

**CATALYTIC PERFORMANCE OF Ni-BASED CERIA-ZIRCONIA  
CATALYSTS FOR HYDROGEN PRODUCTION: EFFECT OF Ni LOADING  
METHOD**

Kulthida Junsai

A Thesis Submitted in Partial Fulfillment 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  
2015

° I 28369518

- 580082

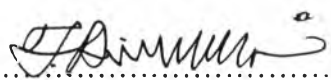
**Thesis Title:** Catalytic Performance of Ni-based Ceria-Zirconia Catalysts  
for Hydrogen Production: Effect of Ni Loading Method  
**By:** Kulthida Junsai  
**Program:** Petroleum Technology  
**Thesis Advisors:** Assoc. Prof. Thirasak Rirksomboon  
Assoc. Prof. Vissanu Meeyoo


---

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


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

**Thesis Committee:**

  
.....  
(Assoc. Prof. Thirasak Rirksomboon)

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

  
.....  
(Asst. Prof. Boonyarach Kitiyanan)

  
.....  
(Assoc. Prof. Manop Charoenchaitrakool)

**ABSTRACT**

5673012063: Petroleum Technology Program

Ms. Kulthida Junsai: Catalytic Performance of Ni-based Ceria-Zirconia Catalysts for Hydrogen Production: Effect of Ni Loading Method

Thesis Advisors: Assoc. Prof. Thirasak Rirksomboon, and  
Assoc. Prof. Vissanu Meeyoo 77 pp.

Keywords: Partial oxidation of methane/ Hydrogen production/ Nickel/ Ceria-Zirconia/ Polyol mediated method

Nickel supported on Ceria-Zirconia mixed oxide catalysts utilizing in catalytic partial oxidation of methane (CPOM) are drastically deactivated by carbon formation. Improving Ni dispersion by acquiring the preparation of small metallic particles on the support has been proposed to reduce coke formation thus increasing the catalytic activity and stability of catalysts. In this study, CeO<sub>2</sub>-ZrO<sub>2</sub> support was prepared by urea hydrolysis with 5, 10, 15 and 25 wt%Ni incorporation using both the polyol mediated and impregnation methods. The catalysts were characterized by several techniques. The CPOM was conducted using a fixed bed reactor to measure activity of catalysts in the temperature range of 400-800 °C at atmospheric pressure. The results showed that nickel of 15 wt% would be an appropriate loading amount in terms of catalytic activity regardless of catalyst preparation methods. However, in terms of catalyst stability the catalyst synthesized by the polyol mediated method provided superior performance on coke resistance.

## บทคัดย่อ

กุลธิดา จันทร์ใส :: สมรรถนะของตัวเร่งปฏิกิริยานิกเกิลออกไซด์บนซีเรียเซอร์โคเนีย สำหรับการผลิตก๊าซไฮโดรเจน โดยศึกษาผลของการเติมนิกเกิลลงบนตัวรองรับ (Catalytic Performance of Ni-based Ceria-Zirconia Catalysts for Hydrogen Production: Effect of Ni Loading Method) อ. ที่ปรึกษา: รศ.ดร. ชีรศักดิ์ ฤกษ์สมบูรณ์ และ รศ.ดร. วิษณุ มีอยู่ 77 หน้า

ตัวเร่งปฏิกิริยานิกเกิลบนซีเรีย-เซอร์โคเนียซึ่งใช้ในการเร่งปฏิกิริยาออกซิเดชันบางส่วนของมีเทนเสื่อมสภาพอย่างรวดเร็วจากการสะสมของคาร์บอน การเพิ่มการกระจายตัวของโลหะนิกเกิลโดยวิธีการเตรียมอนุภาคโลหะขนาดเล็กลงบนตัวรองรับมีวัตถุประสงค์เพื่อลดการสะสมของคาร์บอนและเพิ่มประสิทธิภาพและความเสถียรของตัวเร่งปฏิกิริยา ในงานวิจัยนี้ตัวรองรับโลหะออกไซด์ผสมระหว่างซีเรียและเซอร์โคเนีย ถูกเตรียมโดยวิธีการไฮโดรไลซิสโดยสารละลายยูเรียและเติมโลหะนิกเกิลลงบนตัวรองรับร้อยละ 5 10 15 และ 25 โดยน้ำหนัก ทำโดยวิธีการพอลิออล (polyol) และวิธีการทำให้ชุ่ม จากนั้นได้ศึกษาคุณลักษณะสมบัติของของตัวเร่งปฏิกิริยาที่เตรียมได้โดยวิธีต่างๆ รวมทั้งได้ศึกษาความสามารถในการเกิดปฏิกิริยาออกซิเดชันบางส่วนของมีเทนโดยใช้เครื่องปฏิกรณ์แบบนิ่ง ในช่วงอุณหภูมิ 400 ถึง 800 องศาเซลเซียส ที่ความดันบรรยากาศ ผลการทดลองแสดงให้เห็นว่าการใช้โลหะนิกเกิลร้อยละ 15 โดยน้ำหนักบนตัวรองรับเป็นปริมาณการเติมที่เหมาะสมต่อประสิทธิภาพของตัวเร่งปฏิกิริยาไม่ว่าจะเตรียมตัวเร่งปฏิกิริยาดัวยวิธีใด อย่างไรก็ตามตัวเร่งปฏิกิริยาที่เตรียมด้วยวิธีพอลิออล มีความเสถียรต่อการสะสมตัวของคาร์บอนมากกว่าตัวเร่งปฏิกิริยาที่เตรียมด้วยวิธีการทำให้ชุ่ม

## ACKNOWLEDGEMENTS

First of all, I would like to thank my advisors, Assoc. Prof. Thirasak Rirksomboon and Assoc. Prof. Vissanu Meeyoo who have given me an opportunity to study in this thesis and provided their knowledge, useful recommendations, comments and suggestions throughout my graduate studies.

I am grateful for the partial scholarship and partial funding of the thesis work provided by The Petroleum and Petrochemical College (PPC), Chulalongkorn University as well as Centre for Advanced Materials and Environmental Research (CAMER), Mahanakorn University of Technology for their contributions on partially financial support and work places.

My sincere thanks go to Asst. Prof. Boonyarach Kitiyanan and Assoc. Prof. Manop Charoenchaitrakool for being my thesis committee and for giving me their valuable suggestions.

Finally, I would like to express my sincere thanks to my family and my friends for their love, hearten, and understanding.

## 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	viii
List of Figures	x
<b>CHAPTER</b>	
<b>I INTRODUCTION</b>	1
<b>II THEORETICAL BACKGROUND AND LITERATURE REVIEW</b>	4
2.1 Background	4
2.2 Literature Review	9
<b>III EXPERIMENTAL</b>	23
3.1 Materials	23
3.1.1 Gases	23
3.1.2 Chemicals	23
3.2 Equipment	24
3.2.1 Catalyst Characterization	24
3.3 Methodology	27
3.3.1 Catalyst Preparation	27
3.3.2 Catalytic Activity Testing	28

CHAPTER	PAGE
<b>IV RESULTS AND DISCUSSION</b>	31
4.1 Catalyst Characterization	31
4.1.1 Element Analysis by XRF	31
4.1.2 BET Surface Areas and Degrees of Metal Dispersion	32
4.1.3 X-ray Diffraction (XRD)	33
4.1.4 Temperature-programmed Reduction of Hydrogen by H <sub>2</sub> (TPR)	35
4.1.5 Scanning Electron Microscopy (SEM)	38
4.2 Catalytic Activities for Catalytic Partial Oxidation of Methane	39
4.2.1 Catalytic Activities For CPOM	39
4.2.2 Effect of CH <sub>4</sub> /O <sub>2</sub> Ratio	43
4.2.3 Coke Formation on Catalyst and Catalyst Stability	45
<b>V CONCLUSIONS AND RECOMMENDATIONS</b>	51
5.1 Conclusions	51
5.2 Recommendations	51
<b>REFERENCES</b>	52
<b>Appendix A</b> Experimental Data of Gas Calibration of GC-8A	58
<b>Appendix B</b> Experimental Data of Flow Meter Gas Calibration of Brocks 5850E Mass Flow Controller	62
<b>Appendix C</b> Experimental data of Catalytic Activity Tests for MPO	64
<b>Appendix D</b> Experimental data of Stability Tests for MPO	74
<b>Appendix E</b> Calculation of Metal Surface Area	76
<b>CURRICULUM VITAE</b>	77

## LIST OF TABLES

TABLE		PAGE
2.1	Comparison of technologies for H <sub>2</sub> production from natural gas	7
2.2	Mechanism of methane catalytic partial oxidation	15
4.1	Elemental analysis results for the catalysts synthesized	31
4.2	Textural properties and metal characteristics of the prepared catalysts	33
4.3	Amounts of carbon deposited on the catalysts	48
C1	Catalytic activity test of 5Ni/CZOi catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	64
C2	Catalytic activity test of 5Ni/CZOp catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	65
C3	Catalytic activity test of 10Ni/CZOi catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	66
C4	Catalytic activity test of 10Ni/CZOp catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	67
C5	Catalytic activity test of 15Ni/CZOi catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	68
C6	Catalytic activity test of 15Ni/CZOp catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	69
C7	Catalytic activity test of 25Ni/CZOi catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	70
C8	Catalytic activity test of 25Ni/CZOp catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	71
C9	Catalytic activity test of 15Ni/CZOi catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 4:1)	72



<b>TABLE</b>		<b>PAGE</b>
C10	Catalytic activity test of 15Ni/CZOp catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 4:1)	73
D1	Stability test of 15Ni/CZOi catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	74
D2	Stability test of 15Ni/CZOp catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1)	74
D3	Stability test of 15Ni/CZOi catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 4:1)	75
D4	Stability test of 15Ni/CZOp catalyst (CH <sub>4</sub> /O <sub>2</sub> ratio = 4:1)	75

## LIST OF FIGURES

FIGURE		PAGE
2.1	Thermodynamic representation of the partial oxidation of methane.	6
2.2	Numerous polyalcohol used for the polyol process.	9
2.3	Possible route for methane conversion.	10
2.4	The direct and indirect mechanism for catalytic partial oxidation of methane.	14
2.5	Methane partial oxidation reactor with indirect mechanism.	16
3.1	Schematic of the experimental setup for methane partial oxidation.	29
4.1	XRD patterns of the catalysts: a) CZO, (b) 5Ni/CZOi, (c) 10Ni/CZOi, (d) 15Ni/CZOi, (e) 25Ni/CZOi, (f) 5Ni/CZOp, (g) 10Ni/CZOp, (h) 15Ni/CZOp and (i) 25Ni/CZOp.	34
4.2	H <sub>2</sub> -TPR profiles for supports with a heating rate of 10 °C/min, a reducing gas containing 5 % H <sub>2</sub> in Ar with a flow rate of 50 ml/min. : (a) CZO, (b) 5Ni/CZOi, (c) 10Ni/CZOi, (d) 15Ni/CZOi, (e) 25Ni/CZOi, (f) 5Ni/CZOp, (g) 10Ni/CZOp, (h) 15Ni/CZOp and (i) 25Ni/CZOp.	37
4.3	SEM images of a) CZO, b) 15Ni/CZOi, and c) 15Ni/CZOp .	38
4.4	Methane conversion at different temperature over the investigated catalyst using CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1 and GHSV = 53000 h <sup>-1</sup> .	40
4.5	CO <sub>2</sub> yield at various temperature over the investigated catalyst using CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1 and GHSV = 53000 h <sup>-1</sup> .	41

FIGURE	PAGE
4.6 H <sub>2</sub> yield at various temperature over the investigated catalyst using CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1 and GHSV = 53000 h <sup>-1</sup> .	41
4.7 CO yield at various temperature over the investigated catalyst using CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1 and GHSV = 53000 h <sup>-1</sup> .	42
4.8 Methane conversion and Metal Surface Area as a function of Ni loading at 750 °C using CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1 and GHSV = 53000 h <sup>-1</sup> .	42
4.9 H <sub>2</sub> /CO ratio at various temperature over the investigated catalyst using CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1 and GHSV = 53000 h <sup>-1</sup> .	43
4.10 CH <sub>4</sub> conversion at various temperature over the investigated catalyst using CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1 and 4:1 and GHSV = 53000 h <sup>-1</sup> .	43
4.11 H <sub>2</sub> yield at various temperature over the investigated catalyst using CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1 and 4:1 and GHSV = 53000 h <sup>-1</sup> .	43
4.12 CO yield at various temperature over the investigated catalyst using CH <sub>4</sub> /O <sub>2</sub> ratio = 2:1 and 4:1 and GHSV = 53000 h <sup>-1</sup> .	45
4.13 CH <sub>4</sub> conversion as a function of time over the catalysts investigated at 750 °C (CH <sub>4</sub> /O <sub>2</sub> ratio of 2.0 and 4.0, GHSV=53000 h <sup>-1</sup> ).	46
4.14 H <sub>2</sub> selectivity as a function of time over the catalysts investigated at 750 °C (CH <sub>4</sub> /O <sub>2</sub> ratio of 2.0 and 4.0, GHSV=53000 h <sup>-1</sup> ).	46
4.15 CO and CO <sub>2</sub> selectivity as a function of time over the catalysts investigated at 750 °C (CH <sub>4</sub> /O <sub>2</sub> ratio of 2.0 and 4.0, GHSV=53000 h <sup>-1</sup> )	47

FIGURE		PAGE
4.16	H <sub>2</sub> /CO ratio as a function of time over the catalysts investigated at 750 °C (CH <sub>4</sub> /O <sub>2</sub> ratio of 2.0 and 4.0, GHSV=53000 h <sup>-1</sup> ).	
	The TPO profile of catalysts after reaction at 750 °C	47
4.17	(CH <sub>4</sub> /O <sub>2</sub> ratio of 2.0 and 4.0, GHSV=53000 h <sup>-1</sup> ) an oxidizing gas containing 2% O <sub>2</sub> in He with a flow rate of 40 ml/min.	49
4.18	TEM images of spent catalysts after exposure to reaction at 750°C (CH <sub>4</sub> /O <sub>2</sub> ratio of 2:1, GHSV=53000 h <sup>-1</sup> ).	50
A1	Relationship between area and concentration of methane.	58
A2	Relationship between area and concentration of carbon dioxide.	59
A3	Relationship between area and concentration of hydrogen .	59
A4	Relationship between area and concentration of carbon monoxide.	60
A5	Relationship between area and concentration of oxygen.	60
A6	Relationship between area and concentration of nitrogen.	61
B1	Relationship between SP and flow rate of methane.	62
B2	Relationship between SP and flow rate of air.	62
B3	Relationship between SP and flow rate of helium.	63