

**CATALYTIC DEHYDROXYLATION OF GLYCEROL TO PROPYLENE
GLYCOL OVER COPPER ZINC OXIDE/MAGNESIUM OXIDE
CATALYSTS: EFFECT OF CATALYST PREPARATION**

Siwawut Paengsri

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
2014

I28369798

Thesis Title: Catalytic Dehydroxylation of Glycerol to Propylene Glycol over Copper Zinc Oxide/Magnesium Oxide Catalysts: Effect of Catalyst Preparation

By: Siwawut Paengsri

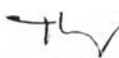
Program: Petroleum Technology

Thesis Advisors: Asst. Prof. Siriporn Jongpatiwut
Assoc. Prof. Thirasak Rirksomboon

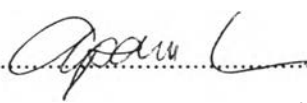
Accepted by The Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

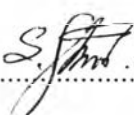

..... College Dean
(Asst. Prof. Pomthong Malakul)

Thesis Committee:


.....
(Asst. Prof. Siriporn Jongpatiwut)


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


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


.....
(Dr. Sutheerawat Samingprai)

ABSTRACT

5573033063: Petroleum Technology Program

Siwawut Paengsri: Catalytic Dehydroxylation of Glycerol to Propylene Glycol over Copper Zinc Oxide/Magnesium Oxide Catalysts: Effect of Catalyst Preparation.

Thesis Advisors: Asst. Prof. Siriporn Jongpatiwut, and Assoc. Prof. Thirasak Rirksomboon 71 pp.

Keywords: Cu-ZnO/ Dehydroxylation/ Glycerol/ Propylene glycol

The present study focused on improving the stability of the catalyst in the presence of an alkali for dehydroxylation of glycerol to propylene glycol. The CuZnO supported on the basic support MgO was investigated in this work. The catalysts were prepared by two different methods—incipient wetness impregnation (IWI) and co-precipitation (COP). Catalytic activity was tested in a packed-bed reactor at 250 °C and 500 psig under hydrogen atmosphere. The co-precipitated catalyst showed higher glycerol conversion and propylene glycol selectivity than the impregnated catalyst. This might be due to the well dispersed and uniform CuO grains in the co-precipitated catalyst. Moreover, AAS results indicated that the co-precipitated catalyst had higher amounts of active sites (Cu) than the impregnated catalyst. The effect of NaOH containing feedstock was also investigated. The results showed that NaOH did not affect stability of the CuZnO/MgO catalysts as compared to the previously investigated CuZnO/Al₂O₃ catalyst. Moreover, it also enhanced the basicity of the catalyst in the presence of MgO and led to higher catalytic activity. Interestingly, the glycerol conversion of the regenerated CuZnO/MgO catalyst prepared by COP was as high as that of the fresh catalyst.

บทคัดย่อ

ศิววุฒิ แพงศรี : การผลิตโพรพิลีนไกลคอลจากกลีเซอรอล โดยตัวเร่งปฏิกิริยาทองแดง และสังกะสีออกไซด์บนแมกนีเซียมออกไซด์: ผลกระทบจากวิธีเตรียมตัวเร่งปฏิกิริยา (Catalytic dehydroxylation of Glycerol to Propylene Glycol over Copper Zinc Oxide/Magnesium Oxide Catalysts: Effect of Catalyst Preparation) อาจารย์ที่ปรึกษา: ผศ. ดร. ศิริพร จงผาดิวุฒิ และ รศ. ดร. ธีรศักดิ์ ฤกษ์สมบูรณ์ 71 หน้า

จุดมุ่งหมายของงานวิจัยนี้ คือ เพื่อปรับปรุงความเสถียรของตัวเร่งปฏิกิริยาต่อระบบที่มีโลหะหมู่ที่หนึ่ง (NaOH) เป็นองค์ประกอบสำหรับการผลิตโพรพิลีนไกลคอลจากกลีเซอรอล ดังนั้นงานวิจัยนี้จึงเลือกที่จะศึกษาตัวเร่งปฏิกิริยาที่มีสมบัติความเป็นเบส ซึ่งก็คือ ทองแดงและสังกะสีออกไซด์บนแมกนีเซียมออกไซด์ (CuZnO/MgO) โดยเตรียมตัวเร่งปฏิกิริยาด้วยเทคนิคที่แตกต่างกัน คือ วิธีเอ็บซุ่ม (incipient wetness impregnation) วิธีการตกตะกอนร่วม (co-precipitation) ตัวเร่งปฏิกิริยาที่เตรียมถูกนำไปทดสอบประสิทธิภาพของการทำปฏิกิริยาในเครื่องปฏิกรณ์แบบต่อเนื่องชนิดเบดนิ่งที่อุณหภูมิ 250 องศาเซลเซียส ภายใต้ความดันของไฮโดรเจนที่ 500 ปอนด์ต่อตารางนิ้ว ผลการทดลองแสดงให้เห็นว่าตัวเร่งปฏิกิริยาที่เตรียมด้วยวิธีตกตะกอนร่วมให้สัดส่วนการทำปฏิกิริยาของกลีเซอรอลและการเลือกเกิดโพรพิลีนไกลคอลมากกว่าตัวเร่งปฏิกิริยาที่เตรียมด้วยวิธีเอ็บซุ่ม ซึ่งผลจากการทดสอบโดยเทคนิค TPR พบว่าตัวเร่งปฏิกิริยาที่เตรียมด้วยวิธีตกตะกอนร่วมนั้น มีขนาดที่เท่ากันและมีการกระจายตัวของตัวเร่งปฏิกิริยาดีกว่าการเตรียมตัวเร่งปฏิกิริยาแบบเอ็บซุ่ม นอกจากนี้ผลการทดสอบตัวเร่งปฏิกิริยาจากเครื่อง AAS ยังแสดงให้เห็นว่า การเตรียมตัวเร่งปฏิกิริยาด้วยวิธีตกตะกอนร่วม มีปริมาณตัวกระตุ้นปฏิกิริยา (ทองแดง) ที่สูงกว่าตัวเร่งปฏิกิริยาที่เตรียมด้วยวิธีเอ็บซุ่มอีกด้วย และเมื่อศึกษาผลกระทบจากโลหะหมู่ที่หนึ่งพบว่า โลหะหมู่ที่หนึ่งที่เติมเข้าไปในสารตั้งต้นนั้น ไม่ส่งผลกระทบต่อความเสถียรของตัวเร่งปฏิกิริยา อีกทั้งยังช่วยเพิ่มสมรรถนะความเป็นด่างให้กับแมกนีเซียมออกไซด์ ส่งผลให้ตัวเร่งปฏิกิริยามีประสิทธิภาพมากขึ้น และนอกจากนี้ยังพบว่า เมื่อนำตัวเร่งปฏิกิริยาทองแดงและสังกะสีออกไซด์บนแมกนีเซียมออกไซด์ที่เตรียมด้วยวิธีตกตะกอนร่วมกลับมาใช้ใหม่ จะให้สัดส่วนการทำปฏิกิริยาของกลีเซอรอล ดีเทียบเท่ากับตัวเร่งปฏิกิริยาดั้งเดิม

ACKNOWLEDGEMENTS

This work would not have been possible if there is no the assistance of the following individuals.

First of all, I greatly appreciate Asst.Prof. Siriporn Jongpatiwut and Assoc. Prof. Thirasak Rirksomboon, my thesis advisors, for providing invaluable recommendations, creative comments, and kindly support throughtout the course of this research work.

I would like to thank Assoc. Prof. Apanee Luengnaruemitchai and Dr. Sutteerawat Samingprai for their kind advice and for being my thesis committee.

The author is grateful for the scholarship and for the research funding of the thesis work provided by The Petroleum and Petrochemical College, and Center of Excellence on Petrochemical and Materials Technology, Chulalongkorn University, Thailand

Special appreciation goes to all of The Petroleum and Petrochemical College's staff who help in various aspects, especially the research affairs staff who kindly help with the analytical instruments used in this work.

For my friends at PPC, I would like to give special thanks for their friendly support, encouragement, cheerfulness, and assistance. Without them, two years in the college will be meaningless for me. I had the most enjoyable time working with all of them.

Finally, I wish to thank my family for moral support, understanding, and always give me greatest love, willpower and financial support until this study completion.

TABLE OF CONTENTS

CHAPTER	PAGE
Title Page	i
Acceptance Pages	ii
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Tables	ix
List of Figures	x
I INTRODUCTION	1
II BACKGROUND AND LITERATURE REVIEW	
2.1 Properties of Glycerol	3
2.1.1 Types of Glycerol	4
2.1.2 Industrial Production of Glycerol	5
2.1.3 Commodity Chemicals Derived from Glycerol	6
2.2 From Glycerol to Propanediols	7
2.2.1 Production of 1,2-Propanediol from Glycerol	9
2.3 The Mechanism of Glycerol Hydrogenolysis to 1,2-PDO	21
2.4 Preparation of Supported Metal Catalysts	22
2.4.1 Impregnation	23
2.4.2 Co-precipitation	23
2.4.3 Sol-Gel Method	24
2.5 Deactivation and Regeneration	27
2.5.1 Poisoning	29

CHAPTER	PAGE
2.5.2 Fouling	31
2.5.3 Thermal Degradation	32
2.5.4 Mechanical Deactivation	35
2.5.5 Corrosion/Leaching	35
III EXPERIMENTAL	
3.1 Materials and Equipment	36
3.1.1 Equipment	36
3.1.2 Chemicals	36
3.2 Experimental Procedure	37
3.2.1 Catalyst Preparation	37
3.2.2 Catalyst Characterization	38
3.3 Feedstock Characterization	40
3.4 Catalytic Activity Measurement	41
3.4.1 Dehydroxylation of Glycerol	41
3.4.2 Product Analysis	42
3.4.3 Comparison of Catalytic Performance	43
3.5 Catalyst Regeneration	43
IV RESULTS AND DISCUSSION	
4.1 Fresh Catalyst Characterization	44
4.2 Catalytic Activity Testing	48
4.2.1 Effect of Catalyst Preparation	48
4.2.2 Effect of NaOH in Feedstock	52
4.3 Catalyst Stability Testing and Catalyst Regeneration	59
4.3.1 Catalytic Stability Testing	59
4.3.2 Catalyst Regeneration	61

CHAPTER	PAGE
V CONCLUSIONS AND RECOMMENDATIONS	
5.1 Conclusions	71
5.2 Recommendations	71
REFERENCE	72
APPENDIX	76
CURRICULAM VITAE	79

LIST OF TABLES

TABLE		PAGE
2.1	Physicochemical properties of glycerol at 20 °C	4
2.2	Specification of glycerol feedstocks	5
2.3	Summary of conversion of glycerol, yield and selectivity of propylene glycol from glycerol over various metal catalysts	13
2.4	Mechanisms of catalyst deactivation	28
2.5	Common poisons classified according to chemical structure	30
2.6	Effects of important reaction and catalyst variables on sintering rates of supported metals based on GPLE data	34
4.1	BET surface area, pore volume, and pore size distribution of the support and the catalysts	45
4.2	The actual and expected metal loading of the catalysts	46
4.3	Concentration of alkali on feedstock, product, and the spent co-precipitated CuZnO/MgO catalysts analyzed by AAS	67
A1	Retention times and response factors of standard chemicals analyzed by a GC/FID (Agilent GC 6890)	78

LIST OF FIGURES

FIGURE		PAGE
2.1	Structure of glycerol.	4
2.2	Overall reaction for production of biodiesel through vegetable oil methanolysis.	5
2.3	Commodity chemicals from glycerol.	6
2.4	Different routes to 1,3-propanediol starting from ethene, propene or glycerol.	9
2.5	Comparison of the reaction routes to 1,2-propanediol starting from propene or glycerol.	10
2.6	Reaction mechanism for conversion of glycerol to propylene glycol.	11
2.7	Possible reaction routes for catalytic hydrogenolysis of glycerol.	12
2.8	Proposed reaction mechanism for conversion of glycerol to propylene glycol.	14
2.9	Reaction scheme of glycerol hydrogenolysis and degradation reactions.	15
2.10	Proposed bifunctional glycerol hydrogenolysis reaction pathways:	16
2.11	Reaction route for the hydrogenolysis of glycerol to glycols.	17
2.12	Proposed reaction for conversion of glycerol to 1,2-PDO.	18
2.13	Reaction scheme of glycerol hydrogenolysis and degradation reactions.	19
2.14	Hydrogenolysis of glycerol to 1,2-PDO.	21
2.15	Schematic diagram showing the various steps of a sol-gel process.	26
2.16	Time scale of deactivation of various catalytic processes.	27

FIGURE	PAGE	
2.17	Major types of deactivation in heterogeneous catalysis.	29
2.18	Conceptual model of poisoning by sulfur atoms of a metal surface during ethylene hydrogenation.	29
2.19	Three kinds of poisoning behavior in terms of normalized activity vs. normalized poison concentration.	31
2.20	Two conceptual models for crystallite growth due to sintering by (A) atomic migration or (B) crystallite migration.	32
3.1	Flow diagram of the system used for dehydroxylation of glycerol.	41
4.1	XRD patterns of the fresh CuZnO/MgO catalysts with different preparation methods.	46
4.2	Temperature programmed reduction (TPR) profiles of the fresh CuZnO/MgO catalysts with different preparation methods.	47
4.3	Plot of (a) Glycerol Conversion and (b) PG Selectivity (c) Acetol Selectivity (d) EG Selectivity as a function of time on stream over the CuZnO/MgO catalysts prepared by different methods. (Reaction conditions: 80 wt.% glycerol feed, 250 °C, 500 psig, H ₂ :glycerol = 4:1, and WHSV = 3.77 h ⁻¹).	48
4.4	The glycerol conversion mechanism (Dasari <i>et al.</i> , 2005).	50
4.5	TPO profiles of the spent CuZnO/MgO catalysts with different preparation methods after 12 h TOS (Reaction conditions: 80 wt.% glycerol feed, 250 °C, 500 psig, H ₂ :glycerol = 4:1, and WHSV = 3.77 h ⁻¹).	51

FIGURE		PAGE
4.6	Plot of (a) Glycerol Conversion and (b) PG Selectivity (c) Acetol Selectivity (d) EG Selectivity as a function of time on stream over the CuZnO based catalysts prepared by different methods. (Reaction conditions: 80 wt.% glycerol feed, 250 °C, 500 psig, H ₂ :glycerol = 4:1, and WHSV = 3.77 h ⁻¹).	53
4.7	TPO profiles of CuZnO/MgO catalysts prepared by different methods on 0.1% NaOH impurities in the glycerol feedstock after 12 h TOS (Reaction conditions: 80 wt.% glycerol feed, 250 °C, 500 psig, H ₂ :glycerol = 4:1, and WHSV = 3.77 h ⁻¹).	55
4.8	Cu (a) and Zn (b) K-edge XANES spectra of the co-precipitated CuZnO/MgO, CuZnO catalysts and reference compounds.	56
4.9	Fourier transform of k ³ -weighed Cu (a) and Zn (b) K-edge EXAFS spectra of the co-precipitated CuZnO/MgO, CuZnO catalysts and reference compounds.	57
4.10	Schematic model for the Cu particles on Zn support, surface alloying, and bulk alloy formation: (a) under oxidation conditions (b) under more reducing conditions (c) strong reducing conditions (d) severe reducing conditions.	59
4.11	Plot of (a) Glycerol Conversion and (b) PG Selectivity as a function of time on stream over the CuZnO/MgO catalysts prepared by co-precipitation methods. (Reaction conditions: 80 wt.% glycerol feed, 250 °C, 500 psig, H ₂ :glycerol = 4:1, and WHSV = 3.77 h ⁻¹).	61

FIGURE		PAGE
4.12	Plot of (a) Glycerol Conversion and (b) PG Selectivity (c) Acetol Selectivity (b) EG Selectivity as a function of time on stream over the CuZnO/MgO catalysts prepared by co-precipitation methods. (Reaction conditions: 80 wt.% glycerol feed, 250 °C, 500 psig, H ₂ :glycerol = 4:1, and WHSV = 3.77 h ⁻¹).	62
4.13	Plot of (a) Glycerol Conversion and (b) PG Selectivity (b) Acetol Selectivity (b) EG Selectivity as a function of time on stream over the CuZnO/MgO catalysts prepared by co-precipitation methods. (Reaction conditions: 80 wt.% glycerol feed, 250 °C, 500 psig, H ₂ :glycerol = 4:1, and WHSV = 3.77 h ⁻¹).	65
4.14	TPO profiles of the spent CuZnO/MgO catalysts after 12 h TOS (a) pure glycerol feedstock (b) 0.1% NaOH containing glycerol feedstock.	68
4.15	XRD patterns of the fresh and regenerate co-precipitated CuZnO/MgO catalysts after 12 h TOS.	69
4.16	Temperature programmed reduction (TPR) profiles of the fresh and regenerate co-precipitated CuZnO/MgO catalysts.	70
A1	Chromatogram of CuZnO/MgO (IWI) on 3 h TOS. analyzed by a GC/FID (Agilent GC 6890).	76
A2	Chromatogram of CuZnO/MgO (COP) on 3 h TOS. analyzed by a GC/FID (Agilent GC 6890).	77
A3	Chromatogram of CuZnO (COP) on 3 h TOS. analyzed by a GC/FID (Agilent GC 6890).	77