

SYNTHESIS OF FIBROUS SILICA SUPPORTED NOBLE METALS
CATALYSTS FOR SYNGAS PRODUCTION VIA PARTIAL OXIDATION OF
METHANE

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UNIVERSITI TEKNOLOGI MALAYSIA

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METHANE

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ABSTRACT

The ever-increasing worldwide energy consumption and released tons of energy-related CO₂ gas into the atmosphere have driven the exploration of syngas in petrochemical industries and synfuels generation from Fischer-Tropsch synthesis (FTS). Among the technologies for syngas generation, catalytic partial oxidation of methane (POM) appears as a promising technique due to its short contact time at high space velocity and mildly exothermicity leading to excellent energy efficiency. However, the catalyst deactivation induced by carbon deposit is always a challenging issue for POM. Thermodynamic equilibrium assessment for POM was conducted in this research by using the Gibbs free energy minimization approach to study the tuning of syngas H₂/CO ratio appropriate for downstream FTS. The results revealed that indirect combustion-reforming pathway was possibly the main contributory factor to the syngas yield during POM. In this research, silica materials with various morphology, namely commercial silica (SiO₂), commercial Mobil Composition of Matter number 41 (MCM-41) and dendritic fibrous KAUST Catalysis Centre 1 (KCC-1) were prepared to study their properties and catalytic activity relationship for POM. The KCC-1 support was synthesized using microwave-assisted microemulsion. The addition of 0.5 wt.% M (M = Ru, Pd or Rh) on KCC-1 support were carried out using wetness impregnation methods to further enhance the POM performance. The catalysts were characterized using X-ray diffraction, N₂ physisorption, transmission electron microscopy, X-ray photoelectron spectroscopy, Fourier-transform infrared spectroscopy, electron spin resonance and Raman spectroscopy measurements. The effects of support morphology and active transition metals addition towards the catalytic performance, stability, resistibility to carbonaceous deposits and high-temperature oxidative regeneration of the KCC-1 supported catalysts were examined over a temperature range of 500–900 °C. Compared to SiO₂ and MCM-41, the high concentration of oxygen vacancies in KCC-1 substantially contributed to the enhancement in POM performance which was highly associated with CH₄ dissociation and adsorption of oxidizing agents (i.e., O₂, CO₂ and H₂O). At 800 °C, turnover rate of CH₄ dropped in the order of Rh/KCC-1 (30.1 min⁻¹) > Pd/KCC-1 (18.1 min⁻¹) > Ru/KCC-1 (15.1 min⁻¹). The in-situ ESR and XPS studies corroborated that the oxygen vacancies were beneficial for the syngas formation by enhancing methane steam reforming and methane dry reforming reaction rates as well as carbon gasification process. Based on the achieved H₂/CO ratio, Rh/KCC-1 appeared as a prospective candidate for use in POM application appropriate for downstream synfuel production. The mechanism-derived kinetic modelling determined that the POM over Rh/KCC-1 followed dual site dissociative adsorption of both CH₄ and O₂ with bimolecular surface reaction as rate-determining step. This study highlighted the new perspectives on the use of KCC-1 supported catalysts in alternative, renewable and sustainable energy technologies with respect to reaction engineering and catalysis, particularly from catalyst synthesis, characterization and application point of view.

ABSTRAK

Penggunaan tenaga di seluruh dunia dan pengeluaran banyak gas karbon dioksida (CO_2) yang berkaitan dengan tenaga ke atmosfera telah mendorong penerokaan singas dalam industri petrokimia dan penjanaan sinbahanapi dari sintesis Fischer-Tropsch (FTS). Antara teknologi untuk penjanaan singas, pengoksidaan separa bermangkin metana (POM) muncul sebagai teknik yang berpotensi kerana masa sentuhannya yang singkat pada halaju ruang yang tinggi dan eksotermisiti ringan yang membawa kepada kecekapan tenaga yang sangat baik. Walau bagaimanapun, penyahaktifan mangkin yang disebabkan oleh karbon sentiasa menjadi isu yang mencabar bagi POM. Penilaian keseimbangan termodinamik untuk POM dijalankan dengan pendekatan peminimuman tenaga bebas Gibbs untuk mengkaji penalaan nisbah singas H_2/CO yang sesuai untuk FTS hiliran. Keputusan mendedahkan bahawa laluan pembaharuan pembakaran yang tidak langsung mungkin merupakan faktor penyumbang utama kepada hasil syngas semasa POM. Dalam penyelidikan ini, bahan silika dengan pelbagai morfologi, iaitu, silika komersial (SiO_2), Komposisi Mobil Matter komersial nombor 41 (MCM-41) dan KAUST Catalysis Center 1 (KCC-1) berserat dendritik disediakan untuk mengkaji sifat mereka dan hubungan aktiviti bermangkin untuk POM. Sokongan KCC-1 disintesis menggunakan mikroemulsi berbantu gelombang mikro. Penambahan 0.5 wt.% M (M = Ru, Pd atau Rh) pada sokongan KCC-1 telah dibuat dengan menggunakan kaedah impregnasi kebasahan untuk meningkatkan lagi prestasi POM. Mangkin dicirikan dengan menggunakan pembelauan sinar-X, fisisorpsi N_2 , mikroskop elektron transmisi, spektroskopi fotoelektron sinar-X, spektroskopi inframerah transformasi Fourier, resonans putaran elektron dan pengukuran spektroskopi Raman. Kesan morfologi sokongan dan penambahan logam peralihan aktif terhadap prestasi mangkin, kestabilan, ketahanan terhadap deposit karbon dan pertumbuhan semula oksidatif suhu tinggi kepada mangkin yang disokong oleh KCC-1 diperiksa dalam julat suhu 500-900 °C. Berbanding dengan SiO_2 dan MCM-41, ketumpuan kekosongan oksigen yang tinggi dalam KCC-1 dengan ketara menyumbang kepada peningkatan prestasi POM yang sangat berkaitan dengan penguraian CH_4 dan perjerapan ejen pengoksidaan (iaitu O_2 , CO_2 dan H_2O). Pada suhu 800 °C, kadar perolehan CH_4 menurun mengikut urutan Rh/KCC-1 (30.1 min^{-1}) > Pd/KCC-1 (18.1 min^{-1}) > Ru/KCC-1 (15.1 min^{-1}). Kajian ESR dan XPS di-situ membuktikan bahawa kekosongan oksigen bermanfaat untuk pembentukan singas dengan meningkatkan pembaharuan wap metana dan kadar reaksi pembaharuan kering metana serta proses gasifikasi karbon. Berdasarkan nisbah H_2/CO yang dicapai, Rh/KCC-1 muncul sebagai calon berpotensi untuk digunakan dalam aplikasi POM yang sesuai untuk penghasilan bahan bakar hilir. Pemodelan kinetik berpandukan mekanisme menunjukkan bahawa POM ke atas Rh/KCC-1 mengikuti perjerapan penceraian dwi-tapak kedua-dua CH_4 dan O_2 dengan reaksi permukaan dwimolekul sebagai langkah penentuan kadar. Kajian ini menyoroti perspektif baharu mengenai penggunaan mangkin yang disokong oleh KCC-1 dalam teknologi tenaga alternatif, boleh diperbaharui dan lestari berkenaan dengan teknik tindak balas dan pemangkinan, terutama dari sudut mangkin sintesis, pencirian dan aplikasi mangkin.

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LIST OF ABBREVIATIONS

ANOVA	-	Analysis of Variance
BBD	-	Box-Behnken Design
BET	-	Brunauer-Emmett-Teller
CCD	-	Central Composite Design
CH ₄ -TPSR	-	Temperature Programmed Surface Reaction of CH ₄
DFT	-	Density Functional Theory
DRM	-	Dry Reforming of Methane
ER	-	Eley Rideal
ESR	-	Electron Spinning Resonance
FESEM	-	Field Emission Scanning Electron Microscopy
FTIR	-	Fourier-Transform Infrared
FTS	-	Fisher-Tropsch synthesis
GHSV	-	Gas Hourly Space Velocity
GTL	-	Gas-to-Liquids
H ₂ -TPR	-	H ₂ Temperature-Programmed Reduction
KCC	-	KAUST Catalysis Center
LH	-	Langmuir-Hinshelwood
MARI	-	Most Abundant Reactive Intermediate
MCM-41	-	Mobil Composition of Matter number 41
NL-DFT	-	Non Localized Density Functional Theory
NPs	-	Nanoparticles
O ₂ -TPSR	-	Temperature Programmed Surface Reaction of O ₂
OFAT	-	One Factor At A Time
OSC	-	Oxygen Storage Capacity
OV	-	Oxygen Vacancies
POM	-	Partial Oxidation of Methane
PSA	-	Pressure Swing Absorption
RDS	-	Rate-Determining Step
RSM	-	Response Surface Methodology
RWGS	-	Reverse Water-Gas Shift

SBA-15	-	Santa Barbara Amorphous number 15
SRM	-	Steam Reforming of Methane
TAP	-	Thin-Zone Temporal Analysis of Products
TEM	-	Transmission Electron Microscopy
TOM	-	Total Oxidation of Methane
TPO	-	Temperature-Programmed Oxidation
TPP	-	Temperature-Partial Pressure
WGS	-	Water-Gas Shift
XANES-POM	-	X-Ray Absorption Near Edge Structure-Partial Oxidation of Methane
XRD	-	X-Ray Diffraction

LIST OF SYMBOLS

kJ	-	Kilojoules
$\Delta H^0_{298\text{K}}$	-	Enthalpy of reaction at room temperature
\rightleftharpoons	-	Reversible reaction pathway
$^{\circ}\text{C}$	-	Degree Celsius
2D	-	Two-dimensional
wt%	-	Weight percentage
h	-	Hours
&	-	And
>	-	Greater than
<	-	Less than
\geq	-	Greater than or equal to
*	-	Adsorbed Intermediate
f	-	Function
ξ	-	External effects on response
kPa	-	Kilopascal
$D_{(\text{Ni})}$	-	Nickel crystallite size
β	-	peak broadness at full width of half maximum intensity
2θ	-	Bragg diffraction angle
θ	-	Theta angle
λ	-	Wavelength
nm	-	Nanometres
R^2	-	Coefficient of determination
exp	-	Exponential
A	-	Pre-exponential factor
R	-	Universal gas constant
k	-	Rate constant
G	-	Gibbs free energy
f_i	-	Fugacity
$\hat{\phi}_i$	-	Fugacity Coefficient

λ_k	-	Lagrange Multiplier
a_{ik}	-	Atom Quantity of Molecular Species
v_m	-	Volume Occupied by an Atom in Bulk Metal
a_m	-	Area Occupied by a Surface Atom
p-value	-	Probability value
P	-	Pressure
T	-	Temperature
g	-	Grams
Min	-	Minutes
s	-	Seconds
mol	-	Mole
Δ	-	Delta
L	-	Litres
m	-	Metres
mL	-	Millilitres
Gt	-	Giga ton
D_{ij}	-	Mass Diffusivity
α	-	Thermal Diffusivity
Le	-	Lewis Number
C_α	-	Adsorbed Surface Carbon
C_β	-	Carbon Filaments
C_v	-	Carbon Whiskers
C_γ	-	Carbide Bulk
C_c	-	Graphitic Platelets

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The depletion of fossil fuel and anthropogenic CO₂ emission has grown exponentially due to the large-scale industrial combustion driven by the increasing global energy demand and economic expansion in recent years. The fossil fuel-based combustion (i.e., coal, natural gas and petroleum) reportedly resulted in 33.5 gigatons of global energy-related CO₂ emission in 2019 and as a result of intensive population growth, it predictably grows by an additional 19.2% in 2050 (Friedlingstein et al., 2019; Peters et al., 2020). Thus, there is a worldwide concern regarding the environment degradation and climate changes, attributed to the present carbon-intensive energy system (Kan et al., 2019). In this context, substituting current fossil fuel-based energy with less carbon-intensive energy sources and reducing the substantial dependency on non-renewable energy are an indispensable and urgent mission. Syngas (mixture of H₂ and CO) emerges as a prospective alternative, which provides feasible building blocks for the downstream production such as hydrogen for fuel cell, methanol in petrochemical industry and synthetic fuels from Fisher-Tropsch synthesis (FTS) (Dos Santos and Alencar, 2020). Although renewable energy is the long-term key to overcome the aforementioned problems, syngas is presently the feasible short-term solution acting as the cushion to smooth the transition towards an effective low-carbon energy system in near future (Minh et al., 2018). To date, the market of syngas and its derivatives was predicted at 2,45,557 MWth and was forecasted to achieve 4,06,860 MWth by 2025 with a 10.6% of compound annual growth rate in between 2020 and 2025 (Research and Markets Ltd, 2020). Additionally, there are five existing commercial-scale gas-to-liquids (GTL) plants implement FTS coupled with syngas production technologies providing 259 Mbpd of synthetic fuel whilst three additional GTL facilities with similar configuration are under development across the world (Lee, 2020).

Amongst the syngas production technologies, steam reforming of methane (SRM) is presently the conventional technology to be deployed in industrial applications due to its abundance of feedstock (i.e., water and methane from natural gas) and high selectivity of H₂ (Abdullah et al., 2017; Minh et al., 2018). However, SRM yields a H₂/CO ratio of 3 with considerable amount of concomitant CO₂ emission, making it unfavorable for direct downstream processes. From industrial and environmental perspectives, the research emphasis has shifted towards dry reforming of methane (DRM) as it transforms greenhouse CO₂ into syngas with a ratio of unity. Nevertheless, for both SRM and DRM technologies, the requirement of auxiliary separation and purification units for tuning syngas ratio to around 2 and high energy supply imposes the overall capital cost (Siang et al., 2018; Subraveti et al., 2020). From the above reasons, partial oxidation of methane (POM) has appeared as a promising candidate to substitute other methane reforming technologies (Elbadawi et al., 2020a). In addition, the POM technology reportedly offers 10–15% and 25–30% lower in the energy requirement and capital investment, respectively compared to SRM (Pantaleo et al., 2016). In fact, POM technology has been implemented in twelve world-wide industrial plants, namely, POX plants by the Linde group since few decades ago and one of the four world's largest POX plants continuously supply 200,000 Nm³/h of syngas to the global gas market till today (The Global Syngas Technologies Council, 2018; Linde, 2020).

Catalytic POM technology undeniably offers practical syngas content for wide-ranging downstream industrial applications with higher cost- and energy-efficiency but it encounters several challenges adversely affecting its catalysis activity as POM owns a complex system consisting of multiple reactions (Enger et al., 2008). In general, metal group VIII, IX and X such as Ni, Co, Fe, Ru, Pd, Rh, Ir and Pt, are widely recognized as the active metals for methane oxidation studies (Bashan and Ust, 2019; He et al., 2020). Despite the non-noble metal catalysts are extensively investigated for methane oxidation studies, the severe deterioration in catalysis activity due to carbon deposition and reoxidation of hosting metal has confined their practicability for industrial purposes. In this context, the emphasis on development of catalyst design respective to noble metal has been renewed with arising concerns from both academic and industrial realms since it possesses great resistance towards reoxidation and carbon deposition as well as excellent ability of CH₄ scission (Zhu et

al., 2013; Kondratenko et al., 2014; Meng et al., 2020; Mishra et al., 2020; Rocha et al., 2020). Particularly, carbon deposition is unavoidable during CH₄ reforming processes at high-temperature zone even though in the presence of noble metal as the active hosting material for a catalyst system (Argyle and Bartholomew, 2015). Additionally, the competitive adsorption of oxidizing agents on catalyst surface under the exceedingly oxidizing environment could affect the carbon elimination associated with the activation of oxidants (Minh et al., 2018). Therefore, exploring a novel catalyst system presents high accessibility of reactants to active sites at a molecular level to facilitate the surface reaction enhancing syngas formation and simultaneously suppressing carbon deposition is essential in POM.

According to the literature (Pantaleo et al., 2016; Ma et al., 2019; Elbadawi et al., 2020b), the reforming catalysts with unique morphological structure or/and comprising of oxygen vacancy are possibly the key to overcome these adverse effects. Wang et al. (2018) reported that fibrous morphology of their nanofibrous-structured Ni catalyst is responsible for the robust long-term catalytic activity which overcomes the mass transfer limitation during POM reaction at high gas space velocity in order to achieve high production. From the computations of Density Functional Theory (DFT) performed by Cheng et al. (2016), the presence of oxygen vacancy reportedly not only enhances the extent of adsorption for the radical-like CH_x (where x = 0–3) fragments from CH₄ molecules but also accelerates the carbon radical adsorption. This was ascribed to the different chemisorbed oxygen (O^{*}) assisted kinetically relevant C–H bond activation mechanism with various levels of O^{*} coverages on catalyst surface depending on the concentration of oxygen vacancy (Chin et al., 2011a; Chin et al., 2011b; Mihai et al., 2012). However, most of the POM investigations associated to oxygen vacancies or distinctive engineered structure of catalyst were studied individually and normally carried out over conventional catalysts instead of active catalyst produced from hierarchical material and advanced synthesis technique. Thus, this study aimed to prepare a highly active and efficient catalyst simultaneously possessing these two features to study the combination effect on the POM performance, kinetic and mechanism.

A new dendritic fibrous nanosilica material, namely KCC-1 (KAUST Catalysis Center) with unique fibrous morphology of dendrimeric silica fibers has recently emerged as the prospective candidate to fulfill the aforementioned requirements (Polshettiwar et al., 2010; Febriyanti et al., 2016). Due to its unique fibrous morphology, KCC-1 possesses high accessible surface area resulting in outstanding catalysis activity and capture of oxidizing agents (Hamid et al., 2017; Peng et al., 2019; Abdulrasheed et al., 2020). Specifically, the silica fibers surrounding the outer surface of KCC-1 providing abundant oxygen vacancy sites could act as platforms to supply labile oxygen ions from adsorbed O^{2-} species, hence significantly tuning the intrinsic nature of hosting metal particles during reaction (Yentekakis et al., 2019; Hussain et al., 2020). These characteristics suggest that employment of KCC-1 in POM process could enormously promote the POM performance in terms of catalytic stability and regenerability. However, comprehensive insight into the correlation between oxygen vacancies and metal-support interaction towards catalytic performance as well as carbonaceous deposition is still vague for KCC-1 supported catalysts in heterogeneous catalytic systems.

To the best of our knowledge, no experimental works about POM performance over dendritic fibrous KCC-1 supported catalysts have been reported to date, particularly in association with the concentration of oxygen vacancies and metal-support interaction. Herein, the POM catalytic behavior of well-characterized M/KCC-1 (where M represents Ru, Pd or Rh) catalysts was studied. The oxygen ion lability characteristic of these materials is greatly reliant on their surface adsorbed oxygen species and the concentration of oxygen vacancies, which ascertain their degree of metal-support interaction on catalyst surfaces. Factually, the intrinsic catalytic activity of catalysts is strongly altered by this property and the investigation of such impacts on the KCC-1 catalyzed POM performance is the main focus of current study. The correlation between oxygen vacancies and catalytic behavior of M/KCC-1 was systematically scrutinized and was rationalized in terms of bifunctional reaction mechanism involving combustion-reforming and Mars-van-Krevelen mechanisms.

1.2 Problem Statement

The syngas production of POM reaction has recently acquired significant interest from researchers since it can reduce the high dependence on carbon-intensive energy systems and produce alternative energy sources, syngas for synthetic fuel generation by providing a practical H₂/CO ratio of 2. However, the POM reaction also faces a number of challenges that need to be addressed, in particular the co-occurrence of several side reactions. It is therefore important to investigate and study the catalytic POM process for potential industrial application.

In fact, trade-offs between the efficiency and stability of heterogeneous catalysts remain the major drawback for the implementation of syngas production through POM. As a mildly exothermic reaction, the equilibrium reactant conversion is favourably achieved at moderated temperatures for POM process. However, numerous undesired parallel side reactions including CH₄ decomposition, reverse Boudouard reaction and reverse water-gas shift, are inevitable at such reaction conditions which eventually adversely affect the product selectivity and catalyst lifespan. In this context, a number of thermodynamic works on operating parameters for POM have been conducted. However, the bibliography of thermodynamic evaluation on POM is still little-known. Therefore, it is important to investigate the thermodynamic behavior of POM under different conditions in order to comprehensively understand its pathway with respect to elimination of carbon deposit and syngas ratio appropriate for FTS application.

Catalyst lifespan is closely depended on the degree of deactivation induced by deposition of carbonaceous species and metal sinterization. Numerous efforts have been dedicated towards enhancement of catalyst stability, many of which have been found to be detrimental to the catalyst activity and similar trends were also obtained vice versa. Hence, it is essential to develop robust catalysts with the required activity and stability suitable of industrial application for the process. Selection of catalytic support for POM reactions is important as it greatly affects the internal and external mass transfer of reactants during reactions. In this study, silica material will be employed as a support due to its crucial silica–metal interface in heterogeneous

catalysis. However, the original silica structure is less active for anchoring the loaded metal particles and hence, the modification of pristine silica material is needed to enhance its catalytic behavior. In this regard, the use of two-dimensional (2D) mesoporous silica supports (i.e., MCM-41 and SBA-15) has been extensively employed in POM due to their high surface area, great thermal resistibility and high pore volume with uniform pore size leading to more accessible active sites. However, these mesoporous silica materials constituents of close-packed spherical empty channels encounter a challenging issue, where the clogging of channels due to partial damage of thin wall or partial metal sintering will results in a loss in catalytic activity.

Apart from support, the active metal acts as the active site is indispensable for POM as it is widely recognized that CH_4 dissociation is a rate-determining step. In general, d-group transition metals such as Rh, Ru, Pd, Pt, Ni, Co, Cu and Fe are widely used as an active metal in POM system. However, similar to the support these transition metals also suffer from numerous setbacks including deposition of carbonaceous species, metal sintering and reoxidation of active metal to inactive metal oxide during POM process. Thus, exploring a novel catalyst system with an effective combination of support and metal is essential to resist the abovementioned problems and simultaneously to achieve an excellent catalytic performance.

Catalyst performance is undeniably depending on the intrinsic behavior of catalyst and operating parameters of reaction. Hence, the screening operating conditions for reaction evaluation is indispensable to attain the best POM performance. Additionally, the bibliographic knowledge about POM mechanistic and kinetic is still vague because of its complexity, particularly for dendritic fibrous transition metal catalysts. The published literature relates to kinetic parameters for POM reaction is still scarce for advanced kinetic evaluation compared to other reforming reactions. Therefore, the best-fit kinetic model based on POM mechanistic is necessitated in order to attain the valuable kinetic parameters benefits the reactor design and optimization of catalyst synthesis.

1.3 Research Hypothesis

The spontaneity and selectivity of POM in comparison to other side reactions to produce the desired product ratio is a function of the Gibbs free energy minimisation, equilibrium temperature and reaction temperature. From the thermodynamic simulations, the range of the suitable operating conditions is determined in terms of minimization of carbon formation and a practical H₂/CO ratio around 2. The uniqueness of the fibrous morphology for mesoporous siliceous KCC-1 support enable a homogeneous dispersion of active metals on the surface of support. In addition, it allows a high accessibility of bulk gaseous reactant to active metallic phase for catalytic heterogeneous reaction due to its non-restricted three-dimensional open structure. As a result, the rate of CH₄ and O₂ adsorption can be extensively accelerated and thus, improvement in kinetic reaction. In comparison with conventional silica-supported catalysts, employment of fibrous KCC-1 is estimated to give a greater catalytic performance owing to its dendritic fibres effectively anchoring metal particles on the site. Subsequently, the resulting fine dispersion of metals can suppress the catalyst deactivation arising from carbonaceous species formation on the surface of catalyst and hence, prolong catalyst lifespan. Additionally, tuning the silica morphology from 2D porous silica to fibrous morphology can raise the basic sites of catalyst that benefits catalytic activity by acting as an active surface for adsorption of CH₄ and O₂ in POM reaction. In fact, tuning the electronic structure and surface morphology of the catalyst support will influence specific defect sites formation of the catalyst, which can increase the basicity of the catalyst due to increasing oxygen deficit. In addition, appropriate selection of metals will promote the reaction activity via facilitation of CH₄ dissociation as the first step of activation for POM. With the employment of response surface methodology (RSM) approach, optimization of POM reaction by selecting appropriate operating conditions (i.e., gas hourly space velocity, temperature and reactant feed composition) will be distinctly ascertained in order to attain the highest reforming performance in terms of syngas yield and syngas ratio. Additionally, the attained data from the various operating parameters can be further be used to fundamentally determine the kinetic parameters with the best-fit kinetic model.

1.4 Research Objectives

The aim of this research work is to synthesize fibrous silica (KCC-1) supported transition metal catalysts with high activity and stability for optimum syngas production via partial oxidation of methane. This is achieved through the following objectives:

1. To evaluate the thermodynamic behavior of POM under various operating conditions including temperature, pressure and reactant feed composition.
2. To compare metal-free (i.e., SiO₂, MCM-41 and KCC-1) and metal-based (i.e., Ru, Pd, Rh) catalysts in terms of their physicochemical attributes and catalytic performances.
3. To optimize the POM process by response surface methodology (RSM) approach for the outperforming fibrous KCC-1 supported catalyst.
4. To determine the kinetics and mechanistic of POM reaction over the outperforming fibrous KCC-1 supported catalyst.

1.5 Research Scope

The emphasis of this study is overcoming some major setbacks encountered by reforming catalyst for syngas production via POM. In this context, thermodynamics of POM, effects of support morphology, effects of active metal catalysts, optimization of POM process, kinetic and mechanistic study of POM have been deliberated upon. The details of the specific research scope are as follows:

1. The thermodynamic behavior of POM reaction was studied by HSC Chemistry software. In this study, few independent variables are chosen, namely, pressure (1–50 bar) (Jang et al., 2016; Nikoo et al., 2011), reaction temperature (from 200 to 1000 °C) (Jang et al., 2016; Nikoo et al., 2011) and feedstock ratio (CH₄:O₂ = 0.5–5) (Jang et al., 2016; Nikoo et al., 2011).

2. Various silica support with different morphology (*viz.*, SiO₂, MCM-41 and KCC-1) and KCC-1 supported noble metal catalysts (i.e., 0.5%Ru/KCC-1, 0.5%Pd/KCC-1, 0.5%Rh/KCC-1) were synthesized by using wetness impregnation technique. Subsequently, their physicochemical attributes were examined. For instance, textural properties (BET surface area, average pore diameter and total pore volume) using Brunauer-Emmett-Teller (BET) method, X-Ray Diffraction (XRD) measurements for crystallinity, Fourier-transform infrared (FTIR) spectroscopy, Raman spectroscopy and electron spinning resonance (ESR) analyses for surface chemistry, H₂ Temperature-Programmed Reduction (H₂-TPR) analyses for catalyst reducibility properties, Transmission Electron Microscopy (TEM) measurements and Field Emission Scanning Electron Microscopy (FESEM) for surface morphology. In addition, deposited carbon quantification and qualification on spent catalyst was ascertained using Temperature-Programmed Oxidation (TPO) measurements, X-ray photoelectron spectroscopy (XPS), XRD, FESEM and TEM. The catalytic performance of all catalysts in POM was scrutinized at gas hourly space velocity of 18000 mL g_{cat}⁻¹ h⁻¹ (Singha et al., 2017; Wang et al., 2018), reaction temperatures of 800 °C (Singha et al., 2017; Wang et al., 2018) and stoichiometric feedstock ratio (CH₄:O₂ = 2:1) (Singha et al., 2017; Wang et al., 2018) for 10 h on-stream.
3. The optimum condition for POM reaction over fibrous KCC-1 supported catalyst (the representative 0.5%M/KCC-1 with best catalytic performance from previous section) was determined by RSM using central composite design (CCD). In this study, few independent variables were chosen for the optimization, namely, gas hourly space velocities (from 15000 to 45000 mL g_{cat}⁻¹ h⁻¹) (Singha et al., 2017; Wang et al., 2018), reaction temperature (from 600 to 900 °C) (Singha et al., 2017; Wang et al., 2018) and feedstock ratio (CH₄:O₂ = 1–3) (Singha et al., 2017; Wang et al., 2018).
4. The study of kinetic rate expressions including simplified power law, Eley Rideal (ER) and Langmuir-Hinshelwood (LH) models was conducted. The best-fit kinetic modelling was determined based on the mechanism derived kinetic rate expressions for POM over the optimum 0.5%M/KCC-1 catalyst.

1.6 Research Significance

In this study, the fibrous siliceous KCC-1 supported catalyst has recently appeared as a new emerging morphology of modified structure for silica materials compared to other material supports. Due to the revolution in microemulsion technique, the formation of fibrous morphology on advanced material is now possible for heterogeneous catalytic system. The uniqueness of fibrous morphology remarkably improves the catalyst properties, which allows bulky mass transfer of gas reactants into the active sites, high thermal stability and high basic sites induced by high oxygen-deficient. As POM is a mild exothermic and short contact time reaction, volume expansion after reaction is inevitable, resulting in competitive adsorption of reactants on catalyst surface, particularly at high temperature. Given the specific feature of fibrous morphology, the accessibility of reactants to the active sites on catalyst surface within short contact time is guaranteed under strongly oxidative surrounding and as a result, the long-term POM activity is sustained.

Additionally, silica fibers of KCC-1 not only offer fibrous morphology but also provide high concentration of oxygen vacancy sites. Since POM also constitutes of indirect combustion-reforming pathway, the employment of fibrous KCC-1 supported catalyst predictably accelerate the oxidant (*viz.*, O₂, CO₂ and H₂O) adsorption-desorption cycle time of catalytic POM reaction leading to an enhancement in reaction kinetics rate, which governs the high POM activity. In the presence of oxygen vacancies, involvement of evolution for secondary catalytic reforming of methane, namely, SRM and DRM will be promoted to boost the conversion of reactants to syngas. Moreover, the labile oxygen ions stored in the oxygen vacancies can largely contribute to the carbon gasification and regenerate the vacancies. This repetitive cycle can further prolong the catalyst lifespan during reaction. Thus, the fundamental studies into the oxygen vacancy effect of fibrous KCC-1 and its synergistic effect with transition metals on CH₄ oxidation can provide applicable guidance to the design and development of catalyst in POM process.

1.7 Thesis Outline

The research is targeted on the development of oxygen vacancy-rich KCC-1 supported catalyst for efficient and sustained syngas production via POM. The thermodynamics of POM and major side reactions were studied to get preliminary information on the dynamics of the POM reaction under various reaction conditions. The dendritic fibrous KCC-1 morphology was not only to enhance the metal dispersion but also to provide high density of oxygen vacancies for facilitating the surface reaction of POM. Introduction of oxygen vacancy sites was done primarily to improve the electrostatic interaction between the support and hosting metal particles, thus leading to an enhancement in the POM performance. The optimization of process parameters, kinetic and mechanistic evaluations were conducted to ensure an optimum operational condition and gain an insight into the fundamental mechanistic understanding for the synthesized catalyst in respect of catalysis, particularly from catalyst synthesis, characterization and application point of view. This thesis therefore consists of five chapters.

Research background of the study area, problem statement, hypothesis, objectives, scope and significance of this research were elaborately discussed in Chapter 1. Chapter 2 presents literature review on contemporary research outputs in areas of global energy demand and its impacts, global syngas market, methods to syngas production, thermodynamic of POM, challenges in POM reaction, strategic design for POM catalyst and reaction kinetics and mechanism. Chapter 3 entails the overall description of materials, methodology, characterizations and experimental procedures applied during the course of the research. Chapter 4 covers the entire results, discussions and their analysis conducted. This includes results on characterization, activity, stability and selectivity of synthesized catalysts, kinetic and mechanism study. Finally, Chapter 5 provides the conclusions drawn from this study and some recommendations proposed for future work.

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LIST OF PUBLICATIONS

List of publications:

1. **Siang, T. J.**, Jalil, A. A., Abdulrasheed, A. A., Hambali, H. U., & Nabgan, W. (2020). Thermodynamic equilibrium study of altering methane partial oxidation for Fischer–Tropsch synfuel production. *Energy*, *198*, 117394.
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3. **Siang, T. J.**, Jalil, A. A., Abdulrahman, A., & Hambali, H. U. (2021). Enhanced carbon resistance and regenerability in methane partial oxidation to syngas using oxygen vacancy-rich fibrous Pd, Ru and Rh/KCC-1 catalysts. *Environmental Chemistry Letters*, 1–10.

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1. **Siang, T. J.**, Jalil, A. A., Hambali, H. U., Abdulrasheedand, A. A., & Azami, M. S. (2019). Dendritic mesoporous Ni/KCC-1 for partial oxidation of methane to syngas. 8th Conference on Emerging Energy and Process Technology (CONCEPT 8- 2019), 27-28 November 2019, Residensi UTM Kuala Lumpur, Malaysia.
2. **Siang, T. J.**, Jalil, A. A., Hambali, H. U., Hussain, I., & bin Mohd, A. M. S. (2019). Catalytic partial oxidation of methane to syngas over perovskite catalysts. 7th Conference on Emerging Energy & Process Technology (CONCEPT 7), 27-28 November 2018, Johor Bahru, Malaysia