***In the Name of Being Supreme the Compassionate the Merciful***

# *Acknowledgment*

First, I would like to thank God for countless blessings all through my life. Without his assistance, no work was possible. There is no doubt that no one can complete his dissertation without a good deal of help along the way. This author is certainly no exception. High on the list of those to thank is my family. I wish to express my gratitude to my dear family for their encouragement, moral support and patience during this work.

Also the special thank is my advisor, Dr. Shahram Sharifnia the major director of the thesis, for his supervision, excellent constructive guidance and support thorough this research.

Deep acknowledgments are offered to Dr. Nahid Shahabadi, for her supervision and support thorough this research.

I would to gratitude to Dr. S.N. Hosseini in department of environmental engineering, Islamic Azad University, Hamedan branch, for all his cooperation.

I am obligated to thank Dr. M. Irandoust who has made helpful suggestion regarding to do this dissertation.

I appreciate all my friends in Catalyst Research Center and the other research lab for the troubles.

Razi University

**Faculty of Chemistry**
**Department of Applied Chemistry**

## M. Sc. Thesis in Applied Chemistry

# Photocatalytic conversion of greenhouse gases ($CO_2$ and $CH_4$) to high value products over $TiO_2$ nano particles/mesh catalyst

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**July 2010**

**Abstract**

Carbon dioxide and methane respectively play a significant role as the main contributors of the greenhouse gases; and their effect on climate has recently received much attention. Therefore, effective utilization of carbon dioxide and methane and conversion of them to high–value products is one of the important topics to be developed nowadays. On the other hand, it is not easy to convert these stable molecules to other useful chemicals at mild reaction conditions.

In the present study, we were studied the conversion of carbon dioxide and methane together to produce useful chemicals at low temperature with a photocatalytic reaction system using nano $TiO_2$ particles coated on stainless steel mesh. The experiments were done under UV irradiation in an appropriate gas-phase batch reactor. GC and GC-MS analysis was used for measuring the concentration of components and identification produced compounds during reaction. In the present work, the influence of six parameters; mesh size of stainless steel mesh, $TiO_2$/mesh dosage, calcination temperature, reactor initial pressure, $CO_2$:$CH_4$:He ratios in the feed and UV light intensity, on the efficiency of the process was investigated. One variable at a time method was applied to design of experiments. On analysis of the results from the experimental studies, optimum experimental conditions were found. Under the optimum experimental conditions, the conversion was 27.9% for $CO_2$ and 33.4% for $CH_4$ with the selectivity of toluene of 66.92%. A high-efficient photoreactor is the first step toward a commercial-scale application to produce chemicals.

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# Chapter One

## Greenhouse Effect and Global Warming

## 1.1. Introduction

According to the Intergovernmental Panel on Climate Change (IPCC, 2005) most of the warming observed over the past 50 years is attributable to human activities. Human influences are expected to continue to change the atmospheric composition throughout the 21st century. Greenhouse gases (GHGs) such as $CO_2$, $CH_4$, $N_2O$, HFCs, PFCs, and $SF_6$ are the primary cause of global warming. The greenhouse gas representing the largest contribution of human activities is carbon dioxide, emissions from fossil fuel combustion [1]. The global concentration of $CO_2$ in the atmosphere is increasing [1] and this accelerates the greenhouse effect. The Kyoto Protocol of 1997 on greenhouse gases (GHGs) emissions has evidenced the necessity to control the emissions not only of $CO_2$, but also of $CH_4$ and $N_2O$ which contributed 7 and 9%, respectively, to the Global Warming Potential (GWP) (with reference to the $CO_2$ equivalent emissions, using GWP values for a 100-year time horizon) [2].

Many factors determine the climate system and for many of them the level of understanding is poor. However, the precise correlation observed over the last 1000 years between change in the earth’s temperature and the atmospheric concentration of greenhouse gases indicates a clear direct relationship. The projected climate change results in an estimated increase in the earth’s temperature of 1–6 $^{\circ}$C, depending on the models. The higher temperatures would be reflected in an increase in sea level, for example, of 0.1-0.9 m which may cause the flooding of large regions in the world [2].

## 1.2. Greenhouse effect

The "greenhouse effect" is the heating of the Earth due to the presence of greenhouse gases. It is named this way because of a similar effect produced by the glass panes of a greenhouse. Shorter-wavelength solar radiation from the sun passes through Earth's atmosphere and then is absorbed by the surface of the Earth, causing it to warm. Part of the absorbed energy is then reradiated back to the atmosphere as long wave infrared radiation. Little of this long wave radiation escapes back into space; the radiation cannot pass through the greenhouse gases in the atmosphere. The greenhouse gases selectively transmit the infrared waves, trapping some and allowing some to pass through into space. The greenhouse gases absorb these waves and reemits the waves downward, causing the lower atmosphere to warm. This process occurs naturally and has kept the Earth's temperature about 59 degrees Fahrenheit warmer than it would otherwise be. Current life on Earth could not be sustained without the natural greenhouse effect.

### 1.2.1. Advantages of greenhouse effect

The presence of carbon dioxide and other gases in the atmosphere produces the greenhouse effect, which keeps the atmosphere warm. The warm atmosphere is very essential for the survival of life on earth in the following ways:

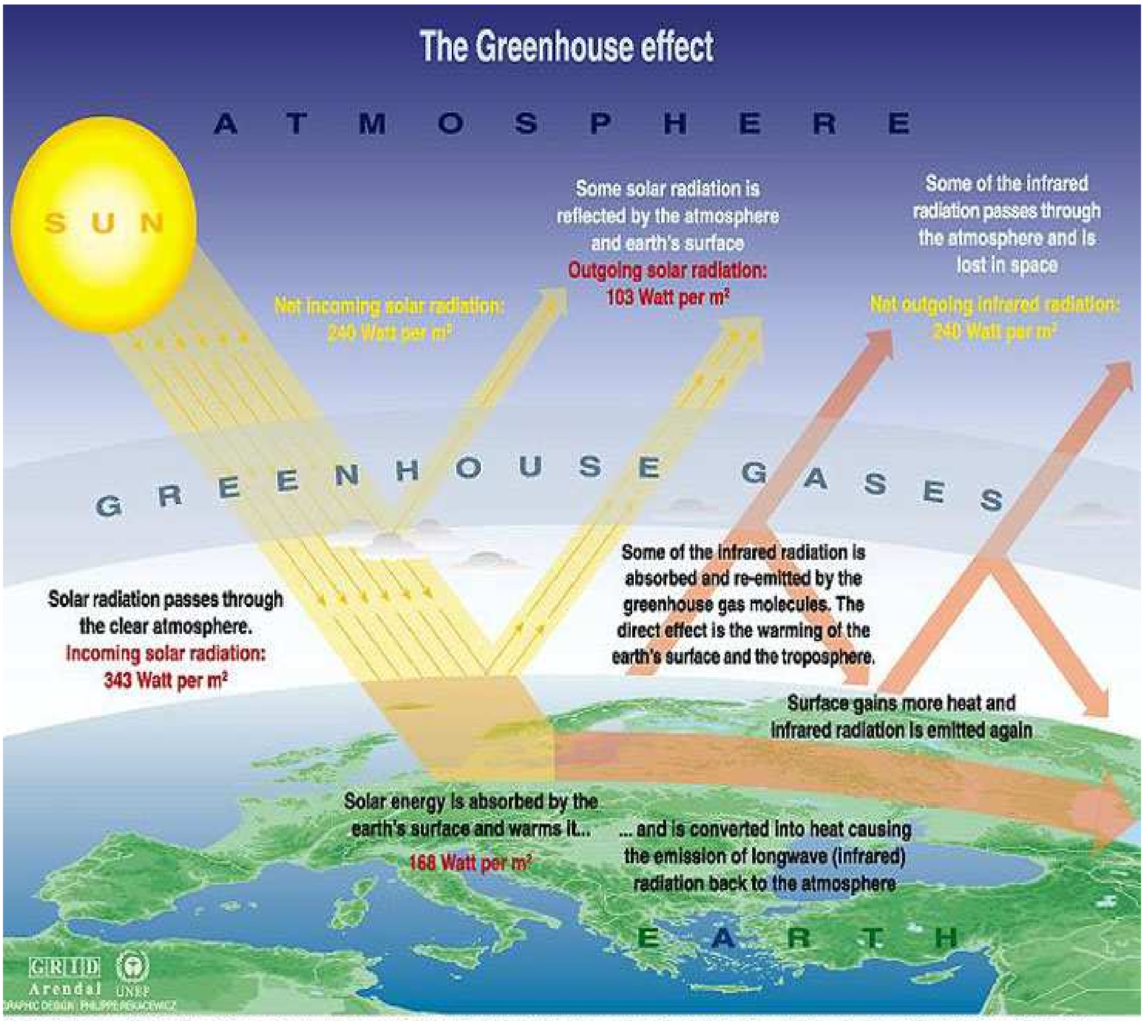
- Precipitation of water, formation of clouds, rainfall etc. Life in the biosphere depends on these resources.

- The warm atmosphere helps in the growth of vegetation and forest etc. These are sources of food, shelter etc.
- This effect helps in rapid bio-degradation of dead plants and animals.

### 1.2.2. Mechanism of greenhouse effect

The Greenhouse Effect is a natural process that warms the Earth, and, in fact, is quite necessary for our survival. Gases in the atmosphere, like water vapor (clouds), carbon dioxide ($CO_2$), methane ($CH_4$), and nitrous oxide ($N_2O$) act as a natural blanket by preventing the sun's heat energy from radiating back into space, much like a greenhouse traps the sun's energy to warm someone's plants even in the middle of winter. The natural greenhouse effect helps warm the Earth's surface by as much as 33$^o$C, and without it, our planet would be too cold for humans to survive.

The Fig 1-1, illustrates the basic processes behind the greenhouse effect. As the sun's energy hits the Earth, some of that energy is absorbed by the earth's crust and by the oceans, warming the planet. The rest of the energy is radiated back toward space as infrared energy. While some of this infrared energy does radiate back into space, some portion is absorbed and re-emitted by water vapor and other greenhouse gases in the atmosphere. This absorbed energy helps to warm the planet's surface and atmosphere just like a greenhouse.




Sources: Okanagan university college in Canada, Department of geography, University of Oxford, school of geography; United States Environmental Protection Agency (EPA), Washington; Climate change 1995, The science of climate change, contribution of working group 1 to the second assessment report of the intergovernmental panel on climate change, UNEP and WMO, Cambridge university press, 1996.

**Fig. 1-1. The schematic of mechanism of greenhouse effect [3]**

### 1.2.3. Factors affecting the greenhouse effect

There are three main factors that directly influence the greenhouse effect: (1) the total energy influx from the sun, which depends on the earth's distance from the sun and on solar activity, (2) the chemical composition of the atmosphere (what gases are present and in what concentrations), and (3) albedo, the ability of the earth's surface to reflect light back into space. The only factor that has changed significantly in the last 100 years is the chemical composition of the atmosphere and that is because of human activity.

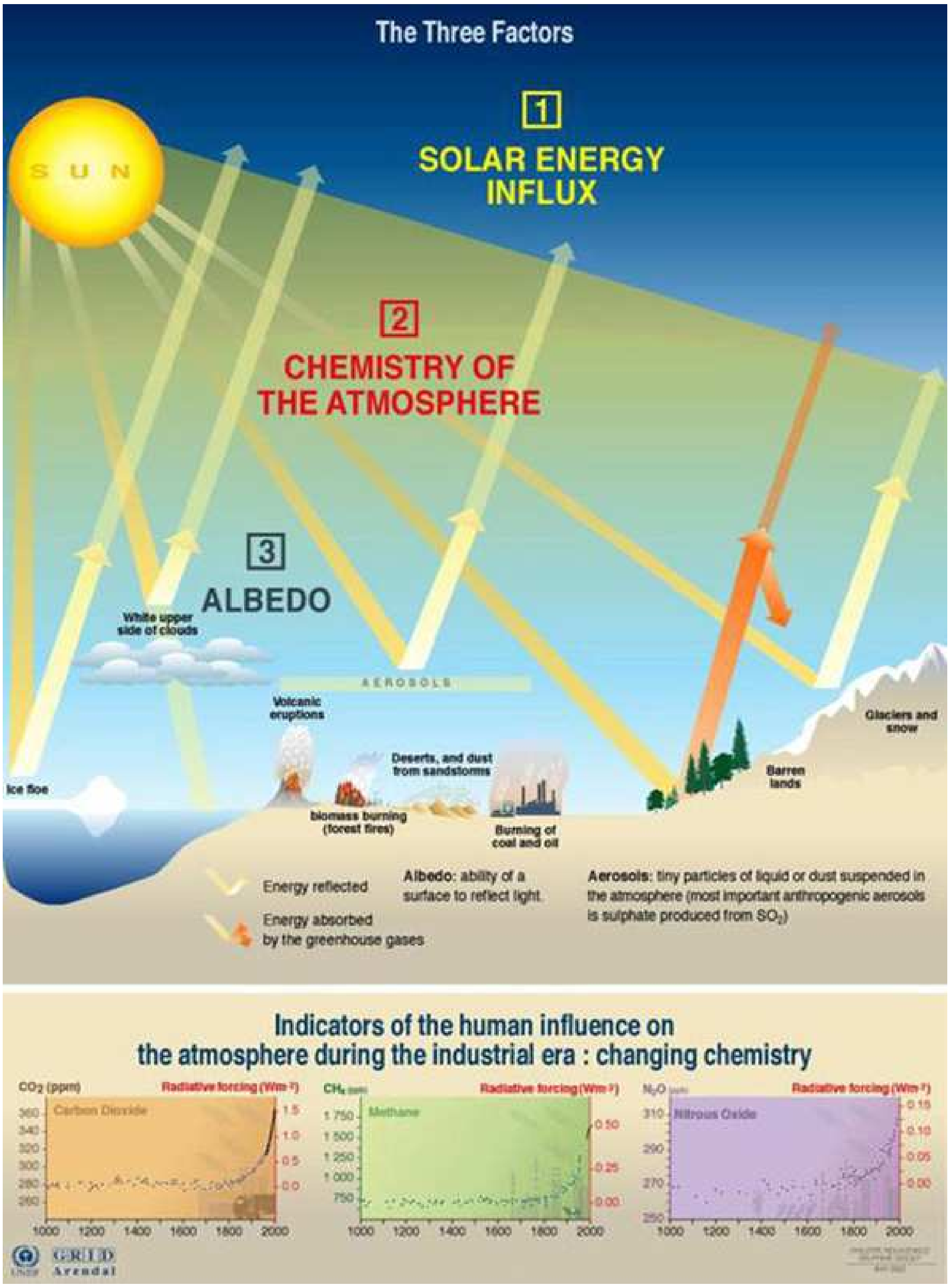



**Fig. 1-2. The schematic of three factors affecting the greenhouse effect [4]**

## 1.3. Contributors to greenhouse effect

Greenhouse gases are gases in an atmosphere that absorb and emit radiation within the thermal infrared range. This process is the fundamental cause of the greenhouse effect**.** In our solar system, the atmospheres of Venus, Mars and Titan also contain gases that cause greenhouse effects**.**

Many greenhouse gases occur naturally in the atmosphere, such as carbon dioxide, methane, water vapor, and nitrous oxide, while others are synthetic. Those that are man-made include the chlorofluorocarbons (CFCs), hydrofluorocarbons (HFCs) and Perfluorocarbons (PFCs), as well as sulfur hexafluoride ($SF_6$). The Table 1-1, lists some of the main greenhouse gases and their concentrations in pre-industrial times and in 1994; atmospheric lifetimes; anthropogenic sources; and Global Warming Potential (GWP). Although some of the gases listed have a larger global warming potential, carbon dioxide ($CO_2$) is the most important greenhouse gas because of its abundance in the atmosphere. Today, atmospheric $CO_2$ concentrations measure over 380 parts per million (ppm), mostly due to fossil fuel use in the energy and transportation sectors.

**Table. 1-1. The main greenhouse gases [5]**

The main greenhouse gases

| Greenhouse gases | Chemical formula | Pre-industrial concentration | Concentration in 1994 | Atmospheric lifetime (years)*** | Anthropogenic sources | Global warming potential (GWP)* |
|---|---|---|---|---|---|---|
| Carbon-dioxide | $CO_2$ | 278 000 ppbv | 358 000 ppbv | Variable | Fossil fuel combustion<br>Land use conversion<br>Cement production | 1 |
| Methane | $CH_4$ | 700 ppbv | 1721 ppbv | 12,2 +/- 3 | Fossil fuels<br>Rice paddies<br>Waste dumps<br>Livestock | 21 ** |
| Nitrous oxide | $N_2O$ | 275 ppbv | 311 ppbv | 120 | Fertilizer<br>industrial processes<br>combustion | 310 |
| CFC-12 | $CCl_2F_2$ | 0 | 0,503 ppbv | 102 | Liquid coolants<br>Foams | 6200-7100 **** |
| HCFC-22 | $CHClF_2$ | 0 | 0,105 ppbv | 12,1 | Liquid coolants | 1300-1400 **** |
| Perfluoromethane | $CF_4$ | 0 | 0,070 ppbv | 50 000 | Production of aluminium | 6 500 |
| Sulphur hexa-fluoride | $SF_6$ | 0 | 0,032 ppbv | 3 200 | Dielectric fluid | 23 900 |

Note : pptv= 1 part per trillion by volume; ppbv= 1 part per billion by volume, ppmv= 1 part per million by volume

* GWP for 100 year time horizon. ** Includes indirect effects of tropospheric ozone production and stratospheric water vapour production. *** On page 15 of the IPCC SAR. No single lifetime for $CO_2$ can be defined because of the different rates of uptake by different sink processes. **** Net global warming potential (i.e., including the indirect effect due to ozone depletion).

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Some greenhouse gases are not often listed. For example, nitrogen trifluoride has a high global warming potential (GWP) but is only present in very small quantities.

The global warming potential (GWP) depends on both the efficiency of the molecule as a greenhouse gas and its atmospheric lifetime. GWP is measured relative to the same mass of $CO_2$ and evaluated for a specific timescale. Thus, if a molecule has a high GWP on a short time scale (say 20 years) but has only a short lifetime, it will have a large GWP on a 20 year scale but a small one on a 100 year scale. Conversely, if a molecule has a longer atmospheric lifetime than $CO_2$ its GWP will increase with time.

The major non-gas contributors to the Earth's greenhouse effect, clouds, also absorb and emit infrared radiation and thus have an effect on radiative properties of the greenhouse gases**.** Water vapor is the most abundant gas and plays the lead role in warming earth causing 36-70% of 'greenhouse effect'. Carbon dioxide contributes 9-26%, methane 4-9% while ozone's share is about 3-7%.

Greenhouse gases, mainly water vapor, are essential to helping determine the temperature of the Earth; without them this planet would likely be so cold as to be uninhabitable. Although many factors such as the sun and the water cycle are responsible for the Earth's weather and energy balance, if all else was held equal and stable, the planet's average temperature should be considerably lower without greenhouse gases.

Although contributing too many other physical and chemical reactions, the major atmospheric constituents, nitrogen ($N_2$), oxygen ($O_2$), and argon (Ar), are not greenhouse gases. This is because homonuclear diatomic molecules such as $N_2$ and $O_2$ and monoatomic molecules such as Ar have no net change in their dipole moment when they vibrate and hence are almost totally unaffected by infrared light. Although heteronuclear diatomics such as carbon monoxide (CO) or hydrogen chloride (HCl) absorb IR, these molecules are short-lived in the atmosphere owing to their reactivity and solubility. As a consequence they do not contribute significantly to the greenhouse effect and are not often included when discussing greenhouse gases**.**

### 1.3.1. The properties of greenhouse gases and their sources

#### 1.3.1.1. Carbon dioxide ($CO_2$)

Carbon dioxide ($CO_2$) is a colorless, odorless, non-flammable gas and is the most prominent Greenhouse gas in Earth's atmosphere. $CO_2$ in our atmosphere acts like a light filter, allowing certain wavelengths (those of visible light) to pass through but absorbing others (especially infra-red light). An important balance exists between concentration of carbon dioxide and life: With less carbon dioxide, more heat would be lost and Earth would be frozen, like mars. With more, more heat would be trapped and our world would be as hot as Venus, at $800^{o}C$, with lakes of molten lead**.**

$CO_2$ is recycled through the atmosphere by the process photosynthesis, which makes human life possible. Photosynthesis is the process of green plants and other organisms transforming light energy into chemical energy. Light Energy is trapped and used to convert carbon dioxide, water, and other minerals into oxygen and energy rich organic compounds. Carbon dioxide is emitted into the air as humans exhale, burn fossil fuels for energy, and deforests the planet. Every year humans add over 30 billion tons of carbon dioxide in the atmosphere by these processes, and it is up thirty percent since 1750.

Burning of petrol alone releases a huge quantity of carbon dioxide into the atmosphere for every 1000 litre petrol consumer, automobile exhaust release nearly 320 kg of carbon dioxide and 2-8 kg of nitrogen oxide, besides various other air pollutants into atmosphere. $CO_2$ concentration have increased from 280 ppm (parts per million) at the down of the industrial revolution to around 370 ppm today. The destruction of forests and the degradation of soils add estimated 5-9 billion tones of $CO_2$ to the atmosphere. Atmospheric concentrations of carbon dioxide have been increasing at a rate of about 0.5 percent per year, and are now about 30 percent above pre-industrial levels**.**