DRY REFORMING OF METHANE OVER NICKEL-TANTALUM SUPPORTED ON FIBROUS ZSM-5 CATALYST FOR PRODUCTION OF SYNTHESIS GAS

HAMBALI UMAR HAMBALI

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy

School of Chemical and Energy Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

NOVEMBER 2020

All praise is due to Allah, by whose honour and Majesty, deeds of virtue are accomplished.

ACKNOWLEDGEMENT

I would like to express utmost gratitude to my supervisor Professor Dr. Aishah Abdul Jalil for her unwavering support, motherly-care, patience and encouragement who made it possible for me to complete this work. Her infectious passion for bridging the fields of catalysis is second to none. It's a privilege to have worked under her great supervision. I acknowledge Late Professor Sugeng Triwahyono (my co-supervisor) for the unforgettable support at the initiation of my PhD journey.

To the entire Green Technology and Advanced Materials (GTAM) research group I extend my warmest gratitude, you are such wonderful and understandable personalities. Thanks Yahya Gambo! You've been a great friend and I really couldn't have done this PhD without you. Did I miss someone? Oh yeah... Special and humongous appreciation to Dr. Abdulrasheed A. Abdulrahman whose outstanding work formed the basis of much of this research. Your helpful discussions, suggestions and yummy meals from your superb chef wife will never be forgotten.

The collaborative nature of my PhD meant that it couldn't have happened without the support of brilliant researchers, namely Tan Ji Siang, Dr. Yusuf Sahul, Dr. Aiza Fatah, Dr. Dai-Viet and Dr. Oki Muraza. Many thanks to the staffs of School of Chemical and Energy Engineering UTM for their support during my study. I also thank the staffs of Unilorin-Nigeria, specifically Prof. D. S. Ogunniyi, Prof. Omodele A. Eleta, Prof. A. S. Abdusalam, Engr. Lydia Jilantikri, Dr. T. E. Odetoye, Dr. A. G. Adeniyi, Engr. Mubaraq Amoloye, Engr. I. A. Mohammed and Engr. Sani Saminu.

To my darling wife (Fatima) and precious son (Umar Jnr.), thank you for the unwavering love, patience and sacrifice. I must also thank my siblings Dr. Idris Umar Hambali, Engr. Shuaibu Umar, Engr. Ahmad Abulfathi and the only princess of the house Saratu Umar Hambali for your support throughout my entire life. Above all I immeasurably appreciate my beloved father and mother for the spiritual and financial support. You have been the rock the family has stood on and an inspiration to us all.

ABSTRACT

Dry reforming of methane (DRM) is an environmentally benign process for production of synthesis gas carbon monoxide (CO) and hydrogen (H_2) with low H_2:CO ratio by utilization of carbon dioxide (CO_2) and methane (CH_4) as feed gas. The large-scale production of syngas via DRM is still in its infancy due to operational constraints exhibited by the several catalysts involved. In this study, microemulsion engineered fibrous ZSM-5 (FZSM-5) support was selected as the support material due to its extended surface area and stabilization of metal particles. In addition, nickel (Ni) loaded on FZSM-5 was prepared by double solvent, physical mixing and wetness impregnation methods. Furthermore, magnesium (Mg), calcium (Ca), tantalum (Ta) and gallium (Ga) promoters were added to Ni/FZSM-5 catalyst using wetness impregnation method. The catalysts were characterized using X-ray diffraction, nitrogen adsorption-desorption isotherm, transmission electron microscope, field-emission scanning electron microscope, Fourier-transform infrared spectrometer, IR-lutidine chemisorption, temperature-programmed desorption with ammonia and CO_2, temperature-programmed reduction with H_2, energy-dispersive X-ray, X-ray photoelectron spectrometer, Raman spectrometer, and thermogravimetric analysis. The effects of active metals, Ni-loading methods, support morphology, promoters, Ni-Ta ratio towards the activity, selectivity and stability of the Ni based catalysts were examined in DRM over a temperature range of 500–800 ^oC and atmospheric pressure. Results revealed that Ni species are highly active for dissociation of the reactants. Ni/FZSM-5 produced superior performance than conventional ZSM-5 supported Ni catalyst. High basicity, surface area and mesoporosity were responsible for the outstanding performance of FZSM-5 supported catalyst. The wetness impregnation catalyst produced superior performance, which was correlated to microscopic dispersion and low surface acidity. The activity of the bimetallic catalysts was in the order: Ni-Ga/FZSM-5 (CH_4= 50.1 %, CO_2= 58.8 %) < Ni-Ca/FZSM-5 (CH_4= 82.9 %, CO_2= 82.7 %) < Ni-Mg/FZSM-5 (CH_4= 86.7 % ,CO_2= 92.3 %) < Ni-Ta/FZSM-5 (CH_4= 91 % ,CO_2= 97.4 %). The side reaction (methane cracking, Boudouard and RWGS) test results indicated that Ni catalyst had high inclination towards methane cracking reaction. The presence of small Ta cations in Ni catalyst was enough to suppress the driving force for agglomeration and coke formation. The optimum CH_4 conversion predicted from the response surface analysis was 96.6 % at reaction temperature of 784.15 °C, CO_2:CH_4 feed ratio of 2.52, and GHSV of 33,760 mL g^{-1} h^{-1}. Experiment carried out with these optimum parameters gave 95.8 % CH_4 conversion with error of 0.8 %. The strong catalytic stability of Ni-Ta/FZSM-5 was due to the small-size and immobilized Ni sites, enhanced reducibility and interaction of catalyst components. This study highlighted the contribution of fibrous structured ZSM-5 support and Ni-Ta catalyst in the quest for potent catalyst development for industrial production of syngas via DRM.

ABSTRAK

Pembentukan semula metana kering (DRM) merupakan satu proses yang mesra alam untuk pengeluaran gas sintesis karbon monoksida (CO) dan hidrogen (H_2) dengan nisbah H_2:CO yang rendah melalui penggunaan karbon dioksida (CO_2) dan metana (CH_4) sebagai gas suapan. Pengeluaran singas berskala besar melalui DRM masih dalam peringkat awal kerana kekangan operasi yang ditunjukkan oleh beberapa mangkin yang terlibat. Dalam kajian ini, sokongan ZSM-5 berserat direka bentuk secara mikroemulsi (FZSM-5) dipilih sebagai bahan sokongan kerana luas permukaannya yang besar dan kestabilan zarah logamnya. Di samping itu, nikel (Ni) yang dimuat pada FZSM-5 disediakan dengan kaedah pelarut berganda, pencampuran fizikal dan impregnasi basah. Selanjutnya, penggalak magnesium (Mg), kalsium (Ca), tantalum (Ta) dan galium (Ga) ditambahkan kepada mangkin Ni/FZSM-5 menggunakan kaedah impregnasi basah. Mangkin tersebut dicirikan menggunakan belauan sinar-X, isoterma penjerapan-penyahjerapan nitrogen, mikroskop elektron penghantaran, mikroskop elektron imbasan pancaran medan, spektrometer inframerah jelmaan Fourier, jerapan kimia IR-lutidina, nyahjerapan dengan amonia dan CO_2 pada suhu terprogram , penurunan dengan H_2 pada suhu terprogram, sinar-X serakan tenaga, spektrometer fotoelektron sinar-X, spektrometer Raman dan analisis termogravimetri. Kesan logam aktif, kaedah pemuatan Ni, morfologi sokongan, penggalak, nisbah Ni-Ta terhadap keaktifan, kememilihan dan kestabilan mangkin berasaskan Ni telah dikaji dalam DRM dengan julat suhu 500–800 ^oC dan pada tekanan atmosfera. Hasil kajian menunjukkan bahawa spesies Ni sangat aktif untuk penguraian bahan tindak balas. Ni/FZSM-5 menghasilkan prestasi unggul berbanding mangkin Ni sokongan ZSM-5 konvensional. Kebesan, luas permukaan dan keliangan meso yang tinggi bertanggungjawab bagi prestasi cemerlang mangkin sokongan FZSM-5. Mangkin impregnasi basah menghasilkan prestasi yang unggul, yang berkorelasi dengan penyebaran mikroskopik dan keasidan permukaan yang rendah. Keaktifan mangkin dwilogam adalah mengikut urutan: Ni-Ga/FZSM-5 (CH_4= 50.1 %, CO_2= 58.8 %) < Ni-Ca/FZSM-5 (CH_4= 82.9 %, CO_2= 82.7 %) < Ni-Mg/FZSM-5 (CH_4= 86.7 % ,CO_2= 92.3 %) < Ni-Ta/FZSM-5 (CH_4= 91 % ,CO_2= 97.4 %). Keputusan ujian (pemecahan metana, Boudard dan RWGS) tindak balas sampingan menunjukkan bahawa mangkin Ni mempunyai kecenderungan tinggi terhadap tindak balas pemecahan metana. Kehadiran sedikit kation Ta dalam mangkin Ni sudah cukup untuk menahan daya pendorong untuk pembentukan pengumpalan dan kok. Penukaran CH_4 optimum yang diramalkan daripada analisis sambutan permukaan adalah 96.6% pada suhu tindak balas 784.15 °C, nisbah suapan CO_2:CH_4 sebanyak 2.52, dan GHSV sebanyak 33,760 mL g^{-1} h^{-1}. Eksperimen yang dijalankan dengan parameter optimum ini memberikan 95.8% penukaran CH_4 dengan ralat sebanyak 0.8%. Kestabilan pemangkinan yang kuat Ni-Ta/FZSM-5 adalah kerana tapak Ni yang bersaiz kecil dan tersekat gerak, peningkatan pengurangan, dan interaksi daripada komponen mangkin. Kajian ini menyerlahkan sumbangan sokongan ZSM-5 yang mempunyai struktur berserat dan mangkin Ni-Ta dalam usaha pembangunan mangkin yang kuat untuk pengeluaran singas industri melalui DRM.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ANOVA	–	Analysis of variance
BBD	–	Box-Behnken design
BET	–	Brunauer–Emmett–Teller
BP	–	British petroleum
BD	–	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
CNG	–	Compressed natural gas
CNT	–	Carbon nanotube
CTAB	–	Cetyl trimethylammonium bromide
DF	–	Degree of freedom
DFT	–	Density functional theory
DOE	–	Design of experiment
DS	–	Double-solvent
DRM	–	Dry reforming of methane
DTA	–	Differential thermal analysis
Ea	–	Energy of activation
EDX	–	Energy-dispersive X-ray spectroscopy
EISA	–	Evaporation-Induced Self-Assembly
FESEM	–	Field emission scanning electron microscopy
FZSM-5	–	Fibrous ZSM-5
FTIR	–	Fourier-transform infrared spectroscopy
GC	–	Gas chromatography
GHG	–	Greenhouse gas
GHSV	–	Gas hourly space velocity
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
JCPDS	–	Joint Committee on Powder Diffraction Standards
KCC-1	–	KAUST catalysis centre number 1
LNG	–	Liquified natural gas
MCM	–	Mobil Composition of Matter
MC	–	Methane cracking
MFI	–	Mordenite Framework Inverted
MS	–	Mean square
MSN	–	Mesoporous silica nanoparticles
NG	–	Natural gas
NLDFT	–	Non-localized density functional theory
OFAT	–	One factor at a time
POM	–	Partial oxidation of methane
PM	–	Physical mixing
PSD	–	Pore size distribution
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
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

WI	–	Wetness impregnation
WGS	–	Water-gas-shift
WMO	–	World meteorological organization
XPS	–	X-ray photoelectron spectroscopy
XRD	–	X-ray powder diffraction
ZSM-5	–	Zeolite Socony Mobil-5

LIST OF SYMBOLS

kJ	–	Kilojoules
ΔH^0_{298K}	–	Enthalpy of reaction at room temperature
$\rightleftharpoons$	–	Reversible reaction pathway
^oC	–	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
$D_{(Ni)}$	–	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
P	–	Pressure
T	–	Temperature
g	–	Grams
Min	–	Minutes
s	–	Seconds
μmol	–	Micromole
kV	–	Kilovolt
Δ	–	Delta
L	–	Litres
m	–	Metres
mL	–	Millilitres
e^-	–	Electron

LIST OF APPENDICES

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The envisaged diminution of crude oil reserves, rapid population growth and stringent environmental policies on emission control has triggered unprecedented research on alternate energy sources. Natural gas (NG) is one of the solutions to this multi-sided challenge, since NG is an abundant (6879 trillion cubic feet) and environmentally benign energy source for power generation and vehicular applications (Chong et al., 2020, Huang et al., 2018). Drawbacks of NG includes low critical temperature as well as high storage and transportation costs, which led to its limited utilization as fuel. Emission of greenhouse gases have been established to be responsible for the current earth's radiative energy imbalance leading to the menace of global warming (Chang et al., 2020). Carbon dioxide and methane constitute the major part of greenhouse gases, with concentration of CO_2 (393.1 ppm) higher than that of CH_4 (1.8 ppm), but the global warming potential of CH_4 still supersedes (Wang et al., 2015). This shows that CH_4 contributes severely to the overall global warming (Chong et al., 2020; Song et al., 2018).

Carbon dioxide management in terms of capture and utilization has received attention in recent years (Norhasyima & Mahlia, 2018; Usman et al., 2015; Wittich et al., 2020). From an industrial standpoint, CO_2 is not only an effluent gas with detrimental environmental footprint, but it’s also an intriguing raw material. Despite the potentials of CO_2 utilization process such as Carbon capture and sequestration (CCS) process, the hugely stored CO_2 has been less utilized. The major alternative to address this problem is utilizing CO_2 as feedstock integrated with CH_4 conversion process to produce syngas (CO and H_2), a versatile feedstock for production of liquid energy carriers and useful chemicals through technologies such as steam reforming (SRM), dry reforming of methane (DRM) and partial oxidation (POM) (Ashok et al., 2020; He et al., 2020; Wittich et al., 2020).

Methane conversion to syngas via DRM is a promising technology in the production of syngas used as an important platform chemical for the synthesis of liquid energy carriers and valuable chemical such as methanol, dimethyl ether and ammonia (Wittich et al., 2020; Zain & Mohamed, 2018). Compared to other methane reforming processes, DRM has several attractive aspects because the process requires less energy and is suitable for NG reserves with high CO_2 content. In addition, DRM produces eco-friendly fuel products via Fischer-Tropsch synthesis to curb the underlying issues associated with storage and transportation of gaseous fuels (Dahan et al., 2019; Pal et al., 2018). The catalyst is considered as a key factor in the DRM reaction. As a result, development of catalyst system capable of maximally producing syngas remains the prime research focus in the last two decades. Despite its environmental and economic potentials, large-scale production of syngas via DRM is still in its infancy due to operational constraints exhibited by the several catalysts involved (Aziz et al., 2019; Das et al., 2019).

A DRM pilot plant has recently been constructed by Linde group in Germany, which was aimed at determining the commercial readiness of DRM technology. The pilot plant uses Ni-based and Co-based catalysts. The plant performance test provided data on longer-term and process parameters, which pave way for investigation of optimization approaches towards development of a more broadly applicable process (Schwab et al., 2015; Wittich et al., 2020). The successfully developed pilot plants are the CALCOR and SPRAG process (Er-Rbib et al., 2012; Schwab et al., 2015). The CALCOR process is only suitable for small-scale operation, with production of CO rich syngas (H_2:CO = 0.43) (Shah & Gardner, 2014). The SPRAG process was designed to combine the characteristics of DRM and SRM process. However, the negative impact of sulphur poisoning reduces the overall activity and stability of the catalyst (Wittich et al., 2020; York et al., 2007). The state of the art DRM technologies seems feasible only in certain scenarios and lack breadth in applicability. Therefore, development of an efficient commercial syngas plant requires greater research efforts towards design of low cost and robust catalyst system that can withstand the harsh conditions of DRM process (Aramouni et al., 2018; Er-Rbib et al., 2012).

Intrinsically, the DRM (Equation 1.1) process involves reaction of CH_4 and CO_2 to produce syngas mixture with equimolar H_2:CO ratio in comparison to SRM (H_2:CO = 3) or POM (H_2:CO = 2) for subsequent Fischer-Tropsch process (Usman et al., 2015). The endothermic nature of the DRM reaction infers high energy requirement and thus high operating cost. Additionally, propagation of competing side reactions during DRM affects the product spectrum and increases the propensity of coke deposition (Danghyan et al., 2020; Pakhare and Spivey, 2014). The side reactions are methane cracking (Equation 1.2), Boudouard reaction (Equation 1.3), and reverse water gas shift reaction (Equation 1.4) (Pal et al., 2018).

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \quad \Delta H^0_{298K}=260.5 \text{ kJ/mol} \tag{1.1}$$

$$CH_4 \rightleftharpoons C + 2H_2 \quad \Delta H^0_{298K} = 75.0 \text{ kJ/mol} \tag{1.2}$$

$$2CO \rightleftharpoons C + CO_2 \quad \Delta H^0_{298K} = -173.0 \text{ kJ/mol} \tag{1.3}$$

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H^0_{298K} = 41.0 \text{ kJ/mol} \tag{1.4}$$

The occurrence of these reactions alters the purity of syngas produced, especially the reverse water gas shift reaction which results in H_2:CO ratio less than unity. The extent of occurrence of these side reactions is evaluated by the deviation of H_2:CO ratio from the ideal stoichiometry.

Generally, catalyst component in terms of active metals, support and promoter is imperative for stellar DRM performance. Ni-based catalysts are suitable for DRM due to their wide availability, high turnover frequency and moderate cost. Nonetheless, they are inclined to fast deactivation due to formation of carbonaceous deposits, usually of encapsulation and graphitic type. Concerted efforts have burgeoned to overcome the severe carbon laydown and Ni catalyst sintering, where several factors have been considered and deliberated for their reduction or elimination. These factors include nature of active metal, type of support, metal dispersion, particle size reduction

and support interactions, basic and acidic properties, change in preparation and metal doping method (Aramouni et al., 2018; Danghyan et al., 2020; Li et al., 2015). It has been substantiated in lots of researches that obtaining an anti-carbon and anti-sintering catalyst by modification of a single factor is difficult to achieve. Hence, collaborative association of various factors is prerequisite for robust and efficient catalyst development.

Several studies have highlighted the impact of catalyst support materials and preparation methods on the activity of Ni-based catalysts for DRM, of which the catalyst structure formed after synthesis also dictates carbon formation and deposition. For any catalyst support to have a potential in industrial applications, several parameters must be met, such as high surface area, high porosity, fine dispersion of metal species, high reducibility, thermal stability, good surface oxygen mobility, surface basicity and low surface acidity (Aziz et al., 2019; Chong et al., 2020; Titus et al., 2017; Usman, et al., 2015). The method of support synthesis and metals loading have demonstrated pivotal effect on overall catalytic performances. Both approaches have overtime emerged as a powerful tool to control interaction of catalyst components in an effort to address the shortcomings of Ni-based catalysts in DRM process.

The development of structured support materials has been conceived to significantly hinder deactivation of Ni catalysts. Many findings attributed the remarkable performance of structured catalyst system to confinement of active metals in the support and enhanced metal-support interaction (Chong et al., 2020; Usman, et al., 2015). Structured supports such as SiO_2 (Cruz-Flores et al., 2020), Al_2O_3 (Shang et al., 2017), SiO_2-Al_2O_3 (Xiang et al., 2016), ZSM-5 (Tang et al., 2014), bi-modal Al_2O_3 (Ma et al., 2020), trimodal hydroxyapatite (Li et al., 2020), trimodal porous silica (Amin et al., 2017), hexagonal mesoporous silica (Sun et al., 2020), core-shell Al_2O_3 (Jabbour et al., 2016) and core-shell SiO_2 (Li et al., 2018; Lu et al., 2018) have thus far been employed in DRM reaction. Fabricating structured materials was achieved via contemporary synthesis techniques, forming catalyst system with mesoporous structure. Lu et al. (2018) synthesized hollow spherical silica support by microemulsion method. Likewise, one-pot micro-emulsion method was applied to fabricate yolk-shell SiO_2 support (Almana et al., 2016). Bawah et al. (2018) developed

mesoporous silicalite-1 zeolite support by adapting the microwave assisted hydrothermal synthesis method. Nevertheless, these approaches have inclinations towards reducing catalytic activity due to the blockage of active sites and mass transfer limitation.

Recent innovation in development of fibrous structured KCC-1 (KAUST Catalysis Centre 1) has found relevant application in the field of drug delivery, chromatographic separation and energy storage due to its unique fibrous morphology and large surface area (Bayal et al., 2016; Febriyanti et al., 2016; Maity & Polshettiwar, 2019; Singh et al., 2016). The fibrous structured support favour high dispersibility of the loaded metal species due to its dendrimeric silica fibres morphology. These characteristics were responsible for its remarkable performances in reactions such as carbon dioxide methanation (Shahul Hamid et al., 2018), organic pollutant degradation (Azami et al., 2020), hydrocarbon isomerization (Jalil et al., 2019; Triwahyono et al., 2019), methane reforming (Wang et al., 2017; Abdulrasheed et al., 2019) and carbon dioxide capture (Maity et al., 2019). Thus, utilizing the KCC-1 synthesis approach could modify the textural, structural and chemical properties of conventional zeolite support. This study involves the development of novel mesostructured fibrous ZSM-5 Ni-based catalyst with fast reaction kinetics and coke tolerance to maximally produce syngas by utilization of gases (CO_2 and CH_4) with potential to cause global warming. The fibrous ZSM-5 offers extended surface area and large pore channels, fine metal dispersion, increased basicity, moderate acidity, thermal stability and confinement of metal particles thereby inducing remarkable performance much better than conventional ZSM-5 support.

1.2 Problem Statement

The rapid population growth and stringent environmental policies on emission control has triggered unprecedented research on alternate energy source. The utilization of greenhouse gas CO_2 as feedstock integrated with CH_4 to produce syngas provides alternative ways for counteracting the energy crises and global warming. However, both the greenhouse gases (CO_2 and CH_4) are highly stable gas molecules

and thus, require high temperatures to have a spontaneous reaction. As a result of this high energy input condition, there are several underlying issues associated with the catalyst system that hinder the commercialization and industrialization of syngas production via DRM process.

The development of an efficient and robust DRM catalyst without compromising activity and stability remains a hurdle. Being a highly endothermic reaction, equilibrium conversion of reactants in DRM is attainable only at high temperatures mostly in the regions above 700 ^{o}C. Despite the meaningful conversion of reactants attained at these temperatures, the DRM process is faced with severe carbon formation due to the carbon rich feed gas and harsh reaction conditions. Moreover, propagation of methane cracking, Boudouard reaction and reverse water gas shift reaction increases the propensity of carbon deposition. The occurrence of these side reactions alters the purity of syngas produced, which results in H_2:CO ratio less than unity. Therefore, commercialization of DRM process is hinged on development of an economically potent catalyst with the required activity, stability and ease of regeneration.

Remarkable DRM performance were obtained over noble metals such as Rh, Ru, Ir, Pt and Pd. Nonetheless, their application is not profitable and sustainable from an industrial standpoint. More so, noble metals are likely vulnerable to sintering at high temperature. As an alternative to the scarce and exorbitant noble metal catalysts, Ni-based catalysts have been the most widely tested. Nickel is relatively abundant with moderate cost and has an activity competitive with those of noble metals. The demerit of Ni-based catalysts is their characteristic swift deactivation due to carbon deposition and sintering. It is worthy of note that the effect of the carbon type, and mechanism of formation during DRM is still much debated and subject of continuous studies in academia. Despite the research successes recorded over recent years in catalyst development with remarkable activity and stability, the quest for novel and economically potent Ni catalysts with enhanced properties and performances is still much desired towards successful commercialization of syngas production via DRM.

Zeolite has been extensively used as a support material for catalysts due to its well define pore structure, universal availability, high affinity for CO_2 as adsorbent, surface acidity, high surface area and intralattice pore volumes. However, it usually contains varying levels of hydration, which leads to structural collapse due to harsh DRM conditions. Its surface contains high concentration of acid sites which often lead to side reactions with inferior stability. Efforts have been made over the years to enhance porosity and moderate the surface acidity for better active metal dispersion and thermal resistance via approaches such as addition of promoters, dealumination and altering Si/Al ratio. Accessibility of reactants to active metal sites is hampered as a result of its intercrystalline mass transfer hinderance, thus, limiting its catalytic performances.

This research is therefore geared primarily towards design of a stable ZSM-5 supported Ni catalyst with activity, stability and selectivity suitable for the industrialization of DRM process. Development of fibrous ZSM-5 zeolite support with increased basicity and porosity is crucial in enhancement of CO_2 chemisorption, thermal stability and metal particles dispersion which suppress the driving force for agglomeration and coke formation. Therefore, addressing the shortcomings of cheap and widely available Ni catalyst is imperative in the quest for an economically and industrially potent catalyst for syngas production via DRM.

1.3 Research Hypothesis

To overcome the above-mentioned problems, unique fibrous ZSM-5 support with extended dendrimer surface area and porosity is expected to improve dispersion and accessibility of Ni active sites for improved performance. Synthesis by microemulsion method is presumed to produce a coke and sinter tolerant catalyst with core-shell morphology, where Ni particles are finely dispersed on the spherical structured support. The enhanced mass transfer is expected to increase the accessibility of reactants to active metal sites for faster reaction kinetics. The improved surface basicity of fibrous ZSM-5 support is expected to facilitate formation of distinct adsorptive sites for better activity. The fibrous ZSM-5 support is also expected to

induce stabilization of Ni particles to suppress the driving force for agglomeration and coke formation. It is expected that incorporation of tantalum promoter influence dispersion, reducibility and Ni-support interaction for an improved activity, stability and selectivity of the fabricated catalyst. The tantalum promoter is also expected to hinder the diffusion of monoatomic carbon into the Ni particles which is prerequisite for stable performance in DRM.

1.4 Research Objectives

The aim of this research work is to synthesize a robust bimetallic nickel-based catalyst supported on fibrous ZSM-5 with high activity and stability for optimal production of syngas via dry reforming of methane. This is achieved through the following objectives:

1. To conduct thermodynamic sensitivity analysis and equilibrium computations of dry reforming of methane alongside the occurrence of other competing side reactions using HSC Chemistry software.

2. To synthesize and characterize fibrous ZSM-5 (FZSM-5) supported nickel catalysts and evaluate the effects of nickel loading method, morphology and various promoters on catalytic activity and stability.

3. To investigate the effect of nickel-tantalum ratio on selectivity of dry reforming of methane and other competing side reactions.

4. To optimize the dry reforming of methane reaction parameters over Ni-Ta/FZSM-5 via response surface methodology (RSM).

1.5 Research Scope

This study is focused on addressing the major challenges of nickel-based catalyst for industrial syngas production via DRM. In this perspective, thermodynamics of DRM, effects of active metal catalysts, effects of nickel incorporation method, effects of support morphology, effects of promoter, effect of nickel-tantalum ratio, and optimization of dry reforming of methane have been deliberated upon. The details of the specific research scope are as follows:

1. Thermodynamic study of DRM reaction was conducted using the HSC chemistry 6.0 software. Spontaneity of occurrence of DRM reaction and other side reactions were evaluated as a function of reaction temperature. Temperature range of 100–1000 ^{o}C and a pressure of 1 atm was considered for all analysis. Equilibrium amount of each reactant and products were determined with respect to reaction temperature using the equilibrium compositions module. Effects of co-feeding steam or oxygen on equilibrium H_2:CO ratio and carbon deposition were also conducted at reaction temperature of 600–1000 ^{o}C and pressure of 1 atm.

2. Preparation of fibrous ZSM-5 (FZSM-5) support was achieved using microemulsion technique. The dendrimer structure was developed via mixture of cetyltrimethylammonium bromide (as surfactant), butanol (as co-surfactant), toluene (as oil phase), tetraethyl orthosilicate, Urea, ZSM-5 seed and deionized water. Amount of transition metals (Co, Mo, Mn and Ni) on the support catalysts were adjusted to 5 wt.%. The transition metal catalysts were prepared via impregnation method. The prepared catalysts were characterized by FESEM, N_2-adsorption, XRD and catalytic testing for DRM was conducted at atmospheric pressure and a temperature range of 500–800 ^{o}C. Thereafter, effects of nickel incorporation method, support morphology and promoter on DRM was studied. A series of FZSM-5 supported nickel catalysts namely: Ni/FZSM-5-(DS), Ni/FZSM-5-(PM) and Ni/FZSM-5-(WI) are prepared by double solvent, physical mixing and wetness impregnation methods, respectively. The conventional ZSM-5 and FZSM-5 supported nickel catalyst

were prepared by wet impregnation to evaluate the effect of support morphology. Ni/FZSM-5 with various promoter (Mg, Ca, Ta, Ga) were also prepared to study the effect of promoters. 5 wt% of metal was loaded for monometallic catalysts, while 5 wt% Ni and 1 wt% promoter was loaded for the bimetallic catalysts. As-synthesized catalysts were characterized by XRD, N_2-adsorption, ICP-OES, FESEM-mapping, FTIR-KBr, FTIR-lutidine, TPD, TPR, and XPS. Spent catalysts were characterized for carbon deposition or sintering using XRD, TGA, DTA and TEM. Performance evaluation of catalysts for DRM was conducted at atmospheric pressure and a temperature range of 500–800 ^oC at a GHSV of 30,000 mL g^{-1} h^{-1}, CO_2:CH_4:N_2 ratio of 20:20:60 and reaction kinetics using Arrhenius equation.

3. In order to investigate the effects of nickel-tantalum on selectivity of DRM and other competing side reactions, five catalyst namely: 10Ni, 7Ni-3Ta, 5Ni-5Ta, 3Ni-7Ta, 10Ta are prepared by microemulsion and impregnation method. Physicochemical properties of the catalysts were characterized by XRD TPD, TPR and FTIR-lutidine. Spent catalysts were characterized by TGA, TEM, Raman spectra and O_2-TPO. Catalyst testing was also performed at atmospheric pressure, temperature range of 550–800 ^oC and reaction kinetics using Arrhenius equation. The stability of DRM and competing side reaction tests were performed at reaction temperature of 700 ^oC.

4. Optimization of DRM reaction parameters was carried out with the aid of central composite design (CCD) interface of RSM available on Design Expert software 11.0. The independent variables selected for this optimization are temperature (700–800 ^oC), CO_2:CH_4 feed ratio (1–5) and GHSV (10,000–60,000 mL $g^{-1}h^{-1}$) using 7Ni-3Ta as the catalyst. These variables and their ranges were selected based on preliminary studies conducted and information obtained from literature. CH_4 conversion being the rate determining step of DRM was selected as the response variable to evaluate the optimal performance of the catalyst.

1.6 Research Significance

In this study where carbon laydown is an inevitable accompaniment of syngas production, making catalyst prone to swift deactivation. Thermodynamic study of the reaction will provide preliminary information on the dynamics of DRM and other competing side reactions. A coke tolerant catalyst was thus developed using microemulsion method and applied for the first time in dry reforming of methane. As compared to low surface area and micro structured conventional zeolite supports, the fibrous silica ZSM-5 catalyst has unique morphology with dendrimer like structure. This distinctive morphology with extended surface area, large pore channels, increased basicity and thermal stability is anticipated to tremendously affect the catalytic performance. Active metals supported on fibrous ZSM-5 will be highly dispersed and accessible leading to higher turnover of reactants and thus, a faster reaction kinetics. The optimization study using RSM analysis will provide insights on the effect of process variables and their interactions on FZSM-5 supported bimetallic catalysed DRM process. Hence, this research will be a significant contribution to the research and science community, especially in the effort to counteract the environmental issues associated with greenhouse gases by converting these hazardous gases into value added products.

1.7 Thesis Outline

The research is targeted on the development of modified ZSM-5 supported Ni catalyst for efficient and sustained syngas production via dry reforming of methane. The thermodynamics of DRM and major side reactions were studied to get preliminary information on the dynamics of the DRM reaction. The fibrous ZSM-5 morphology was to enhance metal dispersion which impede crystallite growth for increased activity and stability. Introduction of Ta promoter was done primarily to amplify interaction of catalyst components for stellar DRM performance. The kinetics and optimization of process parameters was conducted to ensure an optimal utilization condition for the synthesized catalyst. This thesis therefore consists of five chapters.

Research background and problem at hand, hypothesis, objectives, scope and significance of this research were discussed in Chapter 1. Chapter 2 presents literature review pertaining to possible pathway to CO_2 emission and utilization, methane sources and conversion routes, catalyst development, challenges of deactivation, effects of metal loading method on catalytic performance and the prospects of mesostructured catalyst system. 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.

REFERENCES

Abdollahifar, M., Haghighi, M., & Sharifi, M. (2015). Dry reforming of methane over nanostructured Co/Y catalyst for hydrogen production: Effect of ultrasound irradiation and Co-loading on catalyst properties and performance. *Energy Conversion and Management*, *103*, 1101–1112.

Abdullah, B., Abd Ghani, N. A., & Vo, D. V. N. (2017). Recent advances in dry reforming of methane over Ni-based catalysts. *Journal of Cleaner Production*, *162*, 170–185.

Abdulrasheed, A. A., Jalil, A. A., Hamid, M. Y. S., Siang, T. J., Fatah, N. A. A., Izan, S. M., & Hassan, N. S. (2019). Dry reforming of methane to hydrogen-rich syngas over robust fibrous KCC-1 stabilized nickel catalyst with high activity and coke resistance. *International Journal of Hydrogen Energy*, 1–13.

Abou Rached, J., Cesario, M. R., Estephane, J., Tidahy, H. L., Gennequin, C., Aouad, S., Aboukaïs, A., & Abi-Aad, E. (2018). Effects of cerium and lanthanum on Ni-based catalysts for CO_2 reforming of toluene. *Journal of Environmental Chemical Engineering*, *6*(4), 4743–4754.

Aghamohammadi, S., Haghighi, M., Maleki, M., & Rahemi, N. (2017). Sequential impregnation vs. sol-gel synthesized Ni/Al_2O_3-CeO_2 nanocatalyst for dry reforming of methane: Effect of synthesis method and support promotion. *Molecular Catalysis*, *431*, 39–48.

Ahmed, A. H. (2014). Zeolite-encapsulated transition metal chelates: Synthesis and characterization. *Reviews in Inorganic Chemistry*, *34*(3), 153–175.

Akri, M., Zhao, S., Li, X., Zang, K., Lee, A. F., Isaacs, M. A., Xi, W., Gangarajula, Y., Luo, J., Ren, Y., Cui, Y., Li, L., Su, Y., Pan, X., Wen, W., Pan, Y., Wilson, K., Li, L., Qiao, B., Ishii, H., Liao, Y., Wang, A., Wang, X., & Zhang, T. (2019). Atomically dispersed nickel as coke-resistant active sites for methane dry reforming. *Nature Communications*, *10*(1), 1–10.

Al-Fatesh, A. S., Hanan atia, Ibrahim, A. A., Fakeeha, A. H., Singh, S. K., Labhsetwar, N. K., Shaikh, H., & Qasim, S. O. (2019). CO_2 reforming of CH_4: Effect of Gd as promoter for Ni supported over MCM-41 as catalyst. *Renewable Energy*, *140*, 658–667.

Aleksandrov, H. A., Pegios, N., Palkovits, R., Simeonov, K., & Vayssilov, G. N. (2017). Elucidation of the higher coking resistance of small versus large nickel nanoparticles in methane dry reforming via computational modeling. *Catalysis Science and Technology*, *7*(15), 3339–3347.

Alipour, Z., Rezaei, M., & Meshkani, F. (2014). Effect of Ni loadings on the activity and coke formation of MgO-modified Ni/Al_2O_3 nanocatalyst in dry reforming of methane. *Journal of Energy Chemistry*, *23*(5), 633–638.

Alirezaei, I., Ha, A., & Rahimpour, M. R. (2018). Syngas production in chemical looping reforming process over ZrO_2 promoted Mn-based catalyst. *Journal of CO_2 Utilization*, *23*, 105–116.

Almana, N., Phivilay, S. P., Laveille, P., Hedhili, M. N., Fornasiero, P., Takanabe, K., & Basset, J. M. (2016). Design of a core–shell $Pt–SiO_2$ catalyst in a reverse microemulsion system: Distinctive kinetics on CO oxidation at low temperature. *Journal of Catalysis*, *340*, 368–375.

Alper, E., & Yuksel Orhan, O. (2017). CO_2 utilization: Developments in conversion processes. *Petroleum*, *3*(1), 109–126.

Amin, M. H., Sudarsanam, P., Field, M. R., Patel, J., & Bhargava, S. K. (2017). Effect of a Swelling Agent on the Performance of Ni/Porous Silica Catalyst for CH_4-CO_2 Reforming. *Langmuir*, *33*(40), 10632–10644.

Aramouni, N. A. K., Touma, J. G., Tarboush, B. A., Zeaiter, J., & Ahmad, M. N. (2018). Catalyst design for dry reforming of methane: Analysis review. *Renewable and Sustainable Energy Reviews*, *82*, 2570–2585.

Argyle, M. D., & Bartholomew, C. H. (2015). Heterogeneous catalyst deactivation and regeneration: A review. *Catalysts*, *5*(1), 145–269.

Arku, P., Regmi, B., & Dutta, A. (2018). A review of catalytic partial oxidation of fossil fuels and biofuels: Recent advances in catalyst development and kinetic modelling. *Chemical Engineering Research and Design*, *136*, 385–402.

Arora, S., & Prasad, R. (2016). An overview on dry reforming of methane: Strategies to reduce carbonaceous deactivation of catalysts. *RSC Advances*, *6*(110), 108668–108688.

Ashok, J., Dewangan, N., Das, S., Hongmanorom, P., Wai, M. H., Tomishige, K., & Kawi, S. (2020). Recent progress in the development of catalysts for steam reforming of biomass tar model reaction. *Fuel Processing Technology*, *199*, 106252.

Ay, H., & Üner, D. (2015). Dry reforming of methane over CeO_2 supported Ni, Co and Ni-Co catalysts. *Applied Catalysis B: Environmental*, *179*, 128–138.

Ayodele, O. B., Sulaimon, A. A., Alaba, P. A., & Tian, Z. Y. (2020). Influence of metakaolinization temperature on the structure and activity of metakaolin supported Ni catalyst in dry methane reforming. *Journal of Environmental Chemical Engineering*, *8*(1), 103239.

Ayodele, B. V., & Cheng, C. K. (2015). Modelling and optimization of syngas production from methane dry reforming over ceria-supported cobalt catalyst using artificial neural networks and Box-Behnken design. *Journal of Industrial and Engineering Chemistry*, *32*, 246–258.

Azami, M. S., Jalil, A. A., Hitam, C. N. C., Hassan, N. S., Mamat, C. R., Adnan, R. H., & Chanlek, N. (2020). Tuning of the electronic band structure of fibrous silica titania with g-C_3N_4 for efficient Z-scheme photocatalytic activity. *Applied Surface Science*, *512*, 145744.

Aziz, A., Jalil, A. A., Wongsakulphasatch, S., & N. Vo, D. V. (2019). Understanding the Role of Surface Basic Sites of Catalyst in Co_2 Activation of Dry Reforming of Methane: a Short Review. *Catalysis Science & Technology*, 35–45.

Bartholomew, C. H., & Argyle, M. D. (2015). Advances in catalyst deactivation and regeneration. *Catalysts*, *5*(2), 949–954.

Bawah, A. R., Malaibari, Z. O., & Muraza, O. (2018). Syngas production from CO_2 reforming of methane over Ni supported on hierarchical silicalite-1 fabricated by microwave-assisted hydrothermal synthesis. *International Journal of Hydrogen Energy*, *43*(29), 13177–13189.

Bayal, N., Singh, B., Singh, R., & Polshettiwar, V. (2016). Size and Fiber Density Controlled Synthesis of Fibrous Nanosilica Spheres (KCC-1). *Scientific Reports*, *6*, 1–11.

Beltra, Y., Fernandez, C., Pecchi, G., & Jimenez, R. (2017). Dry reforming of methane on grafted-supported Rh catalysts: effect of the metal-support interaction on the reaction rate. Reaction Kinetics, Mechanisms and Catalysis, *120*, 459–475.

Bezerra, M. A., Santelli, R. E., Oliveira, E. P., Villar, L. S., & Escaleira, L. A. (2008). Response surface methodology (RSM) as a tool for optimization in analytical chemistry. *Talanta*, *76*(5), 965–977.

Bian, Z., & Kawi, S. (2018). Sandwich-Like Silica@Ni@Silica Multicore–Shell Catalyst for the Low-Temperature Dry Reforming of Methane: Confinement Effect Against Carbon Formation. *ChemCatChem*, *10*(1), 320–328.

Bian, Z., & Kawi, S. (2020). Preparation, characterization and catalytic application of phyllosilicate: A review. *Catalysis Today*, *339*, 3–23.

Biscardi, J. A., Meitzner, G. D., & Iglesia, E. (1998). Structure and density of active Zn species in Zn/H-ZSM5 propane aromatization catalysts. *Journal of Catalysis*, *179*(1), 192–202.

BP (2017) BP Statistical Review of World Energy June 2013. Tech. rep., BP.

Budiman, A. W., Song, S. H., Chang, T. S., Shin, C. H., & Choi, M. J. (2012). Dry Reforming of Methane Over Cobalt Catalysts: A Literature Review of Catalyst Development. *Catalysis Surveys from Asia*, *16*(4), 183–197.

Bui, M., Adjiman, C. S., Bardow, A., Anthony, E. J., Boston, A., Brown, S., Fennell, P. S., Fuss, S., Galindo, A., Hackett, L. A., Hallett, J. P., Herzo, H. J., Jackson, G., Kemper, J., Krevor, S., Maitland, G. C., Matuszewski, M., Metcalfe, I. S., Petit, C., Puxty, G., Reimer, J., Reiner, D. M., Rubin, E. S., Scott, S. A., Shah, N., Smit, B., Trusler, J. P. M., Webley, P., Wilcox, J., & Dowell, N. M. (2018). Carbon capture and storage (CCS): The way forward. *Energy and Environmental Science*, *11*(5), 1062–1176.

Cardonne, S. M., Kumar, P., Michaluk, C. A., & Schwartz, H. D. (1995). Tantalum and its alloys. *International Journal of Refractory Metals and Hard Materials*, *13*(4).

Carvalho, D. C., de Souza, H. S. A., Filho, J. M., Oliveira, A. C., Campos, A., Milet, E. R. C., de Sousa, F. F., Padron-Hernandez, E., & Oliveira, A. C. (2014). A study on the modification of mesoporous mixed oxides supports for dry reforming of methane by Pt or Ru. *Applied Catalysis A: General*, *473*, 132–145.

Chang, S., Yang, X., Zheng, H., Wang, S., & Zhang, X. (2020). Air quality and health co-benefits of China's national emission trading system. *Applied Energy*, *261*, 114226.

Chen, M., Wang, Y., Yang, Z., Liang, T., Liu, S., Zhou, Z., & Li, X. (2018). Effect of Mg-modified mesoporous Ni/Attapulgite catalysts on catalytic performance and resistance to carbon deposition for ethanol steam reforming. *Fuel*, *220*, 32–46.

Chen, Y. W., & Wang, W. J. (2000). Carbon dioxide reforming of methane to synthesis gas over Ni/MgO-Al_2O_3-$AlPO_4$ catalysts. *American Chemical Society, Division of Petroleum Chemistry, Preprints*, *45*(1), 125–127.

Chong, C. C., Cheng, Y. W., Bahari, M. B., Teh, L. P., Abidin, S. Z., & Setiabudi, H. D. (2020). Development of nanosilica-based catalyst for syngas production via CO_2 reforming of CH_4: A review. *International Journal of Hydrogen Energy*.

Climate Action Tracker, 2018. Climate Action Tracker. Available at: http://climateactiontracker.org/publications/

Cormos, A. M., Dinca, C., Petrescu, L., Andreea Chisalita, D., Szima, S., & Cormos, C. C. (2018). Carbon capture and utilisation technologies applied to energy conversion systems and other energy-intensive industrial applications. *Fuel*, *211*, 883–890.

Cuéllar-Franca, R. M., & Azapagic, A. (2015). Carbon capture, storage and utilisation technologies: A critical analysis and comparison of their life cycle environmental impacts. *Journal of CO_2 Utilization*, *9*, 82–102.

Dahan, M., Komarala, E., Fadeev, L., Chinnam, A. K., Shlomovich, A., Lipstman, S., Padi, S. A., Haustein, H., Gozin, M., & Rosen, B. A. (2019). Methane dry reforming catalyst prepared by the co-deflagration of high-nitrogen energetic complexes. *Journal of Materials Chemistry A*, *7*(1), 141–149.

Danghyan, V., Calderon Novoa, S., Mukasyan, A., & Wolf, E. E. (2018). Pressure dilution, a new method to prepare a stable Ni/fumed silica catalyst for the dry reforming of methane. *Applied Catalysis B: Environmental*, *234*, 178–186.

Danghyan, V., Kumar, A., Mukasyan, A., & Wolf, E. E. (2020). An active and stable NiOMgO solid solution based catalysts prepared by paper assisted combustion `synthesis for the dry reforming of methane. *Applied Catalysis B: Environmental*, *273*, 119056.

Das, S., Sengupta, M., Patel, J., & Bordoloi, A. (2017). A study of the synergy between support surface properties and catalyst deactivation for CO_2 reforming over supported Ni nanoparticles. *Applied Catalysis A: General*, *545*, 113–126.

Das, S., Shah, M., Gupta, R. K., & Bordoloi, A. (2019). Enhanced dry methane reforming over Ru decorated mesoporous silica and its kinetic study. *Journal of CO2 Utilization*, *29*, 240–253.

Das, S., Thakur, S., Bag, A., Gupta, M. S., Mondal, P., & Bordoloi, A. (2015). Support interaction of Ni nanocluster based catalysts applied in CO_2 reforming. J*ournal of Catalysis, 330*, 46–60.

Davis, M. E. (2002). Ordered porous materials for emerging applications. *Nature*, *417*(6891), 813–821.

de la Cruz-Flores, V. G., Martinez-Hernandez, A., & Gracia-Pinilla, M. A. (2020). Deactivation of Ni-SiO_2 catalysts that are synthetized via a modified direct synthesis method during the dry reforming of methane. *Applied Catalysis A: General*, *594*, 117455.

Degnan, T. F., Chitnis, G. K., & Schipper, P. H. (2000). History of ZSM-5 fluid catalytic cracking additive development at Mobil. *Microporous and Mesoporous Materials*, *35–36*, 245–252.

Drobná, H., Kout, M., Sołtysek, A., González-Delacruz, V. M., Caballero, A., & Čapek, L. (2017). Analysis of Ni species formed on zeolites, mesoporous silica and alumina supports and their catalytic behavior in the dry reforming of methane. *Reaction Kinetics, Mechanisms and Catalysis*, *121*(1), 255–274.

Edenhofer, O., Jakob, M., Creutzig, F., Flachsland, C., Fuss, S., Kowarsch, M., Lessmann, K., Mattauch, L., Siegmeier, J., & Steckel, J. C. (2015). Closing the emission price gap. *Global Environmental Change*, *31*, 132–143.

Ennaert, T., Van Aelst, J., Dijkmans, J., De Clercq, R., Schutyser, W., Dusselier, M., Verboekend, D., & Sels, B. F. (2016). Potential and challenges of zeolite chemistry in the catalytic conversion of biomass. *Chemical Society Reviews*, *45*(3), 584–611.

Er-Rbib, H., Bouallou, C., & Werkoff, F. (2012). Production of synthetic gasoline and diesel fuel from dry reforming of methane. *Energy Procedia*, *29*, 156–165.

Erdogan, B., Arbag, H., & Yasyerli, N. (2018). SBA-15 supported mesoporous Ni and Co catalysts with high coke resistance for dry reforming of methane. *International Journal of Hydrogen Energy*, *43*(3), 1396–1405.

Estephane, J., Aouad, S., Hany, S., El Khoury, B., Gennequin, C., El Zakhem, H., Nakat, J. E., Aboukaïs, A., & Aad, E. A. (2015). CO_2 reforming of methane over Ni-Co/ZSM5 catalysts. Aging and carbon deposition study. *International Journal of Hydrogen Energy*, *40*(30), 9201–9208.

Ewbank, J. L., Kovarik, L., Diallo, F. Z., & Sievers, C. (2015). Effect of metal-support interactions in Ni/Al_2O_3 catalysts with low metal loading for methane dry reforming. *Applied Catalysis A: General*, *494*, 57–67.

Fan, M. S., Abdullah, A. Z., & Bhatia, S. (2010). Utilization of greenhouse gases through carbon dioxide reforming of methane over $Ni\text{-}Co/MgO\text{-}ZrO_2$: Preparation, characterization and activity studies. *Applied Catalysis B: Environmental*, *100*(1–2), 365–377.

Fatah, N. A. A., Triwahyono, S., Jalil, A. A., Salamun, N., Mamat, C. R., & Majid, Z. A. (2017). n-Heptane isomerization over molybdenum supported on bicontinuous concentric lamellar silica KCC-1: Influence of phosphorus and optimization using response surface methodology (RSM). *Chemical Engineering Journal*, *314*, 650–659.

Febriyanti, E., Suendo, V., Mukti, R. R., Prasetyo, A., Arifin, A. F., Akbar, M. A., Triwahyono, S., Marsih, I. N., & Ismunandar (2016). Further Insight on the Definite Morphology and Formation Mechanism of Mesoporous Silica KCC-1. *Langmuir, 32(23)*, 5802–5811.

Fernández-Amador, O., Francois, J. F., Oberdabernig, D. A., & Tomberger, P. (2020). The methane footprint of nations: Stylized facts from a global panel dataset. *Ecological Economics*, *170*, 106528.

Firmansyah, M. L., Jalil, A. A., Triwahyono, S., Hamdan, H., Salleh, M. M., Ahmad, W. F. W., & Kadja, G. T. M. (2016). Synthesis and characterization of fibrous silica ZSM-5 for cumene hydrocracking. *Catalysis Science and Technology*, *6*(13), 5178–5182.

Fouskas, A., Kollia, M., Kambolis, A., Papadopoulou, C., & Matralis, H. (2014). Boron-modified Ni/Al_2O_3 catalysts for reduced carbon deposition during dry reforming of methane. *Applied Catalysis A: General*, *474*, 125–134.

Frontera, P., Macario, A., Aloise, A., Antonucci, P. L., Giordano, G., & Nagy, J. B. (2013). Effect of support surface on methane dry-reforming catalyst preparation. *Catalysis Today*, *218–219*, 18–29.

Galadima, A., & Muraza, O. (2019). Zeolite catalyst design for the conversion of glucose to furans and other renewable fuels. *Fuel*, *258*, 115851.

García-Diéguez, M., Finocchio, E., Larrubia, M. Á., Alemany, L. J., & Busca, G. (2010). Characterization of alumina-supported Pt, Ni and PtNi alloy catalysts for the dry reforming of methane. *Journal of Catalysis*, *274*(1), 11–20.

Ghanbari, T., Abnisa, F., & Wan Daud, W. M. A. (2020). A review on production of metal organic frameworks (MOF) for CO_2 adsorption. *Science of the Total Environment*, *707*, 135090.

Giehr, A., Maier, L., Schunk, S. A., & Deutschmann, O. (2018). Thermodynamic Considerations on the Oxidation State of Co/γ-Al_2O_3 and Ni/γ-Al_2O_3 Catalysts under Dry and Steam Reforming Conditions. *ChemCatChem*, *10*(4), 751–757.

Goodarzi, F., Herrero, I. P., Kalantzopoulos, G. N., Svelle, S., Lazzarini, A., Beato, P., Olsbye, U., & Kegnæs, S. (2020). Synthesis of mesoporous ZSM-5 zeolite encapsulated in an ultrathin protective shell of silicalite-1 for MTH conversion. *Microporous and Mesoporous Materials*, *292*, 109730.

Guczi, L., Stefler, G., Geszti, O., Sajó, I., Pászti, Z., Tompos, A., & Schay, Z. (2010). Methane dry reforming with CO_2: A study on surface carbon species. *Applied Catalysis A: General*, *375*(2), 236–246.

Guerrero-Pérez, M. O. (2019). The fascinating effect of niobium as catalytic promoting agent. *Catalysis Today*.

Guilera, J., Del Valle, J., Alarcón, A., Díaz, J. A., & Andreu, T. (2019). Metal-oxide promoted Ni/Al_2O_3 as CO_2 methanation micro-size catalysts. *Journal of CO_2 Utilization*, *30*, 11–17.

Guisnet, M., & Ribeiro, F. R. (2011). *Deactivation and Regeneration of Zeolite Catalysts*. Imperial College Press.

Guo, H., Cheng, Q., Jin, Z., Wang, D., Xu, G., & Liu, Y. (2016). Thermochemical processing of fuels involving the use of molecular oxygen. *RSC Advances*, *6*(104), 102231–102248.

Gür, T. M. (2016). Comprehensive review of methane conversion in solid oxide fuel cells: Prospects for efficient electricity generation from natural gas. *Progress in Energy and Combustion Science*, *54*, 1–64.

Hamid, M. Y. S., Firmansyah, M. L., Triwahyono, S., Jalil, A. A., Mukti, R. R., Febriyanti, E., Suendo, V., Setiabudi, H. D., & Nabgan, W. (2017). Oxygen vacancy-rich mesoporous silica KCC-1 for CO_2 methanation. *Applied Catalysis A: General*, *532*, 86–94.

Han, J. W., Park, J. S., Choi, M. S., & Lee, H. (2017). Uncoupling the size and support effects of Ni catalysts for dry reforming of methane. *Applied Catalysis B: Environmental*, *203*, 625–632.

Hao, Z., Zhu, Q., Jiang, Z., Hou, B., & Li, H. (2009). Characterization of aerogel Ni/Al_2O_3 catalysts and investigation on their stability for CH_4-CO_2 reforming in a fluidized bed. *Fuel Processing Technology*, *90*(1), 113–121.

He, L., Fan, Y., Bellettre, J., Yue, J., & Luo, L. (2020). A review on catalytic methane combustion at low temperatures: Catalysts, mechanisms, reaction conditions and reactor designs. *Renewable and Sustainable Energy Reviews*, *119*, 109589.

Heracleous, E., Lee, A. F., Wilson, K., & Lemonidou, A. A. (2005). Investigation of Ni-based alumina-supported catalysts for the oxidative dehydrogenation of ethane to ethylene : structural characterization and reactivity studies, *231*, 159–171.

Horlyck, J., Lawrey, C., Lovell, E. C., Amal, R., & Scott, J. (2018). Elucidating the impact of Ni and Co loading on the selectivity of bimetallic NiCo catalysts for dry reforming of methane. *Chemical Engineering Journal*, *352*, 572–580.

Horn, R., & Schlögl, R. (2015). Methane Activation by Heterogeneous Catalysis. *Catalysis Letters*, *145*(1), 23–39.

Hossain, M. A., Ayodele, B. V., Cheng, C. K., & Khan, M. R. (2019). Optimization of renewable hydrogen-rich syngas production from catalytic reforming of greenhouse gases (CH_4 and CO_2) over calcium iron oxide supported nickel catalyst. *Journal of the Energy Institute*, *92*(1), 177–194.

Huang, K., Miller, J. B., Huber, G. W., Dumesic, J. A., & Maravelias, C. T. (2018). A General Framework for the Evaluation of Direct Nonoxidative Methane Conversion Strategies. *Joule*, *2*(2), 349–365.

Huang, T., Huang, W., Huang, J., & Ji, P. (2011). Methane reforming reaction with carbon dioxide over SBA-15 supported Ni-Mo bimetallic catalysts. *Fuel Processing Technology*, *92*(10), 1868–1875.

Imperor-Clerc, M., Bazin, D., Appay, M. D., Beaunier, P., & Davidson, A. (2004). Crystallization of β-MnO_2 Nanowires in the Pores of SBA-15 Silicas: In Situ Investigation Using Synchrotron Radiation. *Chemistry of Materials*, *16*(9), 1813–1821.

Izan, S. M., Triwahyono, S., Jalil, A. A., Majid, Z. A., Fatah, N. A. A., Hamid, M. Y. S., & Ibrahim, M. (2019). Additional Lewis acid sites of protonated fibrous silica@BEA zeolite (HSi@BEA) improving the generation of protonic acid sites in the isomerization of C6 alkane and cycloalkanes. *Applied Catalysis A: General*, *570*, 228–237.

Izhab, I., Asmadi, M., & Saidina Amin, N. A. (2020). Methane dry reforming using oil palm shell activated carbon supported cobalt catalyst: Multi-response optimization. *International Journal of Hydrogen Energy*.

Jabbour, K., El Hassan, N., Davidson, A., Casale, S., & Massiani, P. (2016). Factors affecting the long-term stability of mesoporous nickel-based catalysts in combined steam and dry reforming of methane. *Catalysis Science and Technology*, *6*(12), 4616–4631.

Jabbour, Karam, Massiani, P., Davidson, A., Casale, S., & El Hassan, N. (2017). Ordered mesoporous "one-pot" synthesized Ni-Mg(Ca)-Al_2O_3 as effective and remarkably stable catalysts for combined steam and dry reforming of methane (CSDRM). *Applied Catalysis B: Environmental*, *201*, 527–542.

Jalil, A. A., Gambo, Y., Abdulrasheed, A. A., & Asli, U. A. (2019). Platinum - promoted fibrous silica Y zeolite with enhanced mass transfer as a highly selective catalyst for n - dodecane hydroisomerization. *International Journal of Energy Research*.

Jang, J. G., Kim, G. M., Kim, H. J., & Lee, H. K. (2016). Review on recent advances in CO_2 utilization and sequestration technologies in cement-based materials. *Construction and Building Materials*, *127*, 762–773.

Jeong, H., Kim, K. I., Kim, D., & Song, I. K. (2006). Effect of promoters in the methane reforming with carbon dioxide to synthesis gas over Ni/HY catalysts. *Journal of Molecular Catalysis A: Chemical*, *246*(1–2), 43–48.

Jiang, S., Lu, Y., Wang, S., Zhao, Y., & Ma, X. (2017). Insight into the reaction mechanism of CO_2 activation for CH_4 reforming over NiO-MgO: A combination of DRIFTS and DFT study. *Applied Surface Science*, *416*, 59–68.

Jin, Z., Liu, S., Qin, L., Liu, Z., Wang, Y., Xie, Z., & Wang, X. (2013). Methane dehydroaromatization by Mo-supported MFI-type zeolite with core-shell structure. *Applied Catalysis A: General*, *453*, 295–301.

Jing, J., Wei, Z., Zhang, Y., Bai, H., & Li, W. (2020). Carbon dioxide reforming of methane over MgO-promoted Ni/SiO_2 catalysts with tunable Ni particle size. *Catalysis Today*.

Johnson, G. R., & Bell, A. T. (2016). Effects of Lewis acidity of metal oxide promoters on the activity and selectivity of Co-based Fischer-Tropsch synthesis catalysts. *Journal of Catalysis*, *338*, 250–264.

Kaengsilalai, A., Luengnaruemitchai, A., Jitkarnka, S., & Wongkasemjit, S. (2007). Potential of Ni supported on KH zeolite catalysts for carbon dioxide reforming of methane. *Journal of Power Sources*, *165*(1), 347–352.

Kahle, L. C. S., Roussière, T., Maier, L., Herrera Delgado, K., Wasserschaff, G., Schunk, S. A., & Deutschmann, O. (2013). Methane dry reforming at high temperature and elevated pressure: Impact of gas-phase reactions. *Industrial and Engineering Chemistry Research*, *52*(34), 11920–11930.

Kang, W., Guo, H., & Varma, A. (2019). Noble-metal-free NiCu/CeO_2 catalysts for H_2 generation from hydrous hydrazine. *Applied Catalysis B: Environmental*, *249*, 54–62.

Karakaya, C., & Kee, R. J. (2016). Progress in the direct catalytic conversion of methane to fuels and chemicals. *Progress in Energy and Combustion Science*, *55*, 60–97.

Károlyi, J., Németh, M., Evangelisti, C., Sáfrán, G., Schay, Z., Horváth, A., & Somodi, F. (2018). Carbon dioxide reforming of methane over Ni–In/SiO_2 catalyst without coke formation. *Journal of Industrial and Engineering Chemistry*, *58*, 189–201.

Kathiraser, Y., Oemar, U., Saw, E. T., Li, Z., & Kawi, S. (2015). Kinetic and mechanistic aspects for CO_2 reforming of methane over Ni based catalysts. *Chemical Engineering Journal*, *278*, 62–78.

Kawi, S., Kathiraser, Y., Ni, J., Oemar, U., Li, Z., & Saw, E. T. (2015). Progress in Synthesis of Highly Active and Stable Nickel-Based Catalysts for Carbon Dioxide Reforming of Methane. *ChemSusChem*, *8*(21), 3556–3575.

Khajenoori, M., Rezaei, M., & Meshkani, F. (2015). Dry reforming over CeO_2-promoted Ni/MgO nano-catalyst: Effect of Ni loading and CH_4/CO_2 molar ratio. *Journal of Industrial and Engineering Chemistry*, *21*, 717–722.

Kleijnen, J. P. C. (2015). Response surface methodology. *International Series in Operations Research and Management Science*, *216*, 81–104.

Kim, S. H., Kang, P. W., Park, O. O., Seol, J. B., Ahn, J. P., Lee, J. Y., & Choi, P. P. (2018). A new method for mapping the three-dimensional atomic distribution within nanoparticles by atom probe tomography (APT). *Ultramicroscopy*, *190*, 30–38.

Kim, W. Y., Jang, J. S., Ra, E. C., Kim, K. Y., Kim, E. H., & Lee, J. S. (2019). Reduced perovskite $LaNiO_3$ catalysts modified with Co and Mn for low coke formation in dry reforming of methane. *Applied Catalysis A: General*, *575*, 198–203.

Kosinov, N., Liu, C., Hensen, E. J. M., & Pidko, E. A. (2018). Engineering of Transition Metal Catalysts Confined in Zeolites. *Chemistry of Materials*, *30*(10), 3177–3198.

Kumar, H., Sarma, A. K., & Kumar, P. (2020). A comprehensive review on preparation, characterization, and combustion characteristics of microemulsion based hybrid biofuels. *Renewable and Sustainable Energy Reviews*, *117*, 109498.

Larmier, K., Chizallet, C., & Raybaud, P. (2015). Tuning the metal-support interaction by structural recognition of cobalt-based catalyst precursors. *Angewandte Chemie - International Edition*, *54*(23), 6824–6827.

Lee, S., & Shantz, D. F. (2005). Zeolite growth in nonionic microemulsions: Synthesis of hierarchically structured zeolite particles. *Chemistry of Materials*, *17*(2), 409–417.

Li, Baitao, Lin, X., Luo, Y., Yuan, X., & Wang, X. (2018). Design of active and stable bimodal nickel catalysts for methane reforming with CO_2. *Fuel Processing Technology*, *176*, 153–166.

Li, Bin, Yuan, X., Li, B., & Wang, X. (2020). Impact of pore structure on hydroxyapatite supported nickel catalysts (Ni/HAP) for dry reforming of methane. *Fuel Processing Technology*, *202*, 106359.

Li, J., Miao, P., Li, Z., He, T., Han, D., Wu, J., Wang, Z., & Wu, J. (2015). Hydrothermal synthesis of nanocrystalline H[Fe, Al]ZSM-5 zeolites for conversion of methanol to gasoline. *Energy Conversion and Management*, *93*, 259–266.

Li, K., Pei, C., Li, X., Chen, S., Zhang, X., Liu, R., & Gong, J. (2020). Dry reforming of methane over $La_2O_2CO_3$-modified Ni/Al_2O_3 catalysts with moderate metal support interaction. *Applied Catalysis B: Environmental*, *264*, 118448.

Li, L., Anjum, D. H., Zhu, H., Saih, Y., Laveille, P. V., D'Souza, L., & Basset, J. M. (2015). Synergetic effects leading to coke-resistant NiCo bimetallic catalysts for dry reforming of methane. *ChemCatChem*, *7*(3), 427–433.

Li, Z., Das, S., Hongmanorom, P., Dewangan, N., Wai, M. H., & Kawi, S. (2018). Silica-based micro- and mesoporous catalysts for dry reforming of methane. *Catalysis Science and Technology*, *8*(11), 2763–2778.

Li, Z., Mo, L., Kathiraser, Y., & Kawi, S. (2014). Yolk-satellite-shell structured Ni-Yolk@Ni@SiO_2 nanocomposite: Superb catalyst toward methane CO_2 reforming reaction. *ACS Catalysis*, *4*(5), 1526–1536.

Lin, B., Wei, K., Ma, X., Lin, J., & Ni, J. (2013). Study of potassium promoter effect for Ru/AC catalysts for ammonia synthesis. *Catalysis Science Technology*, *3*, 1367.

Liu, D., Lau, R., Borgna, A., & Yang, Y. (2009a). Carbon dioxide reforming of methane to synthesis gas over Ni-MCM-41 catalysts. *Applied Catalysis A: General*, *358*(2), 110–118.

Liu, D., Quek, X. Y., Cheo, W. N. E., Lau, R., Borgna, A., & Yang, Y. (2009b). MCM-41 supported nickel-based bimetallic catalysts with superior stability during carbon dioxide reforming of methane: Effect of strong metal-support interaction. *Journal of Catalysis*, *266*(2), 380–390.

Liu, H., Hadjltaief, H. B., Benzina, M., Gálvez, M. E., & Da Costa, P. (2019). Natural clay based nickel catalysts for dry reforming of methane: On the effect of support promotion (La, Al, Mn). *International Journal of Hydrogen Energy*, *4*, 246–255.

Liu, K., Zhao, X., Ren, G., Yang, T., Ren, Y., Lee, A. F., Su, Y., Pan, X., Zhang, J., Chen, Z., Yang, J., Liu, X., Zhou, T., Xi, W., Luo, J., Zeng, C., Matsumoto, H., Liu, W., Jiang, Q., Wilson, K., Wang, A., Qiao, B., Li, W., & Zhang, T. (2020). Strong metal-support interaction promoted scalable production of thermally stable single-atom catalysts. *Nature Communications*, *11*(1), 1–9.

Liu, Y., Wang, Y., & Huang, D. (2019). Supercritical CO_2 Brayton cycle: A state-of-the-art review. *Energy*, *189*, 115900.

Liu, Z., Lustemberg, P., Gutiérrez, R. A., Carey, J. J., Palomino, R. M., Vorokhta, M., Grinter, D. C., Ramírez, P. J., Matolín, V., Nolan, M., Ganduglia-Pirovano, M. V., Senanayake, S. D., & Rodriguez, J. A. (2017). In Situ Investigation of Methane Dry Reforming on Metal/Ceria (111) Surfaces: Metal–Support Interactions and C−H Bond Activation at Low Temperature. *Angewandte Chemie - International Edition*, *56*(42), 13041–13046.

Lovell, E., Jiang, Y., Scott, J., Wang, F., Suhardja, Y., Chen, M., Huang, J., & Amal, R. (2014). CO_2 reforming of methane over MCM-41-supported nickel catalysts: Altering support acidity by one-pot synthesis at room temperature. *Applied Catalysis A: General*, *473*, 51–58.

Lu, Y., Guo, D., Ruan, Y., Zhao, Y., Wang, S., & Ma, X. (2018). Facile one-pot synthesis of Ni@HSS as a novel yolk-shell structure catalyst for dry reforming of methane. *Journal of CO_2 Utilization*, *24*, 190–199.

Ma, Q., Han, Y., Wei, Q., Makpal, S., Gao, X., Zhang, J., & Zhao, T. S. (2020). Stabilizing Ni on bimodal mesoporous-macroporous alumina with enhanced coke tolerance in dry reforming of methane to syngas. *Journal of CO_2 Utilization*, *35*, 288–297.

Ma, S., Chen, G., Guo, M., Zhao, L., Han, T., & Zhu, S. (2014). Path analysis on CO_2 resource utilization based on carbon capture using ammonia method in coal-fired power Plants. *Renewable and Sustainable Energy Reviews*, *37*, 687–697.

Madadi, S., Charbonneau, L., Bergeron, J. Y., & Kaliaguine, S. (2020). Aerobic epoxidation of limonene using cobalt substituted mesoporous SBA-16 Part 1: Optimization via Response Surface Methodology (RSM). *Applied Catalysis B: Environmental*, *260*, 118049.

Maity, A., Belgamwar, R., & Polshettiwar, V. (2019). Facile synthesis to tune size, textural properties and fiber density of dendritic fibrous nanosilica for applications in catalysis and CO_2 capture. *Nature Protocols*, *14*(7), 2177–2204.

Maity, A., & Polshettiwar, V. (2017). Dendritic Fibrous Nanosilica for Catalysis, Energy Harvesting, Carbon Dioxide Mitigation, Drug Delivery, and Sensing. *ChemSusChem*, *10*(20), 3866–3913.

Marmarshahi, S., Niaei, A., Salari, D., Abedini, F., Abbasi, M., & Kalantari, N. (2015). Evaluating the Catalytic Performance of $La_{1-x}Ce_xNi_{1-y}Zn_yO_3$ Nanostructure Perovskites in the Carbon Dioxide Reforming of Methane. *Procedia Materials Science*, *11*(2008), 616–621.

Mattos, L. V., Jacobs, G., Davis, B. H., & Noronha, F. B. (2012). Production of hydrogen from ethanol: Review of reaction mechanism and catalyst deactivation. *Chemical Reviews*, *112*(7), 4094–4123.

Miedziak, P. J., Kondrat, S. A., Sajjad, N., King, G. M., Douthwaite, M., Shaw, G., Brett, G. L., Edwards, J. K., Morgan, D. J., Hussain, G., & Hutchings, G. J. (2013). Physical mixing of metal acetates: Optimisation of catalyst parameters to produce highly active bimetallic catalysts. *Catalysis Science and Technology*, *3*(11), 2910–2917.

Miller, M. K., & Forbes, R. G. (2009). Atom probe tomography. *Materials Characterization*, *60*(6), 461–469.

Mishra, A., Shafiefarhood, A., Dou, J., & Li, F. (2019). Rh promoted perovskites for exceptional "low temperature" methane conversion to syngas. *Catalysis Today*.

Moradi, G., Khezeli, F., & Hemmati, H. (2016). Syngas production with dry reforming of methane over Ni/ZSM-5 catalysts. *Journal of Natural Gas Science and Engineering*, *33*, 657–665.

Movasati, A., Alavi, S. M., & Mazloom, G. (2019). Dry reforming of methane over CeO_2-$ZnAl_2O_4$ supported Ni and Ni-Co nano-catalysts. *Fuel*, *236*, 1254–1262.

Myint, M. N. Z., Yan, B., Wan, J., Zhao, S., & Chen, J. G. (2016). Reforming and oxidative dehydrogenation of ethane with CO_2 as a soft oxidant over bimetallic catalysts. *Journal of Catalysis*, *343*, 168–177.

Nataj, S. M. M., Alavi, S. M., & Mazloom, G. (2018). Modeling and optimization of methane dry reforming over Ni–Cu/Al_2O_3 catalyst using Box–Behnken design. *Journal of Energy Chemistry*, *27*(5), 1475–1488.

Németh, M., Sáfrán, G., Horváth, A., & Somodi, F. (2019). Hindered methane decomposition on a coke-resistant Ni-In/SiO_2 dry reforming catalyst. *Catalysis Communications*, *118*, 56–59.

Ni, J., Chen, L., Lin, J., & Kawi, S. (2012a). Carbon deposition on borated alumina supported nano-sized Ni catalysts for dry reforming of CH_4. *Nano Energy*, *1*(5), 674–686.

Ni, J., Chen, L., Lin, J., & Kawi, S. (2012b). Carbon deposition on borated alumina supported nano-sized Ni catalysts for dry reforming of CH_4. *Nano Energy*, *1*(5), 674–686.

Ni, J., Zhao, J., Chen, L., Lin, J., & Kawi, S. (2016). Lewis Acid Sites Stabilized Nickel Catalysts for Dry (CO_2) Reforming of Methane. *ChemCatChem*, *8*(24), 3732–3739.

Niu, J., Du, X., Ran, J., & Wang, R. (2016). Dry (CO_2) reforming of methane over Pt catalysts studied by DFT and kinetic modeling. *Applied Surface Science*, *376*, 79–90.

Niu, J., Ran, J., & Chen, D. (2020). Understanding the mechanism of CO_2 reforming of methane to syngas on Ni@Pt surface compared with Ni(111) and Pt(111). *Applied Surface Science*, *513*(111), 145840.

Norhasyima, R. S., & Mahlia, T. M. I. (2018). Advances in CO_2 utilization technology: A patent landscape review. *Journal of CO_2 Utilization*, 323–335.

Oemar, U., Kathiraser, Y., Mo, L., Ho, X. K., & Kawi, S. (2016). CO_2 reforming of methane over highly active La-promoted Ni supported on SBA-15 catalysts: Mechanism and kinetic modelling. *Catalysis Science and Technology*, *6*(4), 1173–1186.

Özdemir, H., Öksüzömer, M. A. F., & Gürkaynak, M. A. (2014). Effect of the calcination temperature on Ni/$MgAl_2O_4$ catalyst structure and catalytic properties for partial oxidation of methane. *Fuel*, *116*, 63–70.

Pakhare, D., Shaw, C., Haynes, D., Shekhawat, D., & Spivey, J. (2013). Effect of reaction temperature on activity of Pt- and Ru-substituted lanthanum zirconate pyrochlores ($La_2Zr_2O_7$) for dry (CO_2) reforming of methane (DRM). *Journal of CO_2 Utilization*, *1*, 37–42.

Pakhare, D., & Spivey, J. (2014). A review of dry (CO_2) reforming of methane over noble metal catalysts. *Chem. Soc. Rev.*, *43*(22), 7813–7837.

Pal, D. B., Chand, R., Upadhyay, S. N., & Mishra, P. K. (2018). Performance of water gas shift reaction catalysts: A review. *Renewable and Sustainable Energy Reviews*, *93*, 549–565.

Pan, Y. X., Kuai, P., Liu, Y., Ge, Q., & Liu, C. J. (2010). Promotion effects of Ga_2O_3 on CO2 adsorption and conversion over a SiO_2-supported Ni catalyst. *Energy and Environmental Science*, *3*(9), 1322–1325.

Park, J. H., Heo, I., & Chang, T. S. (2019). Dry reforming of methane over Ni-substituted CaZrNiOx catalyst prepared by the homogeneous deposition method. *Catalysis Communications*, *120*, 1–5.

Peddakasu, G. B., Velisoju, V. K., Kandula, M., Gutta, N., VR Chary, K., & Akula, V. (2019). Role of group V elements on the hydrogenation activity of Ni/TiO_2 catalyst for the vapour phase conversion of levulinic acid to Γ-valerolactone. *Catalysis Today*, *325*, 68–72.

Perego, C., & Millinib, R. (2013). Porous materials in catalysis: Challenges for mesoporous materials. *Chemical Society Reviews*, *42*(9), 3956–3976.

Phan, T. S., Sane, A. R., Rêgo de Vasconcelos, B., Nzihou, A., Sharrock, P., Grouset, D., & Pham Minh, D. (2018). Hydroxyapatite supported bimetallic cobalt and nickel catalysts for syngas production from dry reforming of methane. *Applied Catalysis B: Environmental*, *224*, 310–321.

Pinheiro, A. N., Valentini, A., Sasaki, J. M., & Oliveira, A. C. (2009). Highly stable dealuminated zeolite support for the production of hydrogen by dry reforming of methane. *Applied Catalysis A: General*, *355*(1–2), 156–168.

Polo-Garzon, F., He, M., & Bruce, D. A. (2016). Ab initio derived reaction mechanism for the dry reforming of methane on Rh doped pyrochlore catalysts. *Journal of Catalysis*, *333*, 59–70.

Polshettiwar, V., Cha, D., Zhang, X., & Basset, J. M. (2010). High-surface-area silica nanospheres (KCC-1) with a fibrous morphology. *Angewandte Chemie - International Edition*, *49*(50), 9652–9656.

Quincoces, C. E., de Varga, S. P., Grange. P., M., & Gonzalez, M. G. (2002). Role of Mo in CO_2 reforming of CH_4 over Mo promoted Ni/Al_2O_3 catalysts. *Materials Letters 56*, 698–704.

Quindimil, A., De-La-Torre, U., Pereda-Ayo, B., González-Marcos, J. A., & González-Velasco, J. R. (2018). Ni catalysts with La as promoter supported over Y- and BETA- zeolites for CO_2 methanation. *Applied Catalysis B: Environmental*, *238*, 393–403.

Rakić, T., Kasagić-Vujanović, I., Jovanović, M., Jančić-Stojanović, B., & Ivanović, D. (2014). Comparison of Full Factorial Design, Central Composite Design, and Box-Behnken Design in Chromatographic Method Development for the Determination of Fluconazole and Its Impurities. *Analytical Letters*, *47*(8), 1334–1347.

Rase, H. F. (2005). *Handbook of Commercial catalysts*. *Chem. Ind. London* (Vol. (12)).

Rego de Vasconcelos, B., Pham Minh, D., Martins, E., Germeau, A., Sharrock, P., & Nzihou, A. (2019). Highly-efficient hydroxyapatite-supported nickel catalysts for dry reforming of methane. *International Journal of Hydrogen Energy*.

Rogelj, J., Den Elzen, M., Höhne, N., Fransen, T., Fekete, H., Winkler, H., Schaeffer, R., Sha, F., Riahi, K., & Meinshausen, M. (2016). Paris Agreement climate proposals need a boost to keep warming well below 2 °c. *Nature*, *534*(7609), 631–639.

Rogers, J. L., Mangarella, M. C., D'Amico, A. D., Gallagher, J. R., Dutzer, M. R., Stavitski, E., Miller, J. T., & Sievers, C. (2016). Differences in the Nature of Active Sites for Methane Dry Reforming and Methane Steam Reforming over Nickel Aluminate Catalysts. *ACS Catalysis*, *6*(9), 5873–5886.

Ruckenstein, E., & Wang, H. Y. (2000). Carbon dioxide reforming of methane to synthesis gas over supported cobalt catalysts. *Applied Catalysis A: General*, *204*, 257–263.

Sajjadi, S. M., & Haghighi, M. (2018). Impregnation vs. sol-gel and sol-gel-plasma dispersion of nickel nanoparticles over Al_2O_3 employed in combined dry reforming and partial oxidation of greenhouse gases to syngas. *International Journal of Hydrogen Energy*, *43*(32), 15014–15029.

Saraswat, S. K., & Pant, K. K. (2011). Ni-Cu-Zn/MCM-22 catalysts for simultaneous production of hydrogen and multiwall carbon nanotubes via thermo-catalytic decomposition of methane. *International Journal of Hydrogen Energy*, *36*(21), 13352–13360.

Sarkar, B., Tiwari, R., Singha, R. K., Suman, S., Ghosh, S., Acharyya, S. S., Mantri, K., Konathala, L. N. S., Pendem, C., & Bal, R. (2012). Reforming of methane with CO_2 over Ni nanoparticle supported on mesoporous ZSM-5. *Catalysis Today*, *198*(1), 209–214.

Schulz, L. A., Kahle, L. C. S., Delgado, K. H., Schunk, S. A., Jentys, A., Deutschmann, O., & Lercher, J. A. (2015). On the coke deposition in dry reforming of methane at elevated pressures. *Applied Catalysis A: General*, *504*, 599–607.

Schwab, E., Milanov, A., Schunk, S. A., Behrens, A., & Schödel, N. (2015). Dry reforming and reverse water gas shift: Alternatives for syngas production? *Chemie-Ingenieur-Technik*, *87*(4), 347–353.

Shah, M., Bordoloi, A., Nayak, A. K., & Mondal, P. (2019). Effect of Ti/Al ratio on the performance of Ni/TiO_2-Al_2O_3 catalyst for methane reforming with CO_2. *Fuel Processing Technology*, *192*, 21–35.

Shah, M., Das, S., Nayak, A. K., Mondal, P., & Bordoloi, A. (2018). Smart designing of metal-support interface for imperishable dry reforming catalyst. *Applied Catalysis A: General*, *556*, 137–154.

Shah, Y. T., & Gardner, T. H. (2014). Dry reforming of hydrocarbon feedstocks. *Catalysis Reviews - Science and Engineering*, *56*(4), 476–536.

Hamid, M. Y. S., Triwahyono, S., Jalil, A. A., Che Jusoh, N. W., Izan, S. M., & Tuan Abdullah, T. A. (2018). Tailoring the Properties of Metal Oxide Loaded/KCC-1 toward a Different Mechanism of CO_2 Methanation by in Situ IR and ESR. *Inorganic Chemistry*, *57*(10), 5859–5869.

Shang, Z., Li, S., Li, L., Liu, G., & Liang, X. (2017). Highly active and stable alumina supported nickel nanoparticle catalysts for dry reforming of methane. *Applied Catalysis B: Environmental*, *201*, 302–309.

Sheng, K., Luan, D., Jiang, H., Zeng, F., Wei, B., Pang, F., & Ge, J. (2019). Ni_xCo_y Nanocatalyst Supported by ZrO_2 Hollow Sphere for Dry Reforming of Methane: Synergetic Catalysis by Ni and Co in Alloy. *ACS Applied Materials and Interfaces*, *11*(27), 24078–24087.

Siang, T. J., Singh, S., Omoregbe, O., Bach, L. G., Phuc, N. H. H., & Vo, D. V. N. (2018). Hydrogen production from CH4 dry reforming over bimetallic Ni–Co/Al_2O_3 catalyst. *Journal of the Energy Institute*, *91*(5), 683–694.

Sidik, S. M., Triwahyono, S., Jalil, A. A., Aziz, M. A. A., Fatah, N. A. A., & Teh, L. P. (2016). Tailoring the properties of electrolyzed Ni/mesostructured silica nanoparticles (MSN) via different Ni-loading methods for CO_2 reforming of CH_4. *Journal of CO_2 Utilization*, *13*, 71–80.

Singh, R., Bapat, R., Qin, L., Feng, H., & Polshettiwar, V. (2016). Atomic Layer Deposited (ALD) TiO_2 on Fibrous Nano-Silica (KCC-1) for Photocatalysis: Nanoparticle Formation and Size Quantization Effect. *ACS Catalysis*, *6*(5), 2770–2784.

Singh, S., Kumar, R., Setiabudi, H. D., Nanda, S., & Vo, D. V. N. (2018). Advanced synthesis strategies of mesoporous SBA-15 supported catalysts for catalytic reforming applications: A state-of-the-art review. *Applied Catalysis A: General*, *559*, 57–74.

Singh, S., Nguyen, T. D., Siang, T. J., Phuong, P. T. T., Huy Phuc, N. H., Truong, Q. D., Vo, D. V. N. (2020). Boron-doped Ni/SBA-15 catalysts with enhanced coke resistance and catalytic performance for dry reforming of methane. *Journal of the Energy Institute*, *93*(1), 31–42.

Sokefun, Y. O., Joseph, B., & Kuhn, J. N. (2019). Impact of Ni and Mg Loadings on Dry Reforming Performance of Pt/Ceria-Zirconia Catalysts. *Industrial and Engineering Chemistry Research*, *58*(22), 9322–9330.

Song, C., Liu, Q., Ji, N., Deng, S., Zhao, J., Li, Y., Song, Y., & Li, H. (2018). Alternative pathways for efficient CO_2 capture by hybrid processes—A review. *Renewable and Sustainable Energy Reviews*, *82*, 215–231.

Soria, M. A., & Rodemerck, U. (2013). Applied Catalysis B : Environmental Transient studies of low-temperature dry reforming of methane over. *Applied Catalysis B, Environmental*, *129*, 450–459.

Stroud, T., Smith, T. J., Le Saché, E., Santos, J. L., Centeno, M. A., Arellano-Garcia, H., Odriozola, J. A., & Reina, T. R. (2018). Chemical CO_2 recycling via dry and bi reforming of methane using Ni-Sn/Al_2O_3 and Ni-Sn/CeO_2-Al_2O_3 catalysts. *Applied Catalysis B: Environmental*, *224*, 125–135.

Sun, F., & Zeng, W. (2020). Electric field effects on hydrogen/methane oxidation: A reactive force field based molecular dynamics study. *International Journal of Hydrogen Energy*.

Sun, H., Zhang, Q., Wen, J., Tang, T., Wang, H., Liu, M., Ning, P., Deng, L., & Shi, Y. (2020). Insight into the role of CaO in coke-resistant over Ni-HMS catalysts for CO_2 reforming of methane. *Applied Surface Science*, *521*, 146395.

Sun, L., Tan, Y., Zhang, Q., Xie, H., Song, F., & Han, Y. (2013). Effects of Y_2O_3-modification to Ni/γ-Al_2O_3 catalysts on autothermal reforming of methane with CO_2 to syngas. *International Journal of Hydrogen Energy*, *38*(4), 1892–1900.

Sun, N., Wen, X., Wang, F., Peng, W., Zhao, N., Xiao, F., Wei, W., Sun, Y., & Kang, J. (2011). Catalytic performance and characterization of Ni-CaO-ZrO_2 catalysts for dry reforming of methane. *Applied Surface Science*, *257*(21), 9169–9176.

Suyetin, M., Peskov, M. V., & Schwingenschlögl, U. (2020). Methane sorption in a family of qzd-MOFs: A multiscale computational study. *Chemical Engineering Journal*, *384*, 123296.

Taherian, Z., Yousefpour, M., Tajally, M., & Khoshandam, B. (2017). A comparative study of ZrO_2, Y_2O_3 and Sm_2O_3 promoted Ni/SBA-15 catalysts for evaluation of CO_2/methane reforming performance. *International Journal of Hydrogen Energy*, *42*(26), 16408–16420.

Takenaka, S., Kato, E., Tomikubo, Y., & Otsuka, K. (2003). Structural change of Ni species during the methane decomposition and the subsequent gasification of deposited carbon with CO_2 over supported Ni catalysts. *Journal of Catalysis*, *219*(1), 176–185.

Tang, M., Xu, L., & Fan, M. (2014). Effect of Ce on 5 wt% Ni/ZSM-5 catalysts in the CO2 reforming of CH4 reaction. *International Journal of Hydrogen Energy*, *39*(28), 15482–15496.

Tathod, A. P., Hayek, N., Shpasser, D., Simakov, D. S. A., & Gazit, O. M. (2019). Mediating interaction strength between nickel and zirconia using a mixed oxide nanosheets interlayer for methane dry reforming. *Applied Catalysis B: Environmental*, *249*, 106–115.

Teh, L. P., Triwahyono, S., Jalil, A. A., Firmansyah, M. L., Mamat, C. R., & Majid, Z. A. (2016). Fibrous silica mesoporous ZSM-5 for carbon monoxide methanation. *Applied Catalysis A: General*, *523*, 200–208.

Therdthianwong, S., Therdthianwong, A., Siangchin, C., & Yongprapat, S. (2008). Synthesis gas production from dry reforming of methane over Ni/Al_2O_3 stabilized by ZrO_2. *International Journal of Hydrogen Energy*, *33*(3), 991–999.

Tian, D., Zeng, C., Wang, H., Cheng, X., Zheng, Y., Xiang, C., Wei, Y., Li, K., & Zhu, X. (2017). Effect of transition metal Fe adsorption on CeO_2 (110) surface in the methane activation and oxygen vacancy formation: A density functional theory study. *Applied Surface Science*, *416*, 547–564.

Titus, J., Goepel, M., Schunk, S. A., Wilde, N., & Gläser, R. (2017). The role of acid/base properties in $Ni/MgO\text{-}ZrO_2$–based catalysts for dry reforming of methane. *Catalysis Communications*, *100*, 76–80.

Triwahyono, S., Jalil, A. A., Izan, S. M., Jamari, N. S., & Fatah, N. A. A. (2019). Isomerization of linear C5–C7 over pt loaded on protonated fibrous silica@Y zeolite (Pt/HSi@Y). *Journal of Energy Chemistry*, *37*, 163–171.

Tsai, H. L., & Wang, C. S. (2008). Thermodynamic equilibrium prediction for natural gas dry reforming in thermal plasma reformer. *Journal of the Chinese Institute of Engineers*, *31*(5), 891–896.

Tsakoumis, N. E., Rønning, M., Borg, Ø., Rytter, E., & Holmen, A. (2010). Deactivation of cobalt based Fischer-Tropsch catalysts: A review. *Catalysis Today*, *154*(3–4), 162–182.

Turap, Y., Wang, I., Fu, T., Wu, Y., Wang, Y., & Wang, W. (2020). Co–Ni alloy supported on CeO_2 as a bimetallic catalyst for dry reforming of methane. *International Journal of Hydrogen Energy*, *45*(11), 6538–6548.

Usman, M., Wan Daud, W. M. A., & Abbas, H. F. (2015). Dry reforming of methane: Influence of process parameters - A review. *Renewable and Sustainable Energy Reviews*, *45*, 710–744.

Vafaeian, Y., Haghighi, M., & Aghamohammadi, S. (2013). Ultrasound assisted dispersion of different amount of Ni over ZSM-5 used as nanostructured catalyst for hydrogen production via CO_2 reforming of methane. *Energy Conversion and Management*, *76*, 1093–1103.

Vakili, R., Gholami, R., Stere, C. E., Chansai, S., Chen, H., Holmes, S. M., Jiao, Y., Hardacre, C., & Fan, X. (2020). Plasma-assisted catalytic dry reforming of methane (DRM) over metal-organic frameworks (MOFs)-based catalysts. *Applied Catalysis B: Environmental*, *260*, 118195.

Valentini, A., Carreño, N. L. V., Probst, L. F. D., Lisboa-Filho, P. N., Schreiner, W. H., Leite, E. R., & Longo, E. (2003). Role of vanadium in Ni:Al_2O_3 catalysts for carbon dioxide reforming of methane. *Applied Catalysis A: General*, *255*(2), 211–220.

Valle, B., Aramburu, B., Olazar, M., Bilbao, J., & Gayubo, A. G. (2018). Steam reforming of raw bio-oil over Ni/La_2O_3-Al_2O_3: Influence of temperature on product yields and catalyst deactivation. *Fuel*, *216*, 463–474.

Wachs, I. E., Chen, Y., Jehng, J., Briand, L. E., & Tanaka, T. (2003). Molecular structure and reactivity of the Group V metal oxides. *Catalysis Today*, *78*, 13–24.

Wan Mansor, W. N., Abdullah, S., Che Wan Othman, C. W. M. N., Jarkoni, M. N. K., Chao, H. R., & Lin, S. L. (2020). Data on greenhouse gases emission of fuels in power plants in Malaysia during the year of 1990–2017. *Data in Brief*, *30*, 105440.

Wang, M., Joel, A. S., Ramshaw, C., Eimer, D., & Musa, N. M. (2015). Process intensification for post-combustion CO_2 capture with chemical absorption: A critical review. *Applied Energy*, *158*, 275–291.

Wang, M., Zhang, Q., Zhang, T., Wang, Y., Wang, J., Long, K., Song, Z., Liu, X., & Ning, P. (2017). Facile one-pot synthesis of highly dispersed Ni nanoparticles embedded in HMS for dry reforming of methane. *Chemical Engineering Journal*, *313*, 1370–1381.

Wang, Z., Cao, X. M., Zhu, J., & Hu, P. (2014). Activity and coke formation of nickel and nickel carbide in dry reforming: A deactivation scheme from density functional theory. *Journal of Catalysis*, *311*, 469–480.

Wang, H. Y. & Ruckenstein, E. (2000). Carbon dioxide reforming of methane to synthesis gas over supported rhodium catalysts: the effect of support. Applied Catalysis A: General, *204*, 143–152.

Weatherbee, G. D., Rankin, J. L., & Bartholomew, C. H. (1984). Activated adsorption of H_2 on iron: Effects of support, potassium promoter and pretreatment. *Applied Catalalysis, 11(1)*:73–84.

Wei, Q., Yang, G., Gao, X., Yamane, N., Zhang, P., Liu, G., & Tsubaki, N. (2017). Ni/Silicalite-1 coating being coated on SiC foam: A tailor-made monolith catalyst for syngas production using a combined methane reforming process. *Chemical Engineering Journal*, *327*, 465–473.

Wittich, K., Krämer, M., Bottke, N., & Schunk, S. A. (2020). Catalytic Dry Reforming of Methane: Insights from Model Systems. *ChemCatChem*.

Wu, H., Liu, J. X., Liu, H., & He, D. (2019). CO_2 reforming of methane to syngas at high pressure over bi-component Ni-Co catalyst: The anti-carbon deposition and stability of catalyst. *Fuel*, *235*, 868–877.

Xia, D., Chen, Y., Li, C., Liu, C., & Zhou, G. (2018). Carbon dioxide reforming of methane to syngas over ordered mesoporous Ni/KIT-6 catalysts. *International Journal of Hydrogen Energy*, *43*(45), 20488–20499.

Xiang, X., Zhao, H., Yang, J., Zhao, J., Yan, L., Song, H., & Chou, L. (2016). One-Pot Synthesis of Ordered Mesoporous NiSiAl Oxides for Catalyzing CO_2 Reforming of CH_4. *European Journal of Inorganic Chemistry*, *2016*(21), 3396–3404.

Xie, T., Shi, L., Zhang, J., & Zhang, D. (2014). Immobilizing Ni nanoparticles to mesoporous silica with size and location control via a polyol-assisted route for coking- and sintering-resistant dry reforming of methane. *Chemical Communications*, *50*(55), 7250–7253.

Xie, Z., Liao, Q., Liu, M., Yang, Z., & Zhang, L. (2017). Micro-kinetic modeling study of dry reforming of methane over the Ni-based catalyst. *Energy Conversion and Management*, *153*, 526–537.

Xu, D., Xiong, Y., Zhang, S., & Su, Y. (2019). The influence of preparation method of char supported metallic Ni catalysts on the catalytic performance for reforming of biomass tar. *International Journal of Energy Research*.

Yolmeh, M., & Jafari, S. M. (2017). Applications of Response Surface Methodology in the Food Industry Processes. *Food and Bioprocess Technology*, *10*(3), 413–433.

York, A. P. E., Xiao, T. C., Green, M. L. H., & Claridge, J. B. (2007). Methane oxyforming for synthesis gas production. *Catalysis Reviews - Science and Engineering*, *49*(4), 511–560.

Yu, M., Zhu, Y. A., Lu, Y., Tong, G., Zhu, K., & Zhou, X. (2015). The promoting role of Ag in Ni-CeO_2 catalyzed CH_4-CO_2 dry reforming reaction. *Applied Catalysis B: Environmental*, *165*, 43–56.

Zain, M. M., & Mohamed, A. R. (2018). An overview on conversion technologies to produce value added products from CH_4 and CO_2 as major biogas constituents. *Renewable and Sustainable Energy Reviews*, *98*, 56–63.

Zhang, J., & Li, F. (2015). Coke-resistant Ni@SiO_2 catalyst for dry reforming of methane. *Applied Catalysis B, Environmental*, *176–177*, 513–521.

Zhang, T., Liu, Z., Zhu, Y. A., Liu, Z., Sui, Z., Zhu, K., & Zhou, X. (2020a). Dry reforming of methane on Ni-Fe-MgO catalysts: Influence of Fe on carbon-resistant property and kinetics. *Applied Catalysis B: Environmental*, *264*, 118497.

Zhang, Laibao, Cullen, D. A., Zhai, P., & Ding, K. (2020b). Adsorption of Colloidal Metal Nanoparticles via Solvent Engineering. *ACS Catalysis*, *10*(3), 2378–2383.

Zhang, Q., Zhang, T., Shi, Y., Zhao, B., Wang, M., Liu, Q., Wang, J., Long, K., Duan, Y., & Ning, P. (2017a). A sintering and carbon-resistant Ni-SBA-15 catalyst prepared by solid-state grinding method for dry reforming of methane. *Journal of CO_2 Utilization*, *17*, 10–19.

Zhang, Li, Wang, X., Chen, C., Zou, X., Ding, W., & Lu, X. (2017b). Dry reforming of methane to syngas over lanthanum-modified mesoporous nickel aluminate/Γ-alumina nanocomposites by one-pot synthesis. *International Journal of Hydrogen Energy*, *42*(16), 11333–11345.

Zhou, W., Zhang, Q., Zhou, Y., Wei, Q., Du, L., Ding, S., Jiang, S., & Zhang, Y. (2018). Effects of Ga- and P-modified USY-based NiMoS catalysts on ultra-deep hydrodesulfurization for FCC diesels. *Catalysis Today*, *305*, 171–181.

Zhu, H., Rosenfeld, D. C., Anjum, D. H., Sangaru, S. S., Saih, Y., Ould-Chikh, S., & Basset, J. M. (2015). Ni-Ta-O mixed oxide catalysts for the low temperature oxidative dehydrogenation of ethane to ethylene. *Journal of Catalysis*, *329*, 291–306.

APPENDIX E

Publications and Conference Proceedings

List of publications:

1. **Hambali, H. U.**, Jalil, A. A., Abdulrasheed, A. A., Siang, T. J., Nyakuma, B. B., Nabgan, W. & Abdullah, T. A. T. (2020). Effect of Ni-Ta ratio on the catalytic selectivity of fibrous Ni-Ta/ZSM-5 for dry reforming of methane. *Chemical Engineering Science, 227,* 115952.
2. **Hambali, H. U.**, Jalil, A. A., Abdulrasheed, A. A., Siang, T. J., Abdullah, T. A. T., Ahmad, A. & Dai-Viet, N. V. (2020). Fibrous spherical Ni-M/ZSM-5 (M: Mg, Ca, Ta, Ga) catalysts for methane dry reforming: The interplay between surface acidity-basicity and coking resistance. *International Journal of Energy Research, 44,* 5696–5712.
3. **Hambali, H. U.**, Jalil, A. A., Abdulrasheed, A. A., Siang, T. J. & Dai-Viet, N. V. (2020). Enhanced dry reforming of methane over mesostructured fibrous Ni/MFI zeolite: Influence of preparation methods. *Journal of the Energy Institute, 93,* 1535–1543.
4. **Hambali, H. U.**, Jalil, A. A., Abdulrasheed, A. A., Siang, T. J., Fatah, N. A. A., Rahman, A. F. A., Aziz, M. A. H. & Hussain, I. (2020). Effect of transition metals (Mo, Mn and Co) on mesoporous ZSM-5 catalyst activity in carbon dioxide reforming of methane. *Materials Science and Engineering. 808,* 012005.
5. **Hambali, H. U.**, Jalil, A. A., Abdulrasheed, A. A., Siang, T. J. & Augi, A. H. K. CO_2 reforming of methane over Ta-promoted Ni/ZSM-5 fibre-like catalyst: Insights on deactivation behavior and optimization using RSM. *Under review in Chemical Engineering Science.*

6. **Hambali, H. U.**, Jalil, A. A., Triwahyono, S., Jamian, S. F., Fatah, N. A. A., Abdulrasheed, A. A. & Siang, T. J. (2019). Unique structure of fibrous ZSM-5 catalyst expedited prolonged hydrogen atom restoration for selective production of propylene from methanol. International Journal of Hydrogen Energy, 1–14.

Conference Proceedings:

1. **Hambali, H. U.**, Jalil, A. A., Abdulrasheed, A. A., Siang, T. J., Fatah, N. A. A., Rahman, A. F. A., Aziz, M. A. H. & Hussain, I. (2019), Effect of transition metals (Mo, Mn and Co) on mesoporous ZSM-5 catalyst activity in carbon dioxide reforming of methane. 8th Conference on Emerging Energy and Process Technology (CONCEPT 8- 2019), 27-28 November 2019, Residensi UTM Kuala Lumpur, Malaysia.
2. **Hambali, H. U.**, Jalil, A. A., Triwahyono, S., Jamian, S. F., Fatah, N. A. A., Abdulrasheed, A. A. & Siang, T. J. (2019), Unique structure of fibrous ZSM-5 catalyst expedited prolonged hydrogen atom restoration for selective production of propylene from methanol. Energy Security and Chemical Engineering Congress, July 17-19, 2019, Parkroyal Penang Resort, Penang, Malaysia.