. Lin, S.C. King, S.Y. Wu, "Low-level CO in hydrogen-rich gas supplied by a methanol processor for PEMFCs", *Chemical Engineering Science* 66, 5095-5106, 2011.
- [2] C.H. Leu, C.C. Chen, S.C. King, J.M. Huang, S.S. Tzeng, W.C. Chang, "Influence of CuO/ZnO/Al₂O₃ wash-coating slurries on the steam reforming reaction of methanol", *International Journal of Hydrogen Energy* 36, 12231-12237, 2011.
- [3] S.Y. Chin, O.S. Alexeev, M.D. Amiridis, "Preferential oxidation of CO under excess H₂ conditions over Ru catalysts", *Applied Catalysis A: General* 286, 157-166, 2005.
- [4] R.A. Lemons, "Fuel cell for transportation", *Journal of Power Sources* 29, 251-264, 1990.
- [5] Y.H. Kim, E.D. Park, H.C. Lee, D. Lee, K.H. Lee, "Preferential CO oxidation over supported noble metal catalysts", *Catalysis Today* 146, 253-259, 2009.
- [6] H. Igarashi, H. Uchida, M. Suzuki, Y. Sasaki, M. Watanabe, "Removal of carbon monoxide from hydrogen-rich fuels by selective oxidation over platinum catalyst supported on zeolite", *Applied Catalysis A: General* 159, 159-169, 1997.

- [7] M. Echigo, N. Shinke, S. Takami, T. Tabata, "Performance of a natural gas fuel processor for residential PEFC system using a novel CO preferential oxidation catalyst", *Journal of Power Sources* 132, 29-35, 2004.
- [8] J.L. Ayastuy, M.P. Gonzalez-Marcos, J.R. Gonzalez-Velasco, M.A. Gutierrez-Ortiz, MnOx/Pt/Al₂O₃ catalysts for CO oxidation in H₂-rich streams. *Applied Catalysis B: Environmental* 70, 532-541, 2007.
- [9] S.H. Lee, J. Han, K.Y. Lee, "Development of 10-kWe preferential oxidation system for fuel cell vehicles", *Journal of Power Sources* 109, 394-402, 2002.
- [10] S. Kawatsu, "Advanced PEFC development for fuel cell powered vehicles", *Journal of Power Sources* 71, 150-155, 1998.

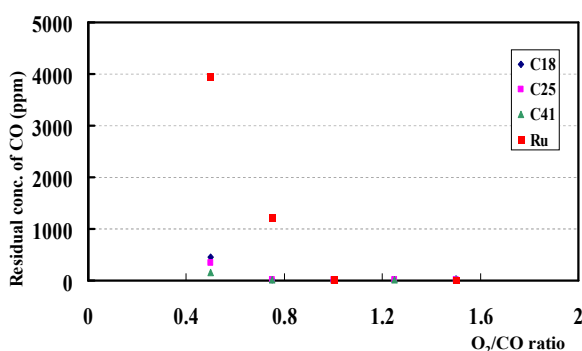


Fig. 1 Comparison of CO PROX activities on Pt and Ru catalysts with varying O₂/CO ratio. Reaction conditions: Pt/Al₂O₃ catalysts (C18, C25 and C41), Ru/Al₂O₃ catalyst, 1% CO, 24% CO₂, 75% H₂.

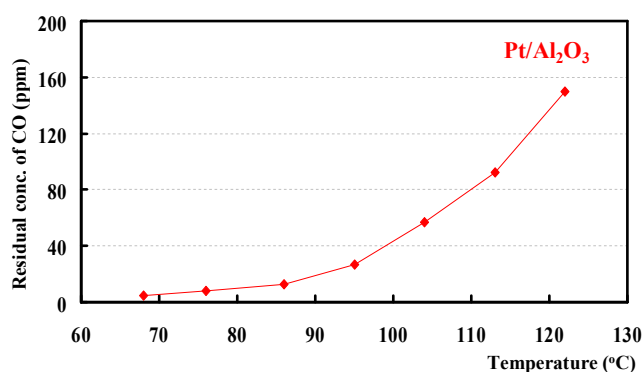


Fig. 2 The CO outlet concentration in the preferential CO oxidation as a function of temperature. Reaction conditions: Pt/Al₂O₃ catalyst (C41) 1% CO, 24% CO₂, 75% H₂.

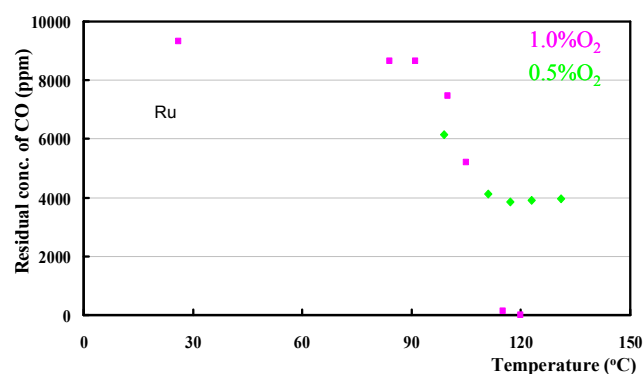


Fig. 3 The CO outlet concentration in the preferential CO oxidation as a function of temperature. Gas composition: Ru/Al₂O₃ catalyst, 1% CO, 24% CO₂, 75% H₂, with a space velocity of 3150 h⁻¹.