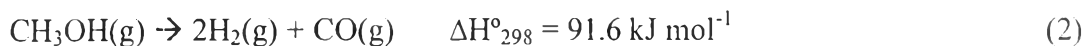# CHAPTER I

INTRODUCTION

As the rapid increases of petroleum fuel consumption and environmental impact, the use of the green technology is of much interest in worldwide to compensate the petroleum fuel with renewable energy. Among the green technologies, proton exchange membrane fuel cell (PEMFC) has recently received much attention on its ability to generate an electrical power for many automobile engines. In addition, PEMFC operates under the low-temperature range of 60–120 °C which is good for cost-saving (Shekhawat *et al.*, 2011); however, the limitation of this fuel cell type is about the high purity requirement of hydrogen (H_2) fuel. The contamination of carbon monoxide (CO) gas in the H_2-rich stream is the major concern because a small amount of CO (10 ppm) can deteriorate the Pt electrode inside the fuel cell and lower its performance (Breen *et al.*, 1999). The high purity H_2 production from renewable sources is the main goal of this work in order to satisfy such requirement of PEMFC.

Among fuels studied, alcohols are more preferable than hydrocarbons because of the low operating temperatures (200–400 °C), especially for methanol (CH_3OH), which is outstandingly attractive to many research groups (Pinzari *et al.*, 2006; Houteit *et al.*, 2006; Amphlett *et al.*, 1994; Alejo *et al.*, 1997) when compared with other oxygenates due to its advantages, such as self handling, easy storing, low cost, and ease of synthesis from a variety of feedstocks (biomass, coal, and natural gas). It contains a relatively high H/C ratio possessing less soot formation, low boiling point, less coke formation, and the absence of C–C bond which is easily broken by using less energy and/or lower reaction temperature. Steam reforming of methanol (SRM) is a conventional process to achieve the high H_2 purity three moles per mole of CH_3OH. Its characteristic is also an endothermic reaction which is more favorable at high temperatures or requires the heat input, as shown in Eq (1),

$$CH_3OH(g) + H_2O(g) \rightarrow CO_2(g) + 3H_2(g) \qquad \Delta H^\circ_{298} = 50 \text{ kJ mol}^{-1} \qquad (1)$$

In fact, the SRM is the combination of methanol decomposition (DM, Eq (2)) and water-gas shift (WGS, Eq (3)) reactions, so the CO formation is possible during the course of reaction (Pinzari *et al.*, 2006).

$$CH_3OH(g) \rightarrow 2H_2(g) + CO(g) \qquad \Delta H^\circ_{298} = 91.6 \text{ kJ mol}^{-1} \qquad (2)$$

$$CO_2(g) + H_2(g) \rightarrow CO(g) + H_2O(g) \qquad \Delta H^\circ_{298} = 41.1 \text{ kJ mol}^{-1} \qquad (3)$$

A methanol fuel processor is a complex device which converts methanol into hydrogen with consecutive CO clean-up by preferential oxidation of CO (PROX). For the catalyst selection, gold (Au) has been an attractive noble metal of being a potential catalyst due to its high catalytic activity in low-temperature CO reduction and H_2 production. Moreover, the Au activity strongly depends on a number of factors such as the preparation technique, the support selection, calcination temperature, gas pretreatment, particle size, and dispersion. Among these factors, the support selection is considered as the first priority for coupling with the gold metal to yield as a whole active catalyst. Among the metal oxide supports, ceria or cerium oxide (CeO_2) has an interesting characteristic with high oxygen vacancies and oxygen storage capacity that can adsorb the oxygen atoms from the feeding reactants, and then release them as the active species to activate the reaction. According to its properties, it would be beneficial to match with the feed in the SRM reaction. Thus, the use of the Au supported over CeO_2 based catalyst shall be the point to begin with. Many catalyst characterizations were made to describe how the catalytic system can change the properties and performance of studied catalysts.

Chapter 3 provides the overview of the catalyst preparations and the experimental testing of methanol fuel processor (MFP). A direction of this development started with the optimization of the SRM unit at the first step, and then the suitable reformate stream was sent to the PROX unit for mainly reducing CO concentration in the last step. In Chapters 4 and 5, the SRM activity was initially tested in the window temperature of 200–400 °C using the Au supported over CeO_2 and CeO_2–Fe_2O_3 catalysts, prepared by the deposition-precipitation method. With aiming to improve the properties of ceria support, the incorporation of Fe^{3+} cationic species into the Ce^{4+} lattice was studied in order to form mixed oxide solid solution support. Many effective parameters were investigated, including catalyst composition, catalyst pretreatment, and feed composition. The results attained in

Chapters 4 and 5 led to the proposal of new metal substitutional to Fe for improving the thermal stability of CeO_2–based mixed oxides.

In Chapter 6, the stability improvement of CeO_2–based mixed oxides was studied by the incorporation of Zr^{4+} cationic species into the Ce^{4+} lattice. The catalytic activity of the Au/CeO_2–ZrO_2 catalysts was tested in the SRM reaction under the temperature range of 200–500 °C. The effective parameters were investigated on the support preparation techniques (co-precipitation (CP) and sol-gel (SG)) and the support composition. The results attained in this chapter led to the proposal of co-depositing gold with another precious metal to become a bimetallic catalyst for enhancing the catalytic activity and stability in the SRM at low temperature.

Being continued from Chapter 6, Chapter 7 aims to improve the catalytic performance of the bimetallic catalyst over the CeO_2–ZrO_2 (CP) support, prepared by deposition-precipitation method. The co-deposition of Cu and Au metals was studied in order to form an active Au–Cu alloy supported over the CeO_2–ZrO_2 solid solution support. Many effective parameters were investigated i.e., pH of deposition, Au/Cu atomic ratio, gas pretreatment, total metal loading, and calcination temperature. The results attained led to the proposal of H_2 purification in the reformate stream by sending it to the PROX unit for reducing CO concentration.

Chapter 8 aims to develop the PROX unit for cleaning up CO gas in the reformate stream, which was exited from the SRM unit. The PROX performance was tested in the temperature range of 90–150 °C using Au/CeO_2 catalyst, prepared by the deposition-precipitation method. The comparison between single-stage and double-stage PROX reactors was conducted on many effective parameters, such as calcination temperature, O_2/CO feed molar ratio, an amount of catalyst, O_2 split ratio, weight split ratio, and reaction temperature. The development of an efficient MFP was described in order for achieving the ultimate goal of rich H_2 and lean CO concentrations in the final product streams.

Although the output CO concentration of the MFP system investigated could not be reduced for use in PEMFC, the main efforts have been emphasized on the hydrogen-rich gas production from methanol via steam reforming of methanol,

which provides the highest hydrogen and the lowest CO concentration. An overview of a fuel processor integrated with a steam reformer and a PROX reactor demonstrated that it is possible to obtain acceptable hydrogen concentration for supplying the system with smooth operation. Lastly, the author would like to share an insight harvested from his investigation to the readers who are interested in the related field as provided in conclusions and recommendations.