



UNIVERSITI PUTRA MALAYSIA

***DEVELOPMENT OF NICKEL CATALYSTS SUPPORTED ON DOLOMITE,
TALC AND ALKALINE SLUDGE FOR CARBON DIOXIDE
REFORMING OF METHANE***

MOHD RAZALI BIN SHAMSUDDIN

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Fulfilment of the Requirements for the Degree of Doctor of Philosophy**

November 2021

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Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chair : Professor Datuk Chm. Ts. Taufiq Yap Yun Hin, PhD
Faculty : Science

Dry reforming (DRM) is an important reaction mainly used in petrochemical industries. Therefore, in DRM reaction which using a nickel catalyst with high activity, stability, low deactivation, and a favourable product ratio with efficient and practical supports are always the challenge. Objectives of this study is to improve catalyst performance of Ni metal with three different types of supports named as dolomite, talcum and alkaline sludge (AS). These basic supports were pre-treated at high temperature (900°C) followed by catalyst preparation via facile wet-impregnation method. Thus, three series of monometallic nickel-based catalyst at different metal loading (5 to 15 wt%) were prepared in order to determine the optimum loading of nickel of each support. The supports and synthesized catalysts were characterized by various physicochemical analysis including X-ray diffraction (XRD), N₂ adsorption-desorption, X-ray fluorescence (XRF), field emission scanning electron microscope (FESEM), transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), temperature programmed reduction of hydrogen (TPR-H₂), temperature programmed desorption of carbon dioxide (TPD-CO₂), temperature programmed desorption of ammonia (TPD-NH₃) and thermogravimetric analysis (TGA). Investigation on supports and prepared catalysts revealed that the phase composition (such as Ni⁰, NiO, NiOH, CaO and MgO) in each of the catalysts highly affected the textural and chemical properties of catalysts. Crystallite and particle size together with high metal degree of dispersion enhanced reducibility. Meanwhile, basic sites highly contributed by O²⁻ ion attributed by Mg and/or Ca in supports. DRM reactions were carried out in stainless steel fixed-bed reactor connected with online GC-TCD. Prior the reaction, 0.1-0.6g of catalyst were loaded into the reactor, reactant (CH₄: CO₂=1:1) flow at 30ml min⁻¹, GHSV from 3000-1500h⁻¹ and reaction temperature varied from 600-950°C. The catalytic performance indicates that 10%NiO/Dolomite and 10%NiO/Talc shows highest CH₄ and CO₂ conversion together with H₂ selectivity and H₂/CO ratio for its series respectively. 10% NiO/Dolomite catalyst recorded CH₄ and CO₂ conversion, χ_{CH_4} ; χ_{CO_2} up to 98% and H₂ selectivity, S_{H_2} =75%; H₂/CO~1:1 at 800°C temperature of reaction. Meanwhile, 10%NiO/Talc was found to be most effective

catalyst with 98% CH₄ and 80% CO₂ conversion respectively (S_{H₂} = 65%; H₂/CO ~1.2) at 700 °C under 1 atm pressure reaction condition. Thus, 15%NiO/AS show higher performance at 800°C compared to its series with 95% CH₄ conversion and more than 80% CO₂ conversion; while for H₂ selectivity and H₂/CO ratio both shows S_{H₂}=50% and 1.5 H₂/CO. Kinetic study reveals that DRM reaction follow dual site associative adsorption Langmuir–Hinshelwood model. Therefore, mechanistic evaluation indicates four routes involves on DRM reaction including CH₄ dissociation at 350-500 °C; followed by *in-situ* reduction of NiO; DRM reaction at temperature >500°C; and some parallel reaction (>800°C). Furthermore, the calculated apparent activation energy of NiO/Dolomite, NiO/Talc and NiO/AS are +115.47, +114.90 and +135.21 kJ mol⁻¹ respectively. and applicable for membrane reactor implementation. Analysis of spend catalysts proves that the formation of graphitic carbon much influence by physical properties of catalyst. Based on optimization studies, 10%NiO/Talc has been applied on long lasting stability test due to excellence catalytic performance. The results show this catalyst can be last up to 400 hours without any significant decreasing on its activity or selectivity. All in all, it can be concluded that the use of basic material contains Mg and/or Ca as support helps in increasing the potential of nickel as the best transition metal for DRM reaction.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PEMBANGUNAN MANGKIN NIKEL TERSOKONG DOLOMITE, TALC DAN ENAPCEMAR BERALKALI UNTUK KARBON DIOKSIDA REFORMASI METANA

Oleh

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Reformasi kering (DRM) merupakan suatu tindak balas utama yang banyak digunakan dalam industri petrokimia. Cabaran dalam mengendalikan tindak balas DRM adalah untuk menghasilkan mangkin nikel dengan aktiviti yang tinggi, stabil, penyahaktifan rendah dan nisbah produk yang tinggi dengan penyokong yang efisien dan praktikal. Objektif kajian ini adalah bagi menambahbaik keupayaan mangkin nikel dengan menggunakan tiga jenis bahan penyokong dinamakan sebagai dolomit, talkum dan enapcemar beralkali (AS). Pra-rawatan bahan penyokong berbes ini dilakukan pada suhu tinggi (900 °C) diikuti dengan penyediaan mangkin melalui kaedah pengisitepuan basah mudah. Tiga siri mangkin monologam berasaskan nikel dengan muatan berbeza (5 ke 15 % bt) telah disediakan untuk mengenalpasti muatan nikel paling optimum bagi setiap bahan penyokong. Penyokong dan mangkin yang terhasil dicirikan melalui pelbagai teknik analisis fizik-ko-kimia seperti pembelauan sinar-X (XRD), penyerapan dan nyahjerap N₂, floresen sinar-X (XRF), mikroskop imbasan elektron pancaran lapangan (FESEM), mikroskop transmisi elektron (TEM), spektroskopi inframerah penukaran Fourier (FTIR), spektroskopi fotoelektron sinar-X (XPS), penurunan suhu terprogram hidrogen (TPR-H₂), suhu terprogram nyahjerapan karbon dioksida (TPD-CO₂), suhu terprogram nyahjerapan ammonia (TPD-NH₃) dan analisis termogravimetrik (TGA). Penelitian terhadap penyokong dan mangkin yang disediakan menunjukkan adanya komposisi fasa (seperti Ni⁰, NiO, NiOH, CaO dan MgO) setiap mangkin sangat mempengaruhi ciri-ciri tekstur dan sifat kimia mangkin. Sifat keliangan, kekristalan dan saiz zarah bersama-sama dengan darjah penyerakan logam yang tinggi mempertingkatkan lagi sifat kebolehturunan mangkin. Manakala tapak bes mangkin sangat dipengaruhi oleh ion O²⁻ yang dimiliki oleh Mg dan/atau Ca dalam bahan penyokong. Tindak balas DRM dilakukan dalam reaktor kekatil tetap keluli tahan karat yang disambungkan bersama GC-TCD secara dalam talian. Sebelum tindak balas dijalankan, 0.1-0.6g mangkin dimasukkan ke dalam reaktor, bahan tindak balas (CH₄: CO₂=1:1) dialirkan pada 30ml min⁻¹, GHSV daripada 3000-1500h⁻¹ dan suhu dipelbagaikan daripada 600-950°C. Keputusan penentuan prestasi pemangkinan menunjukkan 10%NiO/Dolomite dan 10%NiO/Talc menghasilkan % penukaran CH₄

dan CO₂ bersama keterpilihan H₂ dan nisbah H₂/CO yang paling tinggi untuk sirinya. Mangkin 10%NiO/Dolomite mencatatkan penukaran CH₄ dan CO₂, (χ_{CH_4} ; χ_{CO_2}) sehingga 98% dan keterpilihan H₂, SH₂=75%; H₂/CO~1:1 pada suhu tindak balas 800°C. Sementara itu, mangkin paling efektif ditunjukkan oleh 10%NiO/Talc dengan penukaran CH₄ sebanyak 98% dan 80% CO₂ (SH₂ = 65%; H₂/CO~1.2) pada suhu 700°C dan tekanan 1 atm. Seterusnya, 15%NiO/AS pula menunjukkan prestasi pemangkinan yang tinggi pada 800°C untuk sirinya dengan 95% penukaran CH₄ dan lebih 80% penukaran CO₂; sementara itu, keterpilihan H₂ dan nisbah H₂/CO pula masing-masing menunjukkan SH₂=50% dan 1.5. Kajian kinetik membuktikan tindak balas DRM ini menuruti model kinetik Langmuir–Hinshelwood bagi penjerapan dua tapak terpisah. Justeru, penilaian mekanisma menunjukkan empat langkah yang terlibat semasa tindak balas DRM termasuklah pemisahan CH₄ pada suhu 350-500°C, diikuti penurunan NiO secara *in-situ*; tindak balas DRM pada suhu >500°C; dan tindak balas selanjur (>800°C). Tambahan pula, tenaga pengaktifan yang dikira menunjukkan NiO/Dolomite, NiO/Talc and NiO/AS masing-masing adalah +115.47, +114.90 dan +135.21 kJ mol⁻¹ dan boleh diaplikasi dalam ujian reaktor membran. Analisis pada mangkin yang telah digunakan membuktikan pembentukan karbon grafit banyak dipengaruhi oleh sifit fizikal. Berdasarkan dapatan kajian pengoptimuman, 10%NiO/Talc telah diaplikasikan bagi ujian kestabilan pada tempoh masa yang panjang disebabkan prestasi pemangkinan yang sangat baik. Keputusan menunjukkan mangkin ini mampu bertahan menghampiri 400 jam tanpa menunjukkan pengurangan yang ketara pada aktiviti dan sifat keterpilihannya. Kesimpulannya, penggunaan bahan berbes sederhana yang mengandungi Mg dan/atau Ca sebagai penyokong dapat membantu meningkatkan potensi nikel sebagai logam peralihan terbaik untuk tindak balas DRM.

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LIST OF ABBREVIATIONS

JCPDS	Joint Committee on Powder Diffraction Standards
ICDD	International Centre for Diffraction Data
BET	Brunauer-Emmett-Teller
DTG	Derivative Thermogravimetric
EDX	Energy Dispersive X-Ray
FESEM	Field Emission Scanning Electron Microscopy
i.d	Internal Diameter
T _{calcination}	Calcination Temperature
TGA	Thermogravimetric Analysis
T _{max}	Temperature at maximum peak
TPD	Temperature Programmed Desorption
TPR	Temperature Programmed Reduction
T _{reaction}	Reaction Temperature
DRM	Dry Reforming of Methane
AS	Alkaline Sludge
XRD	X-ray Diffraction
XRF	X-ray Fluorescent
XPS	X-ray Photoelectron Spectroscopy
TEM	Transmission Electron Microscopy
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared
POME	Palm Oil Mill Effluent
EFB	Empty Fruits Bunch
MF	Mesocarp Fibers

PKS	Palm Kernel Shell
CSTR	Continuous Stirred Tank Reactor
RABR	Reversible Anaerobic Baffled Reactor
MTG	Methanol-to-gas
HFC	Hydrofluorocarbons
PFC	Perfluorocarbons
UNFCC	United Nation Framework of Climate Change
NOAA	National Oceanic and Atmospheric Administrator
IFAD	International Fund for Agricultural Development
SCWG	Super Critical Water Gasification
POX	Partial Oxidation
ATR	Autothermal Reforming
WGS	Water Gas Shift
SR	Steam Reforming
MRs	Membrane Reactor
MCM-41	Mobil Composition of Matter No. 41
SBA-15	Santa Barbara Amorphous-15
MFIBR	Magnetized Fluidized Bed Reactor
HFMBR	Hollow Fiber Membrane Reactor
FIBR	Fluidized-Bed Reactor
FBR	Fixed-Bed Reactor
HMS	Hexagonal Mesoporous Silica
BJH	Barrett- Joyner- Halenda
DFT	Density Functional Theory
CASAXPS MS	Computer Aided Surface Analysis for X-ray Photoelectron Mass spectrometer

GC-TCD	Gas Chromatography Thermal Conductivity Detector
IPCC	International Panel on Climate Change
S _{BET}	Surface area by BET
GHSV	Gas Hourly Space Velocity
W _{cat}	Weight of the catalyst
TPO	Temperature Programmed Oxidation
BE	Binding Energy
ESR	Ethanol Steam Reforming
CNTs	Carbon Nanotubes
FWHM	Full Width at Half-Maximum
PV	Photovoltaic
CAGR	Compound Annual Growth Rate
SCM	Supplementary Cementitious Material

CHAPTER 1

INTRODUCTION

1.1 Background Study

Palm oil industry is one of the biggest contributors for economic growth in Malaysia but at the same time, it also contributes for environmental pollution due to the huge quantities of effluent during oil extraction process. The production of crude palm oil, large amount of waste and by-products are generated. The solid waste streams consist of empty fruit bunch (EFB), mesocarp fruit fibres (MF) and palm kernel shells (PKS). Reuse of these waste streams in applications for heat, steam, compost and to lesser extent power generation are practised widely across Asia. Underutilization of liquid waste stream, known as POME or Palm Oil Mill Effluent, this is generated during the palm oil extraction/decanting process and often seen as a serious environmental issue. Therefore, discharge of POME is subject to increasingly stringent regulations in many palms oil-producing nations.

POME is an attractive feedstock for biogas production and is abundantly available in all palm oil mills. Hence, it ensures continuous supply of substrates at no or low cost for biogas production, positioning it as a great potential source for biogas production. (Chin *et al.*, 2013). Biogas captured from POME can be carried out using several various technologies ranging in cost and complexity. The closed-tank anaerobic digester system with continuous stirred-tank reactor (CSTR), the methane fermentation system employing special microorganisms and the reversible flow anaerobic baffled reactor (RABR) system are among the technologies offered by technology providers, Malaysian Palm Oil Board (2015). Gas production largely depends on the method deployed for biomass conversion and capture of the biogas, and can, therefore, approximately range from 5.8 to 12.75 kg of CH₄ per cubic meter of POME. Application of enclosed anaerobic digestion will significantly increase the quality of the effluent/discharge stream as well as the biogas composition.

Utilization of CH₄ for production of synthetic gas (CO and H₂) has benefits in fulfil energy demand especially on contributing to carbon neutral energy chain. The considerable attention has been paid to catalytic conversion of dry reforming CH₄ for environmental protection as well as neutral energy sources. The interesting part of this reaction is an ability to convert simultaneously two major greenhouse gasses (CO₂ and CH₄) to valuable production of syngas with low H₂/CO molar ratio. The production syngas from catalytic methane reforming can serve as intermediate chemicals for gasoline production by methanol-to-gas (MTG) process or diesel production using Fisher-Tropsch process (Tijmensene *et al.*, 2002; Wood, Nwaoha, & Towler, 2012; Xiong *et al.*, 2011). Furthermore, H₂ is considered as future energy vector due to its benefits on carbon-free formation and can be used directly for thermal combustion or converted into electrical energy for fuel cell application.

Dry reforming of CH_4 is an old technology but presently not fully developed for commercial scale production process for producing syngas and the major route for H_2 production. The considerable efforts have been focused on the development of catalysts for CO_2 reforming of CH_4 to achieve optimum catalytic activity together with lower energy consumption and high resistant of catalyst deactivation. Nevertheless, the challenges of developing an effective catalyst together with efficient support have been major concern amongst researchers around the world. Although catalysts based on noble metals promising particularly good performance due to high stability and activity, however they are pricey and limited in availability.

1.2 Problem Statement

Recently, alternative resource for energy demand was focus on H_2 production as potential future fuel. These options have led to exploration of reaction that can produce H_2 and at the same time reduce the greenhouse gases. In the quest to overcome the constraints, considerable attention has been paid to the CO_2 reforming of CH_4 in view of environmental protection as well as potential industrial application aspects. This process has the merit of using two most prominent components (CO_2 and CH_4) of greenhouse gasses as feedstock to the dry reforming process. However, there are several drawbacks which might be limitation to the process.

The CH_4 dry reforming process is presently not fully develop for commercial scale production compared to steam reforming which utilizes steam in the reforming of CH_4 over catalytic reaction to produce syngas mainly due to challenges of developing suitable catalyst, difficulties in obtaining optimum process conditions and understanding the complex mechanisms of the main and elementary reaction. Although there are many types of catalysts has been proposed for the CO_2 reforming of CH_4 , the suitable and active catalyst for this reaction is still under exploration.

Nevertheless, the challenges of developing an effective catalyst with high activity, stability, less susceptibility to catalyst deactivation, good product ratio together with efficient supports have been the major concern amongst researchers. Transition metal could be the best choice and have been investigated widely for CH_4 dry reforming. Among these metals, noble metal such as platinum (Pt) and palladium (Pd) have been reported to have high activity and selectivity together with anti-coking properties. Instead of these good properties, the noble metal-based catalysts are awfully expensive and limited in availability. On the other hands, nickel-based catalyst has shown good potential for this reaction.

Ni-based catalyst are inexpensive compared to noble metals and readily available. However, major obstacle encountered for dry reforming reaction over Ni based catalyst is the rapid deactivation due to carbon deposition, sintering end up with poisoning of the active site on the catalyst which often reduce activity, selectivity and stability. During catalyst deactivation, coke was form on the active sites which is associated with large Ni particles sizes (more than 10 nm) and low ability of support to adsorb CO_2 that is helpful to gasify the carbon formed on the surface of catalyst. In addition, Ni based

catalysts with weak metal-support interaction showed a tendency to sinter at high reduction temperature.

To overcome all mention problems, mesoporous support with high basicity can be used to enhance Ni dispersion on the support surface and suppress the coke formation. It was expected that incorporated of Ni and dolomite would form a strong metal-support interaction. Hence, the addition of other metal binder to catalyst would result a synergetic effect between both metals and support which is believed will enhance the activity and stability in CO₂ reforming of CH₄.

1.3 Objectives

This research aims to synthesize nickel-based catalysts supported on basic material generally from mineral and industrial waste. Thus, utilization on these materials which is enriched with Mg and/or Ca would improve CO₂ adsorption which is important especially on DRM reaction. This research also focused on the physicochemical properties of the synthesized catalysts and the feasibility of the support from the low-cost material such dolomite, talc and AS. Hence, there are four main objectives in this research.

1. To synthesize nickel catalysts supported on basic material such as dolomite, talc and alkaline sludge (AS)
2. To characterized the prepared nickel catalysts on the textural and chemical properties
3. To optimize reaction conditions for CO₂ reforming of CH₄, based on nickel concentration, temperature, catalyst loading and GHSV towards time-on-stream
4. To evaluate kinetic parameter, reaction mechanisms and stability generated from catalytic performance of the catalyst

1.4 Scope of Research

This study focuses on development of NiO catalysts derived from different support material. Three types of support which contain basic element of Ca and/or Mg have been chosen from mineral and industrial waste named as dolomite, talc and alkaline sludge. To determine the elemental component existed in each of supports, XRF analysis were carried out respectively. Initially, all the supports were pre-treated via calcination process at 900°C to make sure the contamination has been removed before the preparation of catalysts. Therefore, the catalysts were prepared via wet impregnation method and calcined at 600°C to ensure the prepared catalyst was stable at room temperature.

Three series of x NiO/Dolomite, x NiO/Talc and x NiO/AS catalysts ($x = 5, 10, 15$ wt%) undergoes physicochemical characterization via phase and chemical composition

(XRD); surface area and porosity (N_2 adsorption-desorption); surface morphology (FESEM-EDX); reduction behaviour (TPR- H_2); acid-basic sites properties (TPD- NH_3 & TPD- CO_2) and surface analysis of elemental composition & chemical state (XPS). It is believed that the physicochemical properties play an important role in catalytic DRM reaction. Besides, effect of reduction step (reduced and non-reduced catalyst) and reduction environment (H_2 and CH_4) also evaluated to estimate the impact these different condition towards catalytic activity of prepared catalyst. Meanwhile to understand the phenomenon occurred during DRM reaction, such as carbon formation and deactivation of active sites the difference between fresh and spend of the best catalyst on each series were recognized by using TGA/DTG; FESEM & TEM, XRD and TPO analysis.

Consequently, to confirm catalytic activity of the prepared catalysts, the catalytic DRM reaction for isothermal and non-isothermal condition were carried out by using stainless steel micro-reactor connected to online GC-TCD system and Micromeritics Autochem II+ Enhanced Chemisorption Analyzer connected with mass spectrometer (MS). Generally, the parameter of reaction was carried out with a reactant gas mixture consisting of CH_4 and CO_2 in the ratio of 1:1 flowing 30 ml min^{-1} at $800\text{ }^\circ\text{C}$ for 10-hour DRM reaction. In isothermal reaction, the effect of reaction parameter, such as nickel loading (Dolomite, NiO, 5-15%NiO/Dolomite), reaction temperature ($650\text{-}950^\circ\text{C}$), GHSV ($3000\text{-}15000\text{h}^{-1}$), catalyst loading ($0.1\text{-}0.6\text{g}$) towards time dependent reaction (2,3,4,6 and 9 hour) were conducted to examine optimum condition of the catalyst. The optimum condition for the prepared catalysts were determined based on CH_4 & CO_2 conversion together with H_2 & CO selectivity and H_2/CO ratio. Besides, the effect of reduction behaviour carried out in non-isothermal reaction to understand *in-situ* reduction occurred during DRM reaction. The reaction condition was carried out in a continuous-flow of CH_4 : CO_2 (20ml min^{-1}), starting from 400°C to 950°C with a ramp rate of $10\text{ }^\circ\text{C min}^{-1}$.

Further investigation on inside into catalytic activity of NiO series catalysts were evaluated by using non-isothermal data via kinetic and mechanistic of comparative NiO/Dolomite, NiO/Talc and NiO/AS with 10% nickel concentration. Therefore, based on the selected model, the mechanisms of catalytic DRM reaction were discussed comprehensively. Based on Arrhenius plot generated from kinetic assessment, the activation energy (E_a) of NiO-based catalysts were calculated to determine the excellent catalytic activity quantitatively during DRM reaction. Mechanism's study of NiO-based catalysts was predicted using non-linear Langmuir-Hinshelwood kinetic model assisted by Polymath version 6.1 software. Based on model fitted the mechanisms route of catalytic DRM reaction over NiO-based catalysts were analysed by XPS technique.

The interpretation of NiO-based catalysts in term of application on membrane reactor was investigated. The Pd membrane was prepared via electroless plating method and evaluated on physical properties (cross-sectional for thickness determination) and performance (H_2 permeability). The membrane reactor test was carried out reaction condition of 500°C reaction temperature, 25.1cm Pd membrane area, 4.0g weight of catalyst, 15ml-stp min^{-1} for both CO_2 and CH_4 flow rate and W/F value of $1.49 \times 10^4\text{ g}_{\text{cat}}\text{ min mol}^{-1}\text{-CO}_2$. The obtained results were compared with fixed bed reactor to

determine applicability of NiO-based catalysts. Besides, the stability for long-lasting reaction period of NiO-based catalyst were carried out by using 10%NiO/Talc catalyst due to is excellent catalytic performance and potential towards DRM reaction. The test was conducted on fixed bed reactor at 700°C, 30ml min⁻¹ reactant flowrate and more than two weeks of non-stop DRM reaction monitored by GC-TCD. The findings from this research are important specially to proves the parallel reaction involves during DRM reaction of exceptionally long reaction period.

1.5 Organization of the Thesis

The thesis consisted of **ten chapters**. The **Chapter One** introduces the background studies which briefly described Malaysia's Palm Oil Industries producing high concentration of CH₄ and CO₂ from POME. Although CH₄ and CO₂ generated as the waste for these industries, with the proper utilization and treatment the waste can turn out into wealth. DRM reaction could be a better problem solving and promising application with excellent developed catalyst to enhance the reaction for future energy industries. Besides, it also consists of the problem statements, the main objectives of research, and scope of research. The **Chapter Two** consists of comprehensive literature review that based on previous reported of DRM reaction and nickel-based catalysts. In the initial paragraph, the review more focusing on global warming scenario which correlated to greenhouse gasses (CH₄ and CO₂) emission followed by effort to control this problem globally. Next, the literature studies were focused on renewable energy especially in the production of hydrogen as future energy. Therefore, the production of hydrogen intensively discussed particularly on thermochemical routes. The main part of this chapter lies on DRM reaction with details discussion on fundamentals, problems, influence on catalytic activity until the development of effective NiO-based catalysts. Meanwhile, **Chapter 3** covers the material, method and sequential process from NiO-based catalysts development followed by catalytic reaction of DRM until deep investigation beyond the reaction such as kinetic & mechanistic study and long-lasting stability. It also consists of analysis involves during each of the process sequences in term of physicochemical analysis, catalytic activity and related calculation for overall process. Furthermore, the experimental set up in different type of reactor such as fixed bed and membrane system are discussed in this chapter. **Chapter 4** discusses extensively the potential of NiO/Dolomite catalysts series based on physicochemical properties obtained by prepared catalysts. Based on the results, several qualities of the catalyst were identified such as bifunctionality and reducibility at lower temperature are the key point to increase catalytic activity on DRM reaction. However, the explanations on chapter 4 are limited to physicochemical characteristics only. Therefore, **Chapter 5** continued to explain inside into DRM reaction using NiO/Dolomite catalysts regarding XPS perspectives followed by optimization reaction using several parameters such as nickel concentration, temperature of reaction, catalyst loading/weight and GHSV. The kinetic and mechanistic study were conducted by using 10%NiO/Dolomite due to excellent catalytic performance. The details discussion supported by reduction behaviour and *in-situ* reaction of non-isothermal DRM monitored by online MS were carried out to corroborates inside into DRM reaction. Then, **Chapter 6** followed by explained the potential of NiO/Talc in DRM reaction. The physicochemical properties explained excellent catalytic performance of 10%NiO/Talc catalyst with high conversion and selectivity. In addition, spent catalyst analysis was carried out to indicates carbon formation during DRM reaction.

Meanwhile, **Chapter 7** discussed the capability of NiO/AS catalysts towards DRM reaction. Chemical properties such as reducibility, basicity and nickel dispersion were more dominant in enhancing DRM reaction rather than physical characteristics. **Chapter 8** conducted to clarify the comparison study of NiO catalysts in physicochemical properties and kinetic & mechanistic studies by determining E_a of each selected NiO-based catalyst. Consequently, characterization of spent catalysts was carried out to evaluate effect of carbon formation in different supports material. Hence, **Chapter 9** demonstrate the potential of NiO catalyst in membrane reactor system. The catalysts were tested in Pd membrane system at lower reaction temperature (500°C) compared to fixed bed reactor system. Even the results obtained lower than fixed bed reactor, but its promising for new application and comparable with noble metal catalyst ($\text{Ru}/\text{Al}_2\text{O}_3$). Besides, the long-lasting stability test conducted on 10%NiO/Talc for 2 weeks reaction periods. The sides' reaction involves during DRM reaction were explain briefly based on obtained results. Finally, **chapter 10** concludes the significant results and outcomes of this research with few recommendations for future work.

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