PHOTOREDUCTION OF CARBON DIOXIDE AND METHANE TO FORMATE, ACETATE DERIVATIVES AND HYDROGEN OVER IMMOBILIZED TITANIA NANOPARTICLES AND NITROGEN-DOPED TITANIA NANOTUBE ARRAYS

SAEED DELAVARI

A thesis submitted in fulfilment of the
requirements for the award of the degree of
Doctor of Philosophy (Chemical Engineering)

Faculty of Chemical and Energy Engineering
Universiti Teknologi Malaysia

JUNE 2017

To my beloved father, late mother and family members

ACKNOWLEDGEMET

Alhamdulillah, Praise to Allah, first and foremost, I would like to express my sincere and deep appreciation to my supervisor, Professor Dr. Nor Aishah Saidina Amin for her guidance, suggestions and encouragements throughout my Ph.D. study. Countless gratitude too, to Chemical Reaction Engineering Group (CREG) members and all academic staffs of Faculty of Chemical Engineering, for their support and friendship over these years.

I would like to thank all laboratory technicians for their assistance and cooperation throughout the research work in the Faculty of Chemical Engineering and Faculty of Science, Universiti Teknologi Malaysia.

I also wish to express my gratitude and utmost appreciation to my beloved parents, my wife and my daughter, for the endless encouragement throughout these years.

Finally, to all who have involved, whether directly or indirectly, thank you. All the kindness that you gave will be greatest treasure for the whole of my life.

ABSTRACT

The major causes of global warming are mainly attributed to greenhouse gases such as carbon dioxide (CO_2) and methane (CH_4). The conversion of the gases to renewable fuels has stirred interest for greenhouse gas mitigation and energy crises alleviations. The main objective of this study was to develop the nanosized titania (TiO_2) catalyst for selective CO_2 and CH_4 reduction to fuels by using photoreactor. The photoreduction of CO_2 in the presence of CH_4 was studied over immobilized titania nanoparticles on stainless steel mesh. Response surface methodology was used to assess individual and interactive effects of important parameters on conversion. Calcination of coated titania nanoparticles increased the absorption of ultraviolet-visible light while uniform photocatalyst structure commensurate with decreasing agglomeration. The observed maximum conversions were 37.9% and 48.7% for CO_2 and CH_4, respectively. It is apparent that the optimization exercise is more efficient with response surface methodology. The corresponding products selectivity were 4.7%, 4.3%, 3.9%, 41.4% and 45.7% for ethane, acetic acid, formic acid, methyl acetate and methyl formate, respectively. The performance of highly ordered nitrogen-doped titania nanotube arrays were then fabricated by anodization method, used for photoreduction of CO_2 and CH_4. Field emission scanning electron microscopy images of titania nanotube arrays indicated highly ordered and vertically oriented morphology with inside diameter ranging from 3 to 50 nm. Optimum experimental conditions indicated that maximum CO_2 and CH_4 conversion could reach up to 41.5% and 62.2%, respectively. Correspondingly, hydrogen at selectivity of 80.5% and several by-products including carbon monoxide and hydrocarbons such as ethane, propane and ethylene were produced from photoreduction. The quantum efficiency of the photoreactor with immobilized titania nanoparticles coated on stainless steel meshes for methyl formate and methyl acetate were 0.163% and 0.147%, respectively. Furthermore, the quantum efficiency of the photoreactor with nitrogen-doped titania nanotube arrays synthesized by electrochemical anodization method, for hydrogen was 0.294%. Finally, kinetic model using Langmuir-Hinshelwood developed to investigate photocatalytic reduction process, was found to fit well with theexperimental data. In conclusion, photoreactor with nitrogen doped titania nanotube arrays increased CO_2 and CH_4 reduction to fuels as much as 1.7 times.

ABSTRAK

Penyebab utama pemanasan global berpunca daripada gas rumah hijau seperti karbon dioksida (CO_2) dan metana (CH_4). Penukaran gas tersebut kepada bahan api yang boleh diperbaharui telah menarik perhatian bagi pengurangan gas rumah hijau dan krisis tenaga. Objektif utama kajian ini adalah untuk membangunkan mangkin titania bersaiz nano (TiO_2) bagi penurunan CO_2 dan CH_4 terpilih kepada bahan api dengan menggunakan fotoreaktor. Fotopenurunan CO_2 dengan kehadiran CH_4 dikaji terhadap partikel nano titania yang tidak bergerak di atas jejaring keluli tahan karat. Kaedah permukaan gerak balas digunakan untuk menilai kesan individu dan interaktif bagi parameter yang penting dalam penukaran. Pengkalsinan untuk partikel nano titania bersalut meningkatkan penyerapan cahaya nampak-ultraungu manakala struktur seragam fotopemangkin setara dengan mengurangkan penggumpalan. Penukaran maksimum yang diperoleh bagi CO_2 dan CH_4 masing-masing adalah 37.9% dan 48.7%. Ini menunjukkan pengoptimuman menggunakan kaedah permukaan gerak balas adalah lebih cekap. Kememilihan produk yang sepadan masing-masing adalah 4.7%, 4.3%, 3.9%, 41.4% dan 45.7% bagi etana, asid asetik, asid formik, metil asetat dan metil format. Prestasi tertib tatasusunan tiub nano titania yang didopkan dengan nitrogen telah dihasilkan melalui kaedah penganodan, digunakan untuk fotopenurunan bagi CO_2 dan CH_4. Imej-imej mikroskop elektron imbasan pancaran medan bagi tatasusunan tiub nano titania menunjukkan morfologi yang berorientasikan menegak dan tersusun dengan diameter dalaman di antara 3 hingga 50 nm. Kaedah optimum uji kaji menunjukkan penukaran maksimum CO_2 dan CH_4 masing-masing dapat mencecah sehingga 41.5% dan 62.2%. Sejajar dengan itu, hidrogen pada kememilihan sebanyak 80.5% dan beberapa produk sampingan termasuk karbon monoksida dan hidrokarbon seperti etana, propana dan etilena dihasilkan daripada fotopenurunan. Kecekapan kuantum fotoreaktor dengan partikel nano titania yang tidak bergerak di atas jejaring keluli tahan karat bagi metil format dan metil asetat masing-masing adalah 0.163% dan 0.147%. Malahan, kecekapan kuantum fotoreaktor dengan tatasusunan tiub nano titania yang didopkan nitrogen telah disintesis melalui kaedah penganodan elektrokimia untuk hidrogen adalah 0.294%. Akhir sekali, model kinetik yang dibangunkan menggunakan Langmuir-Hinshelwood untuk mengkaji proses penurunan fotopemangkin, didapati sesuai dengan data uji kaji. Kesimpulannya, fotoreaktor dengan tatasusunan mangkin tiub nano titania yang didopkan nitrogen meningkatkan penurunan CO_2 dan CH_4 kepada bahan api sebanyak 1.7 kali.

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LIST OF SYMBOLS

α	-	Intensity factor
c	-	Speed of light
e^-	-	Electron
E	-	Activation energy
$E_{ads, H2O}$	-	Activation energy for H_2O adsorption
$E_{des, H2O}$	-	Activation energy for H_2O desorption
E_p	-	Energy of photon
Ec	-	Conduction band energy
Ev	-	Valence band energy
Eg	-	Band gap energy
E_p	-	Energy of one photon
f	-	Photon flux
h	-	Planks constant
ΔH	-	Change in enthalpy of reaction (kJ/mole)
H	-	Heat of reaction
H_0	-	Null hypothesis
I	-	Light intensity (mW/cm^2)
I_p	-	Photon irradiance
J/Y	-	Joule per year
k	-	Reaction rate constant
k_1	-	Reduction rate constant
k_2	-	Oxidation rate constant
L	-	Length
N	-	Nitrogen
nm	-	Nanometer

P_{CH_4}	-	Partial pressure of methane
TiO_2	-	Titania (titanium dioxide)
V	-	Volt
W	-	Watt
X_i *and* X_j	-	Decoded independent process variables
λ	-	Wavelength
$\varphi_{Overall}$	-	Overall quantum efficiency
θ	-	Fraction of occupied sites
β_0	-	Interception coefficient
ε_a	-	Standard error

LIST OF ABBREVIATIONS

ANOVA	-	Analysis of variance
BDDT	-	Brunauer–Deming–Deming–Teller
BET	-	Brunauer-Emmett-Teller
BJH	-	Barrett–Joyner–Halenda
CCRD	-	Central composite rotatable design
C	-	Concentration
CB	-	Conduction band
CNTs	-	Carbon nanotubes
DC	-	Direct current
ESR	-	Electron spin resonance
FCCCD	-	Face-centred central composite design
FESEM	-	Field-Emission Scanning Electron Microscopy
F-T	-	Fischer-Tropsch
FTIR	-	Fourier-transformed infrared spectroscopy
GHG	-	Greenhouse gas
IPCC	-	Intergovernmental Panel on Climate Change
L-H	-	Langmuir-Hinshelwood
PEG	-	Polyethylene glycol
RGA	-	Residual gas analyzer
RSM	-	Response surface methodology
SEM	-	Scanning Electron Microscope
UV-vis	-	Ultraviolet-Visible
VB	-	Valence band
XPS	-	X-ray Photoelectron spectroscopy
XRD	-	X-ray Diffraction

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Owing to the recent effects of fossil fuel use on the global environment and the limited amount of energy sources, the search for renewable energy sources, such as sunlight, energy crops and wind are inevitable. As shown in Figure 1.1, the Intergovernmental Panel on Climate Change (IPCC) presented that the major worldwide energy sources in 2008 were 34.6% of oil, 28.4% of coal, 22.1% of gas and 2.0% of nuclear energy [1]. On a global basis, it is valued that renewable energy accounted for 12.9% of the total $492 * 10^{18}$ Joules of primary energy supply. Renewable energy contributed roughly 19% of global electricity supply (16% hydropower and 3% other renewable energy) and biofuels contributed 2% of global road transport fuel supply. About 17% of traditional biomass, 8% of modern biomass, 2% of solar thermal and geothermal energy together fuelled 27% of the total global demand for heat. The contribution of renewable energy to primary energy supply varies substantially by country and region [1].

Recent data [2] confirm that consumption of fossil fuels accounts for the majority of global anthropogenic greenhouse gas emissions. Emissions continue to grow and CO_2 concentrations increased to over 390 ppm, or 39% above preindustrial levels, by the end of 2010 [1]. There are various options for lowering greenhouse gas emissions from the energy system while still satisfying the global demand for energy services.

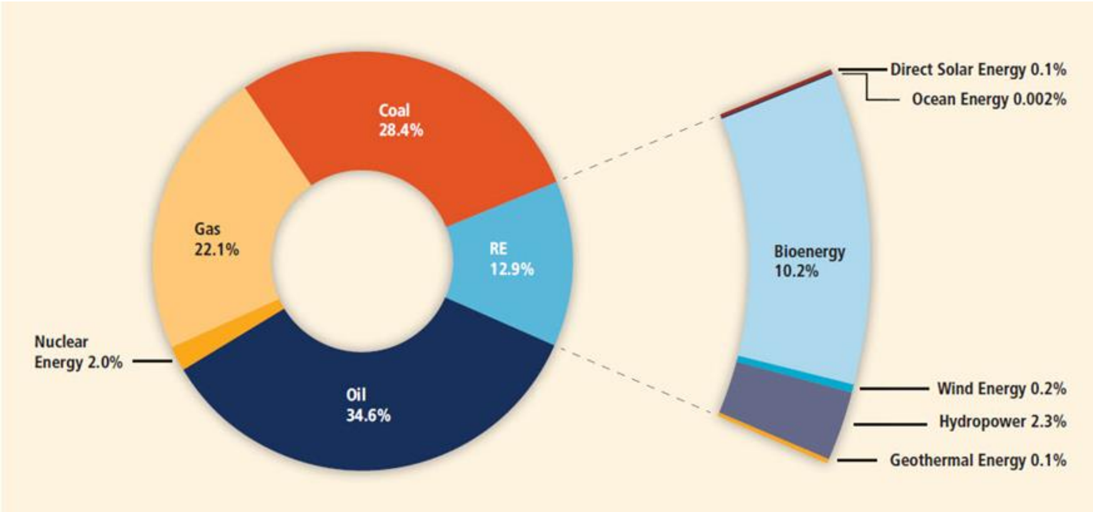

Figure 1.1 The major worldwide energy sources in 2008 [1]

The rapid rise in fossil fuel combustion (including gas flaring) has produced a corresponding rapid growth in CO_2 emissions (Figure 1.2). The amount of carbon in fossil fuel reserves and resources (unconventional oil and gas resources as well as abundant coal) not yet burned has the potential to add quantities of CO_2 to the atmosphere. Global CO_2 emissions for 1940 to 2000 and emissions range for categories of stabilization scenarios from 2000 to 2100 considered in Figure 1.3. In scenarios of CO_2 emission predicted for the year 2050, bioenergy (1.6×10^{20} Joules/Year), direct solar energy (3×10^{19} Joules/Year) and wind energy (2.5×10^{19} Joules/Year) are the major three renewable technologies that must be applied in order to reach the motivated goal that calls to decrease the CO_2 concentration to less than 390 ppm in the atmosphere [1]. Several methods to reduce the CO_2 concentration and prevent CO_2 emissions have been examined: the investigation of the absorption of CO_2 into new or functionalized materials, increment of the dissolved carbonate level and capturing CO_2 [2-6].

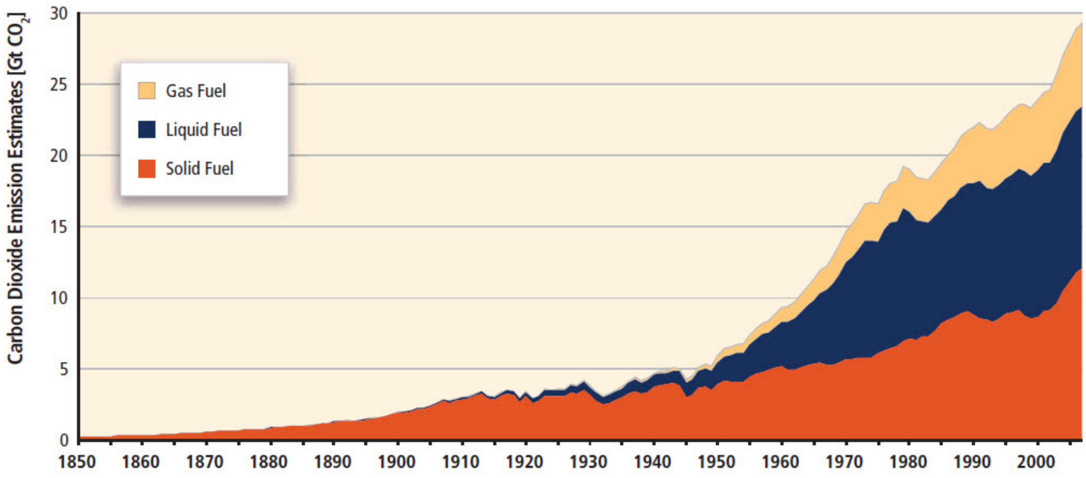

Figure 1.2 Carbon dioxide emissions of burning of fossil fuel (1850 to 2007) [1]

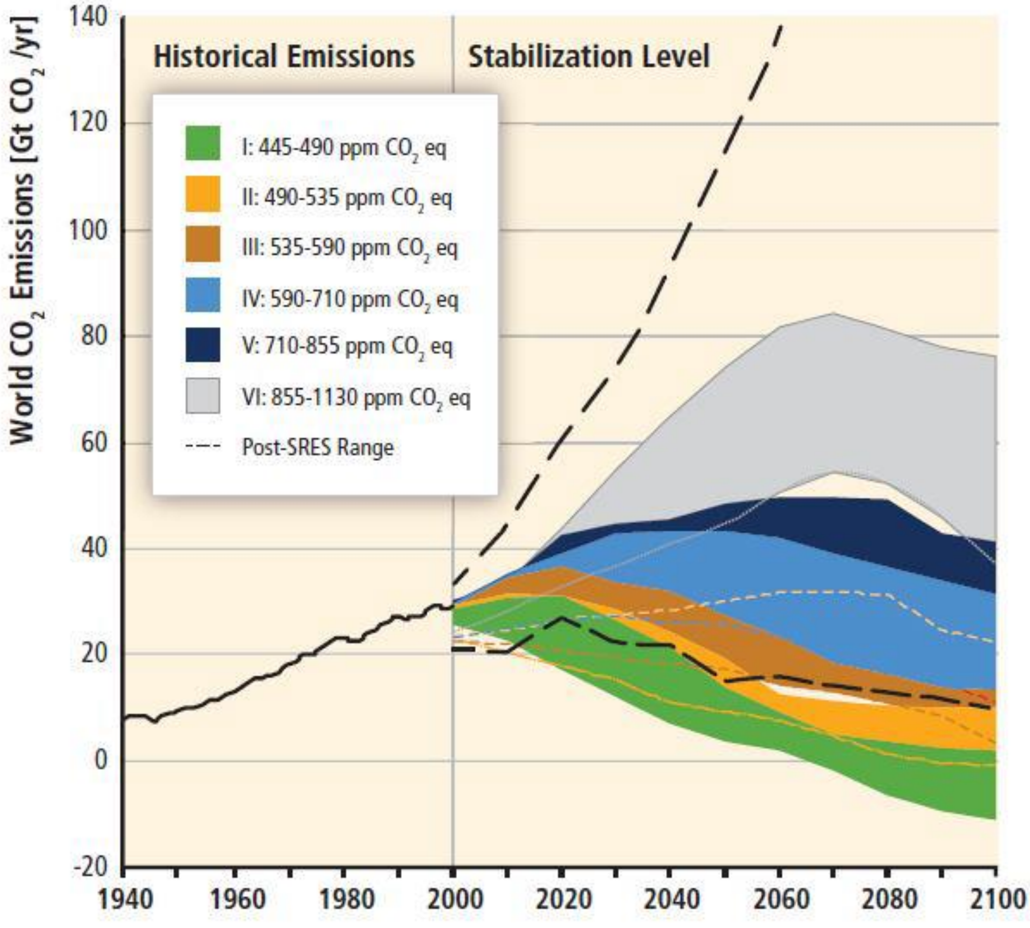

Figure 1.3 Emissions of carbon dioxide between 1940 and 2000 and ranges of emissions for categories between 2000 and 2100 [1]

It is supposedly valuable to capture CO_2 from the atmosphere or plants exhaustion and convert it to hydrocarbon fuels by using sustainable energy sources. This option leads to solving the sustainable energy shortage and global warming problems, simultaneously. In this regard, we need to develop techniques, processes and applications capable of CO_2 conversion at high scale. CO_2 conversion at high scale implies significant challenges [7-9]. C_1 chemistry addresses important subjects including utilization and conversion of CH_4 and CO_2, but it offers no practical conversion technique [4-7]. CH_4 conversion is an oxygenation reaction, while that of CO_2 is a reduction process. The simultaneous process of CO_2 and CH_4 conversion is considered as a perfect redox reaction. The most favorable CO_2 and CH_4 reduction method is by applying photocatalysts since visible light irradiation or UV can reduce it to useful compounds at certain conditions [7-9].

1.2 Introduction to Photocatalysts

Making use of the photocatalytic process to extinguish organic pollutants by oxidation and converting it to hydrocarbon fuels through reduction leads to solving the global warming problems. The use of sunlight for such conversion at accelerated rates with the help of a comparatively economical and nontoxic photocatalyst such as titania (TiO_2), is an attractive alternative for renovation of the deteriorated environment. For this purpose, several photocatalysts, such as TiO_2, CdS, ZnO, WO_3, SnO_2, and Fe_3O_4 have been used. Titania among several semiconductor metal oxides is one of the most favored photocatalysts for the photocatalytic degradation of chemicals and organic dyes [10-18].

1.3 Problem Statement

The major causes of global warming are mainly attributed to greenhouse gases such as carbon dioxide and methane. The carbon-flow between the oceans and atmosphere is considered natural and a yearly excess of CO_2 is added to the cycle by human activities. In order to bring the CO_2 level back to where it was, we need to develop techniques, processes and applications capable of handling CO_2 at high scale. Handling CO_2 at high scale implies significant challenges. C_1 chemistry addresses important subjects including utilization and conversion of CH_4 and CO_2, but it offers no practical conversion technique. Usually, the direct CH_4 and CO_2 conversion to oxygenated mixtures is not promising from the thermodynamical aspect and there is no catalyst available for selective and efficient conversion. CH_4 conversion is an oxygenation reaction, while that of CO_2 is a reduction process. The simultaneous process of CO_2 and CH_4 conversion is considered as a perfect redox reaction. The main challenges ahead in this field are described as below:

Conversion of CO_2 with CH_4 to hydrocarbon fuels is a two-step process which requires higher input energy. On a commercial scale, input energy is provided by the combustion of CH_4, which exacerbates more greenhouse gas emission, leading to uneconomical as well as an unfriendly process to the environment.

Although CO_2 reduction to formate, acetate derivatives and hydrogen through photocatalytic reductions have numerous advantages, yet photocatalysts and reactors under investigations are inefficient to produce high value products with sufficient yield rates and selectivity.

Among semiconductor materials, TiO_2 is widely investigated due to it abundantly available; comparatively cheap and numerous other advantages. However, it has lower light absorption efficiency, trivial photoactivity and selectivity for photocatalytic CO_2 reduction to hydrocarbon fuels.

Existing photoreactors also have lower quantum efficiency due to inefficient harvesting and distribution of light irradiation over the catalyst surface. In addition, such types of reactors have lower exposed surface area, lower catalyst loading, and ineffective adsorption-desorption process and less mass transfer over the catalyst surface, resulting in lower yield rate and selectivity.

1.4 Research Hypothesis

The main focus of this research is to develop a new photocatalytic system for efficiently converting stable CO_2 molecule in the presence of CH_4 to valuable products. In this perspective, nanosized catalysts and a designed reactor could contribute significantly in the photoreduction process. This research also planned to significant improvement of the efficiency of photocatalytic systems that can be achieved by developing appropriate reductants and selecting semiconductors. Therefore, major hypotheses of the research are deliberated as follows:

Titania nanosized catalyst is planned to be designed in such a way which could enable to cross over barriers by providing higher light absorption capacity, controlling of surface reaction for enhancing selectivity and steps ahead toward higher CO_2 and CH_4 conversion. For this purpose titania nanoparticles coated on stainless steel mesh and titania nanotube arrays fabricated by anodizing method as catalysts with a self-designed photocatalytic reactor can provide thrust to wrestle problems of photocatalysis and would help to improve photoactivity and selectivity.

Higher CO_2 and CH_4 reduction and improved photoactivity will be possible through introducing immobilized titania nanoparticles on stainless steel mesh, also titania nanotube arrays fabricated by anodizing method as catalysts. For enhancing the photoactivity of TiO_2 in the visible spectral range would be used the desired band gap narrowing of TiO_2 can be achieved using main-group dopants, such as nitrogen (i.e. TiO_2-xNx).

1.5 Research Objectives

The objectives of this study including;

1) To synthesize and characterize the titania nanoparticles coated on stainless steel mesh and titania nanotube arrays catalysts.
2) To evaluate the catalytic activity of both catalysts on photoreduction of CO_2 and CH_4.
3) To optimize the reaction conditions, including their interaction effect that suitable for the photorcduction.
4) To evaluate the quantum efficiency of the photoreduction over both catalysts.
5) To study the kinetic parameters of the photoreduction over both catalysts.

1.6 Research Scope

The specific research scopes of this study are as follows:

1) Preparation of titania nanoparticles coated on stainless steel mesh and synthesis of nitrogen-doped titania nanotube arrays for addressing the promising catalysts of photocatalytic conversion of CO_2 and CH_4. Furthermore, catalyst characterizations are conducted for samples before and after calcination at different temperatures of titania nanoparticles also, undoped and nitrogen-doped titania nanotube arrays using UV–vis spectra, BET, SEM and XRD in order to investigate the light absorption, agglomeration and surface structure of catalysts.

2) CO_2 and CH_4 molecules were competitively activated by the charge transfer excited complexes and the values of feed ratios influenced the selectivity for the formation of the desired products.

3) Design Of Experiments (DOE) is the first requirement for Response Surface Methodology (RSM) to determine the number of runs that are required to give a reliable measurement of the desired response. The optimization is performed for methane and carbon dioxide conversion responses.

4) The evaluation of photoreactors performances in the field of photocatalysis is vital to compare results under different operating conditions. For this purpose various standard tests such as quantum efficiency and photon flux reported. High quantum efficiencies may be attributed to higher photon absorption due to larger illuminated active surface area.

5) In heterogeneous catalysis, the kinetic expression can be developed for the stable reactants and products in terms of surface concentrations of reactant and product. The reaction mechanism and kinetic model were developed to find out the key parameters in reduction applications.

1.7 Outline of Thesis

This thesis consists of 6 six chapters. Background of the research and problem at hand, research hypothesis, objectives and scope of this study is discussed in chapter 1. Chapter 2 presents a literature review pertaining to possible pathways for CO_2 recycling, fundamentals and progress in CO_2 reduction to hydrocarbon fuels, synthesis and characterization techniques, and description of photocatalytic reactors and development of kinetic models. In chapter 3, general description of research methodology and detailed experimental strategies are discussed. The photoreduction of CO_2 in the presence of CH_4 over immobilized titania nanoparticles on stainless steel mesh and optimization study are deliberated in chapter 4. The description about photoreduction of CO_2 in the presence of CH_4 over nitrogen-doped titania nanotube arrays to hydrogen and optimization using response surface methodology is presented in chapter 5. Finally, 6 contains the overall conclusions of this study and recommendations for the future work.

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