UNIVERSITI TEKNOLOGI MARA

# SYNTHESIS OF SILICA SUPPORTED BIMETALLIC OXIDE (NiCo) CATALYST FOR $CO_2$ METHANATION

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

**Faculty of Chemical Engineering**

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## CONFIRMATION BY PANEL OF EXAMINERS

I certify that a panel of examiners has met on 17th October 2018 to conduct the final examination of Siti Aminah binti Md Ali on her **Doctor of Philosophy** thesis entitled "Synthesis of Silica Supported Bimetallic Oxide (NiCo) Catalyst For $CO_2$ Methanation" in accordance with Universiti Teknologi MARA Act 1976 (Akta 173). The Panel of Examiners recommends that the student be awarded the relevant degree. The panel of Examiners was as follows:

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# ABSTRACT

Methane utilisation has been incentivised in recent years as it is less destructive to the environment than other fossil fuels. This research aims to synthesize and optimize nickel based catalysts for the methanation of carbon dioxide to produce methane. The catalysts were prepared in several series designated as 100Ni, 100Co, 90Ni10Co, 10Ni90Co, 100Ni/$SiO_2$, 100Co/$SiO_2$, 90Ni10Co/$SiO_2$, 10Ni90Co/$SiO_2$, 80Ni20Co/$SiO_2$, 60Ni40Co/$SiO_2$, 50Ni50Co/$SiO_2$, 40Ni60Co/$SiO_2$ and 20Ni80Co/$SiO_2$. The supported Ni-Co catalysts were prepared via a reverse co-precipitation method followed by incipient wetness impregnation method. The supported catalyst was synthesised using tetraethylorthosilicate (TEOS) at various metal ratios and calcination over a range of temperatures (300-500°C). Several characterization techniques were applied to understand the chemical and physical properties of the catalysts in order to optimise the catalyst synthesis process. These techniques included $N_2$ adsorption-desorption (BET), Temperature Programmed Reduction (TPR-$H_2$), X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Thermogravimetric Analysis (TGA) and Scanning Electron Microscopy-Energy Dispersive X-ray (SEM-EDX). The highest $CO_2$ conversion obtained using standard reactor parameters was 49.28% (reaction temperature (350°C), GHSV (30,000 mL/$g_{cat}$.h), reactant ratio $H_2$: $CO_2$ (4:1) for the 80Ni20Co/$SiO_2$ bimetallic catalyst calcined at 500°C. The catalytic performance of the 80Ni20Co/$SiO_2$ catalyst was further optimised in a microactivity reactor where process variables such as temperature (300-500°C), GHSV (15,000 - 75,000 mL/$g_{cat}$.h) and ratio of reactants of $H_2$: $CO_2$ (2:1-8:1) were varied. The highest $CO_2$ conversion obtained was 70.3% at a reaction condition of temperature 400°C, GHSV 15,000 mL/$g_{cat}$.h and a $H_2$: $CO_2$ reactant ratio of 4:1. The stability of the 80Ni20Co/$SiO_2$ catalyst was also assessed. The catalytic activity was stable across the entirety experiment and produced a $CO_2$ conversion of 67% for 120h at which time testing ceased. The kinetic study discovered that the $CH_4$ and CO formation were described by the zero order reaction with the activation energy of 45.09 and 54.47 kJ/mol respectively. The study concludes that the heterogeneous nickel-based catalyst synthesized successfully catalyzed the methanation of $CO_2$ to produce methane at moderate operating conditions.

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# CHAPTER ONE
# INTRODUCTION

## 1.1 Environmental Issue on $CO_2$ Methanation

Greenhouse gases trap that heat in the atmosphere by absorbing infrared radiation. The globe has warmed at an unprecedented rate over the last 150 years due to the accumulation of greenhouse gases in the atmosphere that have been produced from anthropogenic sources (US EPA, 2016). Records of U.S greenhouse gas emissions from 2016 (Figure 1.1) shows that the highest emission is contributed by carbon dioxide (81%), followed by methane (10%), nitrous oxide (6%) and other fluorinated gases (3%).

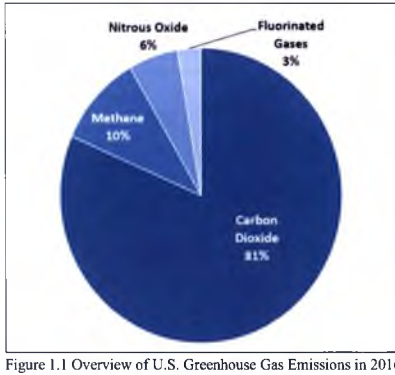


Figure 1.1 Overview of U.S. Greenhouse Gas Emissions in 2016 (US EPA, 2016)

The Global Warming Potential (GWP) of greenhouse gases is very important in determining how much heat will be absorbed by one ton of a gas over a given period of time, relative to one ton of a reference gas (carbon dioxide). Although it has a relatively low GWP, $CO_2$ contributes to the majority of anthropogenic global warming due to its abundance and its long atmospheric lifetime. $CH_4$ has an atmospheric lifetime of