Effect of Gold Loading on CeO$_2$–Fe$_2$O$_3$ for Oxidative Steam Reforming of Methanol

Umpawan Satithai, Apanee Luengnaruemitchai, and Erdogan Gulari

Abstract—In this study, oxidative steam reforming of methanol (OSRM) over a Au/CeO$_2$–Fe$_2$O$_3$ catalyst prepared by a deposition–precipitation (DP) method was studied to produce hydrogen in order to feed a Proton Exchange Membrane Fuel Cell (PEMFC). The support (CeO$_2$, Fe$_2$O$_3$, and CeO$_2$–Fe$_2$O$_3$) were prepared by precipitation and co-precipitation methods. The impact of the support composition on the catalytic performance was studied by varying the Ce/(Ce+Fe) atomic ratio, it was found that the 1%Au/CeO$_2$ calcined at 300 °C exhibited the highest catalytic activity in the whole temperature studied. In addition, the effect of Au content was investigated and 3%Au/CeO$_2$ exhibited the highest activity under the optimum condition in the temperature range of 200 °C to 400 °C. The catalysts were characterized by various techniques: XRD, TPR, XRF, and UV-vis.

Keywords—CeO$_2$, Fe$_2$O$_3$, Gold catalyst, Hydrogen production, Methanol, Oxidative steam reforming.

I. INTRODUCTION

NOWADAYS, hydrogen is considered to be one of the most alternative energy due to it is a renewable energy, clean fuel, non-polluting (no green house gas effect), less fossil fuel consumption, and variety production sources such as splitting water, biomass, solar energy, and so on [1]. Moreover, hydrogen has the potential to run a fuel-cell engine with greater efficiency over an internal combustion engine that can be stored as a liquid state or gas state, which is distributed via pipelines, and has been described as a long term replacement for crude oil and natural gas [2].

In the on-board storage of hydrogen for fuel-cell engines in transportation applications, PEM fuel cell can be used for vehicles. However, the storage has some problems associated with safety, and handling of hydrogen. Methanol has been identified as a highly suitable liquid fuel due to its self handling, low cost, high energy density liquid fuels, high hydrogen–carbon ratio, and no absence of carbon–carbon bond (less coke formation). In addition, it has good availability, low boiling point, no sulfur containing in the fuel, and easy to storage [3], [4].

Normally, a hydrogen-rich gas can be produced from methanol by several methods; steam reforming (SRM), partial oxidation (POM), and oxidative steam reforming of methanol (OSRM) or autothermal reforming of methanol (ATRM) [5]. In this case, OSRM was chosen to be the promising way which combines two reactions: SRM and POM reactions. This operation closes to thermal neutrality or under slightly exothermic condition. This reaction requires lower temperature, resulting in energy saving, fast startup, and quick response of the overall reaction for operating under adiabatic condition [6]. However, OSRM process produces CO as a by-product in appreciable amounts, which poisons the Pt anodes of PEM fuel cells, and also suppresses the hydrogen’s purity [7]. To improve the performance of this reaction, the catalysts should be highly active in terms of high methanol conversion and high hydrogen selectivity (suppression of CO formation).

Gold (Au) catalysts are attractive catalysts because they are highly active and selective for a number of reactions (water-gas shift reaction, selective oxidation of CO in hydrogen-rich stream, and etc.). Compared with the existing commercial catalysts (Copper (Cu) and Palladium (Pd)), Au catalysts can operate at lower temperature [8]. In addition, ceria (CeO$_2$) support is known to improve the stability of catalysts due to its ability to maintain a high dispersion and to change its oxidation state of the cation between Ce$^{3+}$ and Ce$^{4+}$ (redox condition) as an active site [9]. For another interesting support, iron oxide (Fe$_2$O$_3$) is also an attractive support due to an interaction between Au and Fe$_2$O$_3$ could lead to the formation of an active phase at the interface of the catalyst [10]. Nevertheless, the performance of Au catalysts is strongly affected not only from the type of support used, but also from the preparation method including pretreatment conditions [8].

The objective of this research is to study the OSRM over Au/CeO$_2$–Fe$_2$O$_3$ catalysts. The reaction parameters such as the support composition (atomic ratio) of Ce/(Ce+Fe), calcination temperature, and Au content were studied. The catalysts were characterized by X-ray diffraction (XRD), Temperature-Programmed Reduction (TPR), X-ray fluorescence (XRF), and UV-Visible Spectrophotometer.

II. EXPERIMENT

A. Equipment

The system of experiment for oxidative steam reforming of methanol (OSRM) is shown in Figure 1.

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There are 4 main parts in this system: liquid feed section, gas blending section, catalytic reactor section, and analytical instrument section.

B. Liquid Feed System
The mixture of distilled water and methanol was filled in a syringe and this mixture was injected by a syringe pump at a rate of 1.5 ml/hour through a vaporizer for making the vapor of methanol and steam. The methanol vapor and steam were carried by helium, mixed with oxygen stream before entering a catalytic reactor and gas hourly space velocity (GHSV) of 30,000 ml/g-cat. hour were kept constant.

C. Gas Blending System
The pretreatment gas (H<sub>2</sub> or O<sub>2</sub>) and He were delivered from the storage cylinder tank, and then passed through a micron filter in order to remove particles and passed the check valve to prevent reverse flow. The flow rate was controlled by 840 Sierra Instrument model mass flow controller in order to achieve the desired flow rate. All streams were mixed in a mixing chamber before passing through the catalytic reactor.

D. Catalytic Reactor
The OSRM was carried out in a vertical pyrex glass reactor equipped with a chromel-alumel thermocouple (Type K) located in the middle of the reactor, 0.1 g of catalyst was packed between quartz wool plugs. The reactor was installed and electronically heated in the furnace. The temperature of the catalyst bed was controlled and monitored by PID temperature controller equipped with a chromel-alumel thermocouple (Type K).

E. Analytical Instrument
The product gases (e.g. H<sub>2</sub>, CO, CO<sub>2</sub>, and CH<sub>4</sub>) from the reactor were analyzed both qualitatively and quantitatively by a Hewlett Packard 5890 series II gas chromatograph equipped with a thermal conductivity detector (TCD). The column utilized in a gas chromatograph is Carbosphere®, 80/100 mesh, 10 ft x 1/8 inch stainless steel packed column.

F. Preparation of Catalyst and Support
The supports (CeO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>) were prepared by precipitation and co-precipitation methods as the first step. After that, the Au metal was loaded on the prepared supports by a deposition-precipitation (DP) method.

G. Support Preparation
An aqueous solution of 0.1 M Na<sub>2</sub>CO<sub>3</sub> was added dropwise in the aqueous mixture of 0.1 M Ce(NO<sub>3</sub>)<sub>3</sub>, 6H<sub>2</sub>O and 0.1 M Fe(NO<sub>3</sub>)<sub>3</sub>-9H<sub>2</sub>O with suitable amounts under vigorous stirring condition at 80 °C. The mixture was kept at a pH of 8–9 for 1 hour. Excess ions, CO<sub>3</sub><sup>2-</sup> and NO<sub>3</sub><sup>-</sup>, were eliminated by washing with warm deionized water. The suspension was centrifuged in centrifuge HERMLE Z383 at 500 rounds per min. The precipitate was dried at 80 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was labeled and kept in a desiccator. The mixed supports were symbolized as CF(x), where x was the Ce/(Ce+Fe) atomic ratio.

H. Catalyst Preparation
Before adding the metals, the support (CeO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>) was dried in an oven at 110 °C for 12 hours. Hydrogen tetrachloroaurate (III), HAuCl<sub>4</sub>, was weighed for a desired amount, and then dissolved in deionized water under continuous stirring and heating at 80 °C. The dried support was added to a solution and the pH of solution (~8) was adjusted by adding 0.1 M Na<sub>2</sub>CO<sub>3</sub> then the mixture was aged for 1 hour. The suspension was washed by warm deionized water to eliminate the residue ion (CO<sub>3</sub><sup>2-</sup>, Cl<sup>-</sup> and NO<sub>3</sub><sup>-</sup>). The suspension was centrifuged in centrifuge HERMLE Z383 at 500 rounds per min. Deionized precipitate was dried at 110 °C overnight and calcined in air at 400 °C for 4 hours. After calcination, the sample was ground and sieved to 80–120 mesh size, and kept in a desiccator.

I. Calculations
Methanol conversion:

\[ X = \frac{CO + CO_2 + CH_4}{MeOH_{(in)}} \times 100 \% \]  

Hydrogen yield:

\[ Y_{H_2} = X \times S_{H_2} \]  

Hydrogen selectivity:

\[ S_{H_2} = \frac{H_2}{H_2 + CH_4 + CO + CO_2} \times 100 \% \]
After that, the 1% Au metal was loaded on the prepared supports by deposition-precipitation (DP) method. All of them were calcined at 400 °C for 4 hours. Figure 2 shows the methanol conversion and hydrogen yield in the OSRM reaction in the reaction temperature range of 200 °C to 400 °C.

It can be seen that the 1%Au/CF(0.25) exhibited the highest catalytic activity in the whole temperature operating compared with other atomic ratios. The methanol conversion and hydrogen yield reached 91.4%, and 82.8%, respectively, at 400 °C. The mixed supports showed higher methanol conversion, and hydrogen yield than pure support (1%Au/CeO₂, and 1%Au/Fe₂O₃). It has been reported that the addition of Fe into CeO₂ resulted in a remarkable increase in the catalytic performance [11]. In this work, the combination of CeO₂ and Fe₂O₃ can also enhance the OSRM reaction. Consequently, 1%Au/CF(0.25) was chosen as the optimal composition for further study.

X-ray Diffraction (XRD)

The XRD results of CeO₂, 1%Au/CeO₂, 1%Au/CF(0.25), 1%Au/CF(0.75), 1%Au/Fe₂O₃, and Fe₂O₃ calcined at 400 °C are shown in Figure 3. The XRD diffractions of CeO₂ and 1%Au/CeO₂ present a very strong peak at 2θ = 28.5°, which is characteristic of fluorite structure of CeO₂ (111). The other peaks at 33.08, 47.47, 56.33, 59.08, 69.40, 76.69, and 79.067 were corresponding to CeO₂ (200), CeO₂ (220), CeO₂ (311), CeO₂ (222), CeO₂ (400), CeO₂ (331), and CeO₂ (420) for CuKα (1.5406 Å) radiation, respectively [12]. The XRD pattern become broadening, or lower intensity when CeO₂ was mixed with higher amount of Fe₂O₃ as a support, meaning that Fe³⁺ has incorporated in the ceria lattice to form a solid solution [13]. The pure support (1%Au/CeO₂, and 1%Au/Fe₂O₃) has higher crystallinity than the mixed supports, suggesting that the combination of Ce and Fe oxide on the catalyst can reduce the Fe₂O₃ and CeO₂ crystallite sizes [14]. The position of peaks is shifted towards higher 2theta values as the Fe content in the solution. This suggests the formation of a Fe₃CeₓO₃ solid solution, with Fe₂O₃ entering in the fluorite structure of ceria, the lower ionic radius of Fe³⁺ (0.67 Å) compared to Ce³⁺ (0.102 Å) [15]. However, the Au peaks of the prepared catalysts cannot be observed due to low Au content as only 1%wt, indicating either a high dispersion of gold or small Au particle size [16]. The crystallite sizes of catalysts were calculated based on the Scherrer equation and the results are summarized in Table I.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>CRYSSTALLITE SIZES OF THE 1%AU OVER DIFFERENT SUPPORTS</th>
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</thead>
<tbody>
<tr>
<td>Catalysts</td>
<td>CeO₂</td>
</tr>
<tr>
<td>CeO₂</td>
<td>9.69</td>
</tr>
<tr>
<td>1%Au/2CeO₂</td>
<td>9.49</td>
</tr>
<tr>
<td>1%Au/CF(0.75)</td>
<td>8.94</td>
</tr>
<tr>
<td>1%Au/CF(0.5)</td>
<td>7.31</td>
</tr>
<tr>
<td>1%Au/CF(0.25)</td>
<td>6.25</td>
</tr>
<tr>
<td>1%Au/Fe₂O₃</td>
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<tr>
<td>Fe₂O₃</td>
<td>-</td>
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</tbody>
</table>

From Table I, it shows that the mean crystallite sizes of CeO₂, 1%Au/CeO₂, 1%Au/CF(0.75), 1%Au/CF(0.5), and 1%Au/CF(0.25) were 9.96, 9.62, 8.09, 7.27, and 6.87, respectively. It is clearly seen that the addition of Fe decreases the crystallinity of ceria as the incorporation of small Fe ion into the ceria crystal [11].

B. Effect of Calcination Temperature on the Catalytic Performance

To study the effect of the calcination temperature on the activity of 1%Au/CF(0.25), the supports were prepared a co-
precipitation method. After that, the 1% Au metal was loaded on the prepared supports by a deposition-precipitation (DP) method. The catalysts were annealed at three different calcination temperatures of 200, 300, and 400 °C for 4 hours.

Many researchers reported that calcination temperature significantly affect on the activity of catalyst. Figure 4 shows the effect of calcination temperature on the methanol conversion and hydrogen yield of 1% Au/CF(0.25) catalysts. The results showed that methanol conversion increased with increasing calcinations temperature; however, when calcination temperature was increased from 300 °C to 400°C, the methanol conversion, and hydrogen yield slightly decreased. It could be concluded that the appropriate calcination temperature was 300 °C.

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and 5% wt. All catalysts were calcined at 300°C for 4 hours. It is well known that small Au particle size is highly active for many reactions (water-gas shift reaction, selective oxidation of CO in hydrogen rich stream, and etc.) [8]. However, in this study, the result showed that the methanol conversion, and hydrogen yield increased with increasing Au content from 1% to 3% wt and while Au content was increased from 3% to 5% wt the methanol conversion, and hydrogen yield decreased, as shown in Figure 7. The 3% Au content exhibited the highest performance among the catalysts studied.

Temperature-Programmed Reduction (TPR)

Figure 8 shows the TPR patterns of the 1%Au/CF(0.25), 3%Au/CF(0.25), and 5%Au/CF(0.25). The low temperature reduction peak of 100 °C to 150 °C, could be ascribed to the reduction of O\textsubscript{2} species adsorbed on small gold particle, and reduction of ceria surface sites located around gold particle [9]. At this position, the peak of the 3%Au/CF(0.25) was shifted to lower temperature (122 °C) when compared with 1%Au/CF(0.25) and 5%Au/CF(0.25) (148 °C and 132 °C, respectively). The high temperature reduction peak of 300 °C to 400 °C was attributed to the reduction of Fe\textsubscript{2}O\textsubscript{3} to Fe\textsubscript{3}O\textsubscript{4}, the peak of 3%Au/CF(0.25) was slightly decreased to 312 °C, which indicates that Au exerts a positive influence on the ease of Fe\textsubscript{2}O\textsubscript{3} reduction which occurs at lower temperature [21]. The strong metal-metal and metal-support interaction in the prepared catalysts lead to enhance the ability to reduce O\textsubscript{2} from iron oxide. The high temperature reduction peak (600 °C to 650 °C) was attributed to the reduction of Fe\textsubscript{3}O\textsubscript{4} to FeO species. The reduction of Fe\textsubscript{3}O\textsubscript{4} was much less affected by the presence of gold.

X-ray fluorescence (XRF)

In order to analyze the actual metal loading, and composition of Au/CF(0.25) calcined at 300 °C with different Au loadings, XRF technique was used and the results are summarized in Table II.

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Actual Au loading (%)</th>
<th>Ce/(Ce+Fe)</th>
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<td>1%Au/CF(0.25)</td>
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<td>3%Au/CF(0.25)</td>
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<td>5%Au/CF(0.25)</td>
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</table>

IV. CONCLUSIONS

The hydrogen production from OSRM has been studied over Au/CeO\textsubscript{2}–Fe\textsubscript{2}O\textsubscript{3}. Many parameters influenced on the catalytic activity of the catalyst, which are the type of support, mole ratio of support, calcination temperature, Au content, and operating reaction temperature. The 3%Au/CF(0.25) calcined at 300 °C exhibited the highest methanol conversion, and hydrogen yield.

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