CARBON DIOXIDE REDUCTION TO FUELS USING MODIFIED TITANIUM NANOCATALYSTS IN MONOLITH PHOTOREACTOR

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To my beloved father, late mother and family members

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ABSTRACT

Carbon dioxide (CO_2) is the largest contributor to global warming and its conversion to renewable fuels has stirred interest for greenhouse gas mitigation and energy crises alleviations. The photocatalytic CO_2 reduction to fuels is promising, yet existing technologies registered low CO_2 reduction efficiency. The main objective of this study was to develop a microchannel system for selective CO_2 reduction to fuels. Initially, nanocatalysts were investigated using cell type reactor with methane (CH_4) and carbon monoxide (CO) as the main products during CO_2 reduction with water vapour (H_2O) over indium (In)/TiO_2 and montmorillonite (MMT)/TiO_2 catalysts. Yield of CH_4 over TiO_2 was 31.25, enhanced to 244 μmole g-catal.$^{-1}$ h^{-1} using 10% In-doped TiO_2. Loading MMT evidently enhanced TiO_2 performance with CH_4 yield rate 441.5 μmole g-catal.$^{-1}$ h^{-1}. Next, microchannel monolith photoreactor was explored for selective CO_2 reduction using H_2O and hydrogen (H_2) as reducing agents. Yield rate of CO attained was 962 μmole g-catal.$^{-1}$ h^{-1} and selectivity 95%. Performance comparison revealed 183 fold higher yield rate in monolith compared to cell type reactor. Significantly higher monolith reactor performance reached using H_2 reducing agent and co-metal-doped TiO_2 nanocatalysts. Yield rate of CO over nickel (Ni) and In-co-doped TiO_2 reached to 12028 μmole g-catal.$^{-1}$ h^{-1}, higher in order of 1.8 times than copper (Cu)- In/TiO_2, 5.93 times than In/TiO_2, 207.4 times than TiO_2 with performance 902 fold higher than the cell type reactor. Besides, monolith geometry, reaction temperature, feed ratios, metals-content and irradiation time contributed significantly to enhance reactor performances. Quantum efficiency of CO production was 1.04 %, 87 fold higher than reported in literature. Finally, Langmuir-Hinshelwood and kinetic model were developed to investigate adsorption behaviors and photocatalytic oxidation and reduction process, fitted well with experimental data, and assured efficient adsorption-desorption inside microchannels. In conclusion, microchannel monolith photoreactor with modified TiO_2 nanocatalysts could make possible markedly higher CO_2 reduction to fuels with higher selectivity.

ABSTRAK

Karbon dioksida (CO_2) adalah penyumbang terbesar kepada pemanasan global dan penukarannya kepada bahan api diperbaharui telah menimbulkan minat dalam pengurangan gas rumah hijau dan peningkatan krisis tenaga. Terdapat potensi bagi pengurangan fotokimia CO_2 kepada bahan api, namun teknologi sedia ada mendaftarkan ecekapan pengurangan CO_2 yang rendah. Tujuan utama kajian ini adalah untuk membangunkan sistem saluran-mikro bagi pengurangan CO_2 terpilih kepada bahan api. Kajian dimulakan dengan mengkaji mangkin menggunakan reaktor jenis sel dengan gas metana (CH_4) dan gas karbon monoksida (CO) sebagai produk utama semasa pengurangan CO_2 dengan wap air (H_2O) terhadap mangkin indium (In)/TiO_2 dan montmorilonit (MMT)/TiO_2. Hasil CH_4 terhadap TiO_2 sebanyak 31.25 telah meningkaf kepada 244 μmol g-catal.$^{-1}$ h^{-1} menggunakan 10% In-dop TiO_2. Muatan MMT terbukti meningkatkan prestasi TiO_2 dengan kadar hasil CH_4 sebanyak 441.5 μmol g-catal.$^{-1}$ h^{-1}. Seterusnya, reaktor-foto monolit saluran-mikro dikaji lagi untuk penurunan CO_2 terpilih menggunakan H_2O dan hydrogen (H_2) sebagai agen penurunan. Kadar hasil CO yang diperolehi adalah 962 μmol g-catal.$^{-1}$ h^{-1} dengan selektiviti sebanyak 95%. Perbandingan prestasi menunjukkan 183 kali ganda kadar hasil yang lebih tinggi dalam reaktor monolit berbanding reaktor jenis sel. Prestasi terbaik reaktor monolit dicapai secara signifikan menggunakan H_2 sebagai agen penurunan dan mangkin nano ko-logam yang didopkan dengan TiO_2. Kadar hasil CO bagi nikel (Ni) dan In- diko-dopkan dengan TiO_2 mencapai sehingga 12028 μmol g-catal.$^{-1}$ h^{-1} iaitu 1.8 kali lebih tinggi berbanding kuprum (Cu)- In/TiO_2, 5.93 kali berbanding In/TiO_2, 207.4 kali berbanding TiO_2 dengan prestasi sebanyak 902 kali ganda lebih tinggi berbanding reaktor jenis sel. Selain itu, geometri monolit, suhu tindakbalas, nisbah suapan, kandungan logam, dan masa penyinaran menyumbang secara signifikan dalam meningkatkan prestasi reaktor. Kecekapan kuantum bagi penghasilan CO adalah 1.04%, 87 kali lebih tinggi berbanding dengan nilai yang dilaporkan dalam literasi. Akhir sekali, model Langmuir-Hinshelwood dan kinetik dibangunkan untuk mengkaji sifat penjerapan, proses penurunan dan pengoksidaan foto-pemangkin, dilengkapkan dengan data eksperimen dan jaminan keberkesanan penjerapan-nyahpenjerapan dalam saluran mikro. Sebagai kesimpulan, reaktor-foto monolit bersaluran mikro dengan mangkin nano TiO_2 terubahsuai mampu menukarkan CO_2 dengan lebih signifikan kepada bahan api dengan selektiviti yang lebih tinggi.

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α	-	Intensity factor
β	-	Full width at half maximum
c	-	Speed of light
d_h	-	Channel size
D	-	Average particle size
e-	-	Electron
E_{gap}	-	Gap energy
E_{bg}	-	Energy band gap
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
f	-	Photon flux
h	-	Planks constant
ΔH	-	Change in enthalpy of reaction (KJ/mole)
h^+	-	Hole
H	-	Heat of reaction

I	-	Light intensity (mW/cm^2)
I_p	-	Photon Irradiance
k	-	Reaction rate constant
k_1	-	Reduction rate constant
KJ	-	Kilo Joule
k_2	-	Oxidation rate constant
L	-	Length
M	-	Metal
nm	-	Nanometer
N	-	Nitrogen
S	-	Active Site
TiO_2	-	Titanium dioxide
Ti	-	Titanium
Hg	-	Mercury
V	-	Volt
W	-	Watt
λ	-	Wavelength
$\Phi_{overall}$	-	Overall quantum efficiency
ξ	-	Photonic efficiency

LIST OF ABBREVIATIONS

C	-	Concentration
CVD	-	Chemical vapour deposition
CSD	-	Chemical solvent deposition
CPSI	-	Cell per square inch
F-T	-	Fischer-Tropsch
GHG	-	Greenhouse gas
GW	-	Gaga Watt
MTOE	-	Millions tones oil equivalent
MMT	-	Montmorillonite
NHE	-	Normal hydrogen electrode
BET	-	Braunauer-Emmer-Teller
FTIR	-	Fourier Transform Infrared Spectroscopy
FESEM	-	Field Emission Scanning Electron Microscopy
HRTEM	-	High Resolution Transmission Electron Microscopy
L-H	-	Langmuir-Hinshelwood
IUPAC	-	International Union of Pure and Applied Chemistry
SEM	-	Scanning Electron Microscopy
XRD	-	X-ray Diffraction

UV-Vis	-	Ultraviolent-Visible
VLR	-	Visible light responsive
XPS	-	X-ray Photoelectron spectroscopy
TW	-	Terawatt

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CHAPTER 1

INTRODUCTION

1.1 Research Background

Global warming, primarily due to increasing level of carbon dioxide (CO_2) emission from fossil fuels combustion, has aroused considerable concerns [1]. Rapid global energy demand has been driven by a growing world population. Energy requirements will roughly be doubled by 2050 and tripled by the end of this century [2]. In current circumstances, 80 % of primary energy consumption is fulfilled by fossil fuels of which 58 % alone is consumed in the transportation sector [5, 6]. Combustion of these fuels generates greenhouse gases (GHG) especially CO_2, leading to global warming [3-5]. Moreover, GHG contribute many negative effects like increase in sea level, occurrence of acid rain and loss in biodiversity [6-8]. Exploring new energy resources are inevitable to overcome pressing environmental issues, shortage in fossil fuels supply and continuous increase in energy demand [9]. Recently, numerous efforts have been endorsed to reduce CO_2 emission through pre and/or post combustions and also capturing and sequestration. However, these processes are energy intensive, thus uneconomical [10, 11].

Utilizing easily available and renewable carbon resource such as CO_2 for development of carbon based fuels is imperative for the sustainability, since CO_2 is green and cheap, totally abundant, as well as a renewable feedstock [12]. However, the biggest obstacle for establishing industrial processes based on CO_2 is its low energy level. CO_2 is a stable molecule that requires high energy to transform it into useful chemicals and/or fuels. During the last few years, various types of technologies have been investigated for CO_2 reforming to carbon based chemicals and fuels namely, thermal reforming, plasma reforming and photoreduction [13].

In thermal reforming, CO_2 can be converted to synthesis gas (CO, H_2) through an endothermic process by supplying 247 KJ/mole of input energy at temperature range of 800-1000 ^oC and pressure of 8-10 bars over different types of catalysts. The CO_2 reforming of methane (CH_4) is explained by Equation (1.1) [14, 15].

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H = +247 KJ/mol \tag{1.1}$$

In this reaction Equation (1.1), the yield of syngas could increase with temperature; however, high temperature may affect catalyst stability. At higher temperature, more coke is deposited over the catalyst surface causing catalyst deactivation and reactor clogging. At the commercial level, fixed bed reactors are frequently employed for thermal CO_2 reforming with CH_4 to produce synthesis gas. The input energy required for endothermic reaction is supplied by natural gas combustion according to Equation (1.2).

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H = -800 KJ/mol \tag{1.2}$$

Equation (1.2) reveals 1 mole of CH_4 releases 800 KJ of energy but only 70 % of energy can be possibly utilized for efficient process. In this way, 0.44 mole of CH_4 will be necessary to reform 1 mole of CO_2 and 0.44 mole of CO_2 would be released to the atmosphere. Therefore, to produce 2 moles of CO during CO_2 and CH_4 reforming, it would be necessary to utilize 1.44 mole of CH_4 with 0.44 mole of

CO_2 emitted as greenhouse gas. Thus, a net 0.56 mole of CO_2 will be treated by consuming 1.44 mole of natural gas [16].

CO_2 reforming of CH_4 by plasma is considered a new technology that offers better alternatives compared to thermal catalytic processes. Contrary to catalytic reforming, plasma technology has advantages, since reaction takes place at lower temperature and pressure [17]. Nevertheless, higher input energy in terms of electrons and radicals production for reforming reactions is still a challenge. The reforming reactions through plasma are very complex as indicated by Equations (1.3-1.5) [16].

$$CH_4 \xrightarrow{e^* \text{ or pyrolysis}} C + 2H_2 \quad (1.3)$$

$$CO_2 \xrightarrow{e^* \text{ or pyrolysis}} CO + O \quad (1.4)$$

$$C + O \longrightarrow CO \quad (1.5)$$

Equations (1.3) and (1.4) are highly endothermic reactions induced by thermochemical pyrolysis, while Equation (1.5) is a radical reaction. In plasma process, electrons, radicals and ions are produced by applying higher voltages using electricity, but on commercial scale this process is energized by combusting natural gas.

As discussed in Equation (1.2), during complete combustion of one mole of CH_4, about 800 KJ of heat energy is released. In efficient process, 42 % of this energy can be converted to electricity and 67 % of electricity is possible to be utilized in plasma reactions [16]. In this way, to get 2 moles of CO during CO_2 reforming, it would be necessary to burn 1.10 mole of CH_4 and 1.10 moles of CO_2 gas should be released to atmosphere. Besides, achieving higher efficiency inside a plasma reactor at the commercial level is quite challenging [18, 19].

Among energy producing possibilities, thermal and plasma technologies can be used to produce synthesis gas efficiently, yet in both cases there is release of CO_2

to atmosphere. Besides, there is additional consumption of CH_4 in terms of providing input energy as heat. Therefore, technologies pertinent to carbon management, which not only mitigate global temperature, but also meet increasing energy demands economically, are high in the priority list [20]. Recently, photocatalytic CO_2 reduction has gained significant importance towards productions of hydrocarbon fuels and value added chemical such as CO, CH_3OH, CH_4, HCOOH and HCHO. Phototechnology has high potential for reducing CO_2 emissions and partly resolving energy crises [21, 22]. Therefore, CO_2 reduction using UV and/or visible light irradiation could be a potential phototechnology for the sustainability of the society.

1.2 Photocatalytic Carbon Dioxide Reduction

Photocatalytic CO_2 reduction is one of the most promising solutions to both energy crises and global warming, since CO_2 can be reduced to valuable chemicals at relatively low temperature and atmospheric pressure [23, 24]. In recent innovations, the ubiquitous photocatalysis has gained increasing attention as it can operate at normal operating conditions. During photocatalytic CO_2 reduction to hydrocarbon fuels, energy requirement could be provided using sunlight which is a green source of energy. In this technology, stability of catalyst and its performance is affirmed due to mild operating conditions. The photoreduction of CO_2 by using water (H_2O) and/or H_2 as reductant are stated in Equations (1.6) - (1.8).

$$CO_2 + 2H_2O \xrightarrow{hv,\ catalyst} CH_3OH + 3/2\,O_2 \quad (1.6)$$

$$2CO_2 + 2H_2O \xrightarrow{hv,\ catalyst} CO + CH_4 + 3O_2 \quad (1.7)$$

$$2CO_2 + 2H_2 \xrightarrow{hv,\ catalyst} 2CO + CH_4 + O_2 \quad (1.8)$$

Equation (1.6) - (1.8) revealed renewable fuels such as CO, CH_4 and CH_3OH can be produced in single step. Hence, these reactions affirmed phototechnology as the most attractive and a future hope for mitigation of greenhouse gas with production of green fuels for sustainable development [25]. Furthermore, Fischer-

Tropsch (F-T) involves catalytic conversion of CO with H_2 into hydrocarbons. Therefore, with appropriate photocatalyst, the F-T process may proceed in single step in the presence of irradiations to form higher hydrocarbons during CO_2 reduction through Equations (1.9) – (1.12).

$$2CO_2 + 12H^+ + 12e^- \longrightarrow C_2H_4 + 4H_2O \quad (1.9)$$

$$2CO_2 + 14H^+ + 14e^- \longrightarrow C_2H_6 + 4H_2O \quad (1.10)$$

$$3CO_2 + 18H^+ + 18e^- \longrightarrow C_3H_6 + 6H_2O \quad (1.11)$$

$$3CO_2 + 20H^+ + 20e^- \longrightarrow C_3H_8 + 6H_2O \quad (1.12)$$

However, there are certain challenges in practicing this technology on commercial level as lower CO_2 reduction, lesser yield rate and selectivity of fuels has been reported [26, 27]. To make CO_2 conversion approach economically practical and industrially scalable, research should focus on increasing the overall CO_2 photo conversion efficiency and selectivity; thus ultimately efficient photocatalysts and reactors are warranted [22, 28, 29].

The photocatalytic CO_2 reduction with H_2O to formic acid (HCOOH), formaldehyde (HCHO), CH_3OH and CH_4 as the main products was demonstrated three decades ago by Inoue et al. [30]. Since then, various efforts have been taken to design and develop efficient and selective photocatalytic systems for efficient CO_2 photoreduction to value added chemicals [31-33]. However, lower photocatalytic CO_2 reduction to hydrocarbon fuels has been reported during the last decades. Under such circumstances, efficient photocatalytic reactors that can eminently enhance CO_2 conversion and yield rates are inevitable.

Furthermore, since 1978, H_2O has been used as reducing agent for CO_2 reduction to produce various chemicals and fuels. However, the standard reduction potentials of H_2O to produce H_2 is much lower than the standard reduction potential of CO_2 to generate $\bullet CO_2^-$ [34]. Thus, in CO_2 photocatalysis with H_2O, photoreactions are supposedly more favourable to reduce H_2O through water

splitting, instead of CO_2 reduction. Therefore, other reducing agnets such as H_2 are also need to be explored for CO_2 reduction applications [23].

In photocatalytic applications, semiconductor materials also contribute significantly to enhance reduction process. Among various semiconductors, the focus has been on titanium dioxide (TiO_2) as a photocatalyst. TiO_2 has been researched excessively over the past decades due to its encouraging advantages including good photoactivity, relatively low cost, and is abundantly available. It is also chemically/thermally and biologically stable, non-toxic, and possesses higher oxidative potentials [35-37]. In green chemistry, TiO_2 and H_2O are utilized for photocatalytic transformation of CO_2 to hydrocarbon fuels. However, the efficiency of CO_2 reduction with H_2O to CH_4 and higher hydrocarbons over TiO_2 is low due to immediate recombination of photogenerated electron-holes pairs [38-40]. On the other hand, the photocatalytic activity of TiO_2 depends on its crystalline structure, particle size, presence of dopant or charge trapping materials, surface area, and surface hydroxyl groups. Therefore, numerous efforts are attempted to improve its photocatalytic activity for practical applications [41, 42]. The addition of metals and/or sensitizers to TiO_2 could alter TiO_2 band gap to effectively prevent recombination of photogenerated electron-hole pairs [43-45]. Among various dopants, In has ability to produce large number of electrons due to vacant d-orbits and also can hinder photogenerated electron-hole recombination [46, 47]. Poznyak et al. [48] investigated the photo-electrochemical properties of nanocrystalline In_2O_3/TiO_2 composites. It was observed that In_2O_3 in TiO_2 endorsed efficient separation of photogenerated electron-hole pairs. In another study, it was observed that N doped In_2O_3 thin film electrodes were efficient for H_2O splitting [49]. Recently, Kuo et al. [46] reported Ti–In oxy (nitride) with RuO_2 for H_2O splitting and observed higher H_2 yield rate over the In_2O_3/TiO_2 catalyst. Therefore, it is envisaged that In is suitable to improve TiO_2 photocatalytic activity for efficient CO_2 conversion to value added chemicals and fuels.

Furthermore, TiO_2 co-doping with metals has been endorsed as an attractive approach to improve its photoactivity. This is an important research domain in the field of titanium photo activation, even though all the dopants are not always suitable

for this purpose [50]. Thus, in the specific case of photocatalytic CO_2 reduction to hydrocarbon fuels, some metals are more favorable to improve selectivity. Copper and Ni doping are most efficient to enhance selectivity toward higher hydrocarbon and oxygenated compounds [51-53]. Therefore, these metals are considered very important to get the desired product with appropriate selectivity.

On the other hand, mesoporous materials have been considered for improving TiO_2 photocatalytic activity and selectivity because of the high surface area and inhibition of charge particle recombination. The most widely used materials include clay minerals, activated carbon, graphene oxide, carbon nanotubes, zeolites, and silica [54-57]. Abundantly available natural clays and among them, pillared clays, constitute a group of mesoporous materials deemed effective to enhance TiO_2 photocatalytic activity. The clay-TiO_2 heterojunction makes easier for trapping the photogenerated charge particles, improving TiO_2 photoreduction efficiency [58, 59]. The more convincing features of clay materials are; low cost, environmentally friendly, higher surface area and good adsorption capacity [60, 61]. Apart from nanoclays, MMT is a natural layered clay classified as 2:1 groups of phyllosilicates clays in which one octahedral sheet is sandwiched between two silica tetrahedral sheets [62, 63]. MMT is widely used as support to manufacture functional composites as photocatalysts which makes it effective for higher charge trappings. By dispersing MMT into the precursors of the TiO_2 particles, intercalated delaminated clay is formed. This clay-TiO_2 heterojunction not only prepare nano-TiO_2 particles but also immobilize nano- TiO_2 over MMT-clay which is helpful to increase surface activity [64, 65]. The addition of MMT into TiO_2 could also enhance yield rates due to the presence of hydroxyl groups (OH) known to be more suitable for CO_2 adsorption.

During the last 10 years, fixed-bed, catalyst supported and optical fiber reactors have been under investigation for CO_2 photoreduction. The fixed-bed with its lower surface to volume ratio, inefficient light distribution and lower interaction between reactant and catalyst [66] seem not suitable for the photoreduction process. The optical fiber photoreactors, however, fall in the category of efficient photocatalytic reactors. These reactors have been explored for photocatalytic CO_2

reduction, since the exposed surface area to light ratio are larger, delivering light efficiently and uniformly throughout the reactor [67, 68]. However, several disadvantages such as lower adhesion strength, relatively low surface area and only 20-30% of effective total reactor volume hindered the progress of the reactor towards commercialization [69, 70].

Among photocatalytic reactors, the monoliths with large illuminated surface area to reactor volume ratio and efficient light utilization/distribution over the catalyst surface are considerably effective for photocatalytic CO_2 reduction applications. Basically, monolith composed of large number of channels with catalyts usually coated as thin layer along the walls to allow higher surface interaction with irradiation [71, 72]. In addition, higher flow rates in the honeycomb monoliths give lower pressure drops, and its substrate can provide specific surface area 10-100 times more than other types of catalyst supports having the same outer dimensions [66, 73, 74]. In monolith, less dense channels with higher surface area per unit volume are useful for efficient light distribution and increasing mass transfer rate on the catalyst surface. In addition, light distributions along the axial length of the monolith decreases gradually and higher CO_2 mass transfer coefficient can be achieved using shorter monolith length [75].

1.3 Problem Statement

CO_2 reduction to hydrocarbon fuels provides alternative ways for monitoring energy crises and global warming. However, breaking stable CO_2 molecule through thermal reforming is demanding higher input energy. The main challenges ahead in this field are described as below:

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

2. Although, CO_2 reduction to fuels through photocatalytic reductions have numerous advantages, yet photocatalysts and reactors under investigations are inefficient to produce hydrocarbon fuels with sufficient yield rates and selectivity.

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

4. 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 on developing new photocatalytic system for efficiently converting stable CO_2 molecule to hydrocarbon fuels and other value added chemicals. In this perspective, nanosized catalysts and micro structured photoreactors could contribute significantly in the field of phototechnology. This research is planned by touching different research fields for solving basic reactor design problems in the way of getting selective CO_2 photoreduction efficiency for a net zero carbon cycle. Therefore, major hypotheses of the research are deliberated as follows:

1. The single step CO_2 reduction to hydrocarbon fuels is possible through photochemical Fischer-Tropsch process. Nanostructured semiconductor

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 conversion. For this purpose TiO_2 nanoparticles doped and co-doped with metals and modified with micro structured materials can provide thrust to wrestle problems of photocatalysis and would help to improve photoactivity and selectivity.

2. Higher CO_2 reduction toward hydrocarbon fuels and improved photoactivity will be possible through introducing metal ions into titanium structure. The metals that would be used are In, Cu and Ni because of their distinguish features and selective production of hydrocarbon fuels through CO_2 recycling. Besides, micro structured material employed would be pillared MMT-clay. The MMT-clay dispersed into TiO_2 would provide higher charges mobility, higher reduction potential, more CO_2 adsorption and prolonged life time of electron-hole pairs.

3. The lower quantum efficiency of the photoreactor system because of inefficient light distribution over the catalyst surface is intended to overcome employing microchannel monolith photoreactor. The micro structured photoreactor could provide momentum toward goal by wresting fundamental design problems of photoreactors. Monolith will be productive to provide higher illuminated active surface area, higher adsorption-desorption and efficient mass transfer toward catalyst surface. Higher light distribution and harvesting over the catalyst surface would also be possible utilizing microchannels, ultimately stimulating higher quantum efficiency toward efficient CO_2 reduction to selective hydrocarbon fuels. Besides, selection of an efficient reducing agent and optimizing various operating parameters could contribute significantly to maximize CO_2 reduction efficiency at improved selectivity.

1.5 Research Objectives

The aim of this research is to design a monolith photoreactor having microchannels of higher surface area that could serve as light transfer path over the thin layer of nanosized catalysts and capable of enhancing CO_2 reduction and yield rates. Next co-doped nanocatalysts and process operating parameters are deliberated to maximize CO_2 reduction efficiency. Finally, exploring L-H and kinetic models are planned to understand the role of catalysts and photoreactors. The specific objectives of the research are:

1) To synthesize, characterize and test modified titanium nanocatalysts for CO_2 reduction to fuels
2) To design and fabricate a monolith photoreactor suitable for efficient CO_2 reduction to fuels
3) To investigate the effectiveness of various operating parameters on the photoactivity of nanocatalysts in terms of yield and selectivity
4) To study kinetic and reaction rate parameters for understanding the role of nanocatalysts toward optimization of CO_2 reduction.

1.6 Research Scope

This study is focused on resolving some of the fundamental problems pertaining to lower CO_2 reduction efficiency and selectivity. In this perspective, design of monolith and cell type photoreactors, effects of operating parameters on CO_2 reduction efficiency, synthesis and characterization of various doped, co-doped and surface modified nanocatalysts, reaction mechanisms of CO_2 reduction, oxidative-reductive model development and quantum efficiency analysis have been deliberated. Furthermore, the design of photoreactor is limited to the fabricating of monolith photoreactor to maximize yield rates and products selectivity. The CO_2 reduction efficiency is related to maximize yield rates of desired products. Therefore, the specific research scope of this study is as follows:

1) TiO_2 nanoparticles, In/TiO_2 nanoparticles, Cu and Ni co-doped TiO_2 nanoparticles and MMT/TiO_2 nanocomposite photocatalysts are synthesized using sol-gel single step method to investigate the route of CO_2 photoreduction to hydrocarbon fuels. Nanocatalysts characterization are conducted using XRD, SEM, FESEM, HRTEM, FTIR, BET, XPS, DR UV-Visible and PL spectroscopy in order to investigate the phase and crystal structure, surface morphology and mesoporosity, surface area and pore size distribution, metals transitions states and optical properties of catalysts.

2) The role of nanocatalysts for photochemical reduction of CO_2 to hydrocarbon fuels was firstly explored using cell type photoreactor in which catalyst was distributed at the bottom. The light source used was a flash type 500 W Hg lamp with maximum UV-light irradiation intensity at 365 nm operated using high voltage power supply. The reducing agent employed was H_2O vapors for CO_2 photoreduction in gaseous phase.

3) In cell type photoreactor, operating parameters investigated were light intensity, metal loading, reaction temperature, feed ratios, and irradiation times. The reaction mechanism and kinetic model were developed to find out the key parameters in CO_2 reduction applications.

4) The microchannel monolith photoreactor of multiple cell density was used. The cell density employed were 100 and 400 CPSI while the microchannels length varied from 0.5 to 5 cm. The monolith microchannels provide higher interaction surface area between reactants and light irradiations to get higher reduction and yield rates. The nanocatalysts were coated over the microchannels using sol-gel dip coating method, while a reflector type 200 W Hg lamp was employed as source of light irradiations. The photochemical reduction of CO_2 to hydrocarbons was investigated using both H_2O vapours and H_2 as reducing agents. The performance comparison between photoreactors was conducted to investigate the efficiency of microchannel monolith photoreactor.

This research work will be helpful to cross over fundamental problems in photocatalysis employing micro structured photoreactor, while providing a new opportunity for future to overcome energy crises. The single step reduction of CO_2 to renewable fuels through photochemical F-T process with higher yield rates and selectivity are bottom-line benefits enables the process efficient. The microchannel monolith photoreactor and nanocatalysts are intended as an efficient photocatalysis systems for sustainable energy production to get low carbon economy derive for the sustainability of the society.

1.7 Research Outcomes

CO_2 was efficiency reduced to CO, CH_4 and higher hydrocarbons in the presence of different reducing agents and photocatalytic systems, thus confirming sustainable fuel productions. The monolith photoreactor performance was very encouraging while the efficiency found was much higher than ever reported in the literature. However, several outcomes of this research are described below:

- New microchannel monolith photoreactor system to investigate efficient CO_2 reduction to hydrocarbon fuels
- New methods and finding on the development of delaminated TiO_2 MMT for CO_2 reduction to fuels.
- New methods and findings on the synthesis of TiO_2 nanoparticles, Cu and Ni co-doped In-modified TiO_2 nanocatalyst
- New development in reaction rate and kinetic models
- Low-carbon economy shift through CO_2 recycling
- Alternative solutions to energy crises and global warming

1.8 Outline of Thesis

The research is targeted on the development of modified TiO_2 nanocatalysts suitable for efficient CO_2 reduction to hydrocarbon fuels. The microchannel monolith photoreactor was designed to improve photochemical F-T process for higher CO_2 reduction to value added chemicals and hydrocarbon fuels. The optimization of catalysts compositions, investigation of operating parameters, evaluation of reactor performances for higher yield rate, reaction mechanisms and kinetic rate parameters are discussed in different chapters. This thesis consists of eight 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 literature survey 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 characterizations of nanocatalysts and catalysts coated over the microchannels are deliberated in Chapter 4. The description about photocatalytic CO_2 reduction with H_2O vapors over In and MMT modified TiO_2 nanocatalysts using cell type photoreactor is presented in Chapter 5. Chapter 6 explores microchannel monolith photoreactor for photocatalytic CO_2 reduction with H_2O vapors over In and MMT modified TiO_2 nanocatalysts. Chapter 7 investigates the photocatalytic CO_2 reduction with H_2 as reducing agent over doped and co-doped TiO_2 catalysts and employing microchannel monolith photoreactor. Finally, Chapter 8 contains the overall conclusions of this study and recommendations for the future work.

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