

SYNTHESIS AND CHARACTERIZATION OF NICKEL CATALYST
SUPPORTED ON POROUS SILICA OXIDE FOR CARBON DIOXIDE
METHANATION

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DEDICATION

*Specially dedicated to Ayah and Ibu
for the inspiration to take the first step here*

*Beloved, family and friends
for being there for me to take some break in between*

Thank you

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ABSTRACT

Carbon dioxide (CO₂) hydrogenation into methane (CH₄) is a promising technique in environment conservation while producing sustainable fuel to fulfil the energy demand. In this study, mesoporous silica KAUST Catalytic Centre number 1 (KCC-1) with a unique fibrous structure was successfully synthesized and compared with other silica-based catalysts to study the influence of catalyst support morphology on CO₂ methanation. Different transition metals loaded on KCC-1 were prepared by impregnation method to investigate the enhancement of catalytic activity and different mechanism pathways of CO₂ methanation. In addition, the bimetallic promoted KCC-1 catalysts prepared via a co-impregnation method were studied with different promoter loading (2.5-10 wt.%). The catalysts were characterized using X-ray diffraction, nitrogen physisorption, field emission scanning electron microscopy, transmission electron microscopy, Fourier transform infrared (FTIR), pyrrole adsorbed FTIR, CO₂ adsorbed FTIR, nuclear magnetic resonance, hydrogen temperature programmed reduction and electronic spin resonance. Catalytic activity was conducted at 423-723 K under atmospheric pressure. KCC-1 has significantly a higher number of basicity and oxygen vacancy than those of mobil composition of matter number 41 (MCM-41) and commercial silica (SiO₂) which is directly correlated with the CO₂ adsorption and catalytic performance. At 723 K, the CO₂ conversion for KCC-1, MCM-41 and SiO₂ was 9.2, 8.6 and 5.9 %, respectively. For different transition metal loaded on KCC-1, at 673 K, the catalytic activity follows the trend of nickel (Ni/KCC-1) > cobalt (Co/KCC-1) > zinc (Zn/KCC-1) with CH₄ yield of 90.6, 71.6 and 10.8 % respectively. It was discovered that Ni/KCC-1 and Co/KCC-1 follows a dissociative mechanism pathway in which CO₂ molecule was dissociated on the surface of metal before migrating onto KCC-1 surface. The Zn/KCC-1 on the other hand follows an associative mechanism pathway where H₂ plays a role in CO₂ dissociation which primarily occurs on KCC-1 surface. Vanadium (V) outperformed other second metals promoted Ni/KCC-1 such as chromium, manganese, iron, copper and zinc. The reaction light off temperature was lower on V-Ni/KCC-1 (423 K), compared to Ni/KCC-1 (473 K). At 623 K, the CH₄ yield of 7.5V-Ni/KCC-1 reaches 94.4 % while 77.6 % for Ni/KCC-1. This could be attributed to the presence of V mitigated the agglomeration of Ni metal, thus the highly dispersed and exposed Ni active sites. Moreover, the amphoteric properties of V provide additional adsorption sites of CO₂ and in turn influencing the catalyst activity. The optimum CH₄ yield predicted by Response Surface Methodology was 98.6 % at reaction temperature of 641.3 K, GHSV of 10816.13 mL g⁻¹ h⁻¹ and H₂:CO₂ ratio of 5.8. The experiment carried out at these parameters yielded 95.8 % CH₄ with an error of 1.44 %. The presence of O₂ was found to inhibit the activity of the catalyst due to competitive adsorption of gases. This study reported for the first time, the utilization of unique silica morphology KCC-1 as a catalyst support and highlighted the contribution of promoted V-Ni/KCC-1 in the CO₂ methanation research, particularly in the utilization of CO₂ towards greener environment.

ABSTRAK

Penghidrogenan karbon dioksida (CO_2) kepada metana (CH_4) adalah teknik yang berpotensi dalam pemuliharaan alam sekitar disamping menghasilkan bahan api lestari untuk memenuhi permintaan tenaga. Dalam kajian ini, silika mesoliasing KAUST pusat pemangkin bernombor 1 (KCC-1) dengan struktur berserat unik telah disintesis dan dibandingkan dengan mangkin berasaskan silika lain untuk mengkaji pengaruh morfologi penyokong mangkin keatas metanasi CO_2 . Logam peralihan berbeza dimuatkan keatas KCC-1 telah disediakan dengan kaedah pengisitepuan untuk menyiasat penambahbaikan aktiviti pemangkinan dan perbezaan laluan mekanisme dalam metanasi CO_2 . Tambahan pula, mangkin penggalak dwilogam KCC-1 disediakan melalui kaedah pengisitepuan bersama telah dikaji dengan muatan penggalak berbeza (2.5 – 10 wt.%). Mangkin telah dicirikan dengan pembelauan sinar-X, penjerapan fizikal nitrogen, pengimbasan elektron pancaran medan, mikroskopi elektron penghantaran, inframerah jelmaan Fourier (FTIR), FTIR terjerap pirol, FTIR terjerap CO_2 , salunan magnet nuklear, penurunan suhu terprogram hidrogen dan salunan elektronik putaran. Prestasi pemangkin telah dijalankan pada suhu 423-723 K pada tekanan atmosfera. KCC-1 mempunyai bilangan nombor bes dan kekosongan oksigen yang lebih tinggi berbanding komposisi jirim mobil nombor 41 (MCM-41) dan silika komersil (SiO_2) yang secara langsung berhubungkait dengan penjerapan CO_2 dan prestasi pemangkinan. Pada 723 K, penukaran CO_2 bagi KCC-1, MCM-41 and SiO_2 adalah masing-masing 9.2, 8.6 and 5.9 %. Bagi logam peralihan berbeza yang dimuatkan keatas KCC-1, pada 673 K, aktiviti pemangkinan mengikuti urutan nikel (Ni/KCC-1) > kobalt (Co/KCC-1) > zink (Zn/KCC-1) dengan hasil CH_4 sebanyak masing-masing 90.6, 71.6 dan 10.8%. Penemuan bahawa Ni/KCC-1 dan Co/KCC-1 mengikuti laluan mekanisme penceraian di mana molekul CO_2 tercerai di permukaan logam sebelum berpindah ke permukaan KCC-1. Zn/KCC-1 sebaliknya mengikuti laluan mekanisme bersekutu di mana H_2 memainkan peranan dalam penceraian CO_2 yang berlaku terutamanya pada permukaan KCC-1. Vanadium (V) mengatasi penggalak logam kedua Ni/KCC-1 lain seperti kromium, mangan, besi, tembaga dan zink. Permulaan suhu tindak balas adalah lebih rendah pada V-Ni/KCC-1 (423 K), berbanding Ni/KCC-1 (473 K). Pada 623 K, hasil CH_4 oleh 7.5V-Ni/KCC-1 mencapai 94.4% manakala 77.6% untuk Ni / KCC-1 . Hal ini boleh dikaitkan dengan kehadiran V mengurangkan penggumpalan logam Ni, justeru tersebar dan terdedah oleh tapak aktif Ni. Selain itu, sifat-sifat amfoterik V memberikan tapak penjerapan CO_2 tambahan dan seterusnya mempengaruhi aktiviti mangkin. Hasil CH_4 optimum yang diramalkan oleh kaedah sambutan permukaan adalah 98.6% pada suhu tindak balas 641.3 K, GHSV 10816.13 $\text{mL g}^{-1} \text{h}^{-1}$ dan nisbah $\text{H}_2:\text{CO}_2$ 5.8. Eksperimen yang dijalankan pada parameter-parameter ini menghasilkan 95.8% CH_4 dengan ralat 1.44%. Kehadiran O_2 didapati membantut aktiviti mangkin kerana persaingan penjerapan gas. Kajian ini melaporkan buat pertama kali, penggunaan morfologi silika unik KCC-1 sebagai penyokong mangkin dan menekankan sumbangan penggalak V-Ni/KCC-1 dalam kajian metanasi CO_2 , khususnya dalam penggunaan CO_2 ke arah persekitaran yang lebih hijau.

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LIST OF ABBREVIATIONS

APTES	-	3-aminopropyl triethoxysilane
CPB	-	Cetylpyridinium Bromide
CTAB	-	Cetyltrimethylammonium Bromide
Ea	-	Activation energy
ESR	-	Electron Spin Resonance
FESEM	-	Field Emission Scanning Electron Microscopy
FID	-	Flame Ionization Detector
FT	-	Fisher-Tropsch
FTIR	-	Fourier Transform Infrared
FWHM	-	Full width half maximum
GC	-	Gas Chromatography
GHG	-	Greenhouse Gases
GHSV	-	Gas hourly space velocity
JCPDS	-	Joint Committee on Powder Diffraction Standards
KCC	-	KAUST Catalytic Centre
MCM	-	Mobil Composition of Matter
MSN	-	Mesostructured Silica Nanoparticles
NLDFT	-	Non-local density functional theory
NMR	-	Nuclear magnetic resonance
RWGS	-	Reverse water gas shift
SBA	-	Santa Barbara Amorphous
TCD	-	Thermal Conductivity Detector
TEM	-	Transmission Electron Microscopy
TEOS	-	Tetraethylorthosilicate
TPR	-	Temperature Programmed Reduction
XRD	-	X-ray diffraction

LIST OF SYMBOLS

λ	-	wavelength
2θ	-	Bragg angle
$^{\circ}\text{C}$	-	degree celcius
\AA	-	Angstrom
μm	-	micrometer
g	-	gram
wt. %	-	weight percentage
min	-	minutes
mL	-	millilitre
nm	-	nanometer
P	-	pressure
K	-	Kelvin
θ	-	angle

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Increasing greenhouse gases (GHG) concentration in the atmosphere is one of the major problems contributing to global warming. Among the greenhouse gases, carbon dioxide (CO₂) is the heaviest and the most rapidly amplified (Faralli *et al.*, 2017). Huge emission amount over 30 Gt CO₂ per year CO₂ contributes to over 60% of global warming (Albo *et al.*, 2010). This triggered intensive research into CO₂ mitigation. Many previous researchers have discussed CO₂ capture and sequestration in term of various environmental and economic aspects such as fixation in carbonates, geological or ocean storage, or afforestation (Ghedini *et al.*, 2010; Wang *et al.*, 2011). Although various physical and chemical techniques have been proposed for the fixation of exhausted CO₂, their immediate practical application has drawbacks in term of economic factors, safety, efficiency, and dependability (Kim *et al.*, 2010)

Generally, three major pathways have been identified in order to reduce total CO₂ emission into the atmosphere. Firstly, reduction of energy consumption on daily activities. This option requires efficient use of energy. Secondly, reduction of carbon intensive processes which requires switching to the use of non-fossil fuels. Lastly, enhancement of CO₂ sequestration process by the development of technologies for CO₂ capture and utilization. Hence the motivation behind this work is to utilize CO₂ over modified porous silica materials into fuels and to optimize the effectiveness of the conventional silica catalyst towards CO₂ methanation process.

Nowadays, CO₂ has been applied in various industries, e.g., food, soft drink, welding, fire-extinguishers, foaming, propellant, agro-chemistry, or as a solvent/fluid in various process like water treatment packaging, separation, drying-cleaning, etc. Supercritical CO₂ found its growing application as solvent for reactions, polymer

modification and separation process. Although there exist such feasible applications of CO₂ utilization, their implication towards reducing total CO₂ emission were less effective due to small market scale (Huang and Tan, 2014). Thus, converting CO₂ as fuel would open new doors towards more feasible CO₂ utilization.

CO₂ hydrogenation into methane also known as CO₂ methanation or Sabatier reaction (Eq. 1.1) is the most favoured reaction in the series of CO₂ hydrogenation due to its ease of operation and relatively simple process. (Li *et al.*, 2018b). In the Sabatier process, CO₂ reacts with hydrogen in the presence of catalysts to produce methane and water. It is likewise one of the favourable options in order to cut the CO₂ emission in our environment. However, the reduction of CO₂ into methane requires the transfer of eight electrons which leads to significant kinetic limitation.



The reaction is highly exothermic and the removal of heat from the reactor is an important issue. Consequently, processes using high performance catalyst and adequate reactors are needed to achieve acceptable rates and selectivity (Hwang *et al.*, 2012).

Support plays an important role in the catalysis by providing high surface area and porosity to the catalytic system in order to provide abundance active sites. The role of support is not only restricted to adsorption centre for reactant, but also play role in the modification of catalyst properties. Previous study showed that CO₂ hydrogenation over unsupported catalyst is very low compared to supported catalyst (Aziz *et al.*, 2014c). This is due to the fact that supported catalyst is an oxidized phase, which can act as a matrix to enhance the homogeneous distribution of active metals and prevent agglomeration due to crystallite migration. Other than that, the morphology of the support also influences the performance of CO₂ methanation. Hence, in this study, several issues with respect to the morphology of porous silica have been investigated towards the CO₂ adsorption capacity.

Silica is usually chosen as a catalyst support due to high surface area, high mechanical and thermal stabilities and also ease to modify (Zhang *et al.*, 2013). Development of silica catalyst as support have gone through tremendous changes to tailor its properties to fit specific applications. Based on previous studies, open framework silica catalyst with two-dimensional (2D) structure such as mesoporous silica structure MCM-41 and SBA-15 have been attracting great concern over the years because of their potential ability to be a catalyst and behave as great surface-assimilative materials for large molecule of reactant. This is due to their unique properties such as high surface area, homogeneous pore size distribution and plenty of well distributed active sites. However, these porous silica nanomaterials comprised close-packing spherical empty cages with body-centred cubic symmetry which leads to poor accessibility to the active sites inside the pores, thus limiting their application (Zeleňák *et al.*, 2010)

In recent years, fibrous mesostructured silica catalyst (KCC-1) emerged as a new morphological structure and the surface area mainly attributed from the silica fibres (Polshettiwar *et al.*, 2010). In contrast to the two dimensional (2D) porous silica materials with cylindrical pore structure such as MCM-41 and SBA-15, KCC-1 has open silica fibrous, dendritic like structures. Fibrous morphology allows bulk mass transfer of gas reactant, as a consequence, it will shorten the CO₂ adsorption-desorption cycle time and lead to increase in the reaction kinetics. Thus, tremendously affects the catalytic performance (Singh *et al.*, 2016). Previous study showed that KCC-1 had been used in drug delivery system, adsorbent in removing drugs and heavy metals in waste water streams (Singh and Polshettiwar, 2016). Moreover, Patil *et al.* tested KCC-1 in CO₂ adsorption and better adsorption was found on KCC-1 compared to MCM-41 (Patil *et al.*, 2012). Herein, this study utilizes the KCC-1 in the gas phase reaction in order to identify the effect of modified porous silica nanomaterials toward the catalytic activities of CO₂ methanation. It is predicted that the altering of silica morphology from the two dimensional (2D) porous silica into fibrous morphology will optimize the catalytic activities.

Tailoring the surface morphology and electronic structure of the catalyst support is one of the promising approaches for the formation of abundant and specific

surface defect sites on the catalyst surface (Aziz *et al.*, 2014a). This is due to the abundance of oxygen-deficient sites on the catalyst surface which influence the CO₂ attraction, thus increasing the adsorption capabilities of catalyst. Therefore, the nature of the catalyst support such as basic strength, total oxygen vacancies and electron properties of the catalyst support will determine the interaction between the support and the reactant, thus determines the catalytic performance of CO₂ methanation reaction.

Metal loaded on silica-based catalysts were studied vastly in CO₂ methanation reaction. Typically, ruthenium and nickel are the most studied active metal for very long time. The ruthenium is superior in term of catalytic activity and mild reaction condition (Abdel-Mageed *et al.*, 2016). Nickel, on the other hand, also provide comparable activity at lower material cost. Cobalt was also studied as CO₂ methanation catalyst. Since cobalt is well known to perform in Fisher-Tropsch (FT) synthesis (Lögdberg *et al.*, 2017), researcher expected formation of higher hydrocarbon during the reaction. However, upon changing reactant from CO gas to the mixture of CO₂ and H₂ gas, cobalt catalyst displayed methanation favoured catalyst rather than FT catalyst (Bratt, 2016). Akin and co-worker observed that almost 70% of methane was formed using Co/Al₂O₃ catalyst (Akin and Önsan, 1997). Previous study also found that metal such as rhodium, ruthenium, nickel, iridium gave good catalytic activity while zinc, vanadium, chromium and aluminium were inactive for CO₂ methanation (Aziz *et al.*, 2014c).

However, the consensus on different pathways of reactant to product is still not clear. Two major mechanistic routes were proposed: direct hydrogenation route and CO-intermediate route. CO-intermediate route could be further specified by two pathways namely: associative and dissociative pathways. Few researches were conducted on mechanism of CO₂ methanation over different metal-based catalyst (Wang *et al.*, 2011). Major problem of metal-based catalyst for CO₂ methanation is thermal sintering. This phenomenon occurs due to mobilization of metal during elevated temperature (Zeng *et al.*, 2013). One of the main strategies to attenuate this problem is by controlling the metal particle size by either increasing dispersion of metal or immobilization of metal through confinement effect (Gálvez *et al.*, 2015).

Secondary metals or metal oxides as binder and promoter are gaining attention to overcome this limitation and improving activity of the catalyst. Emerging promoter includes cobalt (Wu *et al.*, 2019), magnesium (Bacariza *et al.*, 2017), vanadium (Jalama, 2017), cerium (Wang *et al.*, 2018), and lanthanum (Quindimil *et al.*, 2018). Oxygen exchange capacity of CeO₂ could reversibly store and release oxygen species, this promoting adsorption and desorption of CO₂. Other than that, the presence of CeO₂ over Ni/MCM-41 was found to enhance the dispersion of Ni, thus promoting the activity (Wang *et al.*, 2018). Vanadium showed interesting effect on adsorption of CO_x species. Carabinero *et al.*, concluded that oxygen acceptor-donor properties of vanadium which come from different oxidation states of vanadium promotes activity of carbon gasification of CO₂ to produce CO (Carabineiro *et al.*, 2000). Nicholas *et al.*, found that addition of K₄V₂O₇ produced oxyvanadate ions and in turns promotes the solvent adsorption of CO₂ (Nicholas *et al.*, 2014).

In this thesis, KCC-1 as new morphology of silica was utilized as support for CO₂ methanation. It was expected that due to unique fibrous morphology of KCC-1, both metal dispersion and reactant accessibility would be enhanced. Therefore, three critical modifications were identified and studied which are type of porous silica material with different morphology (KCC-1, MCM-41 and SiO₂), the effect of transition metal type (nickel, cobalt and zinc) and lastly effect of vanadium promoter towards CO₂ methanation activity. Response surface methodology was also utilized to optimize the reaction conditions for the best catalyst.

1.2 Problem Statement

Carbon dioxide (CO₂) is one of the major greenhouse gases that need to be captured and utilized. One of the feasible ways to utilize CO₂ gas is by converting into fuels such as methane. However, the CO₂ methanation reaction is highly exothermic. Therefore, efficient catalyst and catalytic processes are needed. Other than that, the selection of catalyst support for the CO₂ methanation is one of the critical parameters. Common support includes alumina (Al₂O₃), ceria (CeO₂), and silica (SiO₂) were usually chosen due to their ability to disperse the metal and adsorb the reactant. Silica

is usually chosen as a catalyst support due to high surface area, high mechanical and thermal stabilities and also ease to modify. Le et al., (2017) studied methanation reaction over different support such as Al₂O₃, SiO₂, TiO₂ and CeO₂. CeO₂ was found to be perform best due to high surface area, better metal dispersion and strong CO₂ adsorption capabilities. Interestingly, ease of modification properties of silica-based catalyst would allow tuned surface area and CO₂ adsorption capabilities, rendering silica an attractive choice for catalyst support. In general, there is need to design a robust especially highly stable and active catalyst for enhanced low temperature CO₂ methanation.

Two dimensional (2D) mesoporous silica such as MCM-41 and SBA-15 with cylindrical pore structure have been widely used as a catalyst support in CO₂ methanation (Fu *et al.*, 2015). This is due to high surface area, homogeneous pore size distribution and plenty of well distributed active sites for CO₂ adsorption. However, these porous silica materials comprised of closely-packed spherical empty cages which allows only one way of gas flow will lead to poor accessibility of bulk reactant to the active sites located inside the pores, thus limits their applications (Singh and Polshettiwar, 2016).

Metal component of catalysts is the active site for H₂ dissociation in the catalytic reaction of CO₂ methanation. Transition metals have been used as an active metal in heterogeneous catalyst system which showed comparable activity as noble metal-based catalyst. However, transition metal, especially nickel suffers from fast deactivation due to metal sintering. To overcome these problems, immobilization of metal through confinement effect of mesoporous silica was suggested. However, this also leads to accessibility problem as the active metal is located inside of pores (Xu *et al.*, 2011). Other the that, the dispersion of metals was also limited in the confined space.

Although CO₂ methanation could be carried out at moderate temperature with high activity, possibilities of low temperature reaction remain attractive in industrial perspective. This would provide cost efficiency and ensuring safe operation. CO₂ was mainly utilized from high purity sources such as natural gas processing and ammonia

synthesis. However, major CO₂ production comes from power plant (12-15 mol% CO₂), cement (14–33 mol% CO₂), and steel (20–44 mol%) industries were not utilized as scarce report on the influence of impurities. Specifically, the content of flue gas from cement industry includes 77% N₂, 13% CO₂, 5% H₂O, 4% O₂, and trace amount of other gases. Water impurities was studied previously and were found to inhibit methanation reaction (Xu *et al.*, 2003). Research focusing on O₂ impurities should also be carried out in order to utilize CO₂ from this area. Other than that, source of hydrogen should also be taken into consideration. As most hydrogen today is produced from fossil hydrocarbons, its conversion to methane is not a sensible idea unless an inexpensive and renewable source of hydrogen is found (e.g. biomass or water). Provided that hydrogen is generated from renewable energy sources such as water electrolysis (Centi *et al.*, 2009), methanation reaction could be perceived as means of energy storage and transportation.

1.3 Hypothesis

To overcome the above-mentioned problems, unique fibrous morphology of silica could be utilized to promote high accessibility of bulk gas reactants. Therefore, it will shorten the adsorption-desorption cycle of CO₂ reactant, thus increased its kinetics. It was hypothesized that the dispersion of metal on fibrous based silica catalyst will be high and more exposed. This is due to attachment of metal on the dendritic fibres of the silica and not in the pore as with conventional silica. It is also expected that incorporation of different transition metals would lead to different mechanistic pathways. Addition of promoter would result in both increase of CO₂ adsorption sites and allows for reaction to take place at lower temperature. Previous study also shown that addition of promoter could enhance dispersion of metal (Nicholas *et al.*, 2014). The presence of oxygen is expected to negatively affect the reaction as oxidization of metal would passivate the active sites.

1.4 Objective of Study

Objective of this study is to synthesize vanadium promoted nickel supported on silica catalyst for enhanced methanation of carbon dioxide. The objective of this study could be specified as follows;

- 1 To prepare and characterize different silica-based catalysts for CO₂ methanation
- 2 To investigate the effect of different transition metals towards CO₂ methanation activity and mechanism pathway
- 3 To evaluate the effect of second metal promoter and presence of O₂ on CO₂ methanation activity
- 4 To optimize the CO₂ methanation parameters over promoted catalyst by Response Surface Methodology (RSM).

1.5 Scope of Study

The scopes of this study consist of five parts namely: effect of support on CO₂ methanation, effect of metals and promoter on CO₂ methanation, effect of O₂ species and optimization of CO₂ methanation. The details are described as follows:

- I. The effect of supports on CO₂ methanation was studied by preparing a series of silica-based catalysts with different morphology (KCC-1, MCM-41 and SiO₂). KCC-1 was prepared via microemulsion method as reported in previous literature (Febriyanti *et al.*, 2016). The growth of pore size of KCC-1 was controlled by the cationic surfactant cetyltrimmonium bromide (CTAB), while toluene as a non-polar solvent act as a media to retain the surfactant to facilitate the growth of dendrimers. The prepared catalysts were characterized by XRD, N₂ physisorption, FESEM, TEM, UV-DRS, Pyrrole-FTIR, CO₂-

FTIR, ESR, TPR and NMR. Catalytic testing on CO₂ methanation was done at temperature range of 423-723 K and atmospheric pressure.

- II. The effect of metals on CO₂ methanation was studied by preparing a series of transition metal promoted KCC-1 with various metals (Ni, Co, Zn, V, Cr, Mn, Fe and Cu). Preparation of metal promoted on KCC-1 catalysts were synthesized by impregnation method with 5 wt.% metal (Garbarino *et al.*, 2014). From the screening result, three metals (Ni, Co and Zn) were chosen to further analyses to understand the influence of different transition metals. The prepared catalysts were characterized by XRD, N₂ physisorption, FESEM-EDX, Pyrrole-FTIR, and TPR. Catalytic testing on CO₂ methanation was done at temperature range of 423-723 K and atmospheric pressure. The general reaction mechanism of CO₂ methanation over different transition metal was studied using *in situ* CO₂-ESR and *in situ* CO₂+H₂-FTIR spectroscopy.
- III. The effect of second metal promoter on CO₂ methanation was studied with different metals (V, Zn, Cr, Mn, Fe and Cu). Vanadium showed good interaction with CO₂, and was chosen to be further characterized. (Nicholas *et al.*, 2014). A series of vanadium promoted Ni/KCC-1 was prepared with various vanadium loading (2.5, 5, 7.5 and 10 wt. %). Preparation of vanadium promoted Ni/KCC-1 catalysts were synthesized by co-impregnation method. The prepared catalysts were characterized by XRD, N₂ physisorption, Pyrrole-FTIR, CO₂-FTIR and TPR. Catalytic testing on CO₂ methanation was done at temperature range of 423-723 K and atmospheric pressure. The effect of O₂ species on CO₂ methanation was studied using 7.5V-Ni/KCC-1 as a catalyst. Different ratio of O₂:CO₂ was used (0.25, 0.5, 1 and 2). The catalyst was also tested for prolong effect of O₂ species. FTIR O₂ on preadsorbed CO₂ was carried out to investigate the influence of O₂ on CO₂ adsorption.
- IV. The optimum condition for CO₂ methanation over 7.5V-Ni/KCC-1 was identified by RSM using central composite design (CCD) developed by Statistica 6.0 StatSoft. The variables selected in the study are reaction temperature (623-723 K) (Kesavan *et al.*, 2018), GHSV (7500 – 22500 mL g⁻¹

h^{-1}) (Aziz *et al.*, 2015) and H_2 to CO_2 ratio (2-6) (Hoekman *et al.*, 2010). These variables were chosen based on results from literature and preliminary studies that have been conducted. From preliminary results, the activity of the catalyst already reached plateau at temperature 773 K, thus, the lower range of 723 was chosen. The performance of the catalyst was evaluated by analyzing the response of CH_4 yield.

1.6 Significant of Studies

In this study, the KCC-1 supported catalyst is a new and emerging morphology of modified silica nanoparticle catalyst. As compared to other cylindrical silica nanoparticle system such as MCM-41 and SBA-15, KCC-1 has unique fibrous morphology with dendrimer like structure. This fibrous morphology is unique due to several catalyst properties such as allowing bulky mass transfer of gas reactant into the active sites, high thermal stability and high oxygen-defect thus high basic sites. As a consequence, fibrous morphology shortens CO_2 adsorption-desorption cycle time of catalytic reaction which leads to increase in the reaction kinetics. Furthermore, loading of metals on the KCC-1 support will be easier due to the fact that more active metals can be placed onto its open access morphology. Besides, detailed investigation on transition metal loaded KCC-1 and promoted metal KCC-1 reveals different mechanism pathway and higher activity of the catalyst. Optimization by RSM highlighted the factors influencing catalytic methanation. Additionally, it will be a significant contribution to the research and science community, especially in the utilization of the greenhouse gases into more valuable synthetic natural gases.

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