

DRY REFORMING OF METHANE OVER STABILIZED NICKEL-
LANTHANUM SUPPORTED ON FIBROUS KCC-1 CATALYST

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ABSTRACT

Dry reforming of methane (DRM) is a promising technology towards production of synthesis gas (syngas) with low H₂:CO ratio by utilization of gases (CO₂ and CH₄) with potential to cause global warming. This study entails the development of highly active and stable nickel (Ni) based catalyst supported on synthesized fibrous KCC-1 silica (KAUST Catalytic Centre number 1) by in situ one-pot method. The performance and robustness of the synthesized Ni/KCC-1(1P) catalyst to DRM reaction was evaluated and compared to other silica-based Ni catalysts supported by wet impregnation on KCC-1 (Ni/KCC-1(IM)) and conventional silica (Ni/SiO₂). Furthermore, lanthanum (La) was added as a promoter to Ni/KCC-1 also in situ one-pot synthesis and compared to catalysts of single metal loadings of nickel (Ni/KCC-1(1P)) and lanthanum (La/KCC-1(1P)). Fresh and spent catalysts were characterized with the aid of X-ray diffraction, nitrogen adsorption-desorption isotherm, field-emission scanning electron microscope, energy-dispersive X-ray, transmission electron microscope, Fourier-transform infrared spectrometer, IR-pyrrole chemisorption, temperature-programmed reduction with hydrogen and X-ray photoelectron spectrometer, Raman spectrometer, thermogravimetric analysis. The effects of support morphology, synthesis mode and addition of La promoter on the activity and stability of Ni-based catalysts for DRM were studied over a temperature range of 550 – 850 °C and atmospheric pressure. From the results obtained, Ni/KCC-1(1P) produced the best performance in terms of reactants (CO₂, CH₄) conversions in comparison to Ni/KCC-1(IM) and Ni/SiO₂ in the order: Ni/KCC-1(1P) (88 %, 92 %) > Ni/KCC-1(IM) (80 %, 92 %) > Ni/SiO₂ (76 %, 82 %). From the reaction kinetics, low activation energy Ni/KCC-1(1P) at 22.7 kJ/mol facilitated its high activity in comparison to Ni/KCC-1(IM) and Ni/SiO₂ with energy values of 26.5 and 40.9 kJ/mol, respectively. Enhanced surface area, mesoporosity and basicity were responsible for the increased activity of KCC-1 supported catalysts over silica. Activity of Ni/KCC-1(1P) was accompanied by an outstanding stability over 72 h time on stream with negligible activity loss, whereas Ni/KCC-1(IM) and Ni/SiO₂ produced activity losses of 13.4 % and 42.5 %, respectively for CH₄ conversion. The long-term stability was attributed to the confinement effect, core-shell structure and strong metal-support interaction provided by the one-pot mode of synthesis. The introduction of La promoter on Ni/KCC-1 increased its catalytic activity and selectivity for CO production due to enhancement in Ni dispersion and catalyst basicity for CO₂ chemisorption. As a result, the activation energy for CO₂ and CH₄ conversions were reduced by a margin of 10.4 kJ/mol and 2.2 kJ/mol respectively. Based on optimization of reaction conditions for the synthesized catalyst by response surface methodology, DRM reaction temperature of 820 °C, CO₂:CH₄ feed ratio of 2.5 and gas hourly space velocity of 35.5 Lg⁻¹h⁻¹ produced an optimal CH₄ conversion of 97 %. The highlight of this study is the application of the confinement effect and core-shell structure from in situ one-pot synthesis and the fibrous dendrimer morphology of KCC-1 support in the quest for a robust catalyst design for industrialization of syngas production via DRM.

ABSTRAK

Pembentukan semula kering metana (DRM) adalah teknologi yang baik untuk menghasilkan gas sintesis (singas) dengan nisbah $H_2:CO$ rendah menggunakan gas (CO_2 dan CH_4) yang mempunyai potensi untuk penyelesaian pemanasan global. Kajian ini melibatkan sintesis mangkin berasaskan nikel (Ni) yang sangat aktif dan stabil disokong pada silika KCC-1 bergentian yang disintesis (KAUST pusat pemangkin bernombor 1) dengan kaedah satu bekas di situ. Prestasi dan keteguhan mangkin Ni/KCC-1 (1P) yang disintesis terhadap tindak balas DRM dinilai dan dibandingkan dengan mangkin Ni berasaskan silika lain yang disokong secara pengisitepuan basah pada KCC-1 (Ni/KCC-1 (IM)) dan silika konvensional (Ni/SiO₂). Tambahan pula, lantana (La) telah ditambah sebagai penggalak kepada Ni/KCC-1 juga semasa sintesis satu bekas di situ dan dibandingkan dengan mangkin logam tunggal nikel (Ni/KCC-1 (1P)) dan lantana (La/KCC-1 (1P)). Mangkin segar dan terguna dicirikan dengan bantuan pembelauan sinar-X, isoterma penjerapan-penyerapan nitrogen, pengimbasan elektron pancaran medan, dispersi tenaga sinar-X, mikroskopi penghantaran elektron spektrometer, inframerah jelmaan Fourier, kemoterapi IR-pyrrole, penurunan suhu terprogram hidrogen dan spektrometer fotoelektron sinar-X, spektrometer Raman, analisis termogravimetrik. Kesan morfologi sokongan, jenis sintesis dan penambahan penggalak La pada aktiviti dan kestabilan mangkin berasaskan Ni untuk DRM telah dikaji pada julat suhu 550 – 850 °C dan tekanan atmosfera. Keputusan yang diperolehi, Ni/KCC-1 (1P) menghasilkan prestasi terbaik dari segi penukaran bahan tindak balas (CO_2 , CH_4) berbanding Ni/KCC-1 (IM) dan Ni/SiO₂ mengikut urutan: Ni/KCC-1 (1P) (88%, 92%) > Ni/KCC-1 (IM) (80%, 92%) > Ni/SiO₂ (76%, 82%). Dari kinetik tindak balas, tenaga pengaktifan rendah Ni/KCC-1 (1P) pada 22.7 kJ/mol memudahkan aktiviti yang tinggi berbanding dengan Ni/KCC-1 (Ni) dan Ni/SiO₂ dengan nilai tenaga masing-masing adalah 26.5 dan 40.9 kJ/mol. Luas permukaan yang dipertingkatkan, mesolias dan tapak bes bertanggungjawab terhadap peningkatan aktiviti mangkin KCC-1 yang disokong oleh silika. Aktiviti Ni/KCC-1 (1P) disertai dengan kestabilan yang luar biasa melebihi 72 jam dalam aliran dengan kehilangan aktiviti yang dapat diabaikan, manakala Ni/KCC-1 (IM) dan Ni/SiO₂ menghasilkan kehilangan aktiviti masing-masing adalah 13.4% dan 42.5% untuk penukaran CH_4 . Kestabilan jangka panjang adalah disebabkan oleh kesan pembendungan, struktur teras-cengkerang dan interaksi logam-sokong kuat yang disediakan oleh ragam sintesis satu bekas. Pengenalan penggalak La pada Ni/KCC-1 meningkatkan aktiviti pemangkinan dan pemilihan terhadap pengeluaran CO yang disebabkan oleh penambahbaikan dalam penyebaran Ni dan bes mangkin untuk penjerapan kimia CO_2 . Akibatnya, tenaga pengaktifan bagi penukaran CO_2 dan CH_4 masing-masing dikurangkan dengan margin 10.4 kJ/mol dan 2.2 kJ/mol. Berdasarkan pengoptimuman keadaan tindak balas untuk mangkin yang disintesis oleh kaedah sambutan permukaan, suhu tindak balas DRM 820 °C, nisbah suapan $CO_2:CH_4$ 2.5 dan halaju ruang jaman gas $35.5 Lg^{-1}h^{-1}$ menghasilkan penukaran CH_4 optimum sebanyak 97%. Penekanan kajian ini adalah penggunaan kesan pengasingan dan struktur teras-cengkerang dari sintesis satu bekas in situ dan morfologi sokong dendrimer berserat KCC-1 dalam usaha untuk menghasilkan reka bentuk mangkin yang kuat untuk industri pengeluaran singas melalui DRM.

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LIST OF ABBREVIATIONS

ALD	–	Atomic layer deposition
ANOVA	–	Analysis of variance
ATR	–	Autothermal reforming
BASF	–	Badische Anilin und Soda Fabrik
BBD	–	Box-Behnken design
BET	–	Brunauer–Emmett–Teller
BP	–	British petroleum
BR	–	Boudouard reaction
CCD	–	Central composite design
CCS	–	Carbon capture and sequestration
CCU	–	Carbon capture and utilization
CCUS	–	Carbon capture, utilization, and storage
CG	–	Coke gasification
CI	–	Capillary impregnation
CNG	–	Compressed natural gas
C-NTs	–	Carbon nanotubes
CP	–	Co-precipitation
CTAB	–	Cetyl trimethylammonium bromide
DF	–	Degree of freedom
DFT	–	Density functional theory
DOE	–	Design of experiment
DRM	–	Dry reforming of methane
DTA	–	Differential thermal analysis
Ea	–	Energy of activation
EDX	–	Energy-dispersive X-ray spectroscopy
EISA	–	Evaporation-Induced Self-Assembly
FD	–	Factorial design
FESEM	–	Field emission scanning electron microscopy
FTIR	–	Fourier-transform infrared spectroscopy
GC	–	Gas chromatography

GHG	–	Greenhouse gas
GHSV	–	Gas hourly space velocity
GTL	–	Gas to liquids
GWP	–	Global warming potential
HAADF-STEM	–	High-angle annular dark-field-scanning transmission electron microscope
HRTEM	–	High-resolution transmission electron microscopy
HSC	–	Enthalpy (H), entropy (S) and heat capacity (C)
ICP-OES	–	Inductively coupled plasma - optical emission spectrometry
IEA	–	International Energy Agency
IPCC	–	Intergovernmental Panel on Climate Change
IWI	–	Incipient wetness impregnation
JCPDS	–	Joint Committee on Powder Diffraction Standards
KCC-1	–	KAUST catalysis centre number 1
LNG	–	Liquified natural gas
LPR	–	Linde pilot reformer
MCM	–	Mobil Composition of Matter
MD	–	Methane decomposition
MS	–	Mean square
MSN	–	Mesoporous silica nanoparticles
NG	–	Natural gas
NGV	–	Natural gas vehicle
NLDFT	–	Non-localized density functional theory
OCM	–	Oxidative coupling of methane
OFAT	–	One factor at a time
OSC	–	Oxygen storage capacity
POM	–	Partial oxidation of methane
PSD	–	Pore size distribution
RS	–	Raman spectroscopy
RS	–	Raman spectroscopy
RSM	–	Response surface methodology
RWGS	–	Reverse water-gas-shift
SBA	–	Santa Barbara amorphous

SEM	–	Scanning electron microscope
SPRAG	–	Sulphur passivated reforming
SRM	–	Steam reforming of methane
SS	–	Sum of squares
SSITKA	–	Steady-state isotopic transient kinetic analysis
TCD	–	Thermal conductivity detector
TCD	–	Thermal conductivity detector
TEM	–	Transmission electron microscope
TEOS	–	Tetraethyl orthosilicate
TGA	–	Thermogravimetric analysis
TOF	–	Turnover frequency
TOS	–	Time on stream
TPD	–	Temperature-programmed desorption
TPR	–	Temperature-programmed reduction
USCO	–	Union steel corporation
WGS	–	Water-gas-shift
WMO	–	World meteorological organization
XPS	–	X-ray photoelectron spectroscopy
XRD	–	X-ray powder 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
2-D	–	Two-dimensional
wt%	–	Weight percentage
h	–	Hours
&	–	And
>	–	Greater than
<	–	Less than
\geq	–	Greater than or equal to
*	–	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
mA	–	Milliampere
kV	–	Kilovolts
nm	–	Nanometres
R^2	–	Coefficient of determination
exp	–	Exponential
A	–	Pre-exponential factor
R	–	Universal gas constant
k	–	Rate constant
ΔG	–	Change in Gibbs free energy

eV	–	Electronvolt
Å	–	Angstrom
p-value	–	Probability value
t-value	–	Test statistics
P	–	Pressure
T	–	Temperature
g	–	Grams
Min	–	Minutes
s	–	seconds
MHz	–	Mega hertz
µmol	–	Micromole
kV	–	Kilovolt
Δ	–	Delta
L	–	Litres
m	–	Metres
mL	–	Millilitres
e ⁻	–	electron

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

It was estimated at the beginning of 2016 that a total of 6879 trillion cubic feet natural gas (NG) has been discovered in its associated and non-associated form (Huang et al., 2018). Fast depleting crude oil reserves and stringent environmental regulations on emission control has diverted attention to NG as a source of energy for heat, power and vehicular applications. Setbacks to NG for these applications are its characteristic low energy density, low critical temperature, high cost of storage and transportation. As a result of these challenges, utilization of abundant NG reserves as fuel is low resulting to flaring of large volume during exploration of crude oil. Anthropogenic production and emission of greenhouse gases (CH₄, CO₂, H₂O vapour, NO_x) have been established to be responsible for the menace of heat trapping in the Earth's atmosphere known as global warming (Cooper et al., 2018). As at 2011, the World Meteorological Organization (WMO) assessment revealed the atmospheric concentration of CH₄ and CO₂ as 1.8 and 393.1 ppm respectively (Wang et al., 2015a). Despite the low methane concentration relative to that of carbon dioxide, its global warming potential (GWP) is 28-36 times higher than that of CO₂, hence contributing severely to Earth's radiative imbalance (Elvidge et al., 2018; Song et al., 2018).

CO₂ emission poses the greatest threat due to its high energy absorbing efficiency attributed to its large-scale emission and long-term duration in the atmosphere. Capture, sequestration and utilization of CO₂ have been the most effective abatement strategies towards combating this trend (Wang et al., 2015b). Despite the successes attained in Carbon capture and sequestration (CCS), Utilization of immensely stored CO₂ has found limited application. In an effort to curb underutilization, reduce wastage and control generation of greenhouse gases from

gas flaring, CO₂ and NG containing mainly CH₄ are converted to synthetic gas (syngas), an important platform chemical intermediate for production of useful chemicals and synthetic fuels through distinct processes such as steam reforming (SRM), autothermal reforming (ATM), dry reforming of methane (DRM), oxidative coupling (OCM) and partial oxidation (POM) (Wang et al., 2017a), (Bian & Kawi, 2017).

Methane conversion to synthesis gas (syngas) by CO₂ dry reforming is a catalytic induced process producing syngas (a gaseous fuel mixture containing primarily H₂, CO and traces of CO₂) used as a sustainable fuel alternative to fossil fuel and also a precursor for important chemicals such as methanol, ammonia and synthetic hydrocarbon fuel production (Zain & Mohamed, 2018; Paksoy et al., 2015). Advantages of this technology are its suitability for low calorific value CO₂-rich NG, utilization and conversion of CH₄ and CO₂ which are both gases with significant greenhouse tendencies, production of eco-friendly fuel products and their subsequent conversion to liquid fuels through Fischer-Tropsch synthesis to address the inherent storage and transportation problems associated with gaseous fuels (Rafiee et al., 2017; Pal et al., 2018; Dahan et al., 2019). The utilization of cheap and readily available DRM catalysts with performance to maximally produce syngas has been the focal point of research and development in recent times. Despite its economic and environmental potentials, DRM is still an immature industrial process due to the problem associated with catalyst development with a long life-span on stream at a cheap price suitable for profit-oriented commercialization (Park, 2019; Das et al., 2019).

In 2015, Linde group revealed the pioneer pilot plants for dry reforming of methane (DRM). It was a product of concerted research effort in partnership with BASF and others. The Linde Pilot Reformer (LPR) is located near Munich and it uses two catalyst materials; a Nickel-based and a Cobalt-based. The aim is to test-run the LPR to obtain data at longer-term and longer-scale using pilot facility to investigate and optimize different approaches which could be used towards design of a commercial plant for the DRM (Schödel et al., 2015). Obviously, the LPR not only inspired greater research efforts in DRM catalyst design and development, but it is a

step further towards commercial utilization of DRM catalysts for syngas production (Jarvis & Samsatli, 2018; Er-Rbib et al., 2012). The other two industrial pilot plants successfully implemented are the SPRAG and CALCOR projects (Er-Rbib et al., 2012).

Contemporary design of DRM catalysts involved principally the utilization of inherent properties of catalyst components and understanding their complex synergistic interactions for optimum performance and longevity using state-of-the-art theoretical and analytical characterizations. Different catalyst configurations, morphologies and topologies have overtime been tested to evaluate how synergistic component interactions affects active metal dispersion, basicity, redox property, oxygen mobility, particle size, size distribution, reducibility and mass transfer limitations of catalysts (Zhang et al., 2018c; Abdel et al., 2018). These interactions have been linked towards predicting the pathways for establishing DRM reaction kinetics, thermodynamics, mechanisms and reactor design. Trade-offs between catalysts cost and their respective activity, selectivity and stability is the main challenge facing syngas production by dry reforming. Base metals are cheap and abundant catalyst precursors currently applied in dry reforming of methane (DRM) as a replacement to noble metals but their accelerated deactivation due to catalyst sintering, coke formation and deposition on catalyst surface at reforming conditions constitute a major challenge. Catalysts from noble metal precursors such as Ir, Pd, Pt, Rh and Ru have proven to manifest higher activity, selectivity and stability during DRM. Their viability for large scale industrial application is however not economical, attributed to their high cost and scarcity (Serrano-Lotina, 2013; Khajeh et al., 2015).

In a typical DRM system, syngas is produced from endothermic reaction of CH_4 and CO_2 (Equation 1.1) at a lower syngas ratio ($\text{H}_2:\text{CO} = 1$) in comparison to steam reforming ($\text{H}_2:\text{CO} = 3$) or partial oxidation ($\text{H}_2:\text{CO} = 2$) making a suitable path way to Fischer-Tropsch synthesis (Usman, et al., 2015). This endothermic nature of DRM requires high temperature for activity which implies high energy consumption and thus high operating cost. Production of syngas by DRM is however affected by competing side reactions which aid carbon formation and deposition on catalyst such

as methane decomposition (Equation 1.2), Boudouard reaction (Equation 1.4) and reverse water-gas shift (RWGS) reaction (Equation 1.3) (Pal et al., 2018).



From the stoichiometry of the DRM reaction, CO_2 and CH_4 conversions are expected to be equal and the syngas ratio also to be unity. Presence of side reactions and the extent with which they occur are measured by the deviation from products formed from the ideal stoichiometry. RWGS reaction can be confirmed by presence of water at the outlet of the reactor and higher stoichiometric conversion of CO_2 than CH_4 , Boudouard reaction by disproportionation of CO formation and CH_4 decomposition by CH_4 conversion higher than CO_2 conversion (Serrano-Lotina, 2013).

Suitability of different catalysts for DRM has been thoroughly investigated. However, their application has recorded limited successes for commercialization due to their susceptibility to deactivation caused by coke formation and sintering (Gurav et al., 2017; Lovell et al., 2014). Research attention has shifted from noble metals to base metals for economic reasons. Ni-based catalysts have been found to be competitive with noble metals in their catalytic activities at affordable costs (Zhang et al., 2018c). To overcome challenges of coke deposition and sintering of Ni catalyst, various factors have been considered and investigated for their reduction or elimination. These include nature of active metal, incorporating promoters with basic properties, interactions between active metals and support, particle size reduction, change in pre-treatment and preparation route and viability testing for different combinations of metals and supports (Álvarez et al., 2018; Wang et al., 2014b; Li et al., 2015). Lots of researches carried out in DRM have shown that achieving an ideal carbon-resistant and heat stable catalyst by exclusive adjustment of a single parameter is difficult to achieve. Therefore, it is imperative to consider the

collaborative association of various parameters in the design of a robust and efficient DRM catalyst. Attempts to improve coking resistance and catalytic activity have also been made via combination of two or more active metals, support and/or promoters (Guharoy et al., 2018).

Studies recently have shown that catalyst support materials and methods with which they are prepared impact the activity of Ni and Ni-based catalysts for carbon dioxide dry reforming, of which the catalyst structure formed after synthesis also control carbon formation and deposition. This proposes a tendency of obtaining an improved catalytic performance simply by the appropriate choice of the catalyst supports and control of the nickel-support interaction. The method a catalyst is prepared may also affect strongly the types of active species present on the catalyst surface which thereupon determine its final performance. The role played by the method followed in the preparation of catalysts on their overall performances can be classified into two groups namely: (1) method of support synthesis and (2) method of active metal doping on support. Both approaches have overtime been systematically modified and improved to control metal-metal, metal-support, metal-coke, support-coke interactions and their interactions with reactant gases in an effort to eliminate or reduce the setbacks of nickel-based catalysts application during DRM.

Several researches have over the years been conducted in an effort to improve and maintain dispersion of Ni particles, within support structure, to prevent sintering and coking by tuning metal-support, bimetallic, and catalyst-reactants' interaction pathways and mechanisms. One of the contemporary and efficient ways is the confinement of Ni particles in the matrix of mesoporous support materials by one-pot metal-support synthesis, forming catalyst with core-shell structure, with active metals as core and the support providing the protective shell structure. The mesoporous support provides the channels for diffusion of the gaseous reactant molecules and shell to suppress sintering and coke formation (Zhang & Li, 2015; Almana et al., 2016). The adverse effects of coke formation and sintering have previously been tackled via film generation by atomic layer deposition, metal nanoclusters functionalization on the porous support, alloying with high heat resistant metal, and coating of mesoporous support shell structure (Theofanidis et al., 2017; Gould et al.,

2015). However, these approaches have tendencies towards reducing the catalyst activity, attributed to the blockage of active sites and mass transfer limitation.

In recent times, the discovery of KCC-1 has found significant application in the field of drug delivery, chromatographic separation, and energy storage, because of its unique fibrous morphology and extended surface area. Since its discovery, efforts were initially made to enhance its properties for better applications (Febriyanti et al., 2016; Bayal et al., 2016; Singh et al., 2016; Thankamony et al., 2015). Its inherent ability towards minimising diffusion limitation, and resisting Ostwald ripening of the loaded metals related to its well-developed dendrimer networks, facilitate its applications in the field of heterogeneous catalysis, such as Knoevenagel condensation (Bouhrara et al., 2013), production of n-butyl levulinate (Mohammadbagheriet al., 2018), Suzuki coupling (Fihri et al., 2012), and Sabatier reaction (Shahul Hamid et al., 2018). The enhanced pore accessibility and mass transfer makes it a better candidate, as a support over the conventional SiO₂ and other mesoporous silica, such as MSN, MCM-41, and SBA-15 (Shahul Hamid et al., 2017; Sadeghzadeh et al., 2018; Werghi et al., 2018). This study involves the synthesis of a robust Ni based catalyst, supported on fibrous silica (KCC-1) for high activity and stability at high DRM temperature, using one-pot hydrothermal synthesis and the conventional wet impregnation. The fibrous KCC-1 provides enhanced metal dispersion, while the one-pot nickel loading ensures the anticipated long-term stability.

1.2 Problem Statement

The stringent environmental laws and regulations governing the discharge of carbon dioxide and methane into the atmosphere is due to their immense potentials towards affecting the earth's radiative equilibrium through a phenomenon called global warming. Therefore, the storage and utilization of these two greenhouse gases to produce value-added chemicals via dry reforming of methane is indeed an attractive venture with high economy of scale. However, methane and carbon dioxide as reactants are highly stable gas molecules and thus, require high temperatures to

have a spontaneous reaction. As a result of this high temperature reaction condition, there are numerous underlying factors that impede the industrialization and commercialization of the process for syngas production.

Trade-offs between activity and stability of Ni-based catalysts remains the major bottleneck for the actualization of syngas production via DRM. Being a highly endothermic reaction, equilibrium conversion of reactants is attainable only at high temperatures mostly in the regions above 700 °C. DRM reaction at these temperatures produce high conversion of reactants, but is however vulnerable to unwanted and competitive side reactions such as methane cracking, CO disproportionation and RWGS reactions. These side reactions affect the selectivity of the desired products and more so the life span of catalysts used. The catalyst life span is severely affected at high temperature due to deactivation by carbon deposition and active metal sintering. Concerted efforts have overtime been made towards improving catalyst stability, many of which have been found to be detrimental to the catalyst activity and similar trends were also obtained vice versa. Low catalyst activity affects plant productivity while short catalyst lifespan increases operating costs from regeneration or replacement of spent catalysts. It is therefore imperative to develop robust catalysts with the required activity and stability suitable of industrial application of the process.

Catalysts of noble metals such as platinum (Pt), palladium (Pd), rhodium (Rh) and ruthenium (Ru) have been suggested and tested as candidates for DRM because of their high activity and strong resistance to carbon deposition. From the industrial point of view considering the high cost and limited availability of noble metals, their application is not profitable and sustainable. They are likely vulnerable to sintering as well at high temperature. As an alternative to exorbitant noble metal catalysts, nickel-based catalysts have been the most widely tested. Nickel as a transition metal with relatively cheap price and readily available has an activity competitive with those of noble metals. The setback to Ni and Ni-based catalysts is their characteristic rapid deactivation due to carbon deposition and sintering. It is worthy of note that the effect of the type, formation mechanism, and evolution of carbon deposits on deactivation is still much debated and not fully understood. Therefore, a thorough

understanding the carbon types and coking mechanism is also crucial towards tailoring the appropriate resistance required.

Despite the tremendous research successes recorded overtime in catalysts development with excellent activity and stability results, the search for novel and economically viable Ni catalysts with improved properties and performances is still much desired for successful implementation of the industrial and commercial aspect of the process. Research focus are still very much important on catalyst development and tuning of relevant properties and interactions suited for the desired catalyst activity and long-term stability.

Silica has been extensively used as a support material for DRM catalyst development due to its low toxicity, ease of preparation and handling, neutral acidity, low cost, universal availability, strong thermal, swell and shrink resistance. Its porosity has over the years been enhanced in the quest for better active metal dispersion via highly mesoporous silica materials such as SBA-15, MCM-41 and MCM-48. However, the two-dimensional (2-D) structure of these mesoporous silica with empty and closely packed cages has a problem of mass transfer limitations as reported in the work of Singh & Polshettiwar (2019). They allow only one-directional flow across their channels which hamper accessibility of gases to some pores and active sites and thus limit their catalytic performances.

This research is therefore geared primarily towards the design of a robust Ni-based catalyst with activity, stability and selectivity suitable for the industrialization of the DRM process. It is imperative to obtain an activity competitive to those of noble metals, long-term stability by strongly resisting active metal agglomeration and coking, and also providing the required selectivity for the desired products proximal to the stoichiometric $H_2:CO$ ratio. Carbon depositions is the major cause of deactivation but more insight on their types, properties, evolution on catalyst lifespan is critical during catalyst design. Addressing the challenge of low activity and short lifespan of cheap and widely available Ni catalyst is the roadmap towards the DRM commercialization in the nearest future.

1.3 Research Hypothesis

The spontaneity and selectivity of dry reforming of methane 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. The extended dendrimer surface area and porosity provided by the unique fibrous morphological makeup of KCC-1 support is expected to improve the dispersion and accessibility of Ni active sites required for a stellar performance. The enhanced mass transfer is expected to increase the turnover of reactants for faster reaction kinetics. The particle size of Ni crystallites is expected to be smaller due to better dispersion and further apart from one another to minimise the possibility of sintering. Synthesis by one-pot method is presumed to produce a coke and sinter resistance catalyst with core-shell morphology, where Ni particles are dispersed and encapsulated in the fibrous KCC-1 matrix. This gives the catalyst a strong resistance against thermal sintering. The KCC-1 support is also the shell shielding the metals surfaces from exposure to carbon deposition. Addition of lanthanum promoter is expected to improve the catalyst basicity for higher CO₂ conversion and subsequently an improved CO formation. La₂O₃ addition is expected to also enhance the dispersion, reducibility and interaction of Ni with the KCC-1 support, all for an improved activity, stability and selectivity of the synthesized catalyst.

1.4 Research Objectives

The aim of this research work is to synthesize a robust bimetallic nickel-based catalyst supported on fibrous silica with high activity and stability for optimal application in dry reforming of methane. This is achieved through the following objectives:

1. To synthesize and characterize conventional SiO₂ and fibrous KCC-1 supported nickel catalysts with metal loading carried out by wet impregnation and one-pot method.

2. To investigate the effects of lanthanum oxide promoter addition on the activity, stability and selectivity of the bimetallic nickel catalyst for dry reforming of methane.
3. To optimize the dry reforming of methane reaction parameters over synthesized bimetallic nickel-based catalyst via Response Surface Methodology.
4. To carryout thermodynamic sensitivity analysis and equilibrium computations of dry reforming of methane alongside the occurrence of other competing side reactions with the aid of HSC Chemistry software.

1.5 Research Scope

This study is focused on addressing some major setbacks affecting the prospect of nickel-based catalyst for industrial syngas production via dry reforming. In this viewpoint, the effects of silica support morphology, effects of catalyst preparation method, effects of promoter, thermodynamics and optimization of dry reforming of methane have been deliberated upon. The specific details on the adopted scope of this research study are presented as follows:

1. In order to determine the effects of support morphology and preparation techniques, 5 wt% of Ni supported on conventional silica (Ni/SiO₂) and fibrous KCC-1 (Ni/KCC-1(IM)) were prepared by wet impregnation. 5 wt% of Ni supported of fibrous KCC-1 was also prepared by in situ one-pot synthesis (Ni/KCC-1(1P)). The KCC-1 support was synthesized by hydrothermal microemulsion technique using steps prescribed in the work of Febriyanti et al. (2016). The dendrimer structure was developed via mixture of organic phase comprising of toluene, butanol and tetraethyl orthosilicate (TEOS) with the aqueous phase containing cetyltrimmonium bromide (CTAB), urea and deionized water. The as-synthesized catalysts were characterized by XRD, N₂-adsorption, ICP-OES, FESEM-mapping, FTIR-pyrrole, FTIR-KBr and XPS. Spent catalyst were characterized for carbon deposition or sintering using TEM,

Raman spectra, XRD, TGA and DTA. Performance evaluation of catalysts for dry reforming was conducted at atmospheric pressure and a temperature range of 550 – 850 °C at a GHSV of 30,000 mLg⁻¹h⁻¹, CO₂:CH₄: N₂ ratio of 20:20:60, stability test for 72 h time on stream and reaction kinetics using Arrhenius equation.

2. Studying the effects of promoter, which is lanthanum on dry reforming of methane, three catalysts namely: Ni@KCC-1, La@KCC-1 and Ni-La@KCC-1 are prepared by one-pot method. 5 wt% of metal is loaded for monometallic catalysts while 5 wt% Ni and 1 wt% La were loaded for the bimetallic catalyst. Physicochemical properties of catalysts were characterized by XRD, N₂-adsorption, FESEM-EDX, FTIR-pyrrole, TPR, TEM and XPS. Catalyst testing was also performed at atmospheric pressure, temperature range of 550 – 850 °C, GHSV of 30,000 mLg⁻¹h⁻¹, CH₄: CO₂: N₂ ratio of 20:20:60, stability test period of 30 h and reaction kinetics using Arrhenius equation.
3. Optimization was conducted on DRM reaction parameters with the aid of central composite design (CCD) interface of RSM available on StatSoft STATISTICA software 6.0. the independent variables selected for this optimization are reaction temperature (700 – 800 °C), GHSV (10,000 – 50,000 mLg⁻¹h⁻¹) and CO₂:CH₄ ratio (1 – 4) using Ni-La@KCC-1 as the catalyst. These variables and their ranges were selected based on preliminary studies conducted and information obtained from literature. CH₄ conversion being the rate determining step of DRM was selected as the response variable to evaluate the optimal performance of the catalyst.
4. Thermodynamic study of the DRM reaction was conducted using the HSC chemistry 6.0 software. Spontaneity of DRM reaction and other side reactions were evaluated as a function of reaction temperature using the Reaction Equations module on the software. Temperature range considered is 100 – 1000 °C and a pressure of 1 atm for all analysis. Equilibrium amount of each reactant and products in the reactor were also determined with respect to reaction temperature using the Equilibrium Compositions module. Effects of selected side reactions on the equilibrium composition and amount were also conducted in this module at reaction temperature of 100 – 1000 °C and pressure of 1 atm.

1.6 Research Significance

In this study where the reaction is highly endothermic and spontaneous only at high temperature, making catalyst susceptible to swift deactivation and poor product selectivity. A robust catalyst was thus developed using a silica support with distinctive morphology and applied for the first time in the area of dry reforming of methane. The unique fibrous surface structure having bulk of its surface area attributed to its fibres unlike other mesoporous silica support materials such as SBA-15, MCM-41 and MCM-48 whose high surface areas are due to their pores. With the fibrous dendrimer network of KCC-1, accessibility of active sites is significantly increased compare to other forms of silica because some of their pores are not accessible. KCC-1 has also been tested to exhibit an excellent mechanical, thermal and hydrothermal resistance. Ni supported on KCC-1 will be highly dispersed and accessible leading to higher turnover of reactants and thus, a faster reaction kinetics. Synthesis of KCC-1 supported Ni catalyst by one-pot technique will ensure stability of the highly dispersed Ni crystallites by encapsulation on the KCC-1 dendrimer matrix. Ni surfaces will also be protected by the KCC-1 shell against carbon deposits. To complete the facets of DRM catalyst performance enhancement under study, a promoter was introduced to the catalyst to improve its selectivity of syngas production to the appropriate $H_2:CO$ ratio of 1.

1.7 Thesis Outline

The research is targeted at the development of a robust bimetallic Ni-based catalyst supported on fibrous silica KCC-1 by one-pot method, for an efficient and sustained syngas production via dry reforming of methane. The KCC-1 morphology was to improve dispersion Ni and reduce its crystallite size for increased activity. The synthesis method was selected to immobilize the dispersed Ni particles inhibiting the tendency of sintering, and also provides a protective shield to Ni sites against metal deposition. Introduction of La promoter was done primarily to reduce $H_2:CO$ ratio via CO_2 chemisorption and conversion enhancements. The kinetics, thermodynamics and optimization of DRM reaction were conducted to ensure an

optimal utilization condition for the synthesized catalyst. 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 CO₂ emission and utilization, methane as source of energy, methane conversion strategies, catalysts development, challenges of deactivation, effects of synthesis route on catalyst performance and the prospects of development of a robust catalyst. 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 include results on characterization, activity, stability and selectivity of synthesized catalysts. Finally, Chapter 5 provides the conclusions drawn from this study and some recommendations proposed for future work.

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