

SYNTHESIS AND CHARACTERIZATION OF METALS LOADED FIBROUS
MORDENITE ZEOLITE FOR CARBON MONOXIDE METHANATION

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DEDICATION

*Specially dedicated to my beloved Father and Mother
for endless love, encouragement and pray to be successful in my life*

*To my beloved wife, sibling, family and friends
for inspiration and all support to take the first step*

Thank you

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ABSTRACT

Carbon monoxide (CO) methanation is one of the most viable and sustainable ways for methane (CH₄) production to replace fossil fuels (coal, petroleum, and natural gas) and alleviate the adverse environmental impacts of carbon-intensive industries. Thermodynamically, CO methanation is a feasible reaction which can proceed at low temperatures. However, to meet the requirements of reaction kinetics of CO methanation, a suitable and highly active catalyst is mandatory for high CH₄ yield. In this study, fibrous zeolites were successfully synthesized through the microemulsion method using commercial zeolites, namely mordenite (MOR), ZSM-5, and beta zeolite (BEA) as seed. All the zeolite samples were characterized by different techniques, including X-ray diffraction (XRD), nitrogen physisorption, field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), fourier-transform infrared spectroscopy (FTIR), pyrrole adsorbed FTIR, hydrogen temperature-programmed reduction (H₂-TPR) and electron spin resonance (ESR) spectroscopy. The synthesized fibrous mordenite (FSMOR), fibrous ZSM-5 (FSZSM-5) and fibrous beta zeolite (FSBEA) were compared with MOR, ZSM-5 and BEA zeolites to study their activity towards CO methanation. The CH₄ yield was found in the order of FSMOR (50%) > FSZSM-5 (44%) > FSBEA (41%) > MOR (37%) > BEA (25%) > ZSM-5 (21%) at 450°C. The catalytic activity of the synthesized zeolites was strongly correlated to the existence of mesoporosity, inter- and intra-particle pores, intrinsic basic sites, and oxygen vacancies. The fibrous mordenite (FSMOR) displayed superior catalytic activity among all zeolites as a result of the high basicity and oxygen vacancies. To further enhance the catalytic activity, transition metals including Fe, Co, Ni, Ru, Pd, and Ag were loaded on FSMOR by the wet impregnation method. It was found that the transition metals loading significantly improved the catalytic activity towards CO methanation. The Ru-FSMOR unveiled a superior CH₄ yield of 78% at 400°C compared to the other catalysts, in the order of Ru-FSMOR > Ni-FSMOR > Co-FSMOR > Ag-FSMOR. The catalytic performance of the Ru-FSMOR was boosted because of the high reducibility of well-dispersed Ru nanoparticles (Ru-NPs) and the synergistic effect between the Ru-NPs and oxygen vacancies in the FSMOR support. The FSMOR and Ru-FSMOR revealed high stability and suppressed the coke formation caused by the undesired side reactions during CO methanation. Moreover, in the proposed reaction mechanism of CO methanation, it was discovered that the FSMOR and Ru-FSMOR followed an associative reaction pathway via linearly adsorbed CO* as an essential intermediate, dissociated into adsorbed C* to form methane by hydrogenation. For FSMOR, the oxygen vacancies conducted the activation of CO and H₂ into C* and H* during methane formation. Whereas for Ru-FSMOR, the active Ru phase conducted the activation of H₂ and CO molecules followed by migration onto the FSMOR surface to form adsorbed CO* and adsorbed H*. The adsorbed CO* appeared in two forms, namely linear and bridged forms. Based on the above observations, this work provides fundamental insights into the robust catalytic system relating to CO methanation using zeolite-based catalysts with unique fibrous morphology, which can potentially be applied to produce substitute natural gas on a commercial scale.

ABSTRAK

Metanasi karbon monoksida (CO) adalah salah satu cara yang paling sesuai dan mampan bagi pengeluaran metana (CH₄) untuk menggantikan bahan bakar fosil (arang batu, petroleum, dan gas asli) dan mengurangkan kesan buruk industri yang intensif karbon terhadap alam sekitar. Secara termodinamik, metanasi CO adalah tindak balas yang boleh dilaksanakan pada suhu rendah. Walau bagaimanapun, untuk memenuhi keperluan kinetik tindak balas metanasi CO, mangkin yang sesuai dan sangat aktif adalah perlu untuk mendapatkan hasil CH₄ yang tinggi. Dalam kajian ini, zeolit berserat berjaya disintesis melalui kaedah mikroemulsi menggunakan zeolit komersial, iaitu mordenite (MOR), ZSM-5, dan beta zeolite (BEA) sebagai benih. Semua sampel zeolit dicirikan dengan teknik yang berlainan, termasuk pembelauan sinar-X (XRD), fizijerapan nitrogen, mikroskopi elektron pengimbas pemancaran medan (FESEM), mikroskopi elektron penghantaran (TEM), spektroskopi inframerah transformasi Fourier (FTIR), FTIR pirola terjerap, penurunan suhu teraturcara hidrogen (H₂-TPR) dan spektroskopi resonans spin elektron (ESR). Mordenit berserat yang disintesis (FSMOR), ZSM-5 berserat (FSZSM-5) dan beta zeolit berserat (FSBEA) telah dibandingkan dengan zeolit MOR, ZSM-5 dan BEA untuk mengkaji aktiviti mereka terhadap metanasi CO. Hasil CH₄ didapati mengikut urutan FSMOR (50%) > FSZSM-5 (44%) > FSBEA (41%) > MOR (37%) > BEA (25%) > ZSM-5 (21%) pada 450°C. Aktiviti pemangkin zeolit yang disintesis sangat berkaitan dengan kewujudan mesoporositi, liang antara dan intra-partikel, tapak asas intrinsik, dan kekosongan oksigen. Antara semua zeolit yang disintesis, mordenite (FSMOR) menunjukkan aktiviti pemangkin yang unggul kerana kebesan dan kekosongan oksigen yang tinggi. Untuk meningkatkan lagi aktiviti pemangkin, logam peralihan termasuk Fe, Co, Ni, Ru, Pd, dan Ag telah dimuatkan di atas FSMOR dengan kaedah pengisitepuan basah. Didapati bahawa pemuatan logam peralihan telah meningkatkan aktiviti pemangkinan terhadap metanasi CO dengan ketara. Ru-FSMOR menunjukkan hasil CH₄ yang unggul sebanyak 78% pada suhu 400°C berbanding mangkin lain, mengikut urutan Ru-FSMOR > Ni-FSMOR > Co-FSMOR > Ag-FSMOR. Prestasi Ru-FSMOR meningkat kerana keterturunan tinggi nanopartikel Ru yang tersebar dengan baik (Ru-NPs) dan kesan sinergi antara Ru-NP dan kekosongan oksigen dalam penyokong FSMOR. FSMOR dan Ru-FSMOR mendedahkan kestabilan yang tinggi dan menekan pembentukan kok yang disebabkan oleh reaksi sampingan yang tidak diingini semasa metanasi CO. Lebih-lebih lagi, dalam mekanisme tindak balas metanasi CO yang dicadangkan, didapati bahawa FSMOR dan Ru-FSMOR mengikut jalan tindak balas sekutuan melalui CO* yang diserap secara linear sebagai perantara penting, bercerai menjadi C* yang terjerap untuk membentuk metana dengan penghidrogenan. Bagi FSMOR, kekosongan oksigen melakukan pengaktifan CO dan H₂ kepada C* dan H* semasa pembentukan metana. Manakala bagi Ru-FSMOR, fasa Ru aktif melakukan pengaktifan molekul H₂ dan CO diikuti dengan penghijrahan ke permukaan FSMOR untuk membentuk CO* yang terjerap dan H* yang terjerap. CO yang terjerap muncul dalam dua bentuk iaitu bentuk linear dan bentuk bertitisan. Berdasarkan pemerhatian di atas, kajian ini memberikan pandangan asas mengenai sistem pemangkinan yang teguh berkaitan dengan metanasi CO menggunakan mangkin berasaskan zeolit dengan morfologi berserat yang unik, yang berpotensi digunakan untuk menghasilkan gas asli pengganti pada skala komersial.

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Figure 4.33 A plausible mechanism of CO methanation reaction over Ru-FSMOR.

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LIST OF ABBREVIATIONS

H/C	-	Hydrogen to carbon ratio
TOF	-	Turnover Frequency
CTAB	-	Cetyltrimethylammonium Bromide
E_a	-	Activation energy
ESR	-	Electron Spin Resonance
FESEM	-	Field Emission Scanning Electron Microscopy
STP	-	Standard Temperature Pressure
FTS	-	Fisher-Tropsch-Synthesis
FTIR	-	Fourier Transform Infrared
GC	-	Gas Chromatography
GHGs	-	Greenhouse Gases
GHSV	-	Gas hourly space velocity
JCPDS	-	Joint Committee on Powder Diffraction Standards
KCC	-	KAUST Catalytic Centre
MOR	-	Mordenite
BEA	-	Beta zeolite
FSMOR	-	Fibrous mordenite
FSBEA	-	Fibrous beta zeolite
FSZSM-5	-	Fibrous ZSM-5 zeolite
MCM	-	Mobil Composition of Matter
MSN	-	Mesostructured Silica Nanoparticles
NLDFT	-	Non-local density functional theory
RWGS	-	Reverse water gas shift
TCD	-	Thermal Conductivity Detector
TEM	-	Transmission Electron Microscopy
TEOS	-	Tetraethylorthosilicate
TPR	-	Temperature Programmed Reduction
XRD	-	X-ray diffraction

LIST OF SYMBOLS

λ	-	Wavelength
G_T	-	Total Gibbs free energy
R	-	Molar gas constant
ΔG	-	Change in Gibbs free energy
ΔH	-	Enthalpy change
ΔS	-	Entropy change
K_c	-	Equilibrium constant
2θ	-	Bragg angle
$^{\circ}\text{C}$	-	Degree celcius
T	-	Temperature
P	-	Pressure
atm	-	Atmosphere
MPa	-	Mega Pascal
\AA	-	Angstrom
μm	-	Micrometer
g	-	Gram
wt. %	-	Weight percentage
min	-	Minutes
mL	-	Millilitre
nm	-	Nanometer
K	-	Kelvin
Δ	-	Delta
θ	-	Angle
L	-	Litres
s	-	Seconds
μmol	-	Micromole
R^2	-	Coefficient of determination
H	-	Hours

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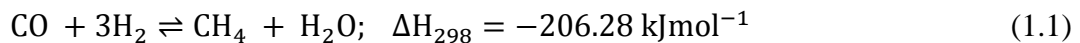
CHAPTER 1

INTRODUCTION

1.1 Research Background

Socio-economic and scientific developments have increased the global energy demand due to the increasing human population, urbanization, and industrialization. The petroleum, coal, and natural gas, known as fossil fuels, serve as the largest sources of energy, currently provide more than 90% of our energy needs (Ozturk *et al.*, 2019). Natural gas (with a significant share of methane) is recognized as an environment amity with high energy density (55.7 kJ g^{-1}) than coal (39.3 kJ g^{-1}) and petroleum (43.6 kJ g^{-1}); it produces a lower amount of CO_2 compared to coal and petroleum (Faria *et al.*, 2018). Therefore, natural gas has received considerable attention, and its consumption has increased by 4.6% in 2018, its highest annual growth rate since 2010, resulting in a shortage of natural gas supply. According to recent reports, the gap between supply and demand will be 200 billion m^3 by 2020 (Tao *et al.*, 2020; Italiano *et al.*, 2020). Unfortunately, the reserves of crude oil and natural gas resources were limited to 40-60 years and the supply of coal in known deposits was projected to be 230 years (Bassano *et al.*, 2020).

The increasing demand and price volatility of natural gas have increased the interest in producing an artificial version of natural gas from syngas ($\text{CO} + \text{H}_2$) derived from biomass, coal or organic solid wastes gasification via carbon monoxide (CO) methanation shown by chemical equation (1.1) as follows:



The produced methane is also called synthetic or substitute natural gas (SNG) or liquid natural gas (LNG) (Italiano *et al.*, 2020). In order to avoid the negative environmental impacts of coal use, Japan, China and most European Union countries have been working on SNG production. SNG has the same properties of natural gas, which can be stored and distributed without additional expenses compared to hydrogen due to the existing infrastructure, including storage facilities, filling stations, and pipeline networks. Hydrogen has many drawbacks, such as explosive, volatile properties, unfavourable compressibility and flammable properties, which render transport and supply to remote areas difficult.

In addition, CO methanation has been widely used in many applications, including coke furnace gas (COG), blast furnace gas (BFG), to mitigate the adverse environmental impact of high-carbon industries. The CO methanation reaction is also used in Fischer-Tropsch synthesis (FTS) and in polymer electrolyte membrane fuel cells to remove trace amounts of CO from the feed gas (Chen *et al.*, 2011; Fatah *et al.*, 2020).

Numerous studies have discovered that CO methanation is thermodynamically a feasible reaction at low temperatures and highly associated with temperature, pressure, and composition of reactants. Simultaneous methanation of CO and CO₂ is often encountered with numerous side reactions, including water gas shift reactions: $\text{CO (g)} + 2\text{H}_2\text{O (g)} \rightleftharpoons \text{CO}_2 \text{(g)} + \text{H}_2 \text{(g)}$, cracking of methane: $\text{CH}_4 \text{(g)} \rightleftharpoons \text{C (s)} + 2\text{H}_2 \text{(g)}$, and Boudouard reaction: $2\text{CO (g)} \rightleftharpoons \text{C (s)} + \text{CO}_2 \text{(g)}$. These reactions affect the methanation process by producing unwanted side products such as coke, which results in the quick deactivation of catalysts during CO methanation (Gao *et al.*, 2012). Therefore, the thermodynamic analysis of CO methanation via Gibbs free energy minimization is an excellent approach to optimize the reaction conditions with minimum impacts of multiple side reactions. Very few thermodynamic studies for CO methanation are available in the open literature (Anderson *et al.*, 1976; Anderson *et al.*, 1986; Gao *et al.*, 2012). However, these studies are less comprehensive and do not cover the thermodynamic considerations of CO methanation in the light of complete thermodynamic parameters such as enthalpy change (ΔH), entropy change (ΔS), and Gibbs energy change (ΔG). In the present study, it will be great to gain an in-depth

understanding of the on-going reactions based on the thermodynamic parameters (ΔH , ΔS , and ΔG).

Regardless of thermodynamically favored CO methanation at low temperatures, a catalyst is mandatory to lower the kinetic energy barrier in chemical conversion of CO and H₂ to methane with an appropriate rate (Gao *et al.*, 2012; Fatah *et al.*, 2020). Therefore, several efforts have been made to develop appropriate catalytic systems for CO methanation using different transition metals (Molybdenum, iron, nickel, cobalt, platinum, rhodium and ruthenium) and supporting materials (Al₂O₃, SiO₂, TiO₂, ZrO₂, MCM-41, SBA-15, and mixed oxides) (Wang *et al.*, 2017). It was found that the molybdenum-based catalysts have the lowest activity for CO methanation. While the iron-based catalysts exhibited a high activity and low methane selectivity towards CO methanation. Nickel and cobalt-based catalysts demonstrated almost similar activity, higher than iron and molybdenum-based catalysts. However, the nickel-based catalysts were easily deactivated at higher temperatures due to metal sintering and carbon deposition during CO methanation. In addition, the platinum, rhodium, and ruthenium-based catalysts illustrated superior catalytic performance towards CO methanation and proved to be more effective than other catalysts due to high stability, anti-sintering, and anti-coking abilities (Ali *et al.*, 2015). Regardless of extensive CO methanation research, synthesizing efficient material and choosing the right metal for a solid catalytic system is one of the major challenges of the CO methanation reaction (Wang *et al.*, 2017).

Supported materials play a substantial role in heterogeneous catalysis by providing high surface area and pore volume for reactant's accessibility to the active sites during the chemical reactions. The purpose of supporting material is not only restricted to adsorption centers for reactants, but they also play a crucial role in modifying of catalyst properties. Previous studies reported that the unsupported catalysts had shown a lower CO methanation activity than the supported catalysts (Aziz *et al.*, 2014; Lakshmanan *et al.*, 2016). In addition, the catalytic performance for CO methanation may be affected by the morphology of the supporting materials. Previously, several studies had been performed for CO methanation using a variety of supporting materials. However, zeolites have not been applied extensively in the CO

methanation reactions as supporting materials. In the present study, CO methanation was performed using zeolites, and their physicochemical properties were examined towards CO methanation.

Zeolites are crystalline, hydrated aluminosilicates consisting of frameworks based on an infinitely extending three-dimensional network of SiO₄ and AlO₄ tetrahedral linking to each other by sharing oxygen atoms. The channels or interconnected voids in the micropore range serve the zeolites with special pore structure, high shape selectivity, activity, and ion exchange characteristics. Therefore, zeolites have attracted considerable attention for a variety of applications such as petrochemicals, pollution control, aromatization of hydrocarbons, alkylation, cracking, and isomerization (Perez-Ramirez *et al.*, 2008; Rahimi *et al.*, 2011). But zeolites have some limitations, affecting their catalytic performance during chemical reactions (Figueiredo *et al.*, 2014). The major drawbacks of zeolites are the relatively small size of channels, cavities, and the lack of interconnection. For example, mordenite, beta zeolite, ZSM-5, and Y zeolite have a problem of diffusion limitation and pore blockage during catalytic reactions (Gackowski *et al.* 2018). Developing new mesopores is an excellent solution to overcome these limitations in conventional zeolites (Firmansyah *et al.*, 2016). Thus, extensive efforts have been made to develop new supporting materials with high mesoporosity to overcome the limitations mentioned earlier.

More recently, KAUST catalysis center-1 (KCC-1), a new fibrous mesostructured silica catalyst, has emerged with a unique fibrous morphology, attributed high mesoporosity and surface area (Polshettiwar *et al.*, 2010). Following this great initiative, a variety of fibrous materials have been synthesized and used efficiently in various chemical reactions, including in CO₂ methanation (Hamid *et al.*, 2017), cumene hydrocracking (Firmansyah *et al.*, 2016), alkane hydrogenolysis (Fihri *et al.*, 2012), phenol hydrogenation (Karakhanov *et al.*, 2017), isomerization (Fatah *et al.*, 2017; Izan *et al.*, 2019), and photocatalysis (Seo *et al.*, 2017). The synthesized fibrous materials exhibited fibrous morphology, resulting in high surface area, large pore volume, and maximum access of reactants to active sites, which could improve catalytic activity. Herein, like the structure of KCC-1, the fibrous silica zeolite-based

supports were synthesized to cover the limitations of commercial based zeolites (MOR, ZSM-5, and BEA) through silica fibrous morphology towards enhanced CO methanation.

In the present study, the thermodynamic analysis was carried out using the Gibbs free energy minimization method to explain the role of various side reactions during CO methanation. The influence of different temperature, pressure, and H₂: CO ratio was investigated towards CO methanation. To conduct CO methanation, different fibrous zeolites, including fibrous mordenite (FSMOR), fibrous ZSM-5 (FSZSM-5), and fibrous beta zeolite (FSBEA) have been prepared through the microemulsion method from commercial mordenite (MOR), ZSM-5 and beta zeolite (BEA), respectively. All the zeolite samples were examined and compared towards CO methanation based on their physicochemical properties. Also, the transition metals such as iron, cobalt, nickel, ruthenium, palladium, and silver were loaded on FSMOR for enhanced CO methanation. Moreover, the possible reaction mechanism was investigated over the metal-free (MOR and FSMOR) and metal-loaded FSMOR (Ru-FSMOR) catalysts using in situ electron spin resonance (ESR) spectroscopy, and in situ Fourier-transform infrared spectroscopy (FTIR) techniques via surface intermediate species formed during the CO methanation reaction.

1.2 Problem Statement

As the quantitative and qualitative growths of industries and technologies are rapidly advancing, more energy will be required globally near future. Developing clean and sustainable energy sources has been strongly emphasized to substitute environment-unfriendly fossil fuels. In this respect, substitute natural gas (SNG) production is one of the most viable approaches using catalytic CO methanation. SNG has attracted much attention in the last decades due to highly efficient eco-friendly energy sources, low price, high H/C ratio, and high calorific value compare to diesel fuels, gasoline, and coal. SNG can be incorporated into existing pipelines, and storage tanks for supply to remote areas (Inga *et al.*, 2017; Zhao *et al.*, 2020).

Despite the economic and environmental potential, the CO methanation reaction faces serious problems associated with the development of highly efficient and stable catalysts. CO methanation is a highly exothermic reaction ($\Delta H = -206$ kJ/mol) and emits a large amount of heat, creating hotspots in the reactors, resulting in deactivating the catalysts. In addition, during CO methanation, coke is produced and deposited on the surface of the catalysts, causing blockages in the pores, and covering the active sites of the catalysts, which causes a decline in catalytic activity (Italiano *et al.*, 2020; Gao *et al.*, 2012; Fatah *et al.*, 2020). To solve these problems, there is an urgent need to design a suitable catalyst with high activity and thermal stability, which can be maintained at high temperatures without deactivation. To design an efficient and active catalyst, supporting material is an essential parameter for CO methanation. Previously, different supporting materials, including SiO₂, Al₂O₃, TiO₂, CeO₂, and ZrO₂ have been effectively used in CO methanation due to their high ability to adsorb CO and high dispersion of metal particles. However, their thermal stability and coke formation are still major challenges towards CO methanation (Wang *et al.*, 2017).

Zeolites have a great potential for use in CO methanation due to microporous-mesoporous structure, high surface area, high thermal stability, and resistance to coke formation. Despite these unique properties, there has been little study of zeolites in CO methanation. This may be due to some of their serious drawbacks, such as regular microporous channels, which cause the reactants to have limited access to the active sites inside the pores. The coke formation easily blocks the micropores and covers the active sites, limiting their application to CO methanation and many other reactions. The preparation of mesoporous zeolites is an intellectual solution to overcome these critical issues by improving the surface area and porosity of the commercial zeolites (Firmansyah *et al.*, 2016; Teh *et al.*, 2016).

The metal components of the catalysts played a decisive role in the catalytic CO methanation by acting as an active phase for hydrogen and CO dissociation. Transition metals have been used as an active phase for CO methanation catalysts, especially nickel, which is the most widely used metal in CO methanation due to its high activity. However, nickel-based catalysts are easily deactivated due to the intense coke deposition and metal sintering (Gao *et al.*, 2015), the major challenges of large-

scale commercial CO methanation. Therefore, the prevention of catalysts deactivation is one of the foremost challenges in CO methanation. It is necessary to choose a suitable transition metal to improve the catalytic activity and high thermal stability for CO methanation at low temperatures.

Despite the simplicity of the CO methanation reaction, the reaction mechanism seems difficult to establish because of the many opinions expressed on the intermediate species during CO methanation (Miao *et al.*, 2016). Despite extensive mechanistic studies, there is no consensus on the mechanism of CO methanation; therefore, the mechanistic understandings of CO methanation reaction is still ongoing. Therefore, it is crucial to elucidate the mechanistic aspects of CO methanation through intermediate surface species formed during CO methanation.

1.3 Hypothesis

To solve the problems described above, the thermodynamic study will be an effective approach to optimize the reaction conditions with minimum impacts of side reactions on CO methanation activity. Fibrous zeolites, including fibrous mordenite (FSMOR), fibrous ZSM-5 (FSZSM-5), and fibrous beta (FSBEA) zeolites of unique fibrous morphology as metal-free catalysts were synthesized using commercial mordenite, ZSM-5, and beta zeolites as seed, respectively. The fibrous zeolites could promote high accessibility of CO and H₂ molecules to the active sites, by providing high surface area, micro-mesoporosity, inter- and intra-particle pores. In addition, the morphology of fibrous zeolites will also promote the intrinsic basicity and oxygen vacancies to enhance CO and H₂ adsorption for CO methanation with less carbon deposition. It is expected that the fibrous morphology will also increase the metal dispersion on fibrous zeolites to improve the catalytic activity and thermal stability towards CO methanation due to the synergistic effect between metal particles and support. It is also anticipated that in situ ESR and in situ FTIR spectroscopic observations will offer a baseline to propose a reaction mechanism via intermediate surface species formed during the CO methanation reaction.

1.4 Objectives of the Study

The purpose of this study is to synthesize metal loaded fibrous zeolite catalysts of high activity and stability for optimal application in CO methanation to produce methane. The set of goals of this study is described as follows:

- 1 To establish the thermodynamics of CO methanation along other competing side reactions using HSC Chemistry 6.0 software.
- 2 To synthesize and characterize the physicochemical properties of fibrous zeolites (FSMOR, FSZSM-5, and FSBEA) and compare them with commercial zeolites (MOR, ZSM-5, and BEA).
- 3 To examine the catalytic activity of the synthesized catalysts as metal-free catalysts towards CO methanation.
- 4 To evaluate the effect of different transition metals over the best performing catalytic support towards CO methanation activity.
- 5 To elucidate reaction mechanism of the CO methanation reaction over metal-free and metal-loaded catalysts.

1.5 Scope of the Study

The scope of this study includes the thermodynamic insights of CO methanation, synthesis and characterizations of fibrous zeolites, their catalytic performance towards CO methanation, and the effect of metals loading on the synthesized catalysts to further enhance CO methanation. Lastly, the mechanistic studies of CO methanation. The details are described as follows:

1. The CO methanation reaction's optimum reaction conditions were investigated by the Gibbs free energy minimization method using HSC Chemistry software 6.0. Different side reactions were investigated based on thermodynamic parameters, including Gibbs free energy (ΔG), enthalpy change (ΔH), and entropy change (ΔS). The effects of temperature (25-1000°C), H₂: CO ratio

(0.5: 1- 5: 1), and pressure (0.1- 3 MPa) were studied towards enhanced CO methanation.

2. The fibrous zeolites (FSMOR, FSZSM-5, and FSBEA) were synthesized by the microemulsion method using the seed of commercial zeolites (MOR, ZSM-5, and BEA). The synthesized FSMOR, FSZSM-5, and FSBEA and the commercial MOR, ZSM-5 and BEA were examined and compared by different types of characterization techniques such as X-ray Diffraction (XRD), N₂ Adsorption-Desorption, Field Emission Scanning Electron Microscopy (FESEM), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), Pyrrole-FTIR, and Electron Spin Resonance (ESR) Spectroscopy.
3. The catalytic CO methanation was performed over FSMOR, FSZSM-5, FSBEA, MOR, ZSM-5, and BEA as metal-free catalysts using hydrogen and carbon monoxide streams with H₂: CO = 5:1 in a micro catalytic fixed-bed reactor in the temperature range of 150-500°C at atmospheric pressure (0.1MPa).
4. The effect of transition metals on CO methanation activity was studied by preparing metal loaded FSMOR catalysts with different transition metals (iron, cobalt, nickel, ruthenium, palladium, and silver). Metal loaded FSMOR catalysts were prepared by the impregnation method using 0.5 wt. % of metal. From the screening result, four metals (cobalt, nickel, ruthenium, and silver) were selected to further investigate the influence of metals loading on the catalytic performance towards enhanced CO methanation. The prepared metal loaded catalysts were characterized by XRD, N₂ Adsorption-Desorption, TEM, Pyrrole-FTIR, and H₂-TPR. The catalytic CO methanation was performed using a micro-catalytic fixed-bed reactor with H₂: CO = 5:1 in the temperature range of 150-500°C at atmospheric pressure (0.1MPa).
5. The possible mechanism of the CO methanation reaction over the MOR and the FSMOR were investigated using in situ (H₂ + CO) electron spin resonance

(ESR) and in situ ($H_2 + CO$) FTIR spectroscopy observations. While the reaction mechanism of CO methanation over Ru-FSMOR was studied using in situ ($H_2 + CO$) Fourier Transform Infrared (FTIR) spectroscopy.

1.6 Significance of the Study

In this study, a thermodynamic study using Gibbs free energy minimization approach sheds light on the optimal reaction conditions for increasing CO methanation by adjusting the temperature, feed ratio and pressure. The fibrous zeolites (FSMOR, FSZSM-5, and FSBEA) were synthesized for CO methanation using the microemulsion method. Compared to other commercial zeolites such as MOR, ZSM-5, and BEA, the synthesized FSMOR, FSZSM-5, and FSBEA have a unique fibrous morphology. This unique fibrous morphology is useful due to a variety of features, including the accessibility of gas reactants to active sites, high thermal stability and oxygen vacancies and high basicity. The fibrous morphology enhances the catalysis process by the adsorption and the activation of CO and H_2 on the active sites during CO methanation. Adding transition metals on FSMOR has further increased CO methanation's catalytic activity due to the synergistic effect between the metal phase and support. In addition, the proposed reaction mechanism over metal-free and metal-based FAMOR offers a better understanding of the catalytic CO methanation. This study will contribute to scientific research and development, particularly in the synthesis of a new robust catalyst for CO methanation to produce substitute natural gas.

1.7 Thesis Outline

This thesis begins with chapter one detailing the research background, problem statement and hypothesis, objectives, scope, and significance of the study. Chapter two reviews the latest developments in catalysis literature related to the CO methanation reaction. Chapter three describes step by step the experimental procedures and characterization techniques for synthesized catalysts for the CO methanation reaction.

While chapter four presents data processing and discussion on physicochemical properties and catalytic performance of the catalysts. Finally, chapter five highlights the conclusions and recommendations for future research.

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APPENDIX G

LIST OF PUBLICATIONS

List of Publication

1. Hussain, I., Jalil, A.A., Mamat, C.R., Siang, T.J., Rahman, A.F.A., Azami, M.S. & Adnan, R.H. (2019). New insights on the effect of the H₂/CO ratio for enhancement of CO methanation over metal-free fibrous silica ZSM-5: Thermodynamic and mechanistic studies. *Energy Conversion and Management*, 199, 112056.
2. Hussain, I., Jalil, A.A., Fatah, N.A.A., Hamid, M.Y.S., Ibrahim, M., Aziz, M.A.A. & Setiabudi, H.D. (2020). A highly competitive system for CO methanation over an active metal-free fibrous silica mordenite via in-situ ESR and FTIR studies. *Energy Conversion and Management*, 211, 112754.
3. Hussain, I., Jalil, A.A., Fatah, N.A.A., Izan, S.M. & Azami, M.S. (2020) Cockscomb-like fibrous silica beta zeolite (FSBEA) as a new engineered catalyst for enhanced CO methanation. *Material Science & Engineering*, 736 042012.
4. Hussain, I., Jalil, A.A., & Aziz, M.A.H., A pivotal role of unique dandelion flower-like structure of modified beta zeolite (@BEA) catalyst in CO hydrogenation to substitute natural gas (SNG). Submitted to International Journal of Hydrogen Energy.
5. Hussain, I., & Jalil, A.A., Synergistic effect of metal phase and oxygen vacancies on ruthenium loaded fibers silica mordenite (Ru-FSMOR) catalyst for enhanced CO methanation. *About to submit*.
6. Hussain, I., & Jalil, A.A., Contemporary thrust and emerging prospects of robust catalytic systems for substitute natural gas production by carbon monoxide methanation. *About to submit*
7. Hussain, I., Jalil, A.A., Hassan, N.S., Hambali, H.U., & Jusoh, N.W.C. (2020). Fabrication and characterization of highly active fibrous silica-mordenite

- (FS@SiO₂-MOR) cockscomb shaped catalyst for enhanced CO₂ methanation. *Chemical Engineering Science*, 228, 115978.
8. Hussain, I., Jalil, A.A., Izan, S.M., Azami, M.S., Kidam, K., Ainirazali, N., & Ripin, A. (2021). Thermodynamic and experimental explorations of CO₂ methanation over highly active metal-free fibrous silica-beta zeolite (FS@SiO₂-BEA) of innovative morphology. *Chemical Engineering Science*, 229, 116015.
 9. Hussain, I., Jalil, A.A., Fatah, N.A.A., Ibrahim, M., Azami, M.S., Fadlun, W., Aziz, H. and Hambali, H.U., (2020) A viable system for carbon dioxide (CO₂) methanation over fibrous silica ZSM-5 for substitute natural gas (SNG). *Material Science & Engineering*, 808, 012037.
 10. Hussain, I., & Jalil, A.A., State of the art and perspectives in robust catalytic systems for chemical conversion of carbon dioxide (CO₂) to substitute natural gas (SNG). *Submitted to journal Renewable & Sustainable Energy Reviews*.

List of Conference Proceedings

1. Hussain, I., Jalil, A.A., Mamat, C.R., Siang, T.J., Azami, M.S. & Hambali, H.U., 2019. Role of Promoters in Hoisting the Catalytic Performance for Enhanced CO Methanation. *Journal of Energy and Safety Technology (JEST)*, 2(1). Conference on Emerging Energy & Process Technology, CONCEPT 2018, Johor Bahru, Malaysia, 27-28 November 2018
2. Hussain, I., & Jalil, A.A, Thermodynamics and catalytic visions of CO₂ methanation over fibrous silica mordenite (FSMOR). 1st Euro-Asia Conference on CO₂ Capture and Utilisation (*EACCO₂CU 2019*), 6-7 August 2019, Kuala Lumpur, Malaysia