

Effect of Gold Loading on $\text{CeO}_2\text{--Fe}_2\text{O}_3$ for Oxidative Steam Reforming of Methanol

Umpawan Satitthai, Apanee Luengnaruemitchai, and Erdogan Gulari

Abstract—In this study, oxidative steam reforming of methanol (OSRM) over a $\text{Au/CeO}_2\text{--Fe}_2\text{O}_3$ 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_2O_3 , and $\text{CeO}_2\text{--Fe}_2\text{O}_3$) were prepared by precipitation and co-precipitation methods. The impact of the support composition on the catalytic performance was studied by varying the $\text{Ce}/(\text{Ce}+\text{Fe})$ atomic ratio, it was found that the 1% $\text{Au}/\text{CF}(0.25)$ 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% $\text{Au}/\text{CF}(0.25)$ 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_2O_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].

U. S., A. L. The Petroleum and Petrochemical College, Chulalongkorn University, Soi Chula 12, Phayathai Road, Pathumwan, Bangkok 10330, Thailand (e-mail: ing_irnac@hotmail.com)

A. L. Center for Petroleum, Petrochemical, and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand (Phone: +66-2-218-4139; fax: +66-2-218-4139; e-mail: apanee.l@chula.ac.th)

E. G. Department of Chemical Engineering, Faculty of Engineer, Michigan University, Michigan 48109, USA

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_2O_3) is also an attractive support due to an interaction between Au and Fe_2O_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 $\text{Au/CeO}_2\text{--Fe}_2\text{O}_3$ catalysts. The reaction parameters such as the support composition (atomic ratio) of $\text{Ce}/(\text{Ce}+\text{Fe})$, 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.

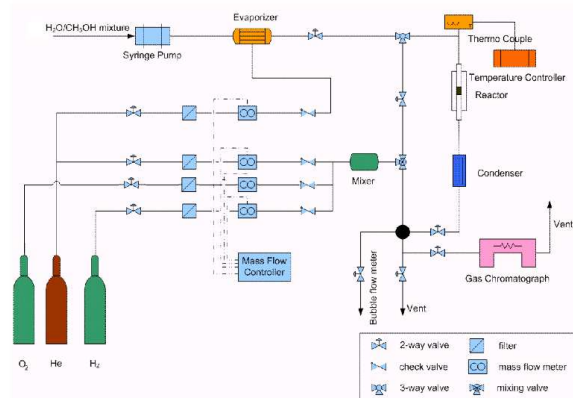


Fig. 1 Schematic of oxidative steam reforming of methanol experimental system

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_2 or O_2), 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 microreactor with an inside diameter of 6 mm at atmospheric pressure and in the temperature range of 200 to 400 °C. 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_2 , CO, CO_2 , and CH_4) 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_2 , Fe_2O_3 , and $CeO_2-Fe_2O_3$) 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_2CO_3 was added dropwise in the aqueous mixture of 0.1 M $Ce(NO_3)_3 \cdot 6H_2O$ and 0.1 M $Fe(NO_3)_3 \cdot 9H_2O$ 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_3^{2-} and NO_3^- , 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_2 , Fe_2O_3 , and $CeO_2-Fe_2O_3$) was dried in an oven at 110 °C for 12 hours. Hydrogen tetrachloroaurate (III), $HAuCl_4$, 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_2CO_3 then the mixture was aged for 1 hour. The suspension was washed by warm deionized water to eliminate the residue ion (CO_3^{2-} , Cl^- and NO_3^-). 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:

$$X = \frac{CO + CO_2 + CH_4}{MeOH_{(in)}} \times 100 (\%) \quad (1)$$

Hydrogen yield:

$$Y_{H_2} = X \times S_{H_2} \quad (2)$$

Hydrogen selectivity:

$$S_{H_2} = \frac{H_2}{H_2 + CH_4 + CO + CO_2} \times 100 (\%) \quad (3)$$

III. RESULTS AND DISCUSSION

A. Effect of Different Supports on the Catalytic Performance of 1%Au loading.

To study effect of different supports on the catalytic performance of 1%Au, the Ce/(Ce+Fe) atomic ratios were varied (0, 0.25, 0.5, 0.75, and 1). The supports were prepared by precipitation and co-precipitation methods as the first step.

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(0.5), 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 $2\theta = 28.5^\circ$, 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 CuK α (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 Fe_xCe_{1-x}O₂ solid solution, with Fe₂O₃ entering in the fluorite structure of ceria, the lower ionic radius of Fe³⁺ (0.67 Å) compared to Ce⁴⁺ (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 I
CRYSTALLITE SIZES OF THE 1%Au OVER DIFFERENT SUPPORTS

Catalysts	Crystallite size (nm)				
	CeO ₂ (111)	CeO ₂ (200)	CeO ₂ (220)	CeO ₂ (311)	Au (111)
CeO ₂	9.69	10.80	8.31	11.03	-
1%Au/CeO ₂	9.49	10.58	8.24	10.16	-
1%Au/CF(0.75)	8.94	9.26	7.03	7.14	-
1%Au/CF(0.5)	7.31	9.65	6.95	5.18	-
1%Au/CF(0.25)	6.25	10.05	6.78	4.14	-
1%Au/Fe ₂ O ₃	-	-	-	-	-
Fe ₂ O ₃	-	-	-	-	-

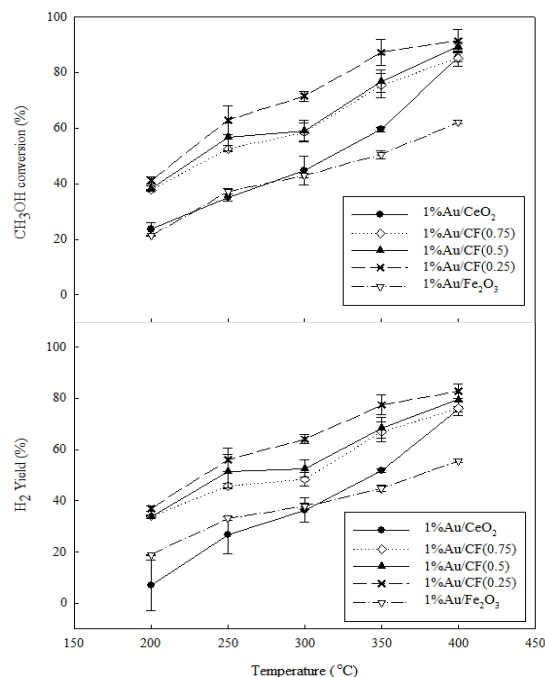


Fig. 2 Effect of Ce/(Ce+Fe) atomic ratio on the methanol conversion and hydrogen yield over 1% wt of Au/CeO₂-Fe₂O₃ catalysts calcined at 400 °C. (Reaction conditions: O₂/H₂O/CH₃OH molar ratio = 0.63:2:1)

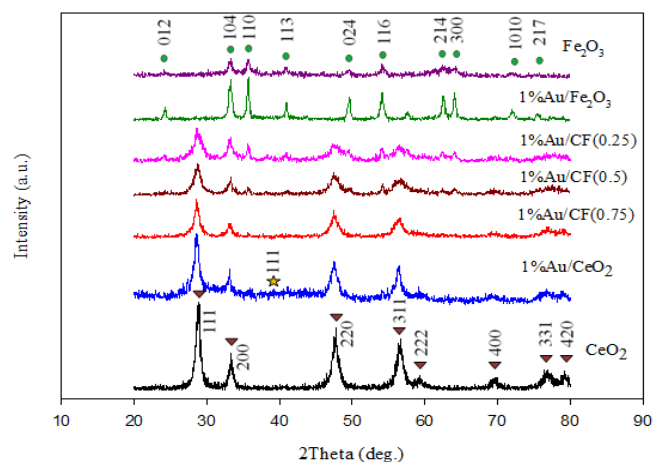


Fig. 3 XRD patterns of supported Au catalysts. : (▼) CeO₂; (●) Fe₂O₃; (★) Au

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), 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.

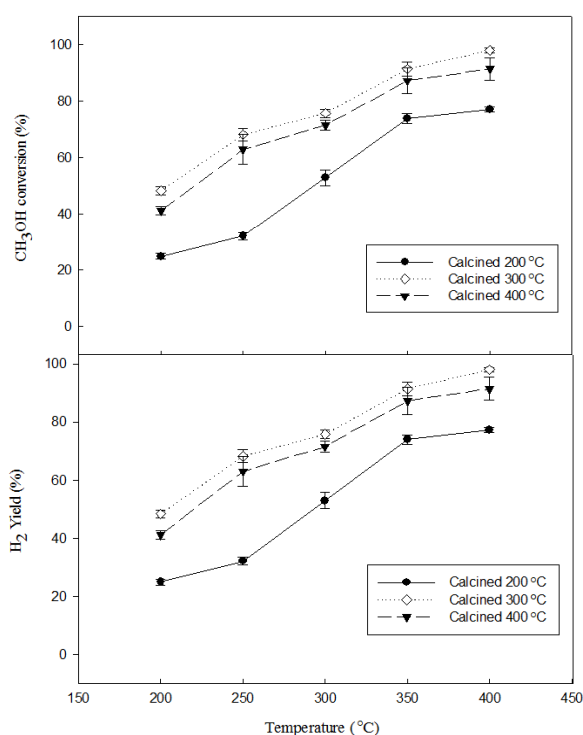


Fig. 4 Effect of calcination temperature on the methanol conversion and hydrogen yield over 1% wt of Au/CF(0.25) catalysts.

Temperature-Programmed Reduction (TPR)

TPR technique was used to study the reduction profiles of the catalysts. Figure 5 shows the TPR profiles of 1%Au/CF(0.25) with various calcination temperatures. The low reduction temperature (100 °C to 200 °C) was attributed to the reduction of Au_xO_y species, the 1%Au/CF(0.25) calcined at 300 °C had a very small peak at 147 °C when compared with other catalysts. The temperature reduction peak of 250 °C to 400 °C was attributed to the reduction of Fe_2O_3 to Fe_3O_4 [18]. The high temperature reduction peak of 600 °C to 650 °C was attributed to the reduction of Fe_3O_4 to FeO species [18]. In this study, it could be concluded that gold metallic (Au^0) exhibited higher activity than gold oxide. According to the reduction of Au_xO_y species peak was small at

147 °C, indicating to low oxide of Au. Corresponding to Ruihui et al., they reported that the active gold particles exist in metallic state (Au^0) [16]

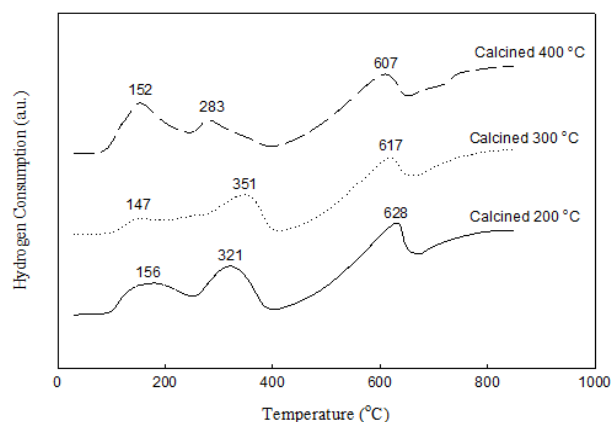


Fig. 5 TPR profiles of 1%Au/CF(0.25) calcined with various calcinations temperature

UV-visible Spectroscopy

There are many research works studied the presence of small Au metal by UV-vis spectroscopy to identify the gold species on support. The gold metallic (Au^0) peak is known to be located between 520–570 nm for gold particle on metal oxides, and gold clusters (Au_n , $1 < n < 10$) can be observed at 280–380 nm [19]. From figure 6, it is clearly seen that calcination temperature of 300 °C have more gold metallic (Au^0) than 200 °C, and 400 °C (calcined at 200 °C, and 400 °C had smaller peak between 520–570 nm than the catalysts calcined at 300 °C) which supported by TPR result. However, the investigation of Au^{3+} was still unclear because of the overlap of combination of support, according to the stacking of ceria oxide and Au^{3+} band, in the range of 200–350 nm and < 250 nm, respectively [20].

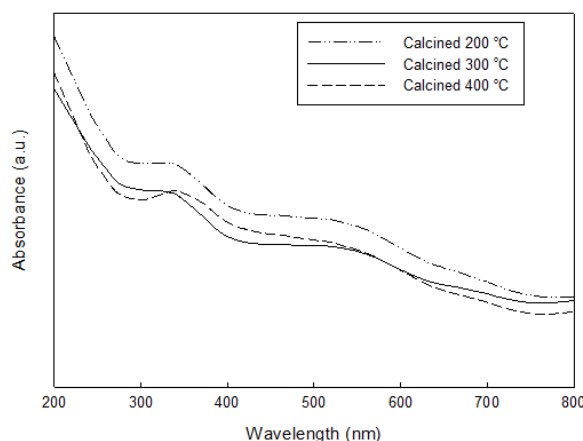


Fig. 6 Diffuse reflectance UV-vis spectra of 1%Au/CF(0.25) calcined with various calcinations temperature

C. Effect of Au Content on the Catalytic Performance

The Au/CF(0.25) were prepared by a deposition-precipitation technique with various Au contents of 1%, 3%,

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 O₂ 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 Fe₂O₃ to Fe₃O₄, 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 Fe₂O₃ 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 O₂ from iron oxide. The high temperature reduction peak (600 °C to 650 °C) was attributed to the reduction of Fe₃O₄ to FeO species. The reduction of Fe₃O₄ was much less affected by the presence of gold.

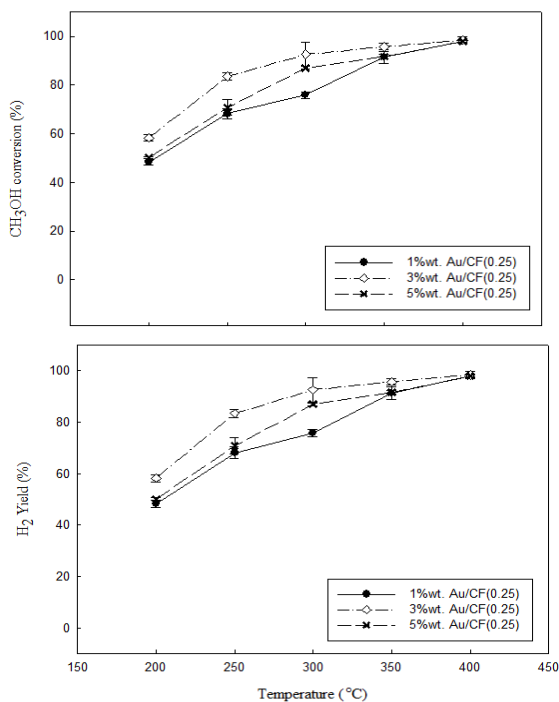


Fig. 7 Effect of Au content on the methanol conversion and hydrogen yield over Au/CF(0.25) catalysts

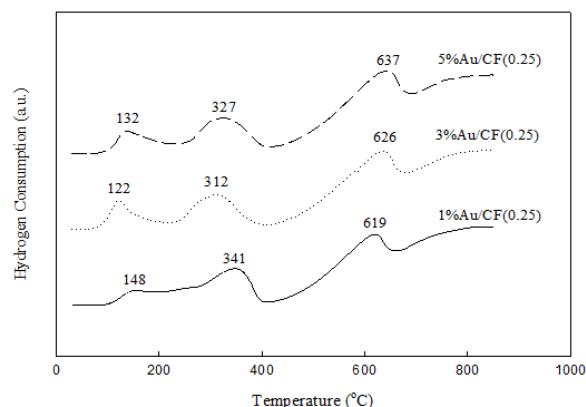


Fig. 8 TPR profiles of Au/CF(0.25) calcined at 300 °C with different Au loadings

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 II
XRF OF 1%Au/CF(0.25) WITH VARIOUS CALCINATIONS TEMPERATURE

Catalysts	Actual Au loading (%)	Ce/(Ce+Fe)
1%Au/CF(0.25)	0.894	0.20
3%Au/CF(0.25)	2.599	0.19
5%Au/CF(0.25)	3.838	0.20

IV. CONCLUSIONS

The hydrogen production from OSRM has been studied over Au/CeO₂-Fe₂O₃. 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.

ACKNOWLEDGMENTS

The authors would like to thank The Petroleum and Petrochemical College, and National Center for Petroleum, Petrochemicals, and Advanced Material, Thailand.

REFERENCES

- [1] K. Faungnawakij, R. Kikuchi, and K. Eguchi, "Thermodynamic evaluation of methanol steam reforming for hydrogen production," *Journal of Power Sources*, vol. 161, pp. 87–94, 2006.
- [2] T. Shishido, Y. Yamamoto, H. Morioka, and K. Takehira, "Production of hydrogen from methanol over Cu/ZnO and Cu/ZnO/Al₂O₃ catalysts prepared by homogeneous precipitation: Steam reforming and oxidative steam reforming," *Journal of Molecular Catalysis A: Chemical*, vol. 268, pp. 185–194, 2007.
- [3] S. Patel, and K.K. Pant, and L. Paturzo, "Hydrogen production by oxidative steam reforming of methanol using ceria promoted copper-alumina catalysts," *Fuel Processing Technology*, vol. 88, pp. 825–832, 2007.
- [4] T. Shishido, Y. Yamamoto, H. Morioka, and K. Takehira, "Production of hydrogen from methanol over Cu/ZnO and Cu/ZnO/Al₂O₃ catalysts

prepared by homogeneous precipitation: Steam reforming and oxidative steam reforming," *Journal of Molecular Catalysis A: Chemical*, vol. 268, pp. 185–194, 2007.

- [5] X. Honga, and S. Ren, "Selective hydrogen production from methanol oxidative steam reforming over Zn–Cr catalysts with or without Cu loading," *International Journal of Hydrogen Energy*, vol. 33, pp. 700 – 708, 2008.
- [6] M. Turco, G. Bagnasco, C. Cammarano, P. Senese, U. Costantino, and M. Sisani, "Cu/ZnO/Al₂O₃ catalysts for oxidative steam reforming of methanol: The role of Cu and the dispersing oxide matrix," *Applied Catalysis B: Environmental*, vol. 77, pp. 46–57, 2007.
- [7] F. Pinzari, P. Patrono, and U. Costantino, "Methanol reforming reactions over Zn/TiO₂ catalysts," *Catalysis Communications*, vol. 7, pp. 696–700, 2006.
- [8] M. Haruta, and M. Date', "Advances in the catalysis of Au nanoparticles," *Applied Catalysis A: General*, vol. 222, pp. 427–437, 2001.
- [9] T. Tabakova, G. Avgouropoulos, J. Papavasiliou, M. Manzoli, F. Boccuzzi, K. Tenchev, F. Vindigni, and T. Ioannides, "CO-free hydrogen production over Au/CeO₂–Fe₂O₃ catalysts: Part 1. Impact of the support composition on the performance for the preferential CO oxidation reaction," *Applied Catalysis B: Environmental*, vol. 101, pp. 256–265, 2011.
- [10] M. Makkee, J.A. Moulijn, , A.R. Overweg, and S.T. Daniells, "The mechanism of low-temperature CO oxidation with Au/Fe₂O₃ catalysts: a combined Mössbauer, FT-IR, and TAP reactor study," *Journal of Catalysis*, vol. 230, pp. 52–65, 2005.
- [11] L. Hongyan, M. Zhiqiang, D. Ling, Q. Jieshan, and L. Changhai, "Preparation of Nanoscale Ce_xFe_{1-x}O₂ Solid Solution Catalyst by the Template Method and Its Catalytic Properties for Ethanol Steam Reforming," *Chinese Journal Catalysis*, vol. 29(5), pp. 418–420, 2008.
- [12] J. Kunming, Z. Huili, and L. Wencui, "Effect of morphology of the ceria support on the activity of Au/CeO₂ catalysts for CO oxidation," *Chinese Journal of Catalysis*, vol. 29, pp. 2089–1092, 2008.
- [13] H. Lin, Z. Ma, L. ding, J. Qiu, and C. Liang, "Preparation of nanoscale Ce_xFe_{1-x}O₂ solid solution catalyst by the template method and its catalytic properties for ethanol steam reforming," *Chinese Journal of Catalysis*, vol. 29, pp. 418–420, 2008.
- [14] K. Sirichaiprasert, A. Luengnaruemitchai, and S. Pongstabodee, "Selective oxidation of CO to CO₂ over Cu–Ce–Fe–O composite-oxide catalyst in hydrogen feed stream," *International Journal of Hydrogen Energy*, vol. 32, pp. 915–926, 2006.
- [15] G. Neri, A. Bonavita, G. Rizzo, S. Galvagno, S. Capone, and P. Siciliano, "Methanol gas-sensing properties of CeO₂–Fe₂O₃ thin films," *Sensors and Actuators B*, vol. 114, pp. 687–695, 2006.
- [16] L. Rui-hui, Z. Cun-man, and M. Jian-xin, "Gold catalysts supported on crystalline Fe₂O₃ for low-temperature CO oxidation," *Chemical Research Chinese University*, vol. 26(1), pp. 98–104, 2010.
- [17] S. Scirè, C. Crisafulli, S. Minicò, G.G. Condorelli, and A.D. Mauro, "Selectivity oxidation of CO in H₂-rich stream over gold/iron oxide: An insight on the effect of catalyst pretreatment," *Journal of Molecular Catalysis A*, vol. 284, pp. 24–32, 2008.
- [18] A. Venugopal, and M. Scurrall, "Low temperature reductive pretreatment of Au/Fe₂O₃ catalysts, TPR/TPO studies and behaviour in the water-gas shift reaction," *Applied Catalysis A: General*, vol. 258, pp. 241–249, 2003.
- [19] S. Park, K. Yoo, H.J. Park, J.C. Lee, and J.H. Lee, "Rapid gold ion recovery from wastewater by photocatalytic ZnO nanopowders," *Journal of Electroceram*, vol. 17, pp. 831–834, 2006.
- [20] R. Zanella, S. Giorgio, C.H. Shin, C.R. Henry, and C. Louis, "Characterization and reactivity in CO oxidation of gold nanoparticles supported on TiO₂ prepared by deposition-precipitation with NaOH and urea," *Journal of Catalysis*, vol. 222, pp. 357–367, 2004.
- [21] F.W. Chang, L.S. Roselin, and T.C. Ou, "Hydrogen production by partial oxidation of methanol over bimetallic Au–Ru/Fe₂O₃ catalysts," *Applied Catalysis A: General*, vol. 334, pp. 147–155, 2008.