Chapter 1

Introduction

The growing world population has had a large effect on the demand for energy. To date, fossil fuels have been used as the main energy sources to support such demand. Unfortunately, fossil fuel reserves are expected to last no longer than 50-100 years. The shortage of energy is thus becoming an important problem for mankind, prompting worldwide searches for alternative energy [1].

One of the interesting alternative energy is energy from hydrogen feeding to a fuel cell creating electricity. A fuel cell unit generates electrical energy from an electrochemical reaction of hydrogen with oxygen, yielding an environmentally benign by product, water [2-4].

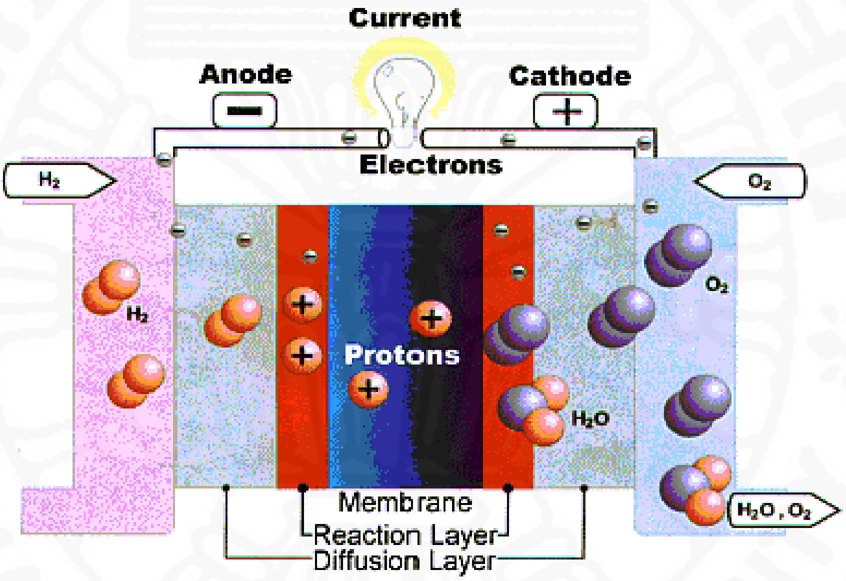

Figure 1 Schematic of hydrogen fuel cell

At the anode side, hydrogen is dissociated to be protons and electrons. The protons are conducted through the membrane to the cathode side, while the electrons are forced to travel through an external circuit to the cathode side and generating electricity. At the cathode side, oxygen reacts with the electrons and protons to form water. The reactions are shown as follows.

Anode: $2H_2 \rightarrow 4H^+ + 4e^-$

Cathode: $O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$

Overall: $2H_2 + O_2 \rightarrow 2H_2O$

Hydrogen fuel cell is considered as one of the promising energy resources in a replacement of fossil fuels. Unfortunately, gathering hydrogen resources is a major obstacle within the production of hydrogen fuel cells. Unlike oxygen which is abundant within the atmosphere, hydrogen could not be easily obtained from any resources without production processes.

Hydrogen can be produced from the reforming reaction of hydrocarbons such as dimethyl ether, ethylene glycol, glycerol, methane, ethanol, methanol, etc [5-9, 46]. Unfortunately, these hydrogen production processes require a high cost of energy expenditure in order to obtain effective hydrogen yields. The dimethyl ether reforming requires the reaction temperature of 573-723 K while the reforming temperature of ethylene glycol is 873-1123 K. The glycerol reforming requires the reaction temperature of 973-1073 K while the reforming temperature of methane is 973-1273 K [10-11]. Even though, the reforming of ethanol requires the low reaction temperature of 473-623 K but the ethanol has been used in various applications such as gasohol and food production. At this stage, methane and ethanol have been widely used as energy resources, so there is no need to spend significant amount of energy to convert methane and ethanol to be hydrogen. One of the attractive hydrocarbons for the hydrogen production from the reforming reaction is methanol. Methanol has a low boiling point and reforming temperature, a high energy density and H/C ratio, can be easily stored and a low cost. There are several reactions for hydrogen production from methanol such as steam reforming, partial oxidation, thermal decomposition and oxidative steam reforming. The reactions are shown as follows.

Steam reforming:

$$CH_3OH + H_2O \longleftrightarrow 3H_2 + CO_2 \qquad \Delta H^0 = 49.5 \text{ kJ/mol}$$

- Hydrogen could be obtained from the reaction of methanol and water. This reaction provided the highest hydrogen among various reactions but it is endothermic reaction, which requires an amount of heat for the reaction.

Partial oxidation:

$$CH_3OH + \tfrac{1}{2}O_2 \longleftrightarrow 2H_2 + CO_2 \qquad \Delta H^0 = -192 \text{ kJ/mol}$$

- Hydrogen could be obtained from the reaction of methanol and oxygen. The reaction provides hydrogen and heat out for the system because this is exothermic reaction. The heat out for system could be accumulated on catalysts which can cause the deactivation of catalyst through the sintering of metal particles. The accumulation of heat, called hot zone, is the major drawback of this reaction.

Thermal decomposition:

$$CH_3OH \longleftrightarrow 2H_2 + CO \qquad \Delta H^0 = 90.6 \text{ kJ/mol}$$

- Hydrogen could be obtained from the decomposition of methanol. This reaction is highly endothermic reaction. So, the major drawback of this reaction is a huge amount of heat required for the reaction and emit amount of CO.

Oxidative steam reforming:

$$5CH_3OH + 4H_2O + \tfrac{1}{2}O_2 \longleftrightarrow 14H_2 + 5CO_2 \qquad \Delta H^0 \approx 0 \text{ kJ/mol}$$

- Hydrogen could be obtained from the combination of steam reforming and partial oxidation reaction by the simultaneous co-feeding of oxygen, steam and methanol through the reactor. By tuning the reactants, the required heat in steam reforming reaction could be supplied by the heat of partial oxidation reaction. However, the hydrogen yield from this reaction is lower than that in steam reforming reaction. In the reaction, besides steam reforming and partial oxidation reaction, other reactions, such as combustion and thermal decomposition, might also occur. So, the oxidative steam reforming is very complex and not yet defined.

This study focuses on methanol steam reforming reaction to produce hydrogen for a fuel cell because this reaction provides the highest hydrogen yield with a moderate consumption of energy. Unfortunately, the process still requires a huge amount of energy in order to produce a high yield of hydrogen. This is a major drawback of hydrogen production from the reforming reaction. Ironically, in order to operate a hydrogen fuel cell, the hydrogen could be obtained from the process with a high cost of energy expenditure. The catalysts have been widely used in order to reduce the energy involved in the reforming reactions. Therefore, the development of catalysts is one of the important parts in the methanol reforming reactions.

The conventional catalysts for this reaction are Cu-Zn based catalysts, which are prepared by precipitation methods. Most Cu-Zn based catalysts and commercial catalysts were prepared by using Cu and Zn contents as high as 60-90 weight percent by the co-precipitation method to produce a high yield of hydrogen [17, 22]. The incipient wetness impregnation over high surface area porous materials has been widely used for many catalyst preparations in order to increase the number of active sites and surface area. Preparation provides an easy method and the use of a small amount of active metal relative to other catalyst preparation methods, which can lower the cost of catalyst production [32]. The literature reports on the use of urea in precipitation of Cu-Zn based catalysts which can improve the activity of the catalysts for hydrogen production. The addition of urea allows the formation of precipitates to have better homogeneity of metal cation distribution in the solution and could yield high surface area precipitates which composed by small pieces of metals stick together in spherical shape [2-5, 17, 41]. Unfortunately, the role of urea in precipitation of Cu-Zn catalyst remains unclear. Impregnation of Cu and Zn on a support of alumina, integrated with the use of urea, might lead to the development of a novel catalyst preparation method for the methanol-steam reforming reaction. The catalyst can exhibit a high activity of hydrogen production without using a high metal loading on the catalyst.

Objective of study

The objective of this work is to study the performance of various Cu-Zn contents impregnated over Al_2O_3 for the methanol reforming reaction. This work also studies the activities of the impregnated Cu-Zn based catalyst over Al_2O_3 with and without the use of urea for hydrogen production from methanol-steam reforming. The performances of the catalysts are also compared with the performance of a commercial one, which is made from a precipitation method. The role of urea in catalyst preparation by impregnation is also investigated. The results of this study can lead to a better understanding of the role of urea in catalyst preparation in order to develop novel catalysts for hydrogen production from the methanol reforming process. The results of this study could lead to a better understanding of the role of catalyst preparation in order to develop novel catalysts for hydrogen production from the methanol reforming process.