PHOTOCATALYTIC REDUCTION OF CARBON DIOXIDE AND METHANE TO LIGHT HYDROCARBONS OVER NITROGEN DOPED TITANIUM DIOXIDE

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To my beloved father, mother and sister

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ABSTRACT

Concerns of fossil fuel reserves depletion and environmental pollution problems have led to increased demand for alternative fuels. Therefore, methods for converting natural gas into useful fuels were considered. The main objective of this study is to develop pathways for photolysis reduction of carbon dioxide and methane. Initially nanocatalyst were investigated using cell type photoreactor with C_2H_6 and C_3H_8 as main products during CO_2 reduction with CH_4 over nitrogen (N) /TiO_2 nanocatalyst. The yield of C_2H_6 over TiO_2 was 35 µmole g^{-1} $catal^{-1}$ enhanced to 166 µmole g^{-1} $catal^{-1}$ using 15% N doped TiO_2. Besides, the effects of parameters such as, CH_4/CO_2 feed ratio, reaction temperature and light irradiation time on yield of reduction of CO_2 was studied. Finally, the central composite design (CCD) was employed to find individual and interactive effects of the mentioned parameter on yields of C_2H_6 was studied. The predicted values of the yield of C_2H_6 were found to be in good agreement with experimental values (R^2= 0.97), which indicate the suitability of the CCD model.

ABSTRAK

Kebimbangan terhadap pengurangan rizab bahan api fosil dan masalah pencemaran alam sekitar telah membawa kepada peningkatan permintaan bagi bahan api alternatif. Oleh itu, kaedah menukarkan gas asli kepada bahan api berguna dipilih. Objektif utama kajian ini adalah untuk membangunkan laluan bagi pengurangan photolysis terhadap karbon dioksida dan metana. Pada permulaan, naocatalyst dikaji dengan menggunakan sel photoreactor dengan C_2H_6 dan C_3H_8 sebagai produk utama bagi pengurangan CO_2 bersama dengan CH_4 terhadap nanocatalyst nitrogen (N)/TiO. Kadar hasil bagi C_2H_6 C terhadap TiO_2 adalah 35 µmole g^{-1} $catal^{-1}$, dipertingkatkan kepada 166 $catal^{-1}$ g $µmole^{-1}$ menggunakan 15% N disaluti oleh TiO_2. Selain itu, kesan parameter seperti, nisbah suapan CH_4/CO_2, suhu tindak balas dan sinaran cahaya masa bagi hasil pengurangan CO_2 telah dikaji. Akhirnya, pusat rekabentuk komposit (CCD) digunakan untuk mencari kesan parameter yang dirujuk di atas secara individu dan interaktif bagi pengahsilan C_2H_6 telah dikaji. Nilai ramalan bagi penghasilan C_2H_6 menunjukkan keputusan yang baik dengan nilai eksperimen (R^2= 0.97), sekaligus menunjukkan kesesuaian penggunaan CCD model.

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LIST OF SYMPOLS

α - Intensity factor
β - Full width at half maximum
c - Speed of light
D - Average Particle size
e^- - Electron
E_{gap} - Gap energy
E_{bg} - Energy band gap
E - Activation energy
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_l - Reduction rate constant
Kj - Kilo Joule
k_2 - Oxidation rate constant
M - Metal
nm - Nanometer
N - Nitrogen
S - Active Site
$TiO2$ - Titanium dioxide
Ti - Titanium

Hg	-	mercury
V	-	Volt
W	-	Watt
λ	-	Wavelength

LIST OF ABBREVIATIONS

C	-	Concentration
CVD	-	Chemical vapor deposition
CSD	-	Chemical solvent deposition
GHG	-	Greenhouse gas
NHE	-	Normal Hydrogen Electrode
BET	-	Braunaure-Element-Teller
FTIR	-	Fourier Transform Infrared Spectroscopy
FESEM	-	Field Emission Scanning Electron Microscopy
HRTEM	-	High Resolution Transmission Electron Microscopy
SEM	-	Scanning Electron Microscopy
XRD	-	X-ray Diffraction
UV-Vis	-	Ultraviolent-Visible
VLR	-	Visible light responses
CCD	-	Central composite design
RSM	-	Response surface methodology
ANOVA	-	Analysis of variance

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CHAPTER 1

INTRODUCTION

1.1 Background of Research

Currently, much of the energy used is produced by fossil fuels. Unfortunately, deposits of fossil fuels reducing too fast owing to industrial developments and other energy requirement. The use of fossil fuels increases air pollution problem, as well as the effect of climate change and global warming. To prevent environmental catastrophe and depleting of the fossil fuel resources a generating notice has developed to replace non-fossil and environmentally friendly energy sources.

Methane is introduced as a greenhouse gas. In the form of natural gas, capacious volumes of methane are extensively accessible in nature. The great supply of this gas cusses it attractive raw substance for fuels and chemical synthesis. Based on the newest reports presently, proven world natural gas supplies are approximate to 6609 trillion cubic feet or about 187 trillion cubic (Figure 1.1) [1]. Because of a large quantity of natural gas are predominantly found in far-off areas (Table 1), Therefore gas exploitation and transportation is so expensive. This problem raises the demand for converting gas into liquids on-site [2-6]. Pipeline and tanker can be transported natural gas liquefied by refrigeration. Though, compressed gas to 80 atm is necessary for transfer gas via these pipelines also for distant market it is possible sometimes pipeline not be accessed [2, 4].

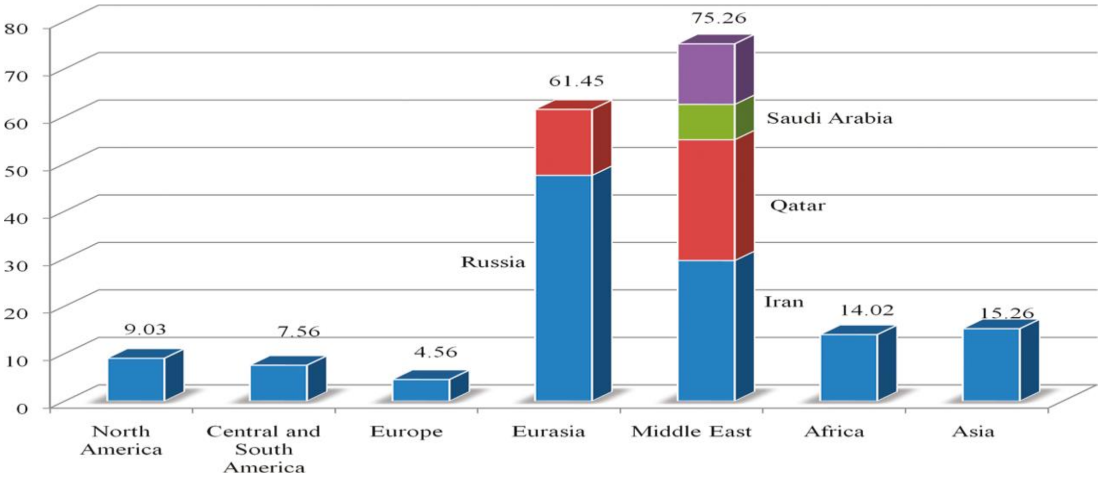

Figure 1.1 World proven reserves of natural gas (10^{12} m^3) [1]

Table 1.1: Location of Natural Gas Reserves (10^{12} m^3) [1]

Type of location	1960	1970	1990
Easy onshore zones	15.8	27.5	60
offshore	1.6	4.5	25
Arctic and Siberia	0.1	7.5	42
Other difficult onshore		0.5	2
world	17.5	40.0	129
share of difficult zones (%)	10	31	53

The most common method for converting methane into higher oxygenates and hydrocarbons are not economical because these methods need to specific conditions like high pressure, temperature and particular catalyst. Thus Scientists encourage finding another method for conversion of carbon dioxide and methane to valuable compounds. Methanol is a favorable compound between the products of methane oxidation because it saves so much of energy of methane. In addition, carry out transportation and storage needs. Methanol can be transformed into useful product and oxygenated fuels or may be used straightly as fuel in industry [7].

Heterogeneous photocatalysis is a developing technology also significant for organic synthesis moreover for water and air cleaning. Scientists have worked in this field for years. Heterogeneous photocatalysis has developed as a specific technique for many usages, with the synthesis processing and characterization of new wide band gap and narrow band gap semiconductor materials. In photocatalysis the selectivity of light source is a very significant [7]. The main goal of this study is the reduction of CO_2 and CH_4 to higher hydrocarbon with mild condition using semiconductor photocatalyst and light.

1.2 Problem Statement of Research

Concerns of fossil fuel reserves depletion and environmental pollution problems have led to increased demand for alternative fuels. Therefore, methods for converting natural gas into useful fuels were considered. One of these methods which is our interest is the photocatalyst reduction of carbon dioxide and methane to hydrocarbons. However, breaking stable CO_2 molecule through thermal reforming requires higher energy. The basic problem in front in this study are explained as below:

i. CO_2 reduction with CH_4 to hydrocarbon fuels is a two-step process which demanded higher energy. However, on industrial, input energy provided by composition of CH_4 causes more greenhouse gases effect, it is also uneconomical as well as unfriendly process to the environment.
ii. CO_2 photocatalysts reduction to fuels have many advantages, yet photocatalysts and reactors under investigations have lower efficiency due to incompetent yield and repartition of light irradiation over the catalyst surface.
iii. TiO_2 semiconductor is widely studied due to great availability, cheap and many other benefits. It's also has lower light adsorption performance, obvious photoactivity and selectivity for photocatalytic CO_2 reduction to fuels

1.3 Objectives of Research

The following are the objectives of this research:

i. To prepare, characterize and test the nitrogen modified TiO_2 nanocatalysts (N-TiO_2) for CO_2 reduction to fuels.
ii. To investigate the effectiveness of various operating parameters on the photoactivity of nanocatalysts in terms of yield
iii. To study central composite design matrix and response surface methodology to design the experiments and evaluate the interactive effects of the three most important operating variables.

1.4 Scope of Research

The following are the scope of this research:

i. TiO_2 nanoparticle, N/TiO_2 nanoparticle are prepared using sol-gel single step method to study the path of CO_2 photoreduction to hydrocarbon fuels. Nanaocatalysts were characterized using X-ray Diffraction (XRD), Field Emission Scanning Electron Microscopy (FESEM), High Resolution Electron Microscopy (HRTEM), Fourier Transfer infrared spectroscopy (FTIR), Brunauer-Emmerr-Teller (BET) Surface Area and UV-Visible Spectrophotometer
ii. Operating parameter such as light intensity, N loading, reaction temperature, feed ratio and irradiation time were investigated in cell photoreactor.
iii. Design expert software was used to study the response surface methodology (RSM) and the effect of three most elements on yield of hydrocarbon and find optimum condition for CO_2 and CH_4 photoreduction.

1.5 Research Hypothesis

Developing photocatalytic system for efficiently converting CO_2 molecule to hydrocarbon fuels is the main focus of this study. Nanosized catalysts and good designed photoreactor could help to achieve this aim. Hence, most hypotheses of the research described as follows:

i. The single step CO_2 reduction to hydrocarbon fuels is possible through photochemical process. Nanostructured semiconductor catalyst is organized to be designed in such a way which could enable to overcome obstacles by providing higher light absorption capacity, controlling of surface reaction for increasing selectivity and steps ahead toward higher CO_2 reduction. For this aim TiO_2 nanoparticles doped with structured material.

ii. Improved photocativity of CO_2 reduction to hydrocarbon fuels will be possible by modified Nonmetal ions to titanium structure. Nitrogen was used because of their determine features and selective production of hydrocarbon fuels.

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