

**CARBON DIOXIDE REFORMING OF METHANE OVER COBALT
SUPPORTED ON ACTIVATED CARBON CATALYSTS FOR SYNGAS
PRODUCTION**

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SUPPORTED ON ACTIVATED CARBON CATALYSTS FOR SYNGAS
PRODUCTION

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ABSTRACT

Carbon dioxide reforming of methane (CDRM) utilizes two major greenhouse gases (GHG) of methane (CH_4) and carbon dioxide (CO_2) for syngas production. The transformation of GHG satisfies the requirements of synthesis processes and is a great interest for reducing gas emission. In this work, cobalt catalysts were synthesized by wet impregnation method onto oil palm shell activated carbon (OPS-AC) and zeolite socony mobil-5 (ZSM-5). The characterizations of supported cobalt catalysts were performed by elemental analysis, Brunauer-Emmett-Teller, thermogravimetric analysis, x-ray diffraction, temperature programmed reduction, temperature programmed desorption, scanning electron microscope, field emission scanning electron microscopy and transmission electron microscopy analysis. In comparison of both supported cobalt catalysts, OPS-AC supported catalysts exhibited superiority in physical and chemical properties than that of ZSM-5. Four manipulated parameters of the micro reactor system namely operating pressure, operating temperature, feedstock ratio of CH_4/CO_2 and gas hourly space velocity (GHSV) were investigated. In catalyst screenings, cobalt 14wt% of OPS-AC (OPS-AC(14)) gave better catalytic performance than cobalt 14wt% of ZSM-5 (ZSM-5 (14)) with 15 % conversion and 60 % yield at 1023 K. The feedstock gases and products of syngas were analyzed by gas chromatography with thermal conductivity detector for yield of hydrogen (H_2) and carbon monoxide (CO) and conversion (CH_4 and CO_2). Then, activity testings of OPS-AC(14) showed high temperature at 1173 K which favoured the conversion (CH_4 , 15 %; CO_2 , 12 %) and yield (H_2 , 80 %; CO, 47 %). However, conversion and yield disfavoured at high pressure of 7 bar and less effect by CH_4/CO_2 ratio and GHSV. Multi-responses of both yields (H_2 and CO) were optimized at 903 °C, 0.88 bar, 1.31 CH_4/CO_2 and 4488 mL/h.g-catalyst for a global optimum value by desirability function analysis. Kinetics study of CDRM was performed for OPS-AC(14) using a power law, Arrhenius plot and equation. The reaction orders of CH_4 and CO_2 were 0.92 and 0.88, respectively which are close to the first order. The average activation energy of CO_2 was lower (66.0 kJ/mol) than that of CH_4 (77.3 kJ/mol). The potential side reactions were graphically plotted using Mathematica.

ABSTRAK

Pembentukan semula metana daripada karbon dioksida (CDRM) menggunakan dua gas utama rumah hijau (GHG) iaitu metana (CH_4) dan karbon dioksida (CO_2) bagi penghasilan singas. Transformasi GHG kepada singas adalah sememangnya memenuhi keperluan proses sintesis dan juga menarik minat dalam menyokong mengurangkan pelepasan gas. Dalam kajian ini, pemangkin kobalt disintesis melalui kaedah impregnasi basah ke atas karbon teraktif tempurung kelapa sawit (OPS-AC) dan zeolit *socony mobil-5* (ZSM-5). Pencirian pemangkin kobalt tersokong dijalankan melalui analisis unsur, Brunauer-Emmett-Teller, analisis termogravimetri, pembelauan sinar-x, penurunan berprogram suhu, penyahjerapan berprogram suhu, mikroskop elektron pengimbas, mikroskop elektron pengimbas pancaran medan dan mikroskop elektron penghantaran. Dalam perbandingan bagi kedua-dua pemangkin kobalt tersokong, OPS-AC mempamerkan prestasi yang lebih baik disebabkan ciri-ciri unggul secara fizikal dan kimia pemangkin tersebut berbanding ZSM-5. Empat parameter yang dimanipulasikan di dalam sistem reaktor mikro seperti tekanan operasi, suhu operasi, nisbah bahan suapan CH_4/CO_2 dan halaju ruang gas setiap jam (GHSV) telah disiasat. Dalam penyaringan mangkin, 14wt% kobalt OPS-AC (OPS-AC(14)) telah memberikan prestasi pemangkin yang lebih unggul daripada 14wt% kobalt ZSM-5 (ZSM-5(14)) dengan 15 % penukaran dan 60 % hasil pada 1023 K. Gas suapan dan produk singas dianalisis menggunakan kromatografi gas dengan pengesan kekonduksian terma untuk hasil hidrogen (H_2) dan karbon monoksida (CO) dan penukaran (CH_4 dan CO_2). Kemudian, pengujian aktiviti pemangkin terhadap OPS-AC(14) menunjukkan suhu tinggi pada 1173 K yang mengutamakan penukaran (CH_4 , 15 %; CO_2 , 12 %) dan hasil (H_2 , 80 %; CO, 47 %). Walau bagaimanapun, penukaran dan hasil berkurangan pada tekanan tinggi sebanyak 7 bar dan kurang berkesan pada nisbah CH_4/CO_2 dan GHSV. Gerak balas berbilang bagi kedua-dua hasil (H_2 dan CO) dioptimumkan pada 903 °C, 0.88 bar, 1.31 CH_4/CO_2 dan 4488 mL/h.g-pemangkin bagi nilai optimum global menggunakan analisis fungsi kebolehinan. Kajian kinetik CDRM telah dijalankan untuk OPS-AC(14) menggunakan hukum kuasa, persamaan dan plot Arrhenius. Kadar tindak balas bagi CH_4 dan CO_2 masing-masing adalah 0.92 dan 0.88 yang menghampiri ke tertib pertama. Tenaga pengaktifan purata untuk CO_2 adalah rendah (66.0 kJ/mol) berbanding dengan CH_4 (77.3 kJ/mol). Tindak balas sampingan yang berpotensi diplotkan secara grafik menggunakan Mathematica.

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LIST OF ABBREVIATIONS

A	-	Ampere
ANOVA	-	Analysis of variance
Bar(g)	-	Bar(gauge)
Cat	-	Catalyst
CBV8014	-	Product name of ZSM-5
CCRD		Central Composite Rotatable Design
CDRM	-	Carbon Dioxide Reforming of Methane
CH ₄	-	Methane
C-H	-	Single bond of carbon and hydrogen atom
cm ²	-	Centimetre square
cm ³	-	Centimetre cubic
CO	-	Carbon Monoxide
Cos	-	Cosine
Co	-	Cobalt
CO ₂	-	Carbon Dioxide
d	-	Desirability
D	-	Overall (global) desirability
DOE	-	Design of experiment
DFA	-	Desirability Function Analysis
E _a	-	Activation Energy
EsB	-	Energy Selective Backscattered
F		Flowrate
Fe	-	Iron
FESEM	-	Field Electron Scanning Electron Microscopy

FTS	-	Fischer-Tropsch Synthesis
FWHM	-	Full Width Half Maximum
g	-	gram
GC		Gas Chromatograph
GHSV	-	Gas Hourly Space Velocity
GHG	-	Greenhouse Gases
GWP	-	Global Warming Potential
h	-	hour
H ₂	-	Hydrogen molecule
H ₂ O	-	Water
HTFT	-	High-temperature Fischer Tropsch
IUPAC	-	International Union of Pure and Applied Chemistry
K	-	Kelvin
kJ	-	kilojoules
LHHW	-	Langmuir –Hinshelwood-Hougen –Watson
ln	-	Natural logarithm
LTB	-	Larger-The-Better
LTCDRM		Low Temperature CO ₂ Reforming of Methane
LTFT	-	Low-temperature Fischer Tropsch
LUT	-	LookUp Table
Min	-	Minute
mL	-	milliliter
MRS	-	Micro Reactor System
MS	-	Mean of Squares
MSDS	-	Material Safety Data Sheet
N	-	Nitrogen
ND	-	Not Detectable
NG	-	Natural Gas
N/A	-	Not Available
Ni	-	Nickel
N ₂	-	Nitrogen molecule
nm	-	nanometre

OPS-AC	-	Oil Palm Shell Activated Carbon
O ₂	-	Oxygen molecule
P	-	Pressure
pm	-	Picometre
Pt	-	Platinum
p/p ^o	-	Relative pressure
Rh	-	Rhodium
RSM	-	Response Surface Methodology
RT	-	Room Temperature
Ru	-	Ruthenium
RWGS	-	Reversed Water Gas Shift
S	-	Sulphur
SEM	-	Scanning Electron Microscopy
SS	-	Sum of Squares
SV	-	Space Velocity
TCD	-	Thermal Conductivity Detector
TEM	-	Transmission Electron Microscopy
TGA	-	Thermal Gravimetric Analysis
TPD	-	Temperature Programmed Desorption
TPR	-	Temperature Programmed Reduction
T	-	Temperature
T _H	-	Higher Temperature Region
T _L	-	Lower Temperature Region
T _p	-	Desorption peak temperature
V	-	Volt
Vol	-	Volume
WGS	-	Water Gas Shift
Wt	-	Weight
XRD	-	X-ray Diffractometer
ZSM-5	-	Zeolite socony mobile-5

LIST OF SYMBOLS

\geq	-	Greater than or equal to
A°	-	Amstrong
π	-	Pi
α	-	Alpha
β	-	Beta
γ	-	Gamma
Δ	-	Delta
θ	-	Theta
λ	-	Lamda
μ	-	micro
%	-	Percent
$^\circ\text{C}$	-	Degree celcius

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CHAPTER 1

INTRODUCTION

1.1 Research Background

A decreased reliance on petroleum is currently demanded worldwide. A forecast on a critical quantity of petroleum and the replenish process which takes many years have paid a great notice to the scientific communities and industries. Many researchers investigated the transformation of nonpetroleum feedstock such as natural gas (NG), coal and biomass into synthetic petroleum products such as gasoline or diesel. Fischer-Tropsch synthesis (FTS) reaction has received attention as one of the methods to synthesize high quality substituted diesel fuels because FTS provides liquid hydrocarbons with practically no S and N compounds. Furthermore, the demand for energy resources in the world has dramatically increased during the last two decades. Globally, the depletion of petroleum resources in the next 50–100 years has rekindled new research and developed interests to convert nonpetroleum feedstock such as NG, coal or biomass to fuels.

Gases of CO₂, CH₄, nitrous oxide and ozone are the primary green house gases (GHG) that contribute to the critical issue of global warming. Therefore, carbon dioxide reforming of methane (CDRM) produces synthesis gases (H₂ and CO), is one of the available methods to utilize two major GHG contributors (CO₂ and CH₄). In the last two decades, huge consideration has been paid on the catalytic

CDRM owing to both commercial and environmental reasons. In addition, CDRM results in a lower H_2/CO ratio if compared with steam reforming and partial oxidation of methane. Hence, lower H_2/CO ratio is favorable for certain chemical processes such as the synthesis of oxygenated compounds, FTS and hydroformylation reactions. In fact, CDRM process simultaneously consumes two important GHG (CO_2 and CH_4) and converts them into a valuable intermediate product of syngas. Therefore, the consumption of two gases in a single process has a great impact on environmental protection. Furthermore, CO_2 is less expensive and a clean oxidant agent for the replacement of pure O_2 . Consequently, the consumption of pure O_2 as an oxidant agent could be avoided or reduced. In short, converting these two GHG into valuable syngas may not only reduce the emission of CO_2 and CH_4 in the atmosphere but also satisfy the requirement of synthesis processes in chemical industries [1].

Emission control of CO_2 as one of GHG is the most demanding environmental policy faces by many countries [2]. One of the key contributors to climate change is due to the uncontrolled emission of CO_2 . Despite the unequivocal evidence that CO_2 is warming the globe, the growth in its emission is inexorable [3]. CH_4 as a primary constituent of NG is also considered as a relatively potent GHG [4]. Methane is more effective for entrapping heat in the atmosphere and its global warming potential (GWP) is approximately 20 times more prevailing at warming the atmosphere than CO_2 . Recently, many researchers have endeavoured to reduce the concentration of both GHG in the atmosphere through their utilization [5]. Therefore, CDRM has equally attracted much attention from both industrial and environmental sectors because of utilizing simultaneously two GHG [6-19] in the substitution of steam with CO_2 as reactant. Aside the advantages of using GHG, another great advantage of CDRM is the very low H_2/CO ratios emerging from the process. A theoretical ratio of H_2/CO lies closely in unity when H_2O is eliminated as a source of H_2 in the “steam” reforming process [20-27]. The unity of H_2/CO fits well for any additional process treatment of the produced syngas or as a feedstock in another chemical industry processes e.g. in FTS [28-35].

Noble metal catalysts were already employed in several industrial plants but soaring in the costs of catalytic materials have made the process less valuable and unprofitable. In order to overcome this drawback, proper selection of appropriate metals is one of the major factors in CDRM research. Thus, the metal catalysts can catalyze CDRM with particular requirements such as resistance to deactivation at high-temperature profiles. The requirement at high temperature is owing to the endothermic of CH₄ conversions and also due to high activation energy (439 kJmol⁻¹) of a strong C-H bond. Therefore, this severe operating at high temperature exacerbates the poor resistance of catalytic materials, which is mainly due to carbon accumulation, or coking, and sintering of both support and active metal particles [36-40].

Many researchers have focused on the development of catalysts which exhibit high activity and stability for CDRM catalytic reaction. Hence, numerous literatures have reported an extensive range of catalysts for CDRM that is basically similar to the choices of catalysts for steam reforming [41-46]. Although noble metal catalysts have been well reported to be more resistant to coking of catalysts, they are widely discouraged to be employed in the industrial application due to high cost and limited in availability. Ni supported catalysts are broadly employed as a substitution for the precious noble metals due to their low price. In addition, Ni based catalyst exhibited high reaction activities but suffered from serious drawbacks caused by metal sintering and carbon deposition onto the active metal sites [47-52]. Therefore, researchers comprehensively investigated more on the augmentation of the catalytic activities of Ni based catalytic systems [53-65]. Even though noble metal catalysts such as Rh, Ru and Pt exhibited high catalytic activity and selectivity with barely carbon deposition, the high cost and limited in availability hinder them for commercialization. Thus, non-noble metal catalysts such as Fe, Ni and Co are lower in cost and more practical. Cobalt based catalyst from the transition metals group has also attracted much attention to the researchers as a substitution of Ni based catalyst [66, 67]. Cobalt has attracted interest as an active metal for CDRM and several variables related to cobalt catalyst such as effect of support, optimization of cobalt content, preparation method addition of small amount of noble metal and the use of Ni-Co bimetallic catalyst were investigated to improve the reaction of CDRM.

1.2 Problem Statements

Problem statements were identified and selected based on the literature reviews, triggered interests of research, potential problems and highlighted future works. Therefore, three identified problem statements have been raised as follows;

The first problem statement was related to a suitability of catalyst to be applied in the reaction process. At an experimental laboratory stage, fewer studies have reported the attempt to utilize oil palm shell activated carbon (OPS-AC) as a support of catalyst in heterogeneous reaction [68, 69]. However, most studies have been using OPS-AC as an adsorbent for the removal of dye, color, and heavy metals [70-73]. Furthermore, other researchers have used OPS-AC as a support for catalyst in biodiesel production, as well as the feedstock in both pyrolysis and gasification. There are studies that have used activated carbon extensively derived from the commercial coconut shell as a support for catalytic reaction but rarely used OPS-AC as the support. Hence, the suitability problem in finding a well-suited support of catalysts which caters the reaction of CDRM is highlighted in this problem statement.

Another problem statement is interrelated to the optimizing molar ratio of feedstock gases which is regarded as the second problem statement. Cobalt based catalysts are considered the most suitable transition metals in terms of giving superior activity and selectivity, lower in water gas shift (WGS) activity, moderate in the operating conditions and comparatively lower in price than the noble metals. Generally, CDRM has a tendency in producing lower molar ratio (1:1) of synthesis gases of CO and H₂. Furthermore, the stoichiometric ratio of 1:1 for syngas (H₂ and CO) is essential for the downstream processes such as FTS using cobalt supported catalysts. Therefore, the identified major problem is to optimize the molar ratio feedstock of GHG (CO₂ and CH₄) by producing unity ratio of syngas for the succeeding production of FT synthetic fuels.

The third identified problem statement is associated with the optimization of temperature and pressure of carbon dioxide reforming of methane (CDRM). However, CDRM is strongly endothermic and requires high temperatures (700 – 900 °C) with the ambient operating pressure of 1 atm. On the contrary, CDRM tends to produce more carbon deposition at elevated pressure. In addition, the key problem of maintaining the entire system at high pressure induces high cost in the actual operation. Therefore, a trial to reduce and optimize higher operating pressure and temperature without adversely affecting the catalytic activity is appreciated due to greater deposition of carbonaceous can hinder the catalytic activities.

1.3 Research Objectives

Research objectives are established based on the respective problem statements and hypothesis. Currently, the research objectives are divided into three main parts, which are:

- (i). To synthesize and characterize cobalt catalysts using two supported materials of OPS-AC and mesoporous zeolite (ZSM-5).
- (ii). To conduct screening and activity testing of catalyst by investigating the performance of the selected catalysts in correlation of product yield with various variables such as feedstock ratios (CH_4/CO_2).
- (iii). To optimize the manipulated variables such as reaction temperature, pressure based on the multi-response optimization of both yields (H_2 and CO).
- (iv). To conduct kinetic studies of the reaction.

1.4 Research Scopes

One of the highlighted research objectives is related to the preparation of catalysts which involves several processes, such as synthesis of catalysts and catalyst characterization. The cobalt-supported catalysts are using two types of porous materials of OPS-AC and mesoporous zeolite (ZSM-5). The cobalt (0–16 wt%) is loaded onto support by wetness impregnation method. The synthesized cobalt supported catalysts are characterized by elemental analysis, TGA, XRD, SEM, FESEM, TEM, TPR, TPD, and BET in order to examine the physical and chemical properties of the respective catalysts.

The second research objective is related to conduct screening and activity testing of catalysts. Design of experiment (DOE) obtained from response surface methodology (RSM) is used to reduced the numbers of unnecessary experiments and to predict the correlations of variables. The cobalt-supported catalysts are screened for the catalyst activity testing using MRS to investigate the catalysts performance. The screened catalyst that gave the best performance in correlation of product yield with four variables (operating temperature, pressure, feedstock ratios (CH_4/CO_2), gas hourly space velocity) is selected for further activity testing of the catalysts.

The third research objective is associated with the optimization of four manipulated variables. Desirability function analysis (DFA) is employed to simultaneously optimize the multiple responses of both H_2 and CO yields. Hence, both yields of H_2 and CO are simultaneously optimized by DFA giving a global optimal condition as the most optimum reaction condition.

As the fourth research objective, a fundamental reaction of kinetic study is also investigated based on the obtained experimental results. Kinetic study of CDRM is performed using a power law, Arrhenius plot and equation. Then, the rate of reactions, rate constants, reaction orders and activation energies are calculated and compared between CH_4 and CO_2 of OPS-AC(14) catalyst.

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