DRY REFORMING OF METHANE USING COLD PLASMA REACTOR FOR DIFFERENT DIELECTRIC MATERIALS AND MODIFIED $MgAl_2O_4$ CATALYSTS

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This thesis is dedicated to my beloved parents and teachers.

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ABSTRACT

Dry reforming of methane (DRM) through dielectric barrier discharge (DBD) plasma is one of the promising techniques to convert greenhouse gases (GHGs) such as methane (CH_4) and carbon dioxide (CO_2) to syngas (H_2, CO) and higher hydrocarbons. In this study, Ni-loaded La_2O_3-$MgAl_2O_4$ mix-matrix support lamella-structure catalyst is prepared using modified co-precipitation followed by hydrothermal and wetness incipient impregnation methods. The catalysts are characterised by X-ray diffraction, field emission scanning electron microscopy, high-resolution transmission electron microscopy, Brunauer-Emmett-Teller with N_2, H_2-temperature-programmed reduction and CO_2-temperature-programmed desorption. The spent catalyst is characterised by scanning transmission electron microscopy, energy dispersive X-ray spectroscopy mapping, thermogravimetric analysis and dielectric properties. DRM activity test is carried-out to determine the influence of reactor configuration and dielectric materials on reactant processing and energy efficiency (EE). The reactor configurations include discharge gap, discharge length, volume discharge and catalyst volume are systematically studied to investigate the plasma-catalytic behaviour. The performance and regeneration of the prepared catalysts are tested in a catalytic-DBD reactor which depicts the CH_4 and CO_2 conversion 84 % and 85.5 %, respectively, while H_2 and CO selectivity are 51 % and 49.5 %, respectively (H_2/CO=1.01) with EE = 0.13 mmol-kJ^{-1} for Ni/La_2O_3-$MgAl_2O_4$ catalyst. The optimum process parameters were examined using multiple response surface methodology through a four-factors, five-level central composite design. The optimum values are feed flow rate = 18.8 mL min^{-1}, feed ratio = 1.05, input power = 125.6 W and catalyst loading = 0.6 g. Finally, from the macroscopic kinetics, the apparent activation energies are calculated as 32.6 kJ mol^{-1}and 35.2 kJ mol^{-1} for CH_4 and CO_2, respectively. The calculated results fitted-well with the experimental results with ±5 error. The catalytic-DBD reactor exhibits encouraging performance for DRM at larger a scale.

ABSTRAK

Pembaharuan kering metana (DRM) melalui plasma penyahcasan rintangan dielektrik (DBD) adalah salah satu teknik yang tampak menjanjikan untuk menukar gas rumah hijau (GHGs) seperti metana (CH_4) dan karbon dioksida (CO_2) kepada gas sintesis (H_2, CO) serta hidrokarbon yang lebih tinggi. Dalam kajian ini, sokongan mangkin berstruktur lamela dibantu campuran-matrik La_2O_3-$MgAl_2O_4$ bermuatan Ni telah disediakan dengan menggunakan kaedah ko-pemendakan terubahsuai diikuti dengan kaedah hidroterma dan kaedah pengisitepuan basah. Mangkin telah dicirikan oleh pembelauan sinar-X, mikroskopi elektron imbasan pancaran medan, mikroskopi elektron transmisi resolusi-tinggi, Brunauer-Emmett-Teller dengan nitrogen (BET), penurunan suhu berprogram dengan hidrogen dan penjerapan suhu teraturcara dengan CO_2. Pasca-reaksi mangkin juga dicirikan oleh mikroskopi elektron transmisi imbasan, penyerakan tenaga sinar-X, analisis termogravimetri dan sifat dielektrik. Ujian aktiviti DRM telah dijalankan untuk menentukan pengaruh konfigurasi reaktor dan bahan dielektrik keatas pemprosesan dan kecekapan tenaga (EE) reaktan. Konfigurasi reaktor termasuk sela penyahcasan, panjang penyahcasan, isipadu penyahcasan dan isipadu mangkin telah dikaji secara sistematik untuk menyiasat kelakuan plasma bermangkin. Prestasi dan penjanaan semula mangkin yang disediakan telah diuji di dalam reaktor mangkin-DBD dimana menunjukkan penukaran CH_4 dan CO_2 masing-masing sebanyak 84% dan 85.5%, serta kememilihan H_2 dan CO masing-masing sebanyak 51% dan 49.5% (H_2/CO=1.01) dengan EE = 0.13 mmol-kJ^{-1} bagi mangkin Ni/La_2O_3-$MgAl_2O_4$. Parameter proses optimum telah dikaji dengan menggunakan kaedah pelbagai respon permukaan melalui reka bentuk empat-faktor, lima-peringkat komposit pusat. Nilai optimum adalah jumlah kadar aliran masukan = 18.8 mL min^{-1}, nisbah masukan = 1.05, kuasa input = 125.6 W dan muatan mangkin = 0.6 g. Akhir sekali, daripada kajian kinetik makroskopik, tenaga pengaktifan yang dikira bagi CH_4 dan CO_2 masing-masing sebanyak 32.6 kJ mol^{-1} dan 35.2 kJ mol^{-1}. Keputusan yang dikira bersesuaian dengan keputusan eksperimen dengan ralat sebanyak ±5. Reaktor mangkin-DBD ini menunjukkan prestasi yang memberangsangkan untuk DRM pada skala besar.

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LIST OF ABBREVIATIONS

BET	-	Brunauer-Emmet-Teller
C	-	Capacitance
DBD	-	Dielectric Barrier Discharge
D_e	-	Diffusion coefficient
D_{gap}	-	Discharge gap
D_L	-	Discharge Length
DRM	-	Dry Reforming of Methane
E	-	Electric field
E_a	-	Activation Energy
EDX	-	Energy Dispersion X-ray
EE	-	Energy Efficiency
f	-	Frequency
FID	-	Flame Ionization Detector
GC	-	Gas Chromatograph
GHG	-	Greenhouse Gas
GHSV	-	Gas Hourly Space Velocity
I	-	Current
PBR	-	Packed Bed Reactor
P_X	-	Partial Pressure
R	-	Gas constant
r	-	Radius
R_T	-	Residence Time
SIE	-	Specific Input Energy
S_X	-	Selectivity
T	-	Temperature
TCD	-	Thermal Conductivity Detector
TEM	-	Transmission Electron Microscopy
TOS	-	Time on Stream
TPD	-	Temperature Programmed Oxidation

TPR	-	Temperature Programmed Reduction
V_D	-	Discharge Volume
V_e	-	Volume of electrode
V_t	-	Volume of tube
X_n	-	Conversion
XRD	-	X-Ray Diffraction
Y	-	Yield

LIST OF SYMBOLS

π	-	Pi
μ	-	Micro
ε	-	Permittivity/Dielectric constant
μ_e	-	Electron mobility
ω	-	Empirical coefficient
γ	-	Gamma
n_x	-	Number of moles of x specie
τ	-	Residence time
EE	-	Energy Efficiency
FID	-	Flame Ionization Detector
GC	-	Gas Chromatograph
GHG	-	Greenhouse Gas
GHSV	-	Gas Hourly Space Velocity
PBR	-	Packed Bed Reactor
P_X	-	Partial Pressure
R	-	Gas constant

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CHAPTER 1

INTRODUCTION

1.1 Research Background

The escalation in energy demand and depletion of fossil fuels are two major challenges for sustainable development. The energy demand and global warming are alarming entities must be addressed on time; otherwise, the world will be facing huge energy crises and serious global warming issues. The global warming caused due to the emissions of Greenhouse Gases (GHGs) which effects climate change, disturbing human and aquatic life (Kennedy *et al.*, 2009). Fossil fuels utilization is one of the major causes of emission of GHGs. The main contributors of GHGs are CH_4 and CO_2, with 16% and 76% share respectively (Lane, 2016; Parker *et al.*, 2018). To address these two distinct threats, different approaches have been made to produce clean energy via utilization of GHGs (Covert *et al.*, 2016; Liu *et al.*, 2003). Over the last decade, researchers are taking key attention to reduce GHG emissions by utilizing them to produce energy for sustainable development. The serious concerns about energy crises have been predicted by researchers by 2035 (Duan *et al.*, 2015b; OECD, 2015). Energy is considered one of the core concerns in developing regions like African countries and Asian countries. The utilization of GHGs to produce energy carriers is yet to commercialized due to serious limitations (Covert *et al.*, 2016; Lane, 2016).

Currently the scientific community is utilizing the GHGs through different technologies to minimize the CO_2 and CH_4 concentration from atmosphere and produce energy, especially reforming technologies i.e., CO_2 or dry reforming of methane (DRM), partial oxidation of methane (POM) (Song *et al.*, 2017), oxidative coupling of methane (OCM) and photocatalytic conversion of methane and CO_2 (Liu

et al., 2003; Tahir and Amin, 2013). One of the promising technique, which is getting much attention from the last decade is DRM (Equation 1.1) for the production of valuable fuels like syngas (H_2, CO) and other HCs (Wang *et al.*, 2018b; Zhang and Verykios, 1994). DRM can be considered via three major approaches (i) thermal DRM and (ii) photo-catalytic DRM (iii) plasma DRM (Bromberg *et al.*, 1998; Eliasson *et al.*, 2000; Jean Marie and Iulian, 2001; Jiang *et al.*, 2002). Plasma DRM is again sub-categorized into two major kinds (i) Thermal plasma (ii) Non-Thermal Plasma (NTP). The plasma is an ionized gas that can be generated by different methods including electric discharges depending upon their energy level, electron temperature and ionic density (Bromberg *et al.*, 1998; Indarto *et al.*, 2008; Neyts *et al.*, 2015; Whitehead, 2016).

In thermal plasmas, the temperature of gas molecules (T_g) and electron (T_e) are in same range $T_e \approx T_g$, that is why thermal plasmas are also known as equilibrium plasmas (Boulos *et al.*, 2016). Thermal plasma is being considered low-economical due to higher input energy, installation cost and difficult to handle due to high reactor temperature and controlled pressure (Toth *et al.*, 2016). Thermal plasma is suitable for the production of liquids fuels, in gas phase processes, the high temperature can erode the high voltage (HV) electrode (Du *et al.*, 2015). The thermal plasma possessing high energy electron having 10 eV with the density of almost 10^5e-m^{-3}. The temperature is considerably high i.e. 5×10^3 to 5×10^4 K (Locke *et al.*, 2006). Thermal plasma producing a higher yield of CO and H_2 (Bromberg *et al.*, 1998; Lee *et al.*, 2010). Nevertheless, the consumption of high energy 10 to 20 MJ-kg^{-1} H_2 and the power density 4 kW-L^{-1} are the main concerns for thermal plasma DRM process (Bromberg *et al.*, 1998; Liu *et al.*, 2010).

NTP is considered as the most suitable technology for the DRM due to its non-thermal equilibrium properties, simple design and lower energy consumption (Eliasson *et al.*, 2000; Lu *et al.*, 2017). Among the NTPs, dielectric barrier discharge (DBD) is more promising for DRM due to its lower energy consumption, simple design and low installation cost (Paulmier and Fulcheri, 2005; Snoeckx and Bogaerts, 2017). Since, DBD plasma operates at room temperature and atmospheric pressure, easy to operate and feedstock versatility makes a more attractive approach

for DRM (Snoeckx *et al.*, 2016b). DBD could generate high energetic species consists of electrons, neutrons, radicals and ions; that excite, ionize and dissociate CH_4 and CO_2 to final products (Eliasson *et al.*, 2000; Kogelschatz, 2003; Li *et al.*, 2007). DBD can be constructed planer and cylindrical orientation using a dielectric material to separate by two electrodes, HV electrode and ground electrode creating a potential difference and accelerate electrons from anode to cathode which creates an electric field. The electrons dissociate the reactant gases and convert into products.

Numerous studies have been undertaken to investigate DRM using DBD plasma at various experimental conditions (Aghamir *et al.*, 2004; Chung *et al.*, 2014; Krawczyk *et al.*, 2014; Wang *et al.*, 2009b) to convert CH_4 and CO_2 to valuable fuels like syngas and higher hydrocarbons (HCs). On the other hand, DBD plasma performance is dependent some of leading process parameters i.e., feed flow rate, feed molar ratio, input power, catalyst loading and reactor temperature (Neyts *et al.*, 2015; Usman *et al.*, 2015; Xin *et al.*, 2011; Yap *et al.*, 2015). Although, DBD plasma has been successfully investigated for DRM application with an appreciable number of desired products, yet foremost concern is the power dissipation, low energy efficiency (EE) and carbon deposition due to methane cracking and Boudouard reactions (Equations 1.2 -1.3). The deposited carbon deactivates the active sites of the catalyst and sometimes leads to the reactor blockage.

$$CH_4 + CO_2 \rightarrow 2\,CO + 2\,H_2 \quad \Delta H^{\circ}_{25^{\circ}C} = 247\ \text{kJ mol}^{-1}\ (\text{DRM}) \tag{1.1}$$

$$CH_4 \rightarrow C + H_2 \quad \Delta H^{\circ}_{25^{\circ}C} = 75\ \text{kJ mol}^{-1}\ (\text{Methane cracking}) \tag{1.2}$$

$$2\,CO \rightarrow C + CO_2 \quad \Delta H^{\circ}_{25^{\circ}C} = -172\ \text{kJ mol}^{-1}\ (\text{Boudouard reaction}) \tag{1.3}$$

To improve the EE and inhibit the carbon formation problem, researchers introduced various catalyst systems to overcome the carbon formation and achieve higher stability in DRM (Brune *et al.*, 2018). The majorly used catalyst are Ni-based due to cheaply available (Pakhare and Spivey, 2014). Another approach which is being practiced currently to synthesise a catalyst using transition and noble metals such as La, Ce, Pt, Rh, Ru, Pd on different supports such as Al_2O_3, SiO_2, SBA, MgO,

MCM and TiO_3 (Fan *et al.*, 2011a; Guo *et al.*, 2015b; Nair and Kaliaguine, 2016; Tu *et al.*, 2011b; Zhu *et al.*, 2008a). Transition and noble metals displayed high catalytic activity along with high resistant to coke deposition (Khani *et al.*, 2016). However, transition and noble metals are expansive compared to conventional non-noble metals. Now by looking into elementary problem, it is required to synthesize a stable catalyst, which can exhibit high resistance to coke deposition and stability towards DRM activity in DBD plasma. The selection of the catalyst must be based on better physico-chemical properties and availability. Keeping in mind, Ni, Mg and Al are available abundantly in earth crust and Al having high surface area, while transition metal like La or Ce can be accommodated in a small amount as co-support to achieve the high stability (Li *et al.*, 2017b). $MgAl_2O_4$ has been used for thermal-DRM previously and reported a good activity towards conversion and selectivity (Damyanova *et al.*, 2012; Habibi *et al.*, 2016b). $MgAl_2O_4$ easily can be modified using co-support to enhance its performance and more resistance to coke. $MgAl_2O_4$ has been reported as strong basic support and it has not been used the DBD plasma DRM. It may be interesting to investigate $MgAl_2O_4$ incorporated with co-support to achieve the stability and coke resistance in DBD DRM.

1.2 Problem Statement

Although, recycling of greenhouse gases (CO_2 and CH_4) into valuable chemicals is an attractive approach to mitigate global warming, breaking stable molecules of CO_2 and CH_4 is a major challenge (Indarto *et al.*, 2008; OECD, 2015; Song, 2002). Among the known technologies, NTP via DBD reactor is the most attractive approach for DRM due to the easy handling, low installation cost and low temperature and pressure operations (Indarto *et al.*, 2008; Jo *et al.*, 2015; Nozaki *et al.*, 2017; Zhou *et al.*, 1998). However, low conversion, selectivity and EE have been reported in DBD plasma DRM and addition of rapid coke formation via Equation 1.2 and 1.3. Due to the carbon deposition, the active site of catalyst are blocked which deactivate catalyst and conversion efficiency reduced to a very unacceptable situation (Pakhare and Spivey, 2014). Coke formation in DBD plasma DRM is the

critical problem identified by many researchers which can be overcome by introducing stable catalysts (Aw *et al.*, 2015). The carbon formation and other reactions like reverse water gas shift (RWGS) (Equation 1.4) reaction, stream generation via DRM (Equation 1.5) made the syngas (H_2/CO) ratio lower than unity. It is inappropriate for further utilisation for downstream processing for liquid fuels via Fischer-Tropsch (FT) synthesis (Maitlis and de Klerk, 2013).

$$H_2 + CO_2 \hat{U} H_2O + CO \qquad D_{25^oC} = -131 \text{ kJ mol}^{-1} \text{ (RWGS)} \tag{1.4}$$

$$2H_2 + CO_2 \hat{U} 2H_2O + C \qquad D_{25^oC} = -90 \text{ kJ mol}^{-1} \text{ (steam generation)} \tag{1.5}$$

Among the known catalysts, Ni-base catalysts are the most widely researched material due to low cost, availability and prolong stability. However, it has been observed lower conversion with lesser products selectivity in Ni-based catalyst (Hafez *et al.*, 2015) due to the rapid carbon formation on the tip of Ni particles. The noble metals like Pt, Rh, Pd, Ru, are displaying high resistance towards coking but the cost is very high and nearly unacceptable for industrial utilisation (Doghachi *et al.*, 2016). Rare earth metals such as La and Ce have high stability in thermal DRM. The Ni/Al_2O_3 and MgO has been used for DBD plasma DRM. Ni/Al_2O_3 exhibited excessive coke formation and Ni/MgO has low catalytic activity, although it resists to coking to some extent due to its basicity (Ganesh, 2013). Then $MgAl_2O_4$ has been synthesised to achieve high surface area and high basicity but the stability was still uncertain. The efficiency of Ni-based $MgAl_2O_4$ supported catalyst could be enhanced by modifying its structure with different rare earth metal oxides like La_2O_3 as co-support. $MgAl_2O_4$ has been solely used in thermal-DRM and reported a better choice for high CO_2 conversion (Zhao *et al.*, 2013). However, up to date no modification of $MgAl_2O_4$ using La_2O_3 as co-support is not stated. Moreover, the preparation methods are also responsible for the major properties like surface area, metal dispersion, basicity, and stability of the catalyst (Muraleedharan and Kaliaguine, 2016).

On the other hand, catalytic DBD plasma reactor is considered as low energy efficient system due to the loopholes in reactor design (Chung and Chang, 2016b).

The most commonly used catalytic DBD reactors are cylindrical fixed bed reactor. The specific design parameters such as discharge gap (D_{gap}), discharge length (D_L, discharge volume (V_D) have not been systematically studied for DBD plasma reactor. The reactor configuration study should have been studied exclusively, suggested by (Awadallah *et al.*, 2014) which can enhance the EE of the DBD plasma reactor. Furthermore, the catalyst incorporation in the DBD reactor is also a challenging task during the calculation of gas hourly space velocity GHSV (h^{-1}) along the V_D (Montoro-Damas *et al.*, 2015). The packing material may also influence the discharge chemistry of DBD plasma which is reported by Jo *et al.* (2013).

Apart from catalyst incorporation in DBD plasma reactor, the effects of dielectric material (reactor tube) on DRM activity has not been systematically studied. Previous studies advocated that dielectric material has a substantial effect on the plasma chemistry (Ozkan *et al.*, 2016a) and affected activity in plasma-based DRM process (Li *et al.*, 2004b). Till date now there is no report published to examine dielectric material performance in DBD plasma DRM activity. Finally, the stability and the H_2/CO ratio is one of the leading problems in DBD DRM to discourse. It is important to figure out the temperature effect in gas heating in DBD plasma to understand its effect on activation energy (E_a).

1.3 Research Hypothesis

The development of a new catalyst required to inhibit coke formation, strong thermal stability and enhance the products selectivity. It is hypothesized that DBD plasma reactor EE could be enhanced using a modified $MgAl_2O_4$ catalyst which has been identified as high basic nature catalyst and tolerant to carbon deposition (Habibi *et al.*, 2016b). Recently, $MgAl_2O_4$ spinel with the high surface area and high basicity has been synthesized for DRM (Guo *et al.*, 2004; Wei *et al.*, 2018). However, the catalyst exhibited low stability without the addition of any active metals or co-support. Addition of active metal improves the catalytic activity but stability is still a major challenge in plasma DRM processes (Messaoudi *et al.*, 2018).

La_2O_3 has shown high stability in thermo-catalytic DRM (Charisiou *et al.*, 2016). The rare earth metal-oxides used in DRM displayed a significant resistant towards carbon formation ascribed to the strong basic nature and carbon-gasification (Li *et al.*, 2017b; Zheng *et al.*, 2015b). La_2O_3 has been employed as a major support in the DRM process owing to its strong basic nature and high metal dispersion capability. La_2O_3, as a mix-matrix support, can prevents the carbon deposition and prolongs catalyst stability owing to its ability to react with CO_2 to form intermediate carbonate $La_2O_2CO_3$ (Liu *et al.*, 2016b; Zeng *et al.*, 2017). The catalytic performance of Ni-impregnated $MgAl_2O_4$ may be improved by adding La_2O_3 as co-support. The Ni interaction with $MgAl_2O_4$ could be enhance by the combined effect of Al and Mg as well as subsequent assistance from La_2O_3 (Li *et al.*, 1992). It is envisaged that the incorporation of La_2O_3 and $MgAl_2O_4$ as mixed-support can enhance the basicity of catalyst, resist Ni particles agglomeration and curtails carbon formation (Al-Fatesh *et al.*, 2014; Li *et al.*, 2017a). Therefore, it is appropriate to synthesize and examine the role of La_2O_3 as co-support in Ni-impregnated $MgAl_2O_4$ in a catalytic-DBD plasma DRM. Recycling or regeneration of the proposed catalyst is highly possible using oxygen and nitrogen as a reducing and purging agent. It may reduce the formed carbon filaments and carbonates to their original states (Lee *et al.*, 2018). The preparation method of the catalyst has a significant influence on the structure/morphology and activity of the material. The materials are prepared using modified co-precipitation followed by hydrothermal method (Li *et al.*, 2017b) shows better structure and stability.

The reactor configuration can contribute in EE of the DBD reactor. The parameters like D_{gap}, D_L and V_D can play a significant role in the performance of the reactor. As these parameters are associated with gas processing capacity including specific input energy (SIE) and EE of DBD reactor (Montoro-Damas *et al.*, 2015). The dielectric material can also play a significant role in DBD plasma performance. It is evident the performance of a DBD reactor is related to the characteristics of the dielectric materials. The materials having high dielectric constant and more resistant to high temperature are considered more suitable for a DBD reactor to hinder power dissipation (Ozkan *et al.*, 2016c). The properties of dielectric material i.e., dielectric constant, morphology and temperature tolerance are the key parameters to consider.

By incorporating the proposed catalyst in a systematic studied DBD reactor, the higher EE, higher H_2/CO ratio and stability is highly expected. The synergistic effect of the plasma-catalysis is vastly targeted in the proposed study.

1.4 Research Objectives

Considering the identified major problems in catalytic-DBD DRM, the main objectives of the present study are follows:

i. To synthesise and characterise of Ni loaded La_2O_3-$MgAl_2O_4$ nano-catalyst for DBD plasma DRM.
ii. To investigate the reactor configuration and dielectric material effect in DBD plasma reactor for DRM.
iii. To investigate the catalytic activity, selectivity and regeneration capability of Ni/La_2O_3-$MgAl_2O_4$ catalyst for DBD plasma DRM.
iv. To optimise process parameter of catalytic-DBD plasma DRM using multiple response surface methodology.
v. To examine the kinetic parameters of catalytic-DBD plasma DRM and fluid modelling for plasma discharge characteristics.

1.5 Scope of the Study

The Ni/La_2O_3-$MgAl_2O_4$ nano-composite is prepared by modified co-precipitation method, followed by hydrothermal process. La_2O_3/$MgAl_2O_4$ is prepared by microemulsion method then impregnated Ni over the mixed-matrix support and calcined. For the sake of comparison, the γ-Al_2O_3, 10% Ni/γ-Al_2O_3, 10% Ni/MgO, 10% Ni/γ-Al_2O_3-MgO, $MgAl_2O_4$ and 10% Ni/$MgAl_2O_4$ prepared and tested in DBD plasma DRM. Ni loading (5-20 %) was investigated to evaluate the plasma-catalytic activity. Detailed characterisation was carried-out to check the physico-chemical

properties of the synthesised catalyst. The prepared samples will be characterized by nitrogen adsorption-desorption (BET), X-ray diffraction (XRD), Raman spectra, Fourier transform infrared spectroscopy (FTIR), H2-temperature programmed reduction (H2-TPR) and CO_2-temperature programmed desorption (CO_2-TPD), field emission scanning electron microscopy (FE-SEM), energy-dispersive X-ray spectroscopy (EDX), transmission electron microscopy (TEM), thermogravimetric analysis (TGA) and dielectric properties. The dielectric properties of the prepared samples were analysed to know the dielectric constant of the catalyst. The DBD plasma reactor is used for DRM to analyse the catalytic activity of the prepared catalyst.

In reactor configuration, D_{gap}, D_L, V_D and catalyst packing were investigated for DBD reactor using prepared samples. The performance of the two different dielectric materials (quartz and alumina) were examined in DBD plasma for different parameters such as GHSV, SIE, feed ratio, and V_D. The reactor configuration such as D_{gap}, and D_L are directly used for the calculation of discharge volume. V_D has a direct relation with GHSV and EE. The prepared samples such as γ-Al_2O_3, Ni/γ-Al_2O_3, Ni/MgO, Ni/γ-Al_2O_3-MgO, $MgAl_2O_4$, Ni/$MgAl_2O_4$ and Ni/La_2O_3-$MgAl_2O_4$ respectively. Various Ni loadings were tested to check the effect on the DBD-DRM. The process parameters optimization was carried out using RSM to investigate the effect of process variables such as flow rate, feed ratio, input power and catalyst loading the conversion of CH_4 and CO_2 as well as the selectivity of products and EE of DBD plasma DRM. The kinetic study was carried out using Power-law model to investigate the rate constants (k) and rate of conversion (X) using Ni/La_2O_3-$MgAl_2O_4$. The COMSOL Multiphysics software was used to investigate the electric properties of Argon-based DBD reactor.

1.6 Significance of the Research

The synthesis of high basic Ni/La_2O_3-$MgAl_2O_4$ shows high catalytic activity and stability in the catalytic-DBD plasma DRM. The regeneration capability of the synthesized material is considered a key step towards the stability of the DBD

plasma DRM process. The H_2/CO is unity in the presented study, a substantial prospective for further utilization in FT synthesis for liquid fuel production. The systematic reactor configuration (DBD reactor) study is investigated to oversee the contribution in the EE of DBD plasma. The reactor configuration study shows the EE can be improved via optimizing the geometric parameters. The kinetic study based on reactor configuration is proposed using Power-law model. The plasma characteristics of the Ar-DBD is presented using fluid modelling approach for various dielectric constant and D_{gap}.

1.7 Organization of the Study

The organization of the study is composed of 8 Chapters. The research background, research problem, research hypothesis, scope and significance of the study is presented in Chapter 1. The extensive literature review on DRM process, catalytic-DBD plasma reactor study, catalyst systems and literature on kinetic and fluid modelling study is drafted in Chapter 2. Chapter 3 provides the research methodology adopted in this study: material synthesis, characterization, reactor setup, catalytic activity calculations, process optimization and kinetic study basic descriptions. Chapter 4 deals with the detail characterization of the synthesized material using various techniques. The DBD reactor design and performance of the material is presented in Chapter 5. Process optimization using RSM is provided in Chapter 6. Chapter 7 is divided into two parts: (i) The macroscopic kinetic study of catalytic-DBD plasma DRM (ii) The fluid modelling study of Ar-based DBD. The conclusion and recommendations of the study is provided in Chapter 8.

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