

**UNIVERSITI TEKNOLOGI MARA**

**PREPARATION OF Cu-Zn BASED  
CATALYSTS VIA ULTRASONIC  
SPRAY PRECIPITATION METHOD  
FOR METHANOL SYNTHESIS**

**MUHAMMAD ZAHIRUDDIN BIN RAMLI**

Thesis submitted in fulfillment  
of the requirements for the degree of  
**Doctor of Philosophy**  
**(Chemical Engineering)**

**Faculty of Chemical Engineering**

**May 2019**

## AUTHOR'S DECLARATION

I declare that the work in this thesis was carried out in accordance with the regulations of Universiti Teknologi MARA. It is original and is the results of my own work, unless otherwise indicated or acknowledged as referenced work. This thesis has not been submitted to any other academic institution or non-academic institution for any degree or qualification.

I, hereby, acknowledge that I have been supplied with the Academic Rules and Regulations for Post Graduate, Universiti Teknologi MARA, regulating the conduct of my study and research.

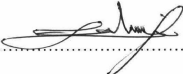
Name of Student : Muhammad Zahiruddin Bin Ramli

Student I.D. No. : 2014852456

Programme : Doctor of Philosophy – EH950

Faculty : Chemical Engineering

Thesis : Preparation of Cu-Zn Based Catalysts via Ultrasonic Spray Precipitation Method for Methanol Synthesis

Signature of Student :  .....

Date : May 2019

## ABSTRACT

The potential of various Cu-Zn-based catalysts in a form of non-hybrid (triple and quadruple metallic) as well as hybrid (multi-metallic with ZSM-5 zeolite) catalyst formulation are being explored for converting CO<sub>2</sub> into methanol. The application of the new preparation method, namely, Ultrasonic Spray Precipitation (USP) is advantageous in improving physicochemical properties of catalysts. This is based on the fact that the spraying action generates microdroplets of catalyst precursors, providing higher surface area contact during the precipitation stage. Meanwhile, the incorporation of an ultrasonic effect can physically alter the surface morphology of the catalyst. This produces much finer and more uniform particles, which also improve the overall physicochemical characteristics. Study on the effect of different preparation methods have shown that the USP-prepared catalyst outperformed the conventionally prepared (CP) catalyst for CO<sub>2</sub> conversion by 20.9% and also improved the methanol selectivity and yield by 2.7% and 27%, respectively. In terms of the elemental composition aspect, the quadruple metallic formulation (CZAZ catalyst) has shown an enhanced characteristics, particularly in reducibility, Cu metal dispersion and total basic sites. These qualities have translated into the highest CO<sub>2</sub> conversion at 20.1% as well as methanol yield at 0.45 g.ml<sup>-1</sup>.h<sup>-1</sup> in CO<sub>2</sub> hydrogenation reaction. On the other hand, by adding zeolite (ZSM-5) in the multi-metallic component in a form of hybrid-catalyst formulation, it improves characteristics such as particle size distribution and its uniformity, bulk surface area and total acid sites, which have reflected the catalyst selectivity, especially in reducing the undesired by-product of CO. These results had proven the role of zeolite in retarding the reverse water gas shift (RWGS) reaction had instead facilitated the consecutive third reaction to shift the equilibrium back into the direction of methanol synthesis and other related hydrocarbons. The influence of reaction condition of temperature and pressure has also aligned with the thermodynamics theoretical calculations. Both non-hybrid (CZAZ) and hybrid (CZAZ-Z) catalysts have exhibited an identical trend in relation to temperature and pressure variations during CO<sub>2</sub> hydrogenation reaction at a fixed gas hourly space velocity (GHSV). The CO<sub>2</sub> conversion and methanol yield increased significantly with increasing pressure but decreased strongly at temperature beyond 520 K. This trend is in-line with the thermodynamic principle that methanol synthesis via CO<sub>2</sub> hydrogenation reaction is exothermic, thus favouring high pressure and low temperature condition. As a conclusion, application of the USP method during preparation stage has proven to enhance the overall physicochemical properties of Cu-Zn based catalysts. These enhancements have promoted better catalytic performance of the catalysts in methanol synthesis with improved CO<sub>2</sub> conversion, methanol selectivity and yield as compared to those of conventional method.

# TABLE OF CONTENTS

	<b>Page</b>
<b>CONFIRMATION BY PANEL OF EXAMINERS</b>	<b>ii</b>
<b>AUTHOR'S DECLARATION</b>	<b>iii</b>
<b>ABSTRACT</b>	<b>iv</b>
<b>ACKNOWLEDGEMENT</b>	<b>v</b>
<b>TABLE OF CONTENTS</b>	<b>vi</b>
<b>LIST OF TABLES</b>	<b>ix</b>
<b>LIST OF FIGURES</b>	<b>x</b>
<b>LIST OF PLATES</b>	<b>xiii</b>
<b>LIST OF SYMBOLS</b>	<b>xiv</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xv</b>
<b>LIST OF NOMENCLATURE</b>	<b>xvii</b>
<b>CHAPTER ONE: INTRODUCTION</b>	<b>1</b>
1.1 Research Background	1
1.2 Problem Statement	4
1.3 Research Hypothesis	5
1.4 Objectives	6
1.5 Scope and Limitation of Study	6
1.6 Significance of Study	7
1.7 Thesis Structure	7
<b>CHAPTER TWO: LITERATURE REVIEW</b>	<b>10</b>
2.1 Introduction	10
2.2 CO <sub>2</sub> Potential	13
2.3 Reactivity of CO <sub>2</sub>	15
2.4 Hydrogenation Reaction	17
2.4.1 Methanol Synthesis Via CO Hydrogenation	19
2.4.2 Methanol Synthesis Via CO <sub>2</sub> Hydrogenation	20
2.5 Catalyst for CO <sub>2</sub> Hydrogenation	21

2.5.1	Reaction Mechanism and Active Sites	26
2.5.2	Role of Basicity and Acidity of Catalysts	30
2.5.3	Physicochemical Properties of Catalysts	31
	2.5.3.1 <i>Surface Area and Porosity</i>	31
	2.5.3.2 <i>Structure, Morphology and Particle Properties</i>	32
	2.5.3.3 <i>Chemisorption Properties</i>	34
2.5.4	Catalyst Deactivation	40
2.6	Catalyst Preparation Techniques	42
	2.6.1 Dropwise-wise Titration	45
	2.6.2 Spraying Techniques	48
	2.6.3 Ultrasonic Influence on Crystallisation	50
2.7	Reaction Conditions	53
2.8	Literature Review Summary	58
 <b>CHAPTER THREE: RESEARCH METHODOLOGY</b>		<b>59</b>
3.1	Introduction	59
	3.1.1 Catalyst Formulation	59
	3.1.2 Catalysts Preparation	60
3.2	Characterization of Catalysts	63
	3.2.1 BET Surface Area	63
	3.2.2 Scanning Electron Microscopy (SEM)	64
	3.2.3 Particle Size Distribution (PSD)	65
	3.2.4 X-ray Diffraction (XRD)	66
	3.2.5 Temperature Programmed Reduction (TPR)	67
	3.2.6 Temperature Programmed Desorption (TPD)	68
	3.2.6.1 <i>TPD – H<sub>2</sub></i>	69
	3.2.6.2 <i>TPD – CO<sub>2</sub></i>	69
	3.2.6.3 <i>TPD – NH<sub>3</sub></i>	69
	3.2.7 Cu Surface Area and Dispersion	69
3.3	Catalyst Testing	70
	3.3.1 Reaction Parameter Setup	71
	3.3.2 Gas Chromatography (GC) Analysis	73