A Review on Photocatalytic Conversion of CO_2

Preeti Pandey
Kalinga University
Email id-preeti.pandey@kalingauniversity.ac.in

Abstract

Due to the huge potential to supply an alternative clean fuel and tackle the problems associated with global warming, photo catalytic conversion of CO_2 to either a renewable fuel or valuable compounds using solar energy has gotten a lot of interest. The creation of innovative photo catalysts for CO_2 photo reduction has been explored, as the current state of photo catalytic CO_2 conversion over metal oxides is examined in this research well as a quick summary of the essential features of artificial photosynthesis. Several critical criteria for high-efficiency CO_2 photo reduction have also been highlighted, as well as the recent development of photo catalytic reactor design for this artificial photosynthesis. Global warming is regarded as one of the most pressing environmental issues confronting humanity. Because carbon dioxide (CO_2) is one of the most common greenhouse gases in the atmosphere, it plays a significant role in global climate change. CO_2 contributes to the rise in global temperature by absorbing and re-emitting infrared radiation. According to the International Panel on Climate Change (IPCC), atmospheric CO_2 levels could reach 590 ppm by 2100, with a 1.9°C rise in global mean temperature. The greenhouse effect will have a global and significant impact in a variety of ways, including ice melting at the poles, rapidly rising sea levels, and increased precipitation around the world.

Keywords: *photo catalytic, nanocomposites, carbon dioxide,*

1. Introduction

Carbon dioxide (CO_2), one of the potential greenhouse gas, is a colourless, odourless and test less gas. It is mainly formed during animal respiration, organic decomposition and combustion of fossil fuels. With the speedy development of society economy, the demand for fossil fuels continuously rises. Currently the worldwide energy expenditure is about 1.5×1010 kW, and it is assumed that it may rich to 2.3×1010 kW by 2050 [1]. The immoderate use of fossil fuels, not only create energy crises, but also release huge amount of greenhouse gas carbon dioxide into the atmosphere. The excessive concentration of carbon dioxide in the atmosphere makes global warming to become a major concern in the recent years [2]. Global warming is nothing but the gradual rise in global temperature, which brought a series of problems, including melting of ice at the earths pole, sea water level rising and irregular weather pattern [3]. Therefore, it is very crucial to discover a promising solution to mitigate such issue [4]. The main methods for the mitigation of CO_2 include the biological fixation of CO_2, the capture and storage of CO_2 and the chemical reduction and utilization of CO_2 [5,6]. However, it is not economically worth to capture and store carbon dioxide as the potential leakage of carbon dioxide is one of the mess. With the decrease in global flora coverage, the natural CO_2 fixation by the green plant also become not feasible. That's why during past few decades researchers are more focused on the discovery of various methods for the artificial reduction of CO_2 [7], which include bio-electrochemical, electrochemical, thermochemical and photo catalytic method. Electrochemical reduction of carbon dioxide is carried out in solution, using an electrochemical cell as an energy source, to reduce CO_2 at the cathode. However, this technology requires additional electricity, which increases the overall cost of this process. Also, the evolution of hydrogen in electrochemical reduction of CO_2 appreciably affect the purity of the product. Bio-electrochemical reduction of carbon dioxide, which utilizes the microorganism as catalyst is a novel method for CO_2 reduction. However, as the microorganisms require living environment for their activity, the bio electrochemical reduction of carbon dioxide only achieved in suitable experimental condition and also at extremely slow rate, which restrict its development in practical purpose. The thermochemical method for the CO_2 reduction requires extremely high temperature, which increase the energy consumption as well as it requires only such catalyst which maintain their catalytic activity at higher temperature. Compared with all the above methods, the photo catalytic conversion of CO_2, using sustainable solar energy is more energy efficient, more economically friendly and more promising, as this process is non-polluting and does not require any extra energy [8].

There is a great importance on the solar energy driven reactions. Solar energy can be used to drive various spontaneous and non-spontaneous reactions. The process is known as Photocatalysis. The photo catalytic conversion of carbon dioxide not only mitigate the global greenhouse effect, but also solves the growing energy crises, by producing useful fuels with higher energy, such as methane (CH_4), methanol (CH_3OH), formic acid (HCOOH), acetaldehyde (HCHO), carbon monoxide (CO) etc. As CO_2 is a stable compound, it is very difficult to make it react with other substances. The C=O bond enthalpy in CO_2 is 805 kJ mol^{-1} [9], which is much elevated than that of C-O (327 kJ mol-

1), C-C (336 kJ mol^{-1}) and C-H (411 kJ mol^{-1}), respectively [10]. For the effective reduction of CO_2, it is very important to overcome the kinetic inertia as well as the thermodynamic energy barrier. Various semiconductor based photocatalyst have been discovered for the effective photoreduction of carbon dioxide in to different liquid and gaseous products. The catalysts used in photoreduction of CO_2 are TiO_2 [11], MgO [12], Ga_2O_3 [13], g-C_3N_4 [14], [Re (bpy) $(CO)_3\{P(OEt)_3\}]^+$ [15] etc. However, among them TiO2 is the most frequently used, because of its high stability, law cost and non-toxicity. But TiO2 has very low photocatalytic activity. So, researchers are more focused on developing many alternative catalyst with higher photocatalytic activity of CO_2 reduction, such as N-TiO_2-001/GR [16], Pt^{2+}-P0/TiO_2 [17], Pt- loaded g-C_3N_4 [18], graphene oxide-CdS [19] and dye/TiO_2/Re(I) [20]. In 1979, found that, a series of semiconductor possess electrical bias under 500W Xe or Hg lamp. Therefore, different products such CH_4, CH_3OH, CO, HCOOH, HCHO etc. are formed when different photocatalyst are employed in the photocatalytic CO_2 conversion [21]. In product selectivity of the CO_2 reduction, the photocatalyst play a very crucial role. Many researches have been conducted on the formation of a single product under visible light in order to reduce the separation cost of the products. However, there is a connection of the product selectivity with the reaction system and routes, which makes it very complicated. Thus not only the catalyst exert a significant effect on the product selectivity, but also the reaction conditions such as pH, reaction system, temperature, pressure and light intensity have a great influence on the product selectivity. This review mainly highlights the advancement in the field of photo catalytic reduction of carbon dioxide, in the view of choosing suitable photo catalyst to form a selective desirable product.

2. Photocatalytic Reduction of Carbon Dioxide

The photo catalytic reduction of CO_2 mimics the process of photosynthesis for green plants, in which the photo catalysts, playing the role of green plants, converts carbon dioxide to valuable chemicals using visible or ultra violet light. The principle behind the photo catalytic conversion of CO_2 is illustrated in figure 1.

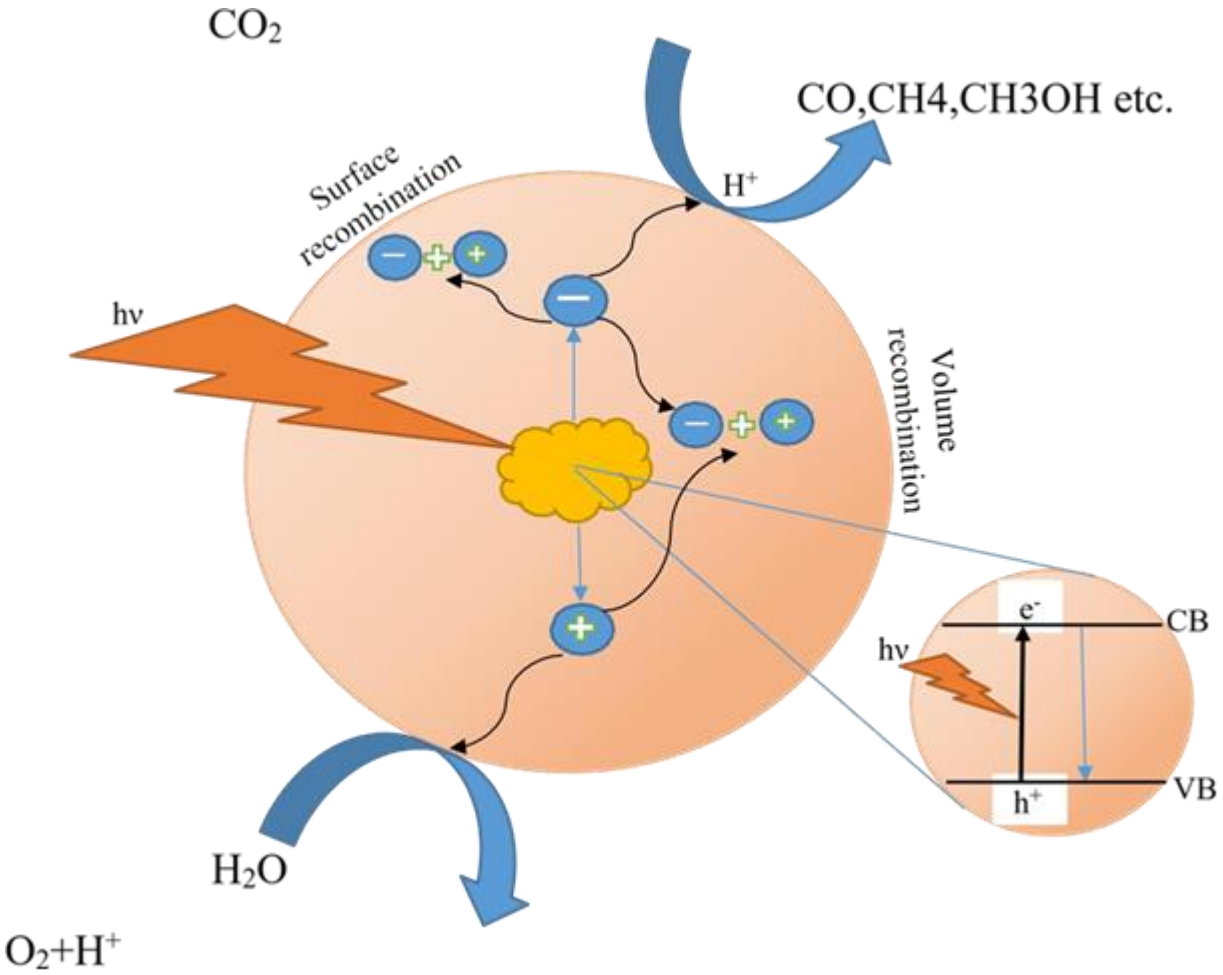

Fig. 1 Schematic diagram of photo catalytic CO_2 reduction

Generally, the overall reaction can be categorized in to four steps: Firstly the activation of the photo catalyst (mainly a semiconductor) takes place by using UV or Visible light from the sun or else by using an illuminated light source. Eventually, the electrons in the valence band (VB) jumps in to the conduction band (CB) of the semiconductor, leading to the formation of hole in the valence band. In this way the electron (e-) and the positive whole (h+) pair is photogenerated, which functions as the reductant and oxidant for reducing and oxidizing the products respectively. Thirdly the separation of electron-hole pair takes place and they transfer to the surface of catalyst. Finally the reduction of CO_2 occurs by utilizing the negative electrons and forms the corresponding reduced products such as CH_4, CH_3OH, CO, HCHO, HCOOH, and other hydrocarbons [22]. The following criteria are generally important for an effective system, required for the photo catalytic reduction of CO_2:

a) The photo-generated whole present on the valence band (VB) of the semiconductor should possess more positive redox potential than that of the redox potential of O_2/H_2O.

b) The photo-generated electrons present on the conduction band (CB) of the semiconductor should possess more negative redox potential than that of the redox potential of CO2 to the formed reduced product (e.g. CH_3OH/CO_2).

c) CO_2 or CO_2^- should be effectively absorbed on the surface of the photo catalyst.

d) The photo catalyst should be highly stable [30,31].

The photo catalytic reduction of CO_2 is mainly carried out in liquid and gas phase system. It has been found that in the gas phase system the major products are CO and CH4, whereas the major products in the liquid phase system are CH_3OH and HCOOH [23,24,25]. Moreover to enhance the photo catalytic activity and product. Many reports suggested that the modification of catalyst by using different metals could boost the reduction of CO_2 to CH_4, due to the increase in electron density on the surface of the catalyst after doping of the metal species [26, 27]. In theory, the formation of CO_2 is easier than that of the formation of CH_4 during the photoreduction of CO_2, as more electrons are required to generate CH_4. But the formation of CO could be arrested by the increasing electron density due to metal doping. The surface electron density can also be increased by constructing a heterojunction. Discovered that CuxO-TiO_2 had inherent p-n heterojunction, which enables excellent light absorption and fast charge separation to the catalysts, enhancing the selectivity for CH_4 generation (221.63 ppm g^{-1} h^{-1}). The CuO supported on the surface of $NaTaO_3$ photo catalyst could enhance the CO_2 absorption and the reaction activity of CO_2 reduction and it was found that the maximum yield of CH3OH was 335.93μmol g^{-1} h^{-1}. For the first time, in 1979, the photo reduction of CO_2 by using semiconductor based photocatalyst, such as TiO_2 and CdS was reported by fujishima and his co-workers. After a few years of research, a series of semiconductors such as CdS, TiO_2, Bi_2WO_6 and ZnO could serve for this purpose. Even so, most of these semiconductor based photocatalysts are photoactive in UV region and their synthesis methods are much more complicated and also uneconomical. Therefore to design and fabricate novel, effective and stable visible light driven (VLD) photocatalysts are the principal challenge in this field [28, 29,30].

Graphitic carbon nitride (g-C3N4) has evolved as a promising photocatalyst due to its excellent physical and chemical properties such as large surface area, high quantum efficiency, interfacial charge separation and transport and feasibility of modification either through the formation of composite or through the incorporation of profitable surface functionalities. It is also desirable and economically feasible alternative catalyst to use in the industries as it can be easily generated from cost effective and abundant raw materials by heating urea, melamine and other nitrogen rich compounds. Furthermore, it can be considered as environmentally friendly, as it does not contain any toxic metal ion and can be easily handled and disposed [31-33].

3. Product Selectivity

The photo catalytic reduction of CO_2 is series of proton-coupled two electron reaction. Based on the above discussion, a number of reduced products including CH_4, CH_3OH, CO, HCOOH, HCHO and CH_3CH_2OH are detected during this process. Some important catalyst and their product selectivity in photo catalytic reduction of CO_2 are listed in Table-1.

Table1. Main catalysts and their product selectivity in photocatalytic reduction of CO_2.

S.No	Catalyst	Main Products	Productivity	Enhanced Mechanism
1	$TiO_2.SiO_2$	CH_4	2.42 μmol·g⁻	Hydrophobicity modification composite photocatalyst
2	$Ti_{30}Si_{70}$MCM-41	CH_4	1.900 μmol·gcat^{-1}· L^{-1}	Sensitization of photosensitizer
3	Ag-MgO-TiO_2	CH_4	37.18 μmol·gcat^{-1}· L^{-1}	Strong local electric field of surfa Plasmon resonance to CO2 reduction
4	Cu_2ZnSnS_4-ZnO	CH_4	138.90 μmol·g^{-1}· L^{-1}	Inherent direct Z scheme heterojunctio
5	V0-rich Pt/Ga_2O_3	CO	21.0 μmol·h⁻	Efficient separation of photoelectro hole pairs on Pt/Ga_2O_3 led by Vo
6	$Bi_4O_5I_2$	CO	19.82 μmol·h^{-1}·g⁻	High lifetime of charge carrier a more electrons in the reaction
7	g-C_3N_4/Bi_2WO_6	CO	5.19 μmol·g^{-1}·h⁻	Band regulation and photosensitizatio p-n heterojunction between monom interfaces
8	Fe_2O_3/Cu_2O	CH_3OH	5.0 μmol·gcat^{-1}	Deposition of Cu nanoparticles
9	Cu/TiO_2	CH_3OH	1.8 μmol·cm^{-2}·h 1	Matching band between SnO2 NR a Fe2O3 Doping of Cu
10	SnO_2NRs/Fe_2O_3 NTs	CH_4/CH_3OH	2.05 mmol·L^{-1}·cm 2	Doping of S Loading of ZnPC
11	Ru(II)multinuclea complexes Ru	HCOOH	TOFHCOOH = 44.9 min^{-1}	[Ru(bpy)3]$^{2+}$supramolecular redo sensitizer

	Ru(CO			
12	Bi_2WO_6	CH_3OH/C_2H_5OH	47.O $\mu mol \cdot g^{-1} \cdot h^{-1}$	Photosensitizer unit with high effecti state Introduction of conducti polymers (polyaniline, polypyrrole, a polythiophene
13	GO-TiO_2 composi	CH_3OH/C_2H_5OH	144 $\mu mol \cdot g^{-1} \cdot h^{-}$	Synergistic interaction of interfa electron transfer between constitue phases
14	Bi_2S_3	$HC(O)OCH_3$	300.94 $\mu mol \cdot g^{-1}$	Special hierarchical structure, good a permeability and high light ability

3.1 Methane (CH4):

The photo catalytic reduction of CO_2 to CH_4 has been more fascinating due to the more stable physical and chemical properties of CH_4. Also it can occurred at a lower potential from the thermodynamic point of view. It was found that, for the photo catalytic conversion of CO_2 to CH_4, TiO_2 is the most frequently used photo catalyst. The catalysis process are usually carried out under UV light at the initial stage of photo catalytic CO_2 reduction. The reduction of CO_2 under UV350 in the TiO_2 suspension system was prominent with the 2-propanol as a hole scavengers. However the lower yield of CH_4 was observed in the oxygen saturated system due to the competition effect of O_2. It could be postulated that, the concentration of O_2 and the whole scavenger (2-propanol) greatly related to the CH_4 production, according to the mechanism [34].

$TiO_2 \xrightarrow{hv} e^- + h^+$

$h^+ + 2^-$ propanol $\longrightarrow$ organic radical + H^+

$CO_2 + 8H^+ + 8e^- \longrightarrow 2H_2O + CH_4$

$e^- + O_2 \longrightarrow O_2^-$

Firstly, CO_2 absorbs on the surface of TiO_2 and accept electrons from the conduction band of the semiconductor (TiO2) under UV radiation. CO_2, then react with the acidic hydrogen to produce a formyl (HC•O) group. Thereafter, the formyl group in acidic solution, get converted in to glyoxal (HOC•HCHO), which subsequently accepts the proton and electron to react with a sacrificial hole scavengers (such as formate, CH_3OH and HCHO) to form acetaldehyde. Finally, the formed acetaldehyde splits in to CO and CH_4 by releasing water through photolysis. From the above mechanism, it was found that, in the photocatalytic conversion CO_2 to CH_4, acidic protons play an important role. However, the pure TiO_2 catalyst exhibits poor ability for the photo-conversion of CO_2 and selectivity for the product due to the deficiency of itself property, such as the wide band gap and fast charge recombination. To solve these drawbacks, doping of the modifiers (Cu, Bi, Ni etc.), having higher catalytic activity and higher reduction potential, has been adopted. It was found the yield of CH_4 over Ni-doped TiO_2 nanoparticles noticeably increased as compared to that of

the pure TiO_2 catalyst, which should be attributed that the band gap of TiO_2 narrowed with the doping of Ni [35]. However, extreme Nickel doping can cause the blockage of pores in TiO_2, resulting in the reduction of the surface area of catalyst and the increase in e^--h^+ recombination. Recently, the doping of Bismuth (Bi) on to the photo catalyst has attracted most interest because Bi, as a semimetal element exhibit the ability of hole trapping and depletion in the absence of a sacrificial agent. Meanwhile the Bi- TiO_2 showed a better absorption capacity of CO_2 than that of pure TiO_2 [36]. Also the photo excitation rate of the composite catalyst was rapid as compared to that of pure TiO_2, thus the photo excited electrons were efficiently transferred to the CO_2 molecule. Simultaneously, water is captured by the holes in the valence band of Bi- TiO_2 and converted in to $^{\bullet}OH$ and $H^{\bullet}$, which undergo reaction with the CO radical, produced from the reduction of CO^{2-} over Bi-TiO_2 to generate CH_4. Pt-TiO_2 photo catalyst was mixed with CdSe quantum dots (2.5 and 6.0 nm) and was sensitized for the photo reduction of CO_2 (40 Pa) with moisture (400 Pa) under visible light [37]. It was found that, the photoexcitaion of electrons becomes more feasible under visible light by the incorporation of CdSe quantum dots in to the photocatalyst. With this system, the photoreduction of CO_2 to CH_4 (major) and CH_3OH (minor) was observed for 4-6 hours. However the catalyst was deactivated due to the oxidation of CdSe quantum dots.

3.2 Carbon Monoxide (CO):

On the basis of the reaction kinetics, it is more feasible to produce carbon monoxide from the photo reduction of carbon dioxide than that of CH_4 and CH_3OH. Because the production of the later requires more number of electrons. It was found that PbS quantum dots (4nm) mixed with Pt/TiO_2 photo catalyst were found to be effective for boosting the photo reduction of CO_2 to CO [30]. The photo excitation of electros between the band gaps of TiO_2, using visible light is very tough. However the photo excitation of electrons between the band gap of PbS quantum dots is feasible using visible light and the excited electrons could be introduced in to the conduction band of TiO_2, resulting in an enhancement in the photo catalytic efficiency of TiO_2. Also CdSe-Pt/TiO_2 was reported to produce carbon monoxide as major product from the photo reduction of CO_2, with a minor amount of CH_4. In recent years, Layered perovskite photo catalyst $A^{2+}La_4Ti_4O_{15}$ (A= Ca, Cs and Ba) were applied to the photo reduction of CO_2 for producing CO as a major product with a minor amount of formic acid. Silver nanoparticle (~10 nm) present on the edge sites of the layered $BaLa_4Ti_4O_{15}$, were found to be effective for the reduction of CO_2 to CO.

$CO_2 + 2H^+ + 2e^-$(Ag-nanoparticles) $CO + H_2O$ E0298K = -0.11V

The photo reduction of CO_2 in water can also achieved using $Na_2Ti_6O_{13}$ nanoparticles to form CO as major products with minor amount of H_2 and O_2 as by-products. The selectivity for CO can be increased up to 60% by carried out the photo catalytic reaction in the basic aqueous solution of Na_2CO_3. The photo catalytic reduction of CO_2 to CO can takes place over alkali and alkaline earth metal ion (Mg^{2+},Na^+,K^+) exchanged hydrogen titanate nanotubes (H-TNTs) in stimulated sunlight. Here, the efficiency of the photo-reduction of CO_2 to CO was mainly enhanced by the ion exchange between H+ and alkali or alkaline earth metal ions.

In addition, the photo catalytic reduction of CO_2 to CO can also be achieved by using environmentally friendly g-C3N4 photo catalyst. The photo catalytic efficiency for the reduction of CO_2 to CO using g-C_3N_4 at visible wavelength can be further improved by the addition of the 0.03 weighted amount of Barbituric acid as a co-monomer in to unmodified g-C_3N_4 sample, derived from urea (NCU) to produce optimum sample (CNU-BA0.03).It was reported that by using CNU-BA0.03, the photo catalytic efficiency for the conversion of CO2 to CO has been increased up to 15 folds in comparison with the CNU. Additionally, some other co-monomers like 2-aminobenzonitrile (ABN), diamino maleonitrile (DAMN) and 3 aminothiophene-3-carbonitrile (ATCN) were also copolymerized with g-C_3N_4 by urea to boost the photo catalytic efficiency. The maximum CO formation was achieved by employing CNU-ATCN0. 03 sample, which has 19-fold greater activity than that of CNU. It was found that, the photo catalytic efficiency of g-C3N4 in the photo catalytic conversion of CO2 to CO can also be enhanced by using g-C_3N_4/N-TiO2 nanocomposite, which was synthesized by doping nitrogen on TiO2 using urea and $Ti(OH)_4$ as precursors. The studied mass ratio of urea to $Ti(OH)_4$ were 50:50 (CT-50), 60:40 (CT-60) and 80:20 (CT-80), among which, the CT-50 sample shows highest CO evolution (5.7μmol) with 12Hr of light irradiation.

3.3 Multi-carbon Products:

Over the last few decades, enormous efforts have been made in the context of phptocatalytic reduction of CO_2. However, the selective formation of C1 products such as CO, CH_4 and CH_3OH can be achieved to a greater extent, but the production of multi-carbon products has still a major challenge in this field. It was found that, a TiO_2-graphene two dimensional (2D) hybrid structure was developed by the research group, which forms an excellent interface through Ti-O-C bond and contain ample Ti^{+3} species on the surface. The graphene based interface permits efficient charge transfer and the photo generated electrons are trapped in the Ti+3 sites synergistically preventing e^--h+ recombination. Due to this synergistic effect, the formation of C_2H_6 in photo reduction of carbon dioxide was favored, whose yield can be enhanced with the graphene content in the hybrid structure. Likewise, the Cu^{+2} sites in CdS-Cu^{+2}/TiO_2 exhibit their role in imprisoning the photo generated electrons, enabling efficient reduction of carbon dioxide to form ethyl alcohol.

3.4 Other Products

During the photo catalytic conversion of CO_2, some other organic products like HCOOH and

HCHO are also produced. It was found the photo reduction of CO_2 to formaldehyde can be achieved in purified water by using various semiconductors such as TiO_2, ZnO, CdS, GaP, SiC and WO_3. Also an aqueous suspension of TiO_2 was found to produce formaldehyde at a rate of 2.0 $\mu molh^{-1}gcat^{-1}$. The photo reduction of CO_2 to formaldehyde can also be achieved under visible irradiation by using $Ba_3Li_2Ti_8O_{20}$ photo catalyst. The catalytic efficiency of $Ba_3Li_2Ti_8O_{20}$ can be enhanced by the incorporation of CuO particles due to the formation of n-p heterostructure between the n-type $Ba_3Li_2Ti_8O_{20}$ and the p-type CuO, which enables the separation of photo generated e^--h+ pair and the accumulation of proton for the conversion of CO_2 to HCHO.

Acetic acid (HCOOH) is also a common product in the photo reduction of CO_2. pH dependent photo catalytic reduction of CO_2 to HCOOH and CH_3OH by using graphene-TiO2 under visible light. When the pH was 8, up to 90% selectivity for HCOOH was achieved. It has been reported that for the reduction of CO_2 to HCOOH, $BiYO_3$ doped with varying amount of Cu, could function as a highly efficient photo catalyst under visible light irradiation. The doping of Cu can not only replace the Bi^{+3} in $BiYO_3$ and the generate oxygen vacancies to encountered electrons and inhibits the recombination of e^--h+ pair, but also decrease the size of the composite catalyst, resulting in an increase of the surface area and decrease of the resistance to surface charge transfer. The formic acid was also detected when an anatase-type TiO_2 powder was inserted in to the supercritical CO_2 and was irradiated under UV-Visible light, followed by water addition.

Acetaldehyde can also produce during the photo catalytic reduction of CO_2. The $NiO/InTaO_4$ photo catalyst were found to be effective for the gas phase Photo reduction of CO_2 using a monolith reactor to form acetaldehyde as a major product along with a minor amount of methanol.

4. Scope for future

In summary, the performance and applications of a wide range of photo catalysts for the conversion of CO_2 to valuable chemicals and fuels are the subject of this review. With a concise overview at the end of each section, the study discusses the surface interaction of photo catalyst with CO_2 molecules in various reaction media and investigates several ways for regulating photo catalyst behavior and final product selectivity. Photo catalytic CO_2 reduction with semiconductors is a long-term solution for lowering CO_2 levels in the environment. The efficiency of a photo catalyst is impacted by a variety of parameters, including CO_2 adsorption and activation, crystal structure, band bending, band gap, surface defects, recombination of charge species and excitation of charge carriers, and photo catalyst size. As a result, while designing, developing, or manufacturing photo catalyst, these factors should be carefully evaluated and adjusted. Advanced in-situ characterization techniques must be used to better visualize and comprehend reaction kinetics, processes, product production, photo catalyst surface alteration in relation to reaction duration, and to assess the rationale for the reduced energy barrier, which remains a mystery. In addition, studies in cohorts with commercialization and large-scale industrial photo catalytic applications should focus on the development of rapid experimental synthesis techniques, charge carrier simulation algorithms, efficient visible light responsive photo catalysts and mathematical models for photo catalytic reduction reactions.

5. Conclusion:

At present days, the global climate change and depletion of energy sources are the most critical issues, world is tackling, due to the worldwide industrialization and population uplifting. The conversion of CO_2 to clean and valuable hydrocarbons under visible radiation or ultra violet radiation by using photo catalyst has been effectively carried out under experimental condition. It has been manifested to be a cost effective technology to solve above two problems. The choice of the suitable catalyst is important to achieve high

efficiency and product selectivity in photo catalytic reduction of CO_2. The catalytic efficiency as well as the product selectivity of a bare photo catalyst can be boost by the modification of the photo catalyst in different ways like metal doping, heterojunction construction and sensitization. TiO_2 is the most frequently used photo catalyst because of its good stability, high activity, and non-toxicity. However recently new types of composite catalysts were emerging because of their very good surface structure and low oxidation potential.

As CO_2 is a chemically inert molecule the reduction of CO_2 require very harsh conditions (i.e. high pressure and high temperature) and large amount of energy input. Hence the photo reduction of CO_2 to valuable chemicals is still only in experimental stage and far apart from the practical application. In the past decades, with extensive efforts, the photo catalytic conversion of CO_2 has witnessed its blossoms but still it encounters bottleneck in particular product selectivity and reaction activity. Therefore finding more effective photo catalyst and improving the efficiency of existing photo catalysts for the photo catalytic reduction of CO_2 is important. The major issues in the photo reduction of CO_2 are the low yield of the reduced product. The yield obtained in the laboratory condition is not sufficient to meet the necessity in practical production. In general, the reduced products are typically, a mixture of various organics as the photo reduction of CO_2 is not selective. The selectivity for a particular product in the photo catalytic reduction of CO_2 can be achieved by modifying the photo catalysts in different ways. In order to further enhance the selectivity and catalytic performance, the future researches are carried out on a suitable optimization of surface properties of the photo catalyst. Meanwhile, light sources also plays a crucial role. In practical the photo catalytic reduction of CO_2 in ultra violet light is quite expensive as huge energy is required for ultra violet excitation. Thus recent researches are slowly transferring to the visible light i.e. the free unlimited source. Also it is useful to discover efficient technology to separate and purify the photo catalytically reduced products. If, it so happens the research on photo catalytic reduction of CO_2 can focus on the yield of the product in place of the selectivity.

To summarize this, there has been a tremendous development in designing and fabrication of different photo catalysts, which shows excellent activity toward the photo catalytic reduction of CO_2. However, researches are going on to further enhance the efficiency of these photo catalysts.

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