

**HYDROGEN PRODUCTION FROM OXIDATIVE STEAM REFORMING  
OF METHANOL OVER Au/CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> CATALYSTS**



Umpawan Satitthai


A Thesis Submitted in Partial Fulfilment of the Requirements  
for the Degree of Master of Science  
The Petroleum and Petrochemical College, Chulalongkorn University  
in Academic Partnership with  
The University of Michigan, The University of Oklahoma,  
Case Western Reserve University, and Institut Français du Pétrole  
2012

551755


**Thesis Title:** Hydrogen Production from Oxidative Steam Reforming of Methanol over Au/CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> Catalysts  
**By:** Umpawan Satitthai  
**Program:** Petrochemical Technology  
**Thesis Advisors:** Assoc. Prof. Apanee Luengnaruemitchai  
Prof. Erdogan Gulari

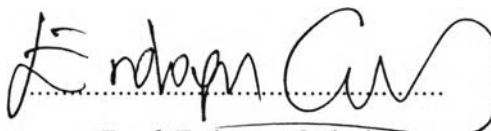
---

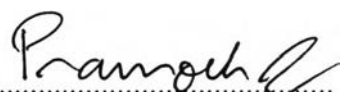
Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

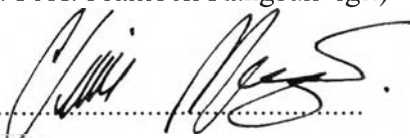
  
..... College Dean  
(Asst. Prof. Pomthong Malakul)

**Thesis Committee:**

  
.....  
(Assoc. Prof. Apanee Luengnaruemitchai)

  
.....  
(Prof. Erdogan Gulari)

  
.....  
(Assoc. Prof. Pramoch Rangsunvigit)

  
.....  
(Assoc. Prof. Vissanu Meeyoo)

**ABSTRACT**

5371033063: Petrochemical Technology

Umpawan Satitthai: Hydrogen Production from Oxidative Steam Reforming of Methanol over Au/CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> Catalysts

Thesis Advisors: Assoc. Prof. Apanee Luengnaruemitchai,  
And Prof. Erdogan Gulari

Keywords: Oxidative Steam Reforming/ Methanol/ Gold Catalyst/ Hydrogen Production/ CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub>

Oxidative steam reforming of methanol (OSRM) over a Au/CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> catalyst prepared by a deposition-precipitation (DP) method was investigated to produce hydrogen for proton exchange membrane fuel cell (PEMFC) applications. 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. The 3%Au/CF(0.25) exhibited the highest activity under optimum conditions of temperatures from 200 °C to 400 °C. The reduction of Au<sub>x</sub>O<sub>y</sub> species and the reduction of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> of 3%Au/CF(0.25) shifted to a lower temperature, resulting in strong metal-metal and metal-support interactions on the prepared catalysts. In addition, the O<sub>2</sub>/H<sub>2</sub>O/CH<sub>3</sub>OH molar ratio of 0.6/2/1 gave the highest catalytic performance.

## บทคัดย่อ

อำพรพรรณ สถิตไทย : กระบวนการผลิตก๊าซไฮโดรเจนจากปฏิกิริยาเปลี่ยนรูปเมทานอลด้วยไอน้ำและก๊าซออกซิเจน โดยใช้ตัวเร่งปฏิกิริยาทองบนซีเรียออกไซด์และไอรอนออกไซด์ (Hydrogen Production from Oxidative Steam Reforming of Methanol over Au/CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> Catalysts) อ. ที่ปรึกษา : รศ. ดร. อาภาณี เหลืองนฤมิตชัย และ ศ. ดร. เอโดแกณ กุลารี่

งานวิจัยนี้ศึกษากระบวนการผลิตก๊าซไฮโดรเจนด้วยกระบวนการเปลี่ยนรูปเมทานอลด้วยไอน้ำและก๊าซออกซิเจน โดยใช้ตัวเร่งปฏิกิริยาทองบนตัวรองรับชนิดซีเรียออกไซด์และไอรอนออกไซด์ ที่เตรียมด้วยวิธีการยึกเกาะควบคู่กับการตกผลึก (Deposition-precipitation) เพื่อนำไปประยุกต์ใช้ใน proton exchange membrane fuel cell (PEMFC) โดยตัวรองรับ (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>) เตรียมด้วยวิธีการตกผลึก ตัวแปรที่ศึกษาที่มีอิทธิพลต่อการเปลี่ยนแปลงของเมทานอล (methanol conversion) เช่น อัตราส่วนโดยโมลของตัวรองรับ อุณหภูมิที่ใช้ในการเตรียมตัวเร่งปฏิกิริยา (calcination temperature) ปริมาณของทองที่ใช้ในการเตรียมตัวเร่งปฏิกิริยา และช่วงของอุณหภูมิที่ใช้ในการเกิดปฏิกิริยาในเตาปฏิกรณ์ขนาดเล็ก ผลการศึกษาพบว่าตัวเร่งปฏิกิริยา 3 wt% Au/CeO<sub>2</sub>-Fe<sub>2</sub>O<sub>3</sub> เตรียมที่อุณหภูมิ 300 °C ให้ผลในการเกิดปฏิกิริยาสูงที่สุด ตลอดทุกช่วงอุณหภูมิที่ทดสอบ (200°C ถึง 400 °C) เนื่องจากที่สภาวะนี้มีการยึกเกาะที่แข็งแรงของโลหะกับโลหะ และโลหะกับตัวรองรับ ยิ่งไปกว่านั้นอัตราส่วนโดยโมลของ O<sub>2</sub>/H<sub>2</sub>O/CH<sub>3</sub>OH ที่ 0.6/2/1 เป็นสภาวะที่เหมาะสมที่สุดต่อการเกิดปฏิกิริยาดังกล่าว

## ACKNOWLEDGEMENTS

The author gratefully acknowledge for the scholarship and funding of the thesis work provided by the Petroleum and Petrochemical College, and by the Center of Excellence on Petrochemicals and Materials Technology, Thailand.

I would like to thankfulness to my advisors and member group. Especially Assoc. Prof. Apanee Luengnaruemitchai that provides suggestion and gives me an idea to troubleshoot problem, I am so appreciate to intimacy for teaching and helping me to understand and get the knowledge. Also for special senior students in the Petroleum and Petrochemical College, Mr. Phatchanon Pipatpratanporn that I would like to thanks for his kind of teaching and helping in laboratory.

My sincere thank to Assoc. Prof. Pramoch Rangsunvigit and Assoc. Prof. Vissanu Meeyoo for being my thesis committee and comment. And this thesis would not have been possible without the knowledge received from all the lecturers and staffs at the Petroleum and Petrochemical College

Finally, I would like to thanks my family for spirit and finance during my study in the Petroleum and Petrochemical College along two years.

## TABLE OF CONTENTS

	<b>PAGE</b>
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	x
List of Figures	xi
<b>CHAPTER</b>	
<b>I INTRODUCTION</b>	<b>1</b>
<b>II THEORETICAL BACKGROUND AND LITERATURE REVIEW</b>	<b>3</b>
2.1 Background	3
2.2 Hydrogen Production from Methanol (CH <sub>3</sub> OH)	3
2.2.1 Steam Reforming of Methanol (SRM)	4
2.2.1.1 Experimental Condition	6
2.2.1.2 Mechanism and Kinetics	9
2.2.2 Partial Oxidation of Methanol (POM)	11
2.2.2.1 Catalytic Activity	12
2.2.2.2 Experimental Condition	13
2.2.3 Oxidative Steam Reforming of Methanol	14
2.2.3.1 Experimental Condition	15
2.2.3.2 Catalytic Activity	18
2.3 Catalysts Development for SRM and OSRM	18
2.3.1 Copper-based Catalysts	19
2.3.2 Non Copper-based Catalysts	20
2.4 Gold Catalyst	21
2.5 Supported Catalyst	24

<b>CHAPTER</b>	<b>PAGE</b>
<b>III EXPERIMENTAL</b>	33
3.1 Materials	33
3.1.1 Reactants	33
3.1.2 Gases	33
3.1.3 Chemicals	33
3.2 Equipment	34
3.2.1 Liquid Feed System	34
3.2.2 Gas Blending System	35
3.2.3 Catalytic Reactor	35
3.2.4 Analytical Instrument	35
3.3 Methodology	36
3.3.1 Preparation of Catalyst and Support	36
3.3.1.1 Support Preparation	36
3.3.1.2 Catalyst Preparation	37
3.3.2 Catalyst Characterization	38
3.3.2.1 BET Surface Area Measurement	38
3.3.2.2 X-Ray Diffraction (XRD)	39
3.3.2.3 Transmission Electron Microscopy (TEM)	40
3.3.2.4 Temperature-Programmed Reduction (TPR)	41
3.3.2.5 Temperature-Programmed Oxidation (TPO)	41
3.3.2.6 UV-vis Spectrophotometer	41
3.3.2.7 X-ray Fluorescence (XRF)	42
3.3.2.8 Fourier Transform Infrared Spectroscopy (FT-IR)	42
3.4 Optimum Condition and Activity Measurement	42

<b>CHAPTER</b>	<b>PAGE</b>
3.4.1 Effect of Support Composition (atomic ratio) of Ce/(Ce+Fe)	42
3.4.2 Effect of Calcination Temperature	43
3.4.3 Effect of Au Content	43
3.4.4 Effect of O <sub>2</sub> Pretreatment	43
3.4.5 Effect of Steam/Methanol (S/M or H <sub>2</sub> O/CH <sub>3</sub> OH) Molar Ratio	43
3.4.6 Effect of O <sub>2</sub> /CH <sub>3</sub> OH Molar Ratio	43
3.4.7 Deactivation Test	44
3.5 Calculation	45
 <b>IV RESULTS AND DISCUSSION</b>	 46
4.1 Au/CeO <sub>2</sub> , Au/ Fe <sub>2</sub> O <sub>3</sub> -CeO <sub>2</sub> , and Au/Fe <sub>2</sub> O <sub>3</sub> Catalysts	46
4.1.1 Effect of Type of Support on the Catalytic Performance of 1% Au Catalyst	46
6.1.1.1 X-ray Diffraction	48
6.1.1.2 X-ray fluorescence	50
6.1.1.3 Surface Area Measurement	51
4.1.2 Effect of Calcination Temperature on the Catalytic Performance	52
4.1.2.1 Temperature-Programmed Reduction	54
4.1.2.2 UV-visible Spectroscopy	55
4.1.2.3 Transmission Electron Micrograph	56
4.1.2.4 X-ray Diffraction	59
4.1.2.5 X-ray fluorescence	60
4.1.2.6 Surface Area Measurement	60
4.1.3 Effect of Au Content on the Catalytic Performance	61
4.1.3.1 Temperature-Programmed Reduction	63
4.1.3.2 UV-visible Spectroscopy	64



<b>CHAPTER</b>	<b>PAGE</b>
4.1.3.3 Transmission Electron Micrograph	65
4.1.3.4 X-ray Diffraction	68
4.1.3.5 X-ray fluorescence	69
4.1.3.6 Surface Area Measurement	69
4.1.4 Effect of Catalyst Pretreatment	70
4.1.5 Effect of H <sub>2</sub> O/CH <sub>3</sub> OH Molar Ratio on the Catalytic Performance	72
4.1.5.1 Fourier Transform Spectroscopy	74
4.1.6 Effect of O <sub>2</sub> /CH <sub>3</sub> OH Molar Ratio on the Catalytic Performance	77
4.1.7 Comparision of Stability between Catalyst Unpretreated and Catalyst Pretreatment	79
4.1.7.1 X-ray Diffraction	80
4.1.7.2 Temperature-Programmed Oxidation	81
<b>V CONCLUSIONS AND RECOMMENDATIONS</b>	<b>83</b>
5.1 Conclusions	83
5.2 Recommendations	84
<b>REFERENCES</b>	<b>85</b>
<b>APPENDICES</b>	<b>92</b>
<b>Appendix A</b> Calibration Curve of Gas Products	92
<b>Appendix B</b> SEM-eds of 3 wt% Au/CF(0.25)	97
<b>CURRICULUM VITAE</b>	<b>99</b>

**LIST OF TABLES**

<b>TABLE</b>		<b>PAGE</b>
2.1	Physical properties of Au	23
4.1	CeO <sub>2</sub> and Au crystallite sizes of the 1%Au catalysts over different supports	50
4.2	XRF of catalysts with calcinations temperature at 400 °C	51
4.3	BET surface areas of catalysts	51
4.4	CeO <sub>2</sub> and Au crystallite sizes of the 1% Au/CF(0.25) with different calcination temperatures	59
4.5	XRF of 1%Au/CF(0.25) with various calcinations temperature	60
4.6	BET surface areas of 1% Au/CF(0.25) with various calcinations temperature	60
4.7	CeO <sub>2</sub> and Au crystallite sizes of the Au/CF(0.25) calcined at 300 °C with different Au loading	68
4.8	XRF results of Au/CF(0.25) calcined at 300 °C with different Au content	69
4.9	BET surface areas of 1%Au/CF(0.25) with various calcinations temperature	69
4.10	Frequency and assignment of carbonate, formate, and intermediate bands of spent 3 wt% Au/CF(0.25) calcined at 300 °C	76

## LIST OF FIGURES

FIGURE	PAGE	
2.1	Simplified process flow diagram for SRM	6
2.2	Effect of reaction temperature in methanol steam reforming reaction	7
2.3	Effect of reaction temperature on product profiles with 0.1 g of 5% Cu/GDC, (a) 210 °C, (b) 240 °C, and (c) 270 °C	8
2.4	The influence of the steam:methanol ratio on CO production	9
2.5	Partial oxidation of methanol over the catalyst Cu <sub>40</sub> Zn <sub>60</sub>	13
2.6	Rates of methanol conversion ( $\Delta$ ) and H <sub>2</sub> ( $\circ$ ) and CO <sub>2</sub> ( $\square$ ) formation at 497 K and copper metallic area ( $\nabla$ ) versus the copper content in the Cu-Zn catalysts	14
2.7	Effect of O <sub>2</sub> /CH <sub>3</sub> OH molar ratio on methanol conversion, hydrogen selectivity and CO selectivity for POM over Au-Ru/Fe <sub>2</sub> O <sub>3</sub> catalysts (calcination temperature, 673 °C; reaction temperature, 523 °C; reaction time, 10 min)	15
2.8	Effect of the temperature on the gas effluent composition in the SRM (a) and OSRM (b) reactions over Zn <sub>10</sub> Ti <sub>90</sub>	17
2.9	Methanol conversion (a) and hydrogen yield (b) as a function of the temperature for Zn <sub>10</sub> Ti <sub>90</sub>	18
2.10	Comparison of methanol conversion and hydrogen production rate for different catalysts as a function of temperature (W/F=15 kg <sub>cat</sub> s <sup>-1</sup> , O/M=0.15 M, S/M=1.5 M, P=1 atm)	19
2.11	Methanol conversion and CO <sub>2</sub> , H <sub>2</sub> , CO selectivities as functions of Cu/Zn ratios over Cu/Zn/SiO <sub>2</sub> catalysts. Reaction conditions: T = 473K; CO <sub>2</sub> /CH <sub>3</sub> OH = 0:3	21
2.12	Turn over frequencies and band-gap measure by STM as a function of the diameter of Au islands deposited on TiO <sub>2</sub>	25

<b>FIGURE</b>	<b>PAGE</b>
2.13 Proposed reaction mechanism for SRM at the Cu/Ce interface	26
2.14 Schematic model of oxidation of CO on as prepared (dried) Au/Fe <sub>2</sub> O <sub>3</sub>	28
2.15 XRD patterns (a) and Raman spectra (b) of different samples of composited oxide catalysts	30
2.16 Ethanol conversion (a) and hydrogen concentration (b) in the effluent of steam reforming of ethanol as a function of reation temperature over different samples	31
2.17 Activity and selectivity towards CO <sub>2</sub> production of Au/CeO <sub>2</sub> (■), Au/Ce75Fe25 (▼), Au/Ce50Fe50 (□), Au/Ce25Fe75 (▲), and Au/Fe <sub>2</sub> O <sub>3</sub> (●) catalysts for the PROX reaction at W/F=0.03gscm <sup>-3</sup> Feed: 1% CO, 1.25% O <sub>2</sub> , 50% H <sub>2</sub> , He	32
3.1 Schematic of oxidative steam reforming of methanol experimental system	34
4.1 Effect of Ce/(Ce+Fe) atomic ratio on the methanol conversion, and concentration of H <sub>2</sub> , CO, and CO <sub>2</sub> over 1 wt% of Au/CeO <sub>2</sub> -Fe <sub>2</sub> O <sub>3</sub> catalysts calcined at 400 °C. (Reaction conditions: O <sub>2</sub> /H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio = 0.6:2:1)	47
4.2 XRD patterns of supported Au catalysts: (▼) CeO <sub>2</sub> ; (●) Fe <sub>2</sub> O <sub>3</sub> ; (•) Au	49
4.3 Effect of calcination temperature on the methanol conversion, and concentration of H <sub>2</sub> , CO, and CO <sub>2</sub> over 1 wt% of Au/CF(0.25) catalysts. (Reaction conditions: O <sub>2</sub> /H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio = 0.6:2:1)	53
4.4 TPR profiles of 1 wt% Au/CF(0.25) with various calcination temperatures	55
4.5 Diffuse reflectance UV-vis spectra of 1%Au/CF(0.25) with various calcination temperatures	56

<b>FIGURE</b>	<b>PAGE</b>
4.6 TEM image of 1% Au/CF(0.25) with various calcination temperatures	58
4.7 XRD patterns of supported Au catalysts: (▼) CeO <sub>2</sub> ; (●) Fe <sub>2</sub> O <sub>3</sub> ; (★) Au	59
4.8 Effect of Au content on methanol conversion, and concentration of H <sub>2</sub> , CO <sub>2</sub> , and CO over Au/CF(0.25). (Reaction conditions: O <sub>2</sub> /H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio = 0.6:2:1)	62
4.9 TPR profiles of Au/CF(0.25) calcined at 300 °C with different Au loadings	64
4.10 Diffuse reflectance UV–vis spectra of Au/CF(0.25) calcined at 300 °C with different Au loading	65
4.11 TEM image of Au/CF(0.25) calcined at 300 °C with different Au loadings	67
4.12 XRD patterns of supported Au catalysts: (▼) CeO <sub>2</sub> ; (●) Fe <sub>2</sub> O <sub>3</sub> ; (★) Au	68
4.13 Effect of O <sub>2</sub> pretreatment on the methanol conversion, and concentration of H <sub>2</sub> , CO <sub>2</sub> , and CO over 3 wt% Au/CF(0.25) catalysts. (Reaction conditions: O <sub>2</sub> /H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio = 0.6:2:1)	71
4.14 Effect of H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio on the methanol conversion, and concentration of H <sub>2</sub> , CO <sub>2</sub> , and CO over 3 wt% Au/CF(0.25) catalysts calcined at 300 °C.	73
4.15 FTIR spectra of 3 wt% Au/CF(0.25) catalysts calcined at 300 °C after reaction. (a) and (b) (1) H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio of 1; (2) H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio of 2; (3) H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio of 3; (4) H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio of 4	75
4.16 Effect of O <sub>2</sub> /H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio on methanol conversion, and concentration of H <sub>2</sub> , CO <sub>2</sub> , and CO over 3 wt% Au/CF(0.25) catalysts calcined at 300 °C.	78

<b>FIGURE</b>	<b>PAGE</b>
4.17 Stability testing of the 3 wt% Au/CF(0.25) at reaction temperature of 350 °C. (Reaction conditions: O <sub>2</sub> /H <sub>2</sub> O/CH <sub>3</sub> OH molar ratio = 0.6:2:1)	79
4.18 XRD patterns of supported Au catalysts: (▼) CeO <sub>2</sub> ; (●) Fe <sub>2</sub> O <sub>3</sub> ; (*) Au	80
4.19 TPO profiles of spent 3 wt% Au/CF(0.25) after reaction temperature 300 °C, and time on stream 12 hour	82