

CHAPTER 1

INTRODUCTION

1.1 Role of carbon dioxide

Presence of carbon dioxide is essential for the photo synthesis process, which forms the lifeline for all the flora and fauna that define the ecology of this earth. In fact, all other forms of life, including human beings, survive on the oxygen which is the by-product of photo synthesis. However, atmospheric CO₂ level has to be within certain limits. The optimum concentration of CO₂ necessary for the bio-network on earth is 300 ppm (Ref). In earlier days, as shown in Fig. 1.1, CO₂ level in the atmosphere and carbon cycle was maintained by a series of natural processes as described below.

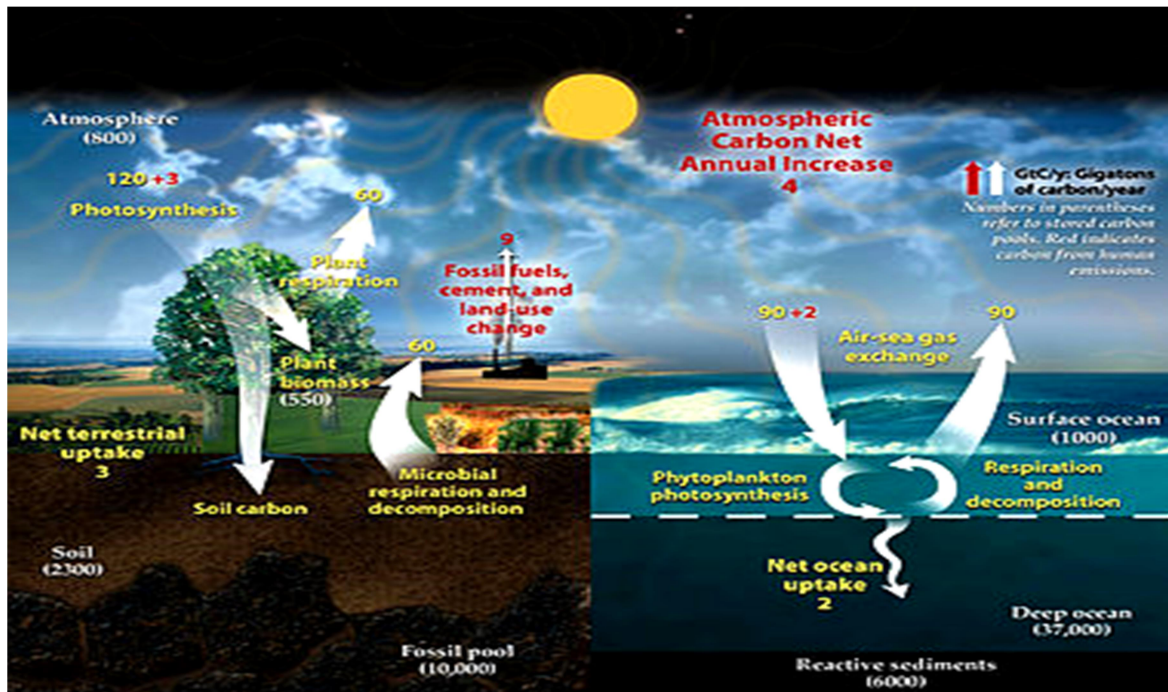


Fig. 1.1 Carbon cycle shows the movement of carbon between land, atmosphere, and oceans in billions of tons of carbon per year. Yellow numbers are natural fluxes; red are human contributions in billions of tons of carbon per year. White numbers indicate stored carbon.(Reproduced from Ref XX)

In modern days, this delicate carbon cycle has been disturbed and atmospheric CO₂ level is gradually increasing. According to the data (Ref) published by International Energy Agency

(IEA), CO₂ emission is exponentially increasing since 1870, (**another Fig showing year-wise increase in atmospheric CO₂ from IEA report to be added**) mainly from the combustion of fossil fuels, in order to meet our energy requirements. Global Total Primary Energy Supply (TPES) has almost doubled, from 1971 to 2012, and 82% of TPES is derived by burning fossil fuels, emitting large quantities of CO₂[1]. One ton of oil releases MT of CO₂ on burning releases **xx MT** of CO₂ (**Ref**). Since energy is essential for economic growth and overall development, increase in atmospheric CO₂ level is expected to be high. CO₂ emissions from the fossil fuels pose serious environmental issues like green-house gas effect and unusual weather patterns. Even though CO₂ is the least effective green house gas per kilogram emitted, it is considered as significant green house gas due to large amount released to the atmosphere from human activities and industrial revolution [2].

Fossil fuels could continue to be our primary source of energy, possibly till the turn of 21st century. Hence globally, serious efforts are on, to keep CO₂ level under control. On one hand, renewable sources of energy like solar, wind, tidal, bio-mass, and geothermal are being harnessed, though to a limited extent as of now, so to minimize the carbon foot print/ CO₂ emission.

Table 1.1 Reactants and their products with CO₂ [Reproduced from Ref.3]

Reactants	Products with CO ₂
Alkane	Syngas, acids, esters, lactones
Cycloalkane	Acids, esters, lactones
Active-H compound	Acids, esters, lactones
Monoalkene	Acids, esters, lactones
Diene ^a	Acids, esters, lactones ^b
Cycloalkene	Acids, esters, lactones, (co)polymers
Substituted hydrocarbon ^c	Acids, esters, lactones, polycarbonates
Alkyne	Lactones, unsaturated organic carbonates
Epoxide	Carbonates, (co)polymers (polycarbonates)
NH ₃ and amine	Symmetrical ureas, aminoacids, (co)polymers
Diamine	Ureas, carbamates, (co)polymers (polyureas)
Imines	Carbamates, (Co)polymers (urethane)

^aAllenes and 1,3-dienes, ^bwith longer C-C chain than the original monomer. ^cDihalogen substituted.

Simultaneously, viable means of capture, storage and sequestration of CO₂ and its conversion to fuels and chemicals are being explored. The task indeed is a challenging one. Conversion of CO₂ by reaction with different organic molecules could result in variety of highly useful products for the fine chemicals industry, is shown in Table 1.1 [3].

However, use of CO₂ as reactant by the chemical industry is only about 0.5 wt% (Ref) of the total anthropogenic CO₂ emissions every year [4]. Hence, several simultaneous approaches are needed to convert CO₂ to fuels and chemicals, so that atmospheric CO₂ level could be maintained at near optimum levels. Such an approach would ultimately lead to the use of CO₂ as sustainable source of energy as well. Considering such a dual benefits, several CO₂ conversion processes, other than those for chemicals manufacture, are being studied with great interest. A list of such CO₂ conversion processes to yield fuels, is presented in the following section.

1.2 Processes for CO₂ conversion

CO₂ is the most oxidized form of carbon and therefore, the only chemical transformation at normal energies, that would be possible, is to reduce it. A wide range of CO₂ conversion/reduction techniques are under investigation [5] which include,

- i. Chemical Reduction by metals which occur at relatively at high temperatures



- ii. Thermo-chemical Conversion



- iii. Radio chemical Method



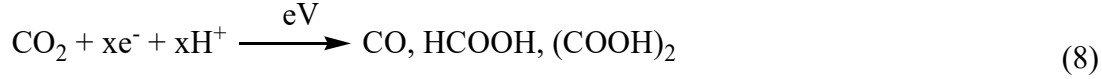
- iv. Photo chemical Conversion



v. Bio-Chemical Conversion

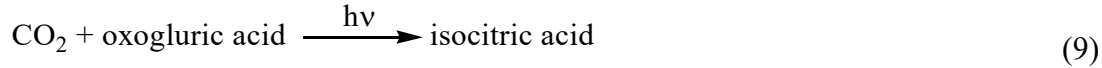


vi. Electro-Chemical Conversion



vii. Bio Photochemical conversion

The bio part of the energy consists in catalysis and information content of an enzyme



viii. Electro photochemical conversion



Conventional catalytic reduction of CO_2 to chemicals (formic acid, methanol, methane etc.) with external hydrogen is feasible [6] but hydrogen from renewable resources is to be utilized, to render the process viable and sustainable.

Amongst the processes listed above, photochemical conversion processes (direct photochemical, photo-electrochemical and photo-biochemical conversions), that utilize abundantly available solar energy, qualify as sustainable processes and hence being pursued with tremendous interest. A brief account of photo catalysis and photosynthesis, which form the basis for all types of photo catalytic conversions in general, and CO_2 reduction in particular, is presented in the following section.

1.3 Photo catalysis and Photo synthesis

Photo catalysis involves an additional means of activation of molecules, besides the normal thermal and chemical catalytic action that facilitate any typical chemical reaction. In simple terms, photo catalysis refers to any reaction that requires simultaneous presence of a photo active catalyst and light energy source [7] and can be expressed as

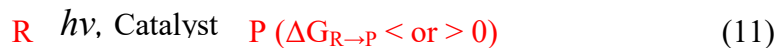


Photo-generated electrons and holes react with adsorbed reactant molecules on a photo active semiconducting catalyst surface, bringing about the reduction or oxidation of the adsorbed

species. The reaction pathways in both processes according to Ravelli et al [8] are illustrated in Fig. 1.2A & B below:

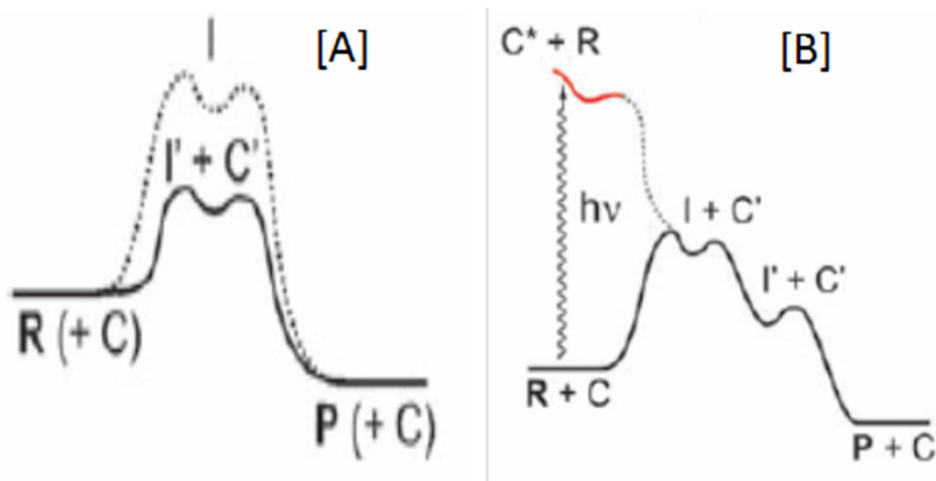
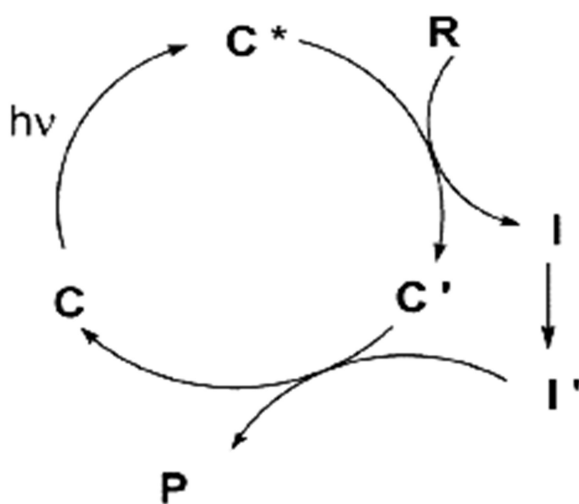


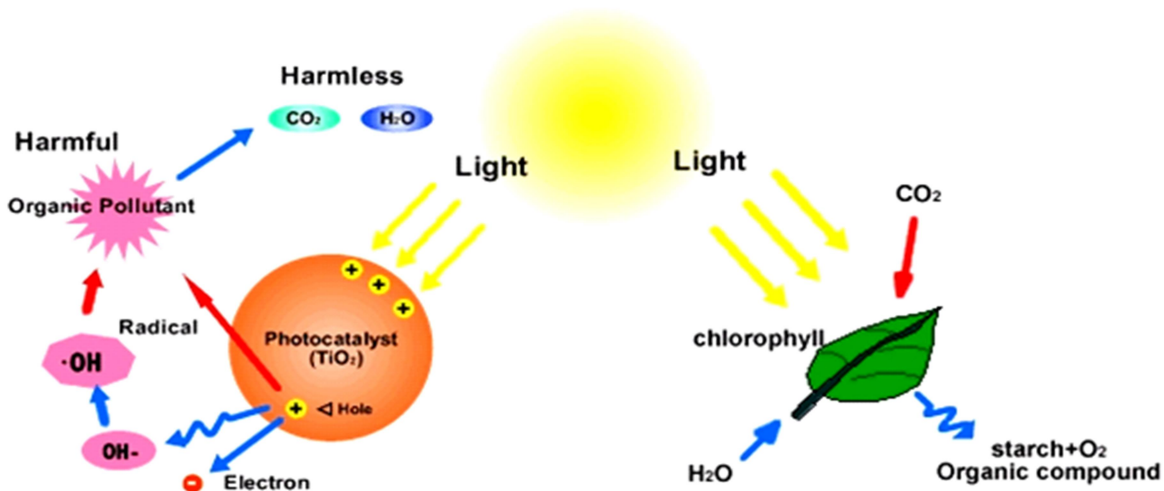
Fig.1.2 Reaction path ways followed [A] in a thermal reaction (R-P) catalyzed by C via intermediate I'; [B] in a photo catalyzed reaction (the catalyst C is active only in the excited state, but the chemical transformation of R occurs entirely on the ground state surface [Reproduced from Ref.8].

The overall reaction cycle in a typical photo catalytic conversion is depicted as shown in Scheme.1.1.



Scheme.1.1. Photo catalytic conversion of R to P by catalyst C [Reproduced from Ref.8]

Historically, photo catalysis has played a pivotal role in the evolution of life on earth. Photo synthesis, the process so vital for the plant life, is essentially a photo catalytic process, involving the conversion of CO_2 and water to carbohydrates, with the release of oxygen into the atmosphere. Chlorophyll acts as collector of solar energy and the conversions take place with the help of a series of enzyme catalysed process steps. This phenomenon of photo synthesis marked the beginning of process of evolution of various forms of life on earth that survive on oxygen. Both photo catalysis and photo synthesis processes utilize the sustainable source of energy, the sunlight, available abundantly at zero cost (Scheme.1. 2).



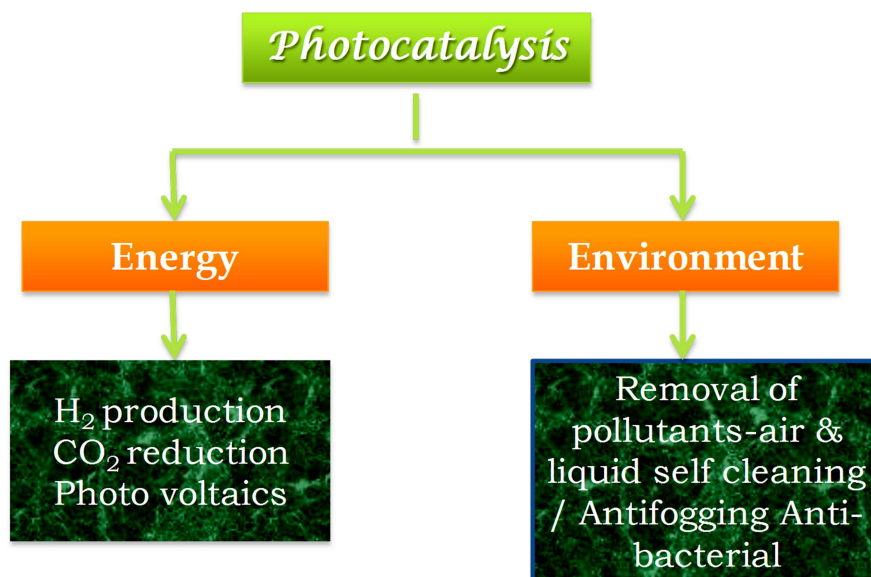
Scheme 1. 2. Photo catalysis and Photosynthesis [Reproduced from Ref.X]

Photo catalytic reduction (PCR) of carbon dioxide by water to yield hydrocarbons, the process commonly referred to as “artificial photosynthesis”, dates back to nearly nine decades, in 1921-22 [Ref]. The process has now attained tremendous importance on global level, since it is considered as one of the means of controlling the current atmospheric carbon dioxide levels (green-house gas effect) by converting it into to fuels and chemicals and the role of CO_2 as source of energy.

1.3.1 Applications of photo catalysis

In the current energy starved scenario on the earth, studies on the science and technology of photo catalytic processes that utilize sunlight, have gained tremendous importance and hence

being explored for a variety of applications. Photo catalysis is an emerging as one of the possible means of providing viable solutions to the challenges related to two major issues on the global front, energy and environment. Solutions in the form of different photo catalytic conversions/ processes, mostly based on titania as the photo catalyst, are represented in Scheme.1.3.



Scheme.1.3. Major applications of photo catalysis

These applications are at various stages of development, with few of them like, self-cleaning, anti-fogging and anti-bacterial applications being practiced already on large scale.

Photo catalytic processes could be utilized for converting solar energy into other useful forms of energy like, hydrogen via splitting of water and hydrocarbons (methane, methanol etc.) which are now collectively termed as “solar fuels”, by photo catalytic reduction of CO₂ with water. Besides, photo catalytic oxidation/ degradation processes help in the elimination of harmful pollutants in air/liquid/water streams in a safe manner, resulting in the conservation of environment. There has been an explosive growth of applications of photo catalysis as evidenced by the fact that from the year 2000 onwards around 1300 international patents (latest figures to be included) per year have been filed, most of them pertaining to the application of titania as photo catalyst for pollution control.

While the practical applications of photo catalysis in the area of pollution control has been demonstrated successfully, the applications on energy front, for hydrogen production by water splitting and hydrocarbons from CO₂ and water are still at infant stages of development.

1.4. CO₂ photo reduction with water- Process features

The CO₂ reduction is a thermodynamically uphill process as illustrated by its standard free energy of formation ($\Delta G^\circ = -394.359 \text{ kJ/mol}$) [9]. Economical CO₂ fixation is possible only if renewable energy, such as solar energy is used as the energy source. Equally difficult is the reduction/ splitting of water using solar radiation to yield hydrogen and hence requires similar combination of activation steps. We can now consider two different processes for CO₂ reduction namely,

- Direct photo reduction of CO₂ using water as a reductant
- Photo catalytic splitting of water to generate hydrogen and further reaction of this hydrogen with carbon dioxide forming C₁–C₂ fuels.

The most ideal and desirable process would then be the simultaneous reduction of CO₂ and water to yield hydrocarbons, which essentially works out to artificial photosynthesis. Photo catalytic process occurs via the direct absorption of photons with energy greater than or equal to the band gap of the photo catalyst, resulting in the generation of electron-hole pairs. The initial excitation and electron energy transfer to the adsorbed reactants on the photo catalyst make chemical reactions in the photo catalytic process possible.

The utilization of solar energy via chemical storage can be achieved by photo catalytic or photo-electrochemical activation of light-sensitive catalytic surfaces. When comparing the two systems, photo catalytic system is simpler, easy to construct and operate. The primary steps involved in the photo catalytic reduction of CO₂ to hydrocarbons include:

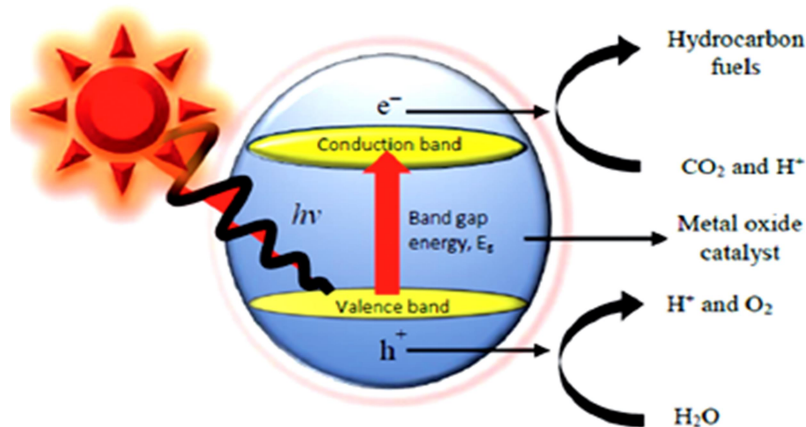


Fig. 1.3 Transformations during photo catalytic reduction CO₂ with water [10] **Reproduced from?** (No Ref. to Fig 1.3 in the text)

- Photo generation of charge carriers by excitation

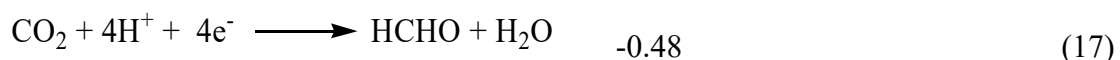
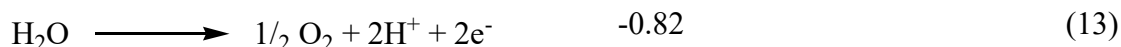
- Bulk diffusion and interfacial transfer of charge carriers to surface species
- Reduction/oxidation and further conversion of surface species to different hydrocarbons

Photo generated electrons bring out the reduction of CO₂ to hydrocarbons and holes facilitate oxidation of water. While the elementary process steps/ mechanism of photo catalytic water splitting have been established to an acceptable level, there is little clarity on the reaction pathways that lead to the conversion of CO₂ to hydrocarbons.

1.4.1 Thermodynamic features

Hydrogen formation from water involves a free energy change (ΔG_0) of 237 kJ/ mol and an enthalpy change (ΔH_0) of 285 kJ/mol; the corresponding values for CO formation from CO₂ are 257 and 283 kJ/mol at 25°C (1atm). Hence, the minimum energy required for water and CO₂ splitting processes are 1.229 and 1.33 eV (per photon) respectively. In theory, the band gap of a photo catalyst used for **splitting/ reduction** of water /CO₂ should be at least 1.33 eV [11]. One, two, four, six and eight electron reduction potentials (vs. NHE) for CO₂ reduction and H₂O oxidation at pH 7 and at 25°C, assuming unit activities for all gaseous and aqueous species are given below [9].

Reaction E^0_{redox} V vs NHE at pH 7



From the above scheme it is clear that CO₂ photo reduction is not a single-step reaction. Upon transfer of one electron, the structure changes from linear to bent configuration, which results in irreversible reduction [5]. Additionally, single electron transfer to CO₂ is highly endergonic, because of the negative adiabatic electron affinity of CO₂.

The initial step in the photo catalytic reduction of CO₂ is the generation of electron-hole pairs upon absorption of photons of energy greater than or equal to the band gap of the photo catalyst. Subsequently, photoelectrons are utilized for the reduction of CO₂ and hole for oxidation of water. However, electron-hole recombination process, which is two to three orders of magnitude faster, competes with the desirable redox processes. Therefore, electron-hole recombination process has to be minimized by some means, to increase the efficiency and improve the rates of CO₂ photo reduction. Besides the recombination, many other factors such as incident light intensity, fraction of the incident light absorbed by the photo catalyst, the type of the catalyst and its particle size, specific surface area, structural and photo-physical properties etc. are known to influence the kinetics of CO₂ photo reduction.

1.4.2 Choice of catalysts - Guiding principles

It is again essential that the photo generated electrons should possess requisite energy, as indicated by the thermodynamic criteria, to facilitate the reduction of CO₂. The chemical potentials of the photo generated electrons and holes highly depend on the band edge positions of the semiconductor. This means that the conduction band bottom energy level of the photo catalyst has to be more negative with respect to the energy for CO₂ reduction and the valence band top has to be more positive with respect to the energy for oxidation of water. Thus, the choice of the catalyst for CO₂ photo reduction with water is determined by the relationship between energy levels of conduction and valence bands vis-a-vis the energies for CO₂ reduction and water oxidation. Pioneering studies on photo electro catalytic reduction of CO₂ on various semiconducting oxides has brought out the basic criteria for the catalytic activity. This guiding principle has been illustrated effectively by Inoue et al. [12] in the relationship between the energy levels of conduction and valence bands and those of the redox couples as depicted in Fig. 1.4.

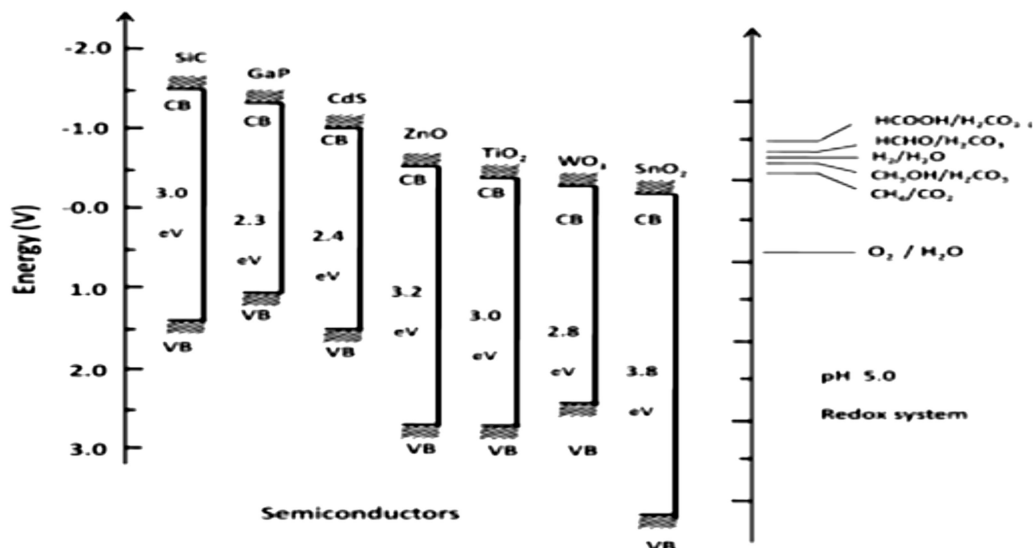


Fig.1.4 Conduction band and valence band potentials for photo catalysts relative to the Energy levels of redox couples in water [12].

Semiconductors like SiC, GaP, CdS, ZnO and TiO₂, which satisfy the above criteria and are active for photo reduction of CO₂ while oxides like WO₃ and SnO₂ whose conduction band levels are below that for CO₂ reduction, have failed to perform. Energy levels of conduction and valence band Vs those for redox couple and the life time of charge carriers, prolonged by reduced recombination, are the two fundamental criteria to be considered for the selection of the efficient photo catalyst for CO₂ photo reduction.

1.5 Catalysts for photo reduction of CO₂ with water

A remarkable feature of PCR of CO₂ is that it could emerge as a carbon neutral process [13], where in carbon emissions are recycled back as useful fuels/chemicals. The process involves two major steps; photo catalytic splitting of water to yield hydrogen, which in turn, helps in the photo reduction of carbon dioxide to different hydrocarbon products in the second step. Design of effective catalysts for such a complex process, involving multi-electron transfer steps, holds the key for the viability of the process.

Although many semiconductors have smaller band gaps and absorb in the visible range (e.g. CdS and Fe₂O₃ with band gap values of 2.4 and 2.3 eV, respectively), just a few of them are catalytically active because the energy levels of either the conduction or valence bands are unsuitable for CO₂ reduction and/or water oxidation (Fig. 1.4). This limitation, together with poor photo-corrosion stability of many semiconductors, limits significantly the number of potential photo catalytic materials for CO₂ photo reduction.

Large-band-gap semiconductors are the most suitable photo catalysts for CO₂ reduction, because they provide sufficient negative and positive redox potentials in conduction bands and valence bands, respectively. The disadvantage of using wide band-gap semi-conductors is the requirement of high energy input [14-18].

1.5.1 The need for modifications in the catalysts

The photo catalytic activity of a typical semiconductor like titania is initiated by the absorption of light energy corresponding to or higher than the band gap energy, resulting in the generation of electrons and holes. The electron-hole pair, on migration to the semiconductor surface, interacts with the adsorbed reactants to facilitate reduction and oxidation process respectively. In the absence of such an energy transfer, the pairs recombine with the loss of energy. Electron-hole recombination process, which is two to three orders of magnitude faster, competes with the desirable redox processes. Therefore, the recombination process needs to be minimized by suitable modifications, to increase the efficiency. Hence modifications in wide band gap semiconductor (band gap engineering) are aimed at dealing with the two major issues, namely, extending light absorption range beyond UV region and arresting the recombination of charge carriers.

By suitable modification of the band gap, i.e., reduction in band gap by creation of additional/impurity energy levels, light absorption range/wavelength could be increased. In the case of titania, light absorption range is increased to cover part of visible region [16, 17]. Arresting the recombination rate increases the life time of photo electrons and holes, thus leading to a corresponding increase in photo catalytic activity.

1.5.2 Major types of modifications in the catalysts

A number of strategies have been devised to bring about the modifications in wide band gap semiconductors, which can be broadly classified as:

- Doping with metal cations and anions
- Coupling with other semiconducting oxides
- Sensitization with light harvesting compounds/dye molecules
- Plasmon resonance induced by specific metals

Excellent and exhaustive reviews describing the changes brought about by these means in the photo-physical properties of the photo catalyst and the consequent improvements observed in the photo-catalytic properties have been compiled [5, 9, 18-29]. The main features of these modifications and the implications in the properties of semiconductors, especially for titania, are summarized in the Table. 1.2, and presented graphically Fig. 1.5

Table 1.2 Implications of different modifications in titania [20]

Modifications	Implications/Mode of action
Doping of metals/metal ions	<ul style="list-style-type: none"> • Act as electron traps and facilitate charge carrier separation • Introduce impurity states and induce visible light absorption • Absorb visible light via surface plasmon resonance (SPR)
Doping of anions	<ul style="list-style-type: none"> • Narrowing of band gap due to mixing of p states of dopants (N, S) with O 2p states in the valance band of TiO₂. • Introduce impurity states above the valence band of titania • Both states induce visible light absorption
Coupling with semi-conductors	<ul style="list-style-type: none"> • A narrow band gap semiconductor, with appropriate energy levels, absorbs visible light and transfers excited electrons into the conduction band of titania. UV light source not needed • Besides visible light activity, effective separation of charge carriers is achieved
Sensitization with light harvesting components /dyes	<ul style="list-style-type: none"> • Light absorbing components can absorb visible light and inject photo-excited electrons into the conduction band of titania. • Besides visible light activity, effective separation of charge carriers is achieved

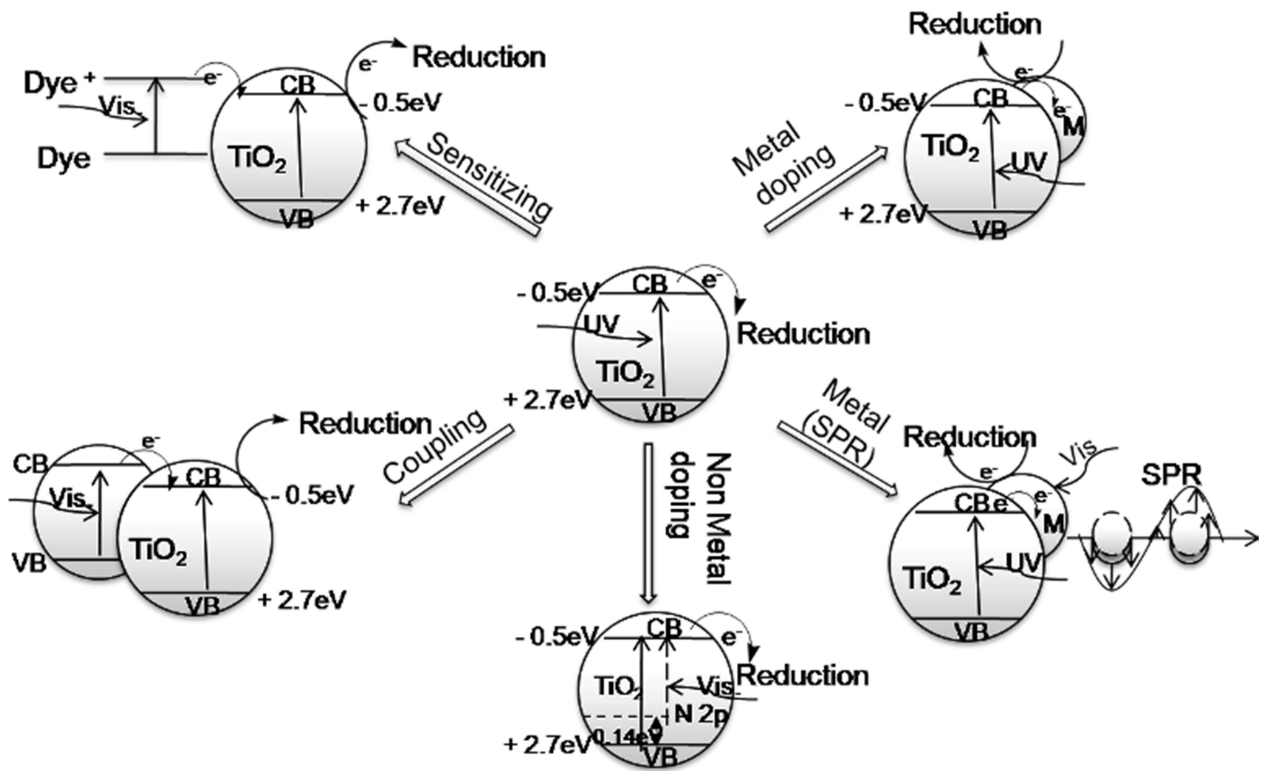


Fig.1.5 Implications of modifiers on the electronic structure of Titanium dioxide [20]

1.6 Influence of experimental parameters

Photo catalytic activities highly depend on the experimental conditions such as, the amount of catalyst, light intensity, lighting area, reactor volume, type of reactor, temperature and pressure etc. Intrinsic properties of semiconductor photocatalyst like, particle/ crystallite size [30], phase composition [31], surface area, surface hydroxyls, lattice defects and the type and level of dopants (metals and non-metals), morphology (powder, nano particles, nano tubes, nano rod and hollow nano spheres), structural features and photo-physical properties influence its performance [15-29]. Photo catalytic activity and phase transition behavior of TiO₂ are significantly influenced by the preparative conditions and methods [32-34]. This explains the wide variations in activity and product patterns observed for the same photo catalyst by different authors. For example, a standard/reference catalyst Degussa P-25 (TiO₂) shows wide difference in efficiency in the results published by different authors during the period 1993 to 2009 as shown in Table. 1.3 (Ref?). Different experimental conditions adopted could be the other major factor that affects yield data, which shows variations in total yield as well as the product patterns.

Hence, rationalization of activity and product patterns in terms of photo-physical properties has been a difficult task.

Table 1.3 CO₂ photo reduction with water on P-25 TiO₂ - Literature reports (Ref?)

Sr. No	Products *	CH ₄	CH ₃ O H	Reactor type	Reactants	Light source	T (K)	Ref.
1	CH ₄ , C ₂ H ₆ CH ₃ OH	0.9	Tr	Quartz cell	CO ₂ in H ₂ O	500W Hg > 310 nm	278	35
2	H ₂ , CO, CH ₄	2.0	Tr	Quartz cell	CO ₂ in H ₂ O	1000W Hg<700 nm	343	36
3	H ₂ , CH ₄ , C _n H _m	4.74 5.68 6.42		Miniaturized reactor	CO ₂ in H ₂ O	200W Hg /Xe <900 nm	278 373 473	37
4	CH ₄ , HCOOH	0.43		SS vessel	CO ₂ / IPA	4200W, Xe		38
5	CH ₄ , CH ₃ OH	0.35		Quartz cell	CO ₂ : H ₂ O 1:5	75W Hg 254 nm	323	39
6	CH ₃ OH	-	6.37	Inner irradiator cell	CO ₂ in NaOH	8W Hg 250 nm	323	40
7	CH ₄ , CH ₃ OH		93.75	Inner irradiator cell	CO ₂ in NaHCO ₃	15 W Hg 365 nm		41
8	CH ₃ - COOH		1.8	Quartz window	Liq. CO ₂	990W Xe Arc lamp		42
9	CH ₄	0.33	-	Quartz cell	CO ₂ : H ₂ O 1:5	100W Hg >250 nm	323	43
10	CH ₄	0.001		Top illumination	CO ₂ : H ₂ O 1:5	4.8W 253.7 nm	311	44
11	CH ₄	14.6		Glass plate	CO ₂ : H ₂ O 1:5	15W 365 nm	296	45
12	CH ₄	3.51		Annular reactor	CO ₂ in NaHCO ₃ / IPA	450WHg	293 -	31 298
13	CH ₃ OH		430	Inner irradiator cell	CO ₂ in NaOH	400W halide 300-600 nm	315	46

* Products – in micro moles per hour per gram of catalyst

1.6.1 Effect of wavelength, band gap and light intensity

Semiconductors absorb light radiation with the threshold wavelength that provides sufficient photon energy to overcome the band gap between the valence and conduction bands. This threshold wavelength, required to promote electrons to the excited state, corresponds to the minimal photon energy and depends on the band-gap energy, e.g. for TiO₂ anatase with band gap energy 3.2 eV, it is about 387.5 nm. Irradiation using the light with shorter wavelength (254 nm) is significantly more effective for the CO₂ reduction using TiO₂ than that with the longer wavelength (350 nm) [47, 48]. The wavelength (λ) of the light used influences the yield of products as observed by Fan et.al [49] in their studies on N (4% w/w) and Ni (6% w/w) co-doped titania for CO₂ reduction with water. For this catalyst formulation, Fan et al [49] observed methanol yields of 482, 253.5 and 120.5 (all in μ moles/g-cat) with radiations of wavelength 254 nm, 365 nm and 400-780 nm respectively, thus clearly bringing out the influence of the wavelength of the light used. Electrons in excited states are produced via electronic transitions the probability of which depends on the light intensity. The CO₂ reduction rate increases linearly with the light intensity and at mid-range light intensities, the photo catalytic reaction rate is dependent on the square root of light intensity. At high light intensities the rate is independent of the light intensity [18].

Variations in the wavelength of radiation used can also affect the rate of formation of products as observed by Liu et al [50] on BiVO₄ catalysts (Table.1.4). Monoclinic BiVO₄ is found to be

Table 1.4 Rates of methanol and ethanol formation with radiations of different wavelengths [Reproduced from Ref. 50]

BiVO ₄	Production rate ^a / μ mol h ⁻¹	300W Xe arc lamp with UV cut off filter	300 W Xe arc lamp without UV cut off filter	36W fluorescent lamp
Monoclinic	Ethanol	21.6	406.6	2.3
	Methanol	0	0	1.8
Tetragonal	Ethanol	1.1	4.9	0.6
	Methanol	0	0	0.6

^a The rate was determined on the basis of the average production rate after 80 min of irradiation

more active than the tetragonal form. Selective formation of ethanol is observed using 300 W UV radiations, with and without UV cut-off filter. But with 36 W lamp, both alcohols are formed at nearly same.

1.6.2 Influence of reaction pressure

Mizuno et al [51] observed that CO₂ photo reduction with water containing dispersed TiO₂ increased with the increase in CO₂ pressure. Increase in the solubility of CO₂ in the liquid phase (water as well as aqueous 0.2N NaOH solution) at elevated pressure and the consequent increase in the concentration CO₂ in the solution phase is responsible for the observed increase in CO₂ reduction (Fig. 1.6). Similar observations on the effect of pressure have been observed by Hisao Hori et al [52].

Kaneco et al [53, 54] studied the CO₂ photo reduction using TiO₂ powders in liquid CO₂ medium. Carbon dioxide has limited solubility in water. Also reduction of CO₂ is competitive with hydrogen formation via water. To overcome this disadvantage, liquid CO₂ system has been explored. **The protonation reaction was performed using water after the end of illumination?** The main reduction product was exclusively formic acid. Tan et al [44, 55] studied the photo catalytic reduction of carbon dioxide using TiO₂ pellets. Pellet increased the contact areas and adsorption capacity. Their yield was significant when compared to thin film coating technique.

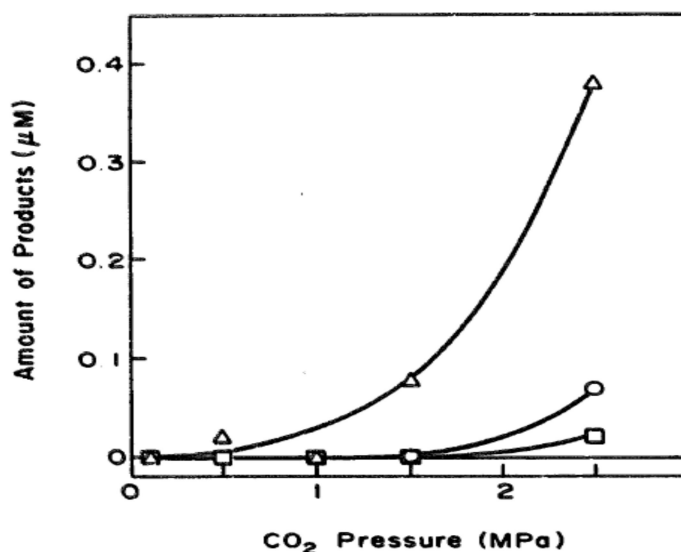


Fig.1.6. Effect of CO₂ pressure on its photo reduction (medium, purified water; irradiation time, 24 h; catalyst, TiO₂): Δ- CH₄, ○-C₂H₄, □- C₂H₆. [Reproduced from Ref.51]

1.6.3 Influence of titania particle size

Koci et al [30] studied the effect of TiO₂ particle size on photo catalytic reduction of carbon dioxide. As the particle size decreased, higher yields of methanol and methane over the TiO₂ nano particles under the illumination of light were obtained. The optimum particle size corresponding to the highest yields of both products was 14 nm (Fig. 1.7). For particles with crystallite sizes < 14 nm, conversions dropped due to a combination of electronic (increase in recombination rates) and optical properties. The observed optimum particle size was a result of competing effects of specific surface area, charge-carrier dynamics and light absorption efficiency.

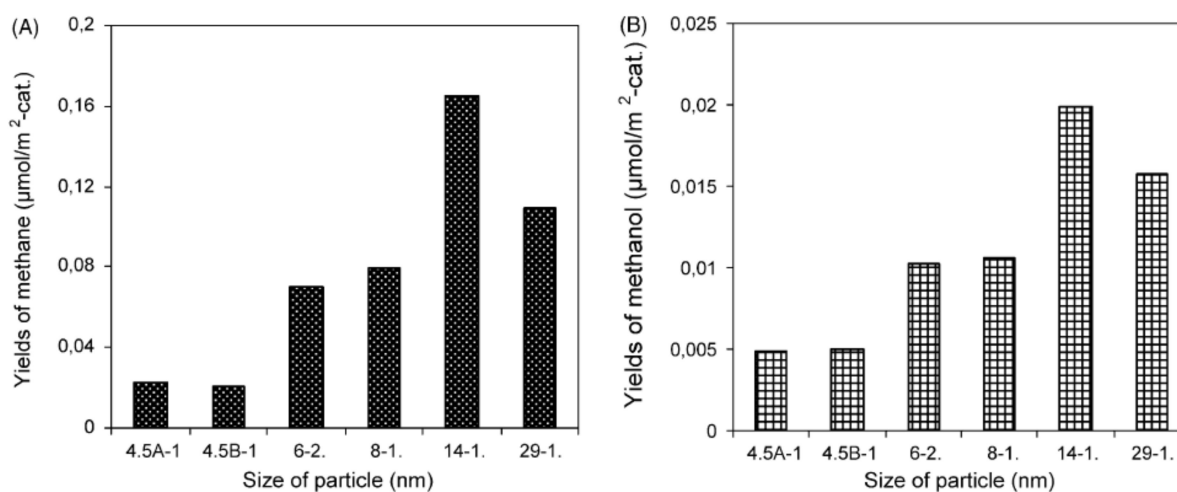


Fig.1.7. A & B Dependence of product yields on particle size of titania (after 24 hrs of irradiation) [Reproduced from Ref.30]

1.6.4 Influence of type of photo reactors and reaction media

The design of photo reactor is an important aspect in CO₂ photo reduction process with water, which could significantly influence the selectivity of products and efficiency of the photo catalyst/process. As stated by O. Ola et al [56], an ideal photo reactor must have uniform light distribution throughout the entire system in order to achieve optimum results. The two parameters which determine the type of photo reactors utilized in CO₂ photo reduction are the phases involved i.e., multiphase, gas-solid, liquid-solid, gas-liquid-solid etc, and the mode of operation i.e., batch, semi-batch or continuous flow of reactants.

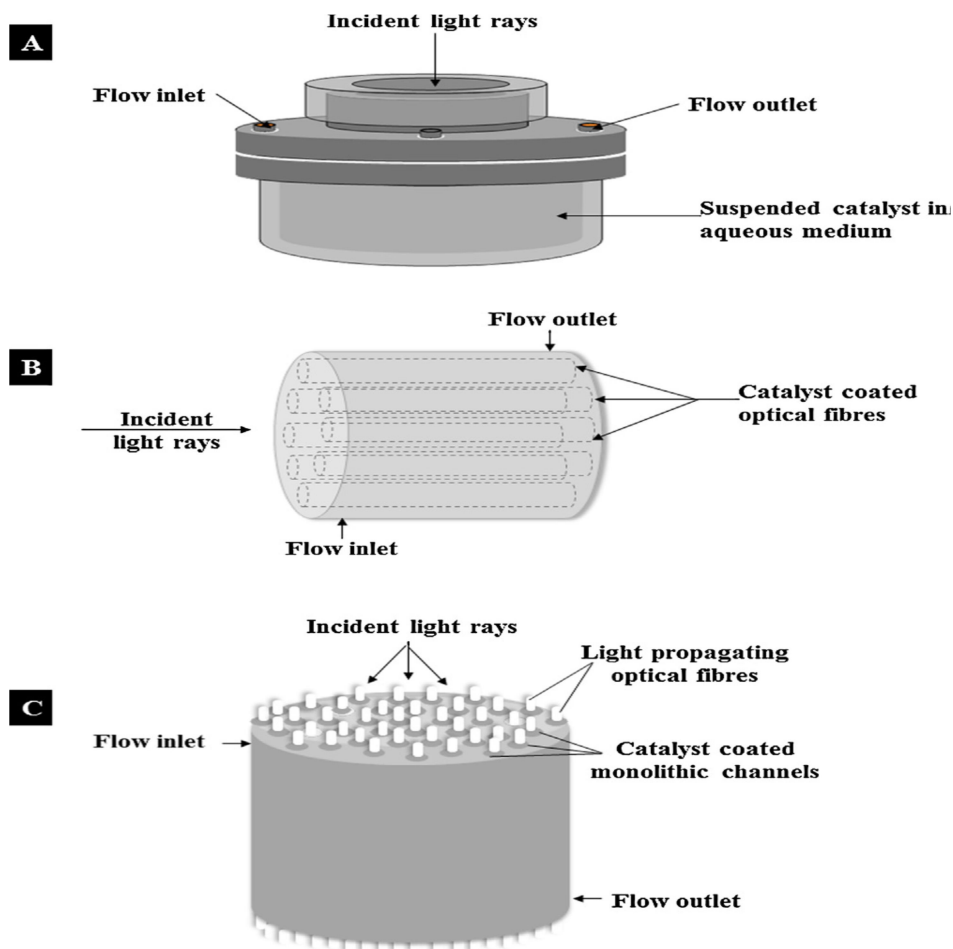


Fig. 1.8. Schematic diagram for different types of photo reactors (A) slurry reactor design with top illumination, (B) optical fiber reactor design with side illumination and (C) internally illuminated reactor with top illumination. (Adapted from Ref. 56).

The photo catalyst can be used in either suspended or immobilized forms in different reactor configurations. Schematic representation of three types of reactor geometry are shown in Fig. 1.8, which are, A. Slurry reactor design with top illumination, B. optical fiber reactor design with side illumination C. internally illuminated reactor with top illumination [56].

Koci et al. [46] studied the influence of reactor geometry on photo reduction of carbon dioxide using two annular batch reactors. The dependence of product yields on the reactor diameter and on the volume of the liquid phase confirmed the fact that the requirement of perfect mixing is difficult with the annular configuration of the reactor. The highest yields of the photo catalytic reduction were achieved in a configuration where the lamp just touches the surface of the liquid in the reactor and the configuration of the reactor was not annular. As shown in Table

1.3/1.5?, different types of photo reactors and reaction medium significantly alter the product selectivity for a commercial P-25 TiO₂ photo catalyst. Advantages and disadvantages of different types of photo reactors for application in CO₂ photo reduction are given in Table 1.5.

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Table 1.5 Advantages and disadvantages of photo reactor systems Adapted from Ref. 56

Reactor design	Advantages	Disadvantages	Ref.
Fluidized and slurry reactor (multiphase)	(I) Temperature gradients inside the beds can be reduced through vigorous movements caused by the solid passing through the fluids (II) Heat and mass transfer rates increase considerable due to agitated movement of solid particles. (III) High catalyst loading	(I) Filters (liquid phase) and scrubbers (gas) are needed. (II) Flooding tends to reduce the effectiveness of the catalyst. (III) Difficulty of separating the catalyst from the reaction mixture (IV) Low light utilization efficiency due to absorption and scattering of the light by the reaction medium (V) Restricted processing capacities due to mass transport limitations	19 [57, 58]
Fixed bed reactor	(I) High surface area (II) Fast reaction time (III) The conversion rate per unit mass of the catalyst is high due to the flow regime close to plug flow (IV) Low operating costs due to low pressure drop Variants of fixed bed designs	(I) Temperature gradient between gas and solid surface is common	[59, 60]
Monolith reactor	(I) High surface to volume ratio and low pressure drop with high flow rate can be achieved. (II) Configuration can be easily modified	(I) Low light efficiency due to opacity of channels of the monolith	[61, 62]
Optical fiber reactor	(I) High surface area and light utilization efficiency. (II) Efficient processing capacities of the catalyst	(I) Maximum use of the reactor volume is not achieved. (II) Heat build-up of fibers can lead to rapid catalyst	[62, 63]

Wu et.al [64-67] applied an optical fibre reactor to the photo reduction of CO₂ with H₂O using TiO₂, Cu/TiO₂, Ag/TiO₂, Cu-Fe/TiO₂-SiO₂ and dye-sensitized Cu-Fe/P25 catalysts coated on optical fibres. Compared with a traditional packed-bed reactor, an optical fibre reactor provides a medium to transmit light uniformly throughout a reactor and hence higher conversion (Table.

1.6) is achieved. In addition, a higher processing capacity is possible because the photo catalyst can be dispersed on the optical fibers with large surface area in a given reactor volume.

Table 1.6 Production rate of methane and ethylene over TiO₂ based-catalysts under artificial light- Influence of the type of photo reactor on reaction rate [64-67]

	Production rate ^a [$\mu\text{mol (gcat)}^{-1} \text{h}^{-1}$]	
	Ethylene	Methane
Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /glass plate	0.049	0.060
Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /optical fiber	0.575	0.914
N3-dye- Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /glass plate	0.033	0.148
N3-dye- Cu(0.5 wt%)-Fe(0.5 wt%)/TiO ₂ /optical fiber	0.562	0.847

^a Production rates were determined on the basis of the average value after 4h of irradiation. The artificial light was in the wavelength range of 320-500 nm with intensity of 225 mW cm⁻².

When CO₂ present in the atmosphere dissolves in water it is mostly present in the form of carbonate. Many authors have studied photo catalytic reduction of carbonate to form various chemicals. Ku et al. [41] studied the photo catalytic reduction of carbonate in aqueous solution by the UV/TiO₂ process. The photo catalytic reduction of carbonate proceeded faster in acidic solutions than in alkaline solutions. The main products of the photo catalytic reduction of carbonate by the UV/TiO₂ reduction process were found to be methanol and methane. A Langmuir–Hinshelwood type kinetic equation was developed for modeling the photo catalytic reduction of carbonate.

Sayama et al [68] investigated the effect of carbonate salt addition on the photo catalytic decomposition of liquid water over Pt–TiO₂ catalyst. It has been found that an addition of carbonate salts to Pt-loaded suspensions led to highly efficient stoichiometric photo- catalytic decomposition of liquid water into H₂ and O₂. Neither the pH nor cation directly contributes to the water splitting. The presence of a high concentration of carbonate ions is essential for the catalytic photodecomposition of water. The carbonate ion affects both the Pt particles and the TiO₂ surface. The Pt was covered with some titanium hydroxide compounds and therefore, the rate of the back reaction (H₂O formation from H₂ and O₂) on the Pt was suppressed effectively in the presence of carbonate ions. On the other hand, the TiO₂ surface was readily covered with

several types of carbonate species. It is considered that these carbonate species aid desorption of O_2 from the TiO_2 surface.

In the place of pure water as the medium for dispersion of the catalysts, in some cases aqueous solution of $KHCO_3$ [46] or $NaOH$ has been used. Martin Reli et al [46, 69] studied different reaction media, such as, $NaOH$, $NaOH + Na_2SO_3$, NH_4OH , $NH_4OH + Na_2SO_3$ to understand the influence of reaction medium on the photo catalytic reduction of carbon dioxide. It was found that $NaOH$ was better reaction medium than NH_4OH for the yields of both gas phase [CH_4 , CO] and liquid phase [CH_3OH] products. Some authors tried with organic reaction media like methanol, propan-2-ol which itself get oxidized during reaction and hence unfavorable for the potential separation of products from CO_2 reduced products [69]. The use of $NaOH$ as reaction medium is also beneficial since OH^- ions act as hole scavengers, thereby retarding electron-hole recombination and simultaneously, alkaline solution increases solubility of CO_2 vis-à-vis pure water [40]

1.6.5 Photo reduction with other reductants

Some researchers have attempted to replace water with other reductants [70]. This provides a high reaction yield and high selectivity to desired products by changing the mechanism. Liu et al. [71] conducted an experiment with CdS in various solvents including water, methanol, ethanol, and 1-propanol with dielectric constants of 80, 33, 24.3, and 20.1, respectively. The results indicated that, if low-dielectric constant solvents or low-polarity solvents are used, CO_2^- anion radicals can be strongly adsorbed on the surface through the carbon atom of another CO_2^- anion radical pre-sorbed on surface Cd sites because these radicals are not completely solvated by low-polarity solvents. Here, CO is produced as the major reduction product of CO_2 . If a high-dielectric-constant solvent is used (e.g., water), the CO_2^- anion radicals can be greatly stabilized by the solvent, resulting in weak interactions with the photo catalyst surface. Similar effects of solvents have been observed on titania embedded in SiO_2 matrices [72]. Subsequently, the carbon atom of the radical tends to react with a proton to produce formic acid. Kaneco et al. [38] and later Dey [73] showed that photo catalytic reduction of CO_2 using TiO_2 suspension in aqueous solutions containing 2-propanol as a hole scavenger leads to the preferential formation of methane.

1.7 Classification of catalyst systems

For the sake of clarity and meaningful comparative study, the catalyst systems studied so far have been grouped in the following manner:

- i. Catalysts based on pure titania
- ii. Titania catalysts modified with metals/metal oxides
- iii. Titania catalysts modified with anions
- iv. Titania catalysts dispersed on meso porous materials
- v. Titania catalysts modified with sensitizers
- vi. Metal oxide catalysts-mono, binary & ternary oxides

Details on the application of these catalysts towards CO₂ photo reduction with water have been compiled in the Tables 1.7 Table 1.14.

Table 1.7 Studies on pure titania based catalysts

S. No.	Catalyst	Type of reactor Used	Conditions		Light Source/ Intensity	Product formation ($\mu\text{mol/g cat}$)	Ref.
			Reactant	Temp. (K)			
1.	TiO ₂	SS Autoclave (Batch mode)	98 kPa -2.5 MPa CO ₂ in NaOH	293	340 nm	HCOOH, CH ₃ OH, CH ₃ CHO, C ₂ H ₅ OH	51
2.	TiO ₂ liq.CO ₂ medium	SS vessel (batch mode)	6.5 MPa CO ₂	293	Xe /(990W)	HCOOH – 0.08	53
3.	TiO ₂ (DegussaP25)	SS vessel (batch mode)	2.8 MPa CO ₂ in 1M IPA	293	Xe / (4.2 kW)	CH ₄ – 1.3.	38
4.	TiO ₂ in CO ₂ Sc	SS vessel	9 MPa CO ₂	308	Xe-990 W/0.96 kWm ⁻² .	HCOOH	54
5.	TiO ₂	Rayonet photo reactor	CO ₂ in IPA	308	350 nm	CH ₄ – 0.3	74
6.	TiO ₂ Pellets	Cylindrical quartz tube	CO ₂ + H ₂ O	308	253.7 nm UVC, 3 x 1.6 W	CH ₄ - 200 ppm	55
7.	TiO ₂	Top – illuminated cell	CO ₂ + H ₂ O	311	253.7nm. UVC/4.8W	CH ₄ – .001, H ₂ ,CO	75
8.	Mixed phase TiO ₂	Annular glass	CO ₂ in aq. NaHCO ₃ +IPA	293– 298	UV-Vis 450 W Hg	CH ₄ . P-25- 5, A- 20, A+R - 50	31
9.	TiO ₂ (14 nm)	Stirred batch annular	CO ₂ in NaOH.	308	254 nm Hg 8W	CH ₃ OH - 0.16	30
10.	P-25, RM- TiO ₂ , UV100	glass reactor with quartz window	Satd CO ₂ in NaOH	298	Hg/300-700 nm, 250 W	CH ₄ , CH ₃ OH, C ₂ H ₅ OH	76
11.	TiO ₂ rod	Stainless steel with quartz window	(CO ₂ + H ₂ O) vapor	RT	300 W Xe lamp	CH ₄ – 5.7/h	77
12.	1D TiO ₂	Cylindrical with quartz window	(CO ₂ + H ₂ O) vapor	RT	400 W Xe lamp	CH ₄ - 1361/h	78
13.	TiO ₂ ultrathin nanosheets	Glass reactor	CO ₂ + H ₂ O vapor	RT	300 W UV Xe lamp	CH ₄ - 5.8 ppm/h	79
14.	Meso TiO ₂	Airtight circulation system	CO ₂ + H ₂ O vapor	RT	300 W Xe lamp	CH ₄ - 1.75, CO - 2.75	80

Table. 1.8. Studies on metal doped titania catalysts

S. No.	Catalyst	Type of reactor Used	Conditions		Light Source/ Intensity	Product formation ($\mu\text{mol/g cat}$)	Ref.
			Reactant	Temp. (K)			
1.	RuO ₂ doped with TiO ₂	Borosilicate glass reactor	CO ₂ + H ₂ O	333	75 W Hg	HCOOH – 1.47, HCHO – 0.13, CH ₃ OH– 0.22, Q E -0.04%	81
2.	Pd/ TiO ₂	Pyrex glass cuvette	CO ₂ in 0.05M NaHCO ₃ & Na ₂ C ₂ O ₄	299	450W Xe/360-nm, cutoff filter	HCOO ⁻ – 4.5	82
3.	Cu/ TiO ₂	SS vessel with a quartz window	28 kgf/cm ² CO ₂ at pH 5.45.	308	450 W UV Xe	CH ₄ – 21.8, C ₂ H ₄ – 26.2, C ₂ H ₆ – 2.7	83
4.	Cu(II)5wt%/ JRC-TiO-4	Flat- bottomed quartz cell.		275	75 W Hg > 290 nm	CH ₄ - 1.5, CH ₃ OH-6.0	84
5.	Cu ₂ O/TiO ₂	Slurry phase quartz reactor	135.6 kPa, CO ₂ in 0.2N NaOH	323	8 W Hg/254 nm	CH ₃ OH – 118.5	85
6.	Cu/TiO ₂	Cylindrical quartz reactor	CO ₂ in 0.2 N NaOH	308	Hg/365 nm	CH ₃ OH - 1000	40
7.	3wt%CuO/ TiO ₂	Horizontal SS vessel	CO ₂ in 1M KHCO ₃	373	10 W UV 2450 1W/cm ²	CH ₃ OH – 2655	86
8.	1.2wt% Cu(I)/ TiO ₂	Continuous optical fiber	1.29 bar CO ₂ : 0.026 bar H ₂ O	348	365 nm	CH ₃ OH - 0.45	65
9.	TiO ₂ , Cu/TiO ₂ , Ag/TiO ₂	optical-fiber	pCO ₂ (1.19 bar), pH ₂ O (0.03 bar)	348	UV/365 nm, 10W/cm ²	CH ₃ OH - TiO ₂ - 2.0. Cu/TiO ₂ - 3.8 Ag/TiO ₂ -4.2	64
10.	Cu-Fe/TiO ₂	Continuous circular Pyrex glass	CO ₂ + H ₂ O	348	250–450 nm, 225 mW/cm ²	CH ₄ – 0.9, C ₂ H ₄ – 0.6, QE - 0.024%	87
11.	Cu & Pt on N doped TiO ₂	SS chambers with quartz window	CO ₂ + H ₂ O	317	Natural sun light AM 1.5 Illumination	CH ₄ -75*, Alkane - 25*, H ₂ - 155*. *ppm cm ⁻² h ⁻¹ .	88
12.	Pt/TiO ₂ nanotube	Fixed bed quartz reactor	CO ₂ in H ₂ O vapor	308	300W Hg/365 nm.	CH ₄ . 3.9	89
13.	7% Ag doped TiO ₂	Annular Reactor	110 kPa CO ₂ in 0.2 M NaOH	308	8W Hg/254 nm	CH ₃ OH - 1.9, H ₂ – 120, CO - 0.9.	90
14.	2 wt% Cu/TiO ₂	SS 316 high-temp. chamber		298	100W Hg/ 365 nm	In-situ IR spectroscopic study	91
15.	N-Ni/TiO ₂		CO ₂ (200 mL/min)	348	λ =365nm 254nm. (15W) 400-780nm	CH ₃ OH – 254nm-482. 365 nm- 253.5 400-700 nm- 120.5	49
16.	Ag doped TiO ₂	Batch stirred Annular reactor	CO ₂ in 0.2 N NaOH	308	8 W Hg/254 & 365 nm, 8 W Hg filled with Ar (400	254 nm light more effective than 365 nm. 400 nm ineffective	48

Table. 1.9. Studies on anion doped titania catalysts

S. No	Photocatalyst	Type of Reactor used	Conditions		Light Source/ Intensity	Product formation $\mu\text{mol/g cat}$	Ref.	
			Reactant	Temp. (K)				
1.	S doped TiO ₂ .	batch reactor	type	CO ₂ + H ₂ O	Sun light	8 mW·cm ⁻² UV lamp	CH ₃ OH, C ₂ H ₅ OH	125
2.	N doped nanotubes	TiO ₂ quartz reactor		CO ₂ in 0.1 N NaOH	308	500W W-Halogen lamp	HCOOH 12475.8±266.7, CH ₃ OH 1132.6±45.4, HCHO -921.6±24.1	- 126 -
3.	N-doped mesoporous with cocatalyst Pt, Ag, Au	Quartz TiO ₂ reactor	tubular	CO ₂ + gaseous H ₂ O	333	350W Xe lamp	CH ₄ - 5.7 in 2 h	127
4.	I doped TiO ₂	Stainless steel with quartz window		(CO ₂ +H ₂ O) vapors	RT	450W Xe lamp		128
5.	N/100	Semi batch		CO ₂ + H ₂ O	RT	-	CH ₃ OH - 23/h	129
6.	g-C ₃ N ₄ -N-TiO ₂ (CT-70)	Gas circulation system	closed	(CO ₂ + H ₂ O) vapors	303	300 W Xe arc lamp	CO - 14.73	130
7.	N-TiO ₂ /spirulina	Slurry reactor		CO ₂ + H ₂ O	RT	13 W lamp	H ₂ - 144.99* CH ₄ -0.48 C ₂ H ₄ - 0.12 C ₂ H ₆ - 0.17 *mmol/g	131

Table. 1.10. Studies on titania supported on different materials

S. No	Catalyst	Type of Reactor used	Conditions		Light Source /Intensity	Product formation $\mu\text{mol/g cat}$	Ref.	
			Reactant	Temp (K)				
1.	TiO ₂ - loaded Nafion films	Cylindrical Press. optical cell with quartz window	high	2000 psia CO ₂ .		990 W Xe	HCOOH CH ₃ OH- CH ₃ COOH -30	-190, 132 280,
2.	MW-CNT supported TiO ₂	SS reactor.		CO ₂ and H ₂ O vapor	308	UV 365 nm	CH ₄ - 58.7, HCOOH- 93.4, C ₂ H ₅ OH- 149.4	45
3.	CdSe/Pt/ hetero structure	TiO ₂ Custom-built photo catalysis cell	3 Torr	H ₂ O vap. 0.3 Torr	308	visible light 420 nm	CH ₄ , CH ₃ OH, CO, H ₂ (CO ₂ conv. rate 0.8 ppm g ⁻¹ h ⁻¹)	133
4.	Graphene TiO ₂ nano Comp.	-				UV - 365 nm	CH ₄ - 8.5	134
5.	CdS-(Bi ₂ S ₃), TNT	Continuous-flow reactor		CO ₂ , NaOH, Na ₂ SO ₃	in 308	500 W Xe	CH ₃ OH - TNT - 102.5, TNTs - CdS - 159.5, TNTs-Bi ₂ S ₃ - 224.6	135
6.	nafion coated	Quartz reactor		CO ₂	in RT	300 W Xe	CH ₄ - 7	136

7.	Pd-TiO ₂ mesoporous TiO ₂ /graphitic carbon microspheres	Stainless reactor	Na ₂ CO ₃ steel CO ₂ +H ₂ O vapor	303	300 W lamp	Xe C ₂ H ₆ - 0.7 CH ₄ - 10.3	137
8.	CNTs@Ni- doped TiO ₂	Quartz reactor	CO ₂ +H ₂ O vapor	RT	visible light λ 400 nm	CH ₄ - 0.145/h	138
9.	graphene- Ti _{0.9} O ₂ spheres	Cylindrical hollow stainless quartz window	CO ₂ +H ₂ O steel vapor	RT	450 W lamp	Xe CO, CH ₄	139
10.	graphene-TiO ₂ nanosheets	Glass reactor	CO ₂ +H ₂ O vapor	RT	300 W lamp	Xe CH ₄ - 8 C ₂ H ₆ - 16.8	140

Table. 1.11. Studies on titania dispersed on porous materials

S. No	Catalyst	Type of Reactor used	Conditions Reactant	Tem p (K)	Light Source /Intensity	Product formation μmol/g cat	Ref.
1.	Q-TiO ₂ embedded in SiO ₂	Quartz cell	CO ₂ in IPA	308	500 W Hg	CO, Formate	72
2.	Pt on (a) Ti- ionexchanged (b) Ti MCM-48 framework	Flat bottom quartz cell. in	734Pa CO ₂	328	75 W Hg/λ > 280 nm	CH ₄ - 12, CH ₃ OH- 2.	141
3.	Pt/TiO ₂ Zeolites	in Quartz cell	CO ₂ in H ₂ O	328	Hg/λ >280 nm.	Ti in O _h sites- CH ₄ , T _d sites- CH ₃ OH	142
4.	Ti- silicalite mol. sieve		CO ₂ , H ₂ O vapor		UV laser 266 nm	CO, HCHO, CH ₃ CHO.	143
5.	Fluorination of Ti- FSM-1	Quartz cell with a flat bottom.	CO ₂ in H ₂ O	323	100 W Hg/λ > 250 nm	Fluorination increases selectivity towards CH ₃ OH	39
6.	TiO ₂ in porous- SiO ₂ thin film.		CO ₂ in H ₂ O	323	100 W Hg/λ > 250 nm	CH ₄ - 70, CH ₃ OH-10	144
7.	Ti -MCM- 41	IR vacuum cell, 3.4 ml	0.1 MPa CO ₂	298	266 nm	CO, O ₂ , H ₂ O confirmed as a e- donor.	145
8.	Ru/TiO ₂ , TiO ₂ /SiO ₂	Inner irradiation type (Batch mode)	CO ₂ in IPA	308	1000 Hg/365 nm.	W CH ₃ OH - 250, CH ₄ - 75.	146
9.	Cu, substitution TiO ₂ - SiO ₂ .	Fe Packed in circulated reactor fibers	bed, CO ₂ + vapor 216	H ₂ O 348	150 W Hg/ 320-500 nm, &500-800 nm	Cu- Fe/TiO ₂ favors C ₂ H ₄ formation, Cu- Fe/TiO ₂ -SiO ₂ favored CH ₄	147
10.	0.5%Cu/Ti SiO ₂	O ₂ - SS wall quartz window. (continuous- flow).	& CO ₂ in vapour	H ₂ O 308	Xe arc source, λ < 650 nm	CO - 60, CH ₄ - 10	148

11.	Cu ₂ O/SiC	XPA-II photochemical reactor	CO ₂ in NaOH & Na ₂ SO ₃ solns.	308	500 W Xe/200 to 700 nm	CH ₃ OH - 191	149
12.	Ti-SBA-15	Combinatorial photo reactors.	CO ₂ in H ₂ O		120 W Hg/280 to 650.	CH ₄ , C ₂ H ₄ , C ₂ H ₆ .	150
13.	Cu/TiO ₂ -SiO ₂	SS wall quartz (continuous flow)	(CO ₂ + H ₂ O) vapour	RT	Xe arc lamp	CO - 10/h CH ₄ - 60/h	151
14.	2 wt% Cu-TiO ₂ -SBA 15	Inner irradiation type (continuous mode)	CO ₂ in NaOH + H ₂ O	+315	500 W halide lamp	CH ₄ - 627/h	152
15.	Kaolinite/TiO ₂	Stirred annular reactor	batch NaOH	RT	8 W Hg lamp	CH ₄ - 4.5 CO - 2.5	153
16.	1, 3 wt% Ce-TiO ₂ /SBA 15	Stainless steel with window	CO ₂ + H ₂ O quartz	RT	450 W Xe lamp	CO - 1	154
17.	Ti-KIT-6/Si-Ti = 100	Pyrex reactor	glass CO ₂ + H ₂ O	RT	300 W UV lamp	CH ₄ - 4.4/h H ₂ - 2.2/h	155
18.	TiO ₂ (20%)/KIT6	Pyrex reactor	glass (CO ₂ + H ₂ O) vapor	RT	300 W lamp	CH ₄ - 44.56 CH ₃ OH - 1.09 CO - 120.54 H ₂ - 44.56	156
19.	Mesoporous g-C ₃ N ₄ flakes	Closed circulation system	gas CO ₂ in NaOH	RT	300 W Xe lamp, visible light λ 420 nm	CH ₃ OH, C ₂ H ₅ OH	157
20.	Si/TiO ₂ nanosphere	Stainless steel cell with window	(CO ₂ + H ₂ O) vapor quartz	RT at 50 psi	355 nm Laser lamp	CH ₃ OH - 197 μM/100 mL	158
21.	Cu/TiO ₂ monoliths	Pyrex reactor	glass (CO ₂ + H ₂ O) vapor	RT	200 W Hg/500 W halogen lamp	H ₂ - 12.5, CH ₃ OH - 4, C ₂ H ₅ OH - 3, CH ₃ CHO - 3	159
22.	TiO ₂ /SiO ₂	Quartz reactor	(CO ₂ + H ₂ O) vapor	298	300 W Xe lamp	CO - 3/h	160
23.	Cu/GO	Cylindrical reactor	(CO ₂ + H ₂ O) vapor	303	300 W halogen lamp	CH ₃ OH - 3/h, CH ₃ CHO - 4/h	161
24.	Ag-MWCNT @ TiO ₂	Quartz reactor	(CO ₂ + H ₂ O) vapor	333	15 W energy saving light	CH ₄ - 6.34, C ₂ H ₆ - 0.68	162
25.	Au-In/TiO ₂	Cylindrical stainless steel with quartz window	CO ₂ + H ₂	RT	200 W Hg lamp	CO - 8982/h	163
26.	Pt-RGO/TiO ₂	Quartz reactor	(CO ₂ + H ₂ O) vapor	333	15 W energy saving light	CH ₄ - 1.7	164
27.	Cu-TiO ₂ /ZSM-5	-	CO ₂ in NaHCO ₃ soln.	298	254 nm UV-lamp	CH ₃ OH - 50.05	165
28.	Ca/Ti _x Si ₄₁ MCM-	Quartz reactor	CO ₂ + H ₂ O (1:2)	303	6 W cm ⁻² Hg lamp	CH ₄ - 82/L	166

Table. 1.12. Studies on different metal oxides

S. No	Catalyst	Type of Reactor used	Conditions		Light Source /Intensity	Product formation μmol/g cat	Ref.
			Reactant	Temp (K)			
1.	Cu/ZrO ₂	Inner irradiation	CO ₂	in 308	400-W Hg	CO - 2.5	167

		quartz reactor	NaHCO ₃ (pH 2.3)		UV Hg		
2.	TiO ₂ ZrO ₂	(P25), Circulating quartz reactor	Pack.bed 1.1 atm CO ₂	316	UV/365 & 254 nm.	TiO ₂ - CH ₄ - .21, CO-0.28, C ₂ H ₆ - 0.2, ZrO ₂ - CO- 1.24 With H ₂ +H ₂ O	168
3.	Pd, Cu Mixed oxides of MgO, ZnO Al ₂ O ₃ ,TiO ₂ , SiO ₂ .	on Batch reactor	CO ₂ in 0.5M KHCO ₃ (pH = 7.5)	308	250 mW Hg.	C ₁ -C ₃ products. Acidic supports- CH ₄ , HCHO, HCOOH. Basic supports-C ₂ H ₆ , C ₂ H ₅ OH, Acetone	169
4.	MgO	Closed static system	CO ₂ & H ₂	308	500 W Hg	CH ₄ ,CO.	170
5.	Ga ₂ O ₃	Closed circulating system- Quartz	CO ₂ : H ₂ : (150:50 μmol).	308	200W Hg-Xe.	CO - 2.1	171
6.	ZrO ₂	Quartz reactor	CO ₂ : H ₂ or CH ₄ = 150:50 (μmol).	308	500W Hg	CO - 9.5	172
7.	Meso Ga ₂ O ₃	Quartz window- closed chamber	CO ₂ in H ₂ O	300	300 W Xe	CH ₄ - 2.9	173
8.	WO ₃ nanosheets	Pyrex glass cell	CO ₂ + H ₂ ORT vapor		300 W Xe visible light λ 420 nm	arc,CH ₄ - 16	174
9.	rectangular sheet-like WO ₃	Stainless steel reaction chamber	CO ₂ + H ₂ ORT vapor		UV Xe lamp	CH ₄ - 0.34	175
10.	W ₁₈ O ₄₉ nanowires	-	CO ₂ + H ₂ ORT vapor		visible light λ 420 nm	CH ₄ - 4000* * ppm/g	176
11.	Porous MgO/TiO ₂	Continuous flow glass reactor	CO ₂ + H ₂ O423 vapor		400 W Xe lamp	CO - 30/h	177
12.	g-C ₃ N ₄ nanosheet	Stainless steel quartz window	withCO ₂ + H ₂ ORT vapor		300 W Xe lamp	CH ₄ - 0.5, CH ₃ CHO - 0.05	178
13.	g-C ₃ N ₄ / Bi ₂ WO ₆	Glass reactor quartz window	withCO ₂ + H ₂ ORT vapor		300 W Xe lamp	CO - 5.19/h	179
14.	CNTs-TiO ₂	Quartz reactor	CO ₂ + H ₂ O	RT	15 W energy saving light bulb	CH ₄ - 1.2	180
15.	CuO nanowire/ZnO	Cylindrical stainless steel with quartz window	(CO ₂ + H ₂ O) vapor	+RT	400 W Xe lamp	CO - 1980/h	181
16.	Fe ₂ O ₃ /Cu ₂ O	Cylindrical stainless steel reactor	(CO ₂ + H ₂ O) vapor	+RT	300 W Xe lamp	CO - 5	182
17.	Rh/Cr ₂ O ₃ /GaN	Pyrex reaction cell	(CO ₂ + H ₂ O) vapor	+RT	300 W Xe lamp	CH ₄ - 85, CO - 100, H ₂ - 3.8	183
18.	ZnS	Fused silica reactor	CO ₂ in Na ₂ S	288	1 kW high-press. Hg (Xe) arc lamp	HCOO ⁻ - 440 μM	184
19.	g-CN	Schlenk flask	CO ₂ in Co- (bpy) ₃ C ₁₂ and TEOA mixture	333	300 W Xe lamp	CO - 10.2, H ₂ - 2.8	185
20.	ZnO/ZnTe	Quartz reactor	CO ₂ + H ₂ O	-	300 W Xe lamp	CH ₄ - 356.51	186

Table 1.13. Studies on mixed metal oxide catalysts

S.	Catalyst	Type of	Conditions	Light Source	Product	Ref
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No	Reactor used	Reactant	Temp (K)	/Intensity	formation $\mu\text{mol/g cat}$
1.	SrTiO ₃ in aq. suspension UHV surf. Anal. chamber -batch	CO ₂ + H ₂ O	Sun light	Natural sunlight	HCOOH, HCHO, 16 CH ₃ OH. QE=0.011%
2.	CaFe ₂ O ₄ Quartz beaker	CO ₂ /0.01 M NaOH (pH 5.8)	308	500-W Hg	CH ₃ OH, HCHO. 187
3.	Pt/ K ₂ Ti ₆ O ₁₃ + Fe-Cu- K/DAY Photoreactor with quartz window	CO ₂ + H ₂ O	308	300W Xe & 150W Hg.	CH ₄ -0.014 188 HCOOH- 3.88 CH ₃ OH -1.45 C ₂ H ₅ OH- 0.35
4.	Pt/ K ₂ Ti ₆ O ₁₃ with Cu/ZnO. Photo reactor with flat quartz window.	CO ₂ + H ₂ O	308	300W Xe- or 150W Hg.	CH ₄ - 0.86, 189 HCOOH- 43.47, CH ₃ OH - 18.93 HCHO -10.97.
5.	ATaO ₃ (A= Li, Na, K) Closed circulating reactor	CO ₂ : H ₂ = 150:50 (μmol)	303	200W Hg-Xe	The order of 190 activity- LiTaO ₃ > NaTaO ₃ > KTaO ₃ . CO - 0.42 on LiTaO ₃
6.	Bi ₂ WO ₆ square nanoplates 230 mL glass reactor	CO ₂ + H ₂ O		300 W Xe	CH ₄ - 6 191
7.	Pt-NaNbO ₃ Pyrex glass	CO ₂ + H ₂ O	308	300-W Xe	CH ₄ -653*, 192 *ppm/h/g
8.	Pt/ NaNbO ₃ Closed Pyrex cell	80 kPa CO ₂ in H ₂ O.	308	300 W Xe	CH ₄ - 0.486 193
9.	Pt/Meso Zn-Ge (ZGON)			($\lambda > 400 \text{ nm}$)	CH ₄ - 26.8*, 194 *ppm/h/g
10.	Ag- ALa ₄ Ti ₄ O ₁₅ (A = Ca, Sr, & Ba) Inner irradiation quartz cell	CO ₂ flow system (15 mL min ⁻¹).		400W Hg	BaLa ₄ Ti ₄ O ₁₅ >SrL 195 a ₄ Ti ₄ O ₁₅ >CaLa ₄ Ti ₄ O ₁₅ . CO, HCOOH
11.	Ni@NiO on InTaO ₄ Pyrex glass (continuous flow)	CO ₂ (3 kg cm ⁻²) H ₂ O	298	100 mW Xe lamp	Methanol - 196 InTaO ₄ < InTaO ₄ -N<Ni@NiO/InTaO ₄ -N.
12.	NiO-InNbO ₄ , Co ₃ O ₄ -InNbO ₄ Pyrex glass (continuous flow)	CO ₂ in 0.2 M KHCO ₃	308	500W halogen H-500; 143 μ W/cm ² ; λ 500-900nm	CH ₃ OH 197 NiO-InNbO ₄ - 1.577 Co ₃ O ₄ -InNbO ₄ - 1.503.
13.	HNb ₃ O ₈ nanobelts Quartz tubular reactor	H ₂ O+CO ₂	318	350 W Xe	CH ₄ - 3.58 198
14.	Zn-Al LDH, Zn-Cu-Ga Quartz reactor	2.3 kPa of CO ₂ + 21.7 kPa of H ₂	305-313	500-W Xe arc lamp	CO - 0.62, 199 CH ₃ OH - 0.17.
15.	FeTiO ₃ / TiO ₂ Pyrex glass	CO ₂ in NaHCO ₃	RT	500W Xe (with cut off)	CH ₃ OH - 0.46 200
16.	CuGaO ₂ , CuGa _{1-x} Fe _x O ₂ SS cell	CO ₂ in H ₂ O	RT	300WXe arc	CO - 9*, *ppm g ⁻¹ h ⁻¹ 201
17.	SiO ₂ - HNb ₃ O ₈ Pillared Quartz tubular reactor	H ₂ O/CO ₂ = 0.14	333	34.8mW Xe arc	cm ⁻² CH ₄ - 2.9 202
18.	Pt/SrTiO ₃ -Rh/ Pt/CuAlGaO ₄ H- Twin reactor	2 mM FeCl ₂ /FeCl ₃	MRT	AM 1.5G	CH ₃ OH - 0.52 203 H ₂ - 0.12

19.	WO ₃ Pt/SrTiO ₃ -Rh/ Pt/CuAlGaO ₄ WO ₃	H- Twin reactor	2 mM- FeCl ₂ /FeCl ₃		AM 1.5G	CH ₃ OH - 8 H ₂ - 1	204
20.	Pt/self-doped SrTiO ₃ □ _δ	-	CO ₂ +H ₂ O water	-	300 W Xe lamp, visible light λ 400 nm	CH ₄ - 0.26/cm ²	205
21.	Ag/ SrTiO ₃	Batch slurry reactor	CO ₂ CH ₃ OH	in 298	Hg lamp	HCOOH	206
22.	Au/ architected SrTiO ₃	leaf-Pyrex reaction cell	CO ₂ +H ₂ O vapor	RT	300 W Xe lamp	CO, CH ₄	207
23.	Pt/Fe ₂ V ₄ O ₁₃ nanoribbons		CO ₂ +H ₂ O vapor		visible light λ 420 nm	CH ₄	208
24.	Pt and RuO ₂ / Na ₂ V ₆ O ₁₆ nanoribbons	Circular reactor	glass CO ₂ +H ₂ O vapor		300 W Xe lamp, visible light λ 420 nm	CH ₄ - 2	209
25.	Bi ₆ Mo ₂ O ₁₅ sub-microwires	-	CO ₂ +H ₂ O vapor	RT	UV Xe lamp	CH ₄ - 17* O ₂ - 250	210
26.	Bi ₂ WO ₆ hollow- microspheres		(CO ₂ +H ₂ O) vapor	RT	visible light λ 420 nm	CH ₃ OH - 33 *ppm,	211
27.	Pt/mesoporous In(OH) ₃	Gas circulation pump	(CO ₂ +H ₂ O) vapor	RT	UV Xe lamp	CH ₄ - 25	212
28.	RuO ₂ /meso ZnGa ₂ O ₄	Glass	(CO ₂ +H ₂ O) vapor	RT	UV Xe lamp	CH ₄ - 145 ppm	213
29.	RuO ₂ /ZnGa ₂ O ₄ nanocubes	Glass reactor	(CO ₂ +H ₂ O) vapor	-	UV Xe lamp	CH ₄ - 2, O ₂ - 21	214
30.	Pt/ ZnAl ₂ O ₄ modified meso ZnGaNO	--	(CO ₂ +H ₂ O) vapor	-	visible light λ 420 nm	CH ₄ - 40	215
31.	Pt/ZIF- 8/Zn ₂ GeO ₄ nanorods	-	CO ₂ bubbled Na ₂ SO ₃	RT	UV Xe lamp	CH ₃ OH - 3	216
32.	Pt & RuO ₂ / sheaf-like, hyperbranched Zn _{1.7} Ge _{1.8} O ₇	Pyrex glass	(CO ₂ +H ₂ O) vapor	RT	visible light λ 420 nm	CH ₄ - 55	217
33.	4.5(ZnGa ₂ O ₄): (Zn ₂ GeO ₄)	Glass reactor	(CO ₂ +H ₂ O) vapor	RT	UV Xe lamp	CH ₄ - 2.75, O ₂ - 17	218
34.	Pt/In ₂ Ge ₂ O ₇ (En) nanowires	Pyrex glass cell	(CO ₂ +H ₂ O) vapor	RT	300 W Xe lamp	CO - 4, O ₂	219
35.	Pt/Zn ₂ SnO ₄	Pyrex glass cell	(CO ₂ +H ₂ O) vapor	RT	UV Xe lamp	CH ₄ - 350	220
36.	layered LDH	Mg-In Closed system	circulation (CO ₂ +H ₂ O) vapor	RT	UV Hg-Xe lamp	CO - 3, O ₂	221
37.	layered Zn- Cu-Ga LDH	Quartz reactor	(CO ₂ +H ₂) vapor	RT	500 W UV Xe lamp	CH ₃ OH, CO	222
38.	Ag/KTaO ₃	Glass reactor	CO ₂ +H ₂ O	RT	300 W Xe lamp	CO - 152.6, H ₂ - 1134, O ₂ - 499.9	223
39.	(MgAl)-LDO grafted TiO ₂	Quartz tube reactor	(CO ₂ +H ₂) vapor	423	100 W He/ Xe lamp	450 W CO - 4/h	224
40.	ZnGaNO nanorod	Glass reactor	CO ₂ +H ₂ O	RT	300 W Xe lamp	CH ₄ - 0.19	225
41.	NiCo ₂ O ₄	with Schlenk reactor	TEOA/ 303		300 W Xe lamp	CO - 35, H ₂ - 5	226

	[Ru(bpy) ₃]Cl ₂ . 6H ₂ O		water/acetoni trile				
42.	SnNb ₂ O ₆	Schlenk reactor	CO ₂ +H ₂ O	RT	300 W Xe lamp	CH ₄ - 110 μL/h	227
43.	MTaO ₃ (M = Li, Na, K)	Pyrex glass cell	CO ₂ +H ₂ O	RT	200 W Hg-Xe arc lamp	CH ₄ - 1.9 nmol/h CO - 4	228
44.	Ag/BaZrO ₃	Cylindrical reactor	quartz(CO ₂ +H ₂ O) vapor	RT	300 W Xe lamp	CH ₄ - 4	229
45.	MnCo ₂ O ₄	-	CO ₂ TEOA	in303	300W Xe lamp	CO - 27, H ₂ -8	230
46.	Cu _x O _y -ZrOCo ^{II} SBA-15	Stainless vacuum cell	infraredCO ₂ diethylamine	inRT	laser	CO	231
47.	Cr doped SrTiO ₃	-	(CO ₂ +H ₂ O) vapor	RT	300W Xe lamp	CH ₄ - 8.8	232
48.	Ca _x Ti _y O ₃	Quartz reactor	CO ₂ +H ₂ O	303	6 W cm ⁻² , UV lamp	CH ₄ - 17	233
49.	C, N/sodium titanate	Stainless steel	(CO ₂ +H ₂ O) vapor	RT	100 W Xe solar simulator	CH ₄ - 9.75/h	234

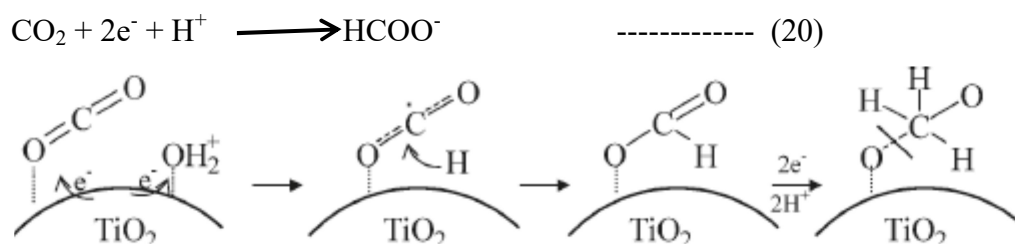
Table 1. 14 Studies on dye sensitized photo catalysts

S. No	Catalyst	Type of Reactor used	Conditions		Light Source /Intensity	Product formation μmol/g cat	Ref.
			Reactant	Temp (K)			
1.	Metal porphyrin / phthalocyanine on Nafion	Glass cell with an optical window.	CO ₂ in TEA	308	500 W tungsten-halogen	HCOOH.	235
2.	Dye([Ru(Bpy) ₃] ²⁺ perylene Di-Imide based) sensitized, Q- yield:Pt onTiO ₂	Glass chamber connected to a vacuum line	0.09 MPa CO ₂ inH ₂ O	298	75 W daylight lamp, 150 W UV	CH ₄ - 0.6.	236
3.	Ruthenium (N ₃)- sensitized Cu-Fe/TiO ₂	Continuous circulating Pyrex glass	CO ₂ + H ₂ O (vapor)	348	Solar 20 mW cm ⁻² , UV lamp 225 mW cm ⁻²	CH ₄ . 0.617	237
4.	CoPc/TiO ₂	Pyrex glass cell (batch mode).	CO ₂ in 0.1N NaOH.	308	500W tungsten-halogen	HCOOH - 300, CH ₃ OH - 10, HCHO - 50.	238
5.	0.7 wt.% CoPc/TiO ₂	In-situ Pyrex glass cell	CO ₂ in 0.1N NaOH.	308	500W tungsten-halogen	HCOOH-1487.6 CH ₃ OH - 93 HCHO - 134.3.	239
6.	Ru/RuOx sensitized TiO ₂	-	CO ₂ + H ₂ O	-	Solar simulator	CH ₄ - 900 μL h ⁻¹	240
7.	Dye sensitized-(perylene diimide derivatives) Pt impregnated on TiO ₂	-	CO ₂ + H ₂ O	RT	75 W daylight lamp	CH ₄ - 0.74	241
8.	N719/TiO ₂	H type reactor	CO ₂ + H ₂ O/ 2 M NaOH	RT	300 W Xe lamp	CH ₃ OH - 178.1/cm ² HCHO - 129.2/cm ²	242
9.	IrOx/SiGe-jn/CC/p-RuCP	Stainless Monolithic shaped device	steelCO ₂ + H ₂ O	RT	Simulated light	solarHCOOH - 50.2, H ₂ - 3.6, O ₂ - 26.4	243
10.	Zinc porphyrin/TiO ₂	Pyrex glass reactor	(CO ₂ + H ₂ O) vapor	RT	300 W Xe-lamp	CO - 8.07/h CH ₄ - 1.01/h	244

detailed experiments, researchers have put forward plausible pathways for CO₂ reduction on TiO₂ surfaces.

Three different reaction pathways depending on the binding mode of CO₂⁻ radical anion on the semiconductor surface have been proposed [245], ie, i) The formaldehyde pathway, ii) The carbene pathway, iii) The glyoxal pathway shown in Fig. 1.9

In the case of Formaldehyde pathway, binding mode of CO₂ through one of the oxygen atom on titanium **atom/ion** ? or carbon atom through surface oxygen atom of TiO₂, favors the formation of .COOH radical, which further combines with .H to form formic acid. As shown in Fig. 1.9 a, final 8 e- reduction product CH₄ was obtained from consecutive reduction of formic acid through HCHO and CH₃OH as intermediate products. These observations find support in a recent publication by Dimitrijevic et al [246], wherein detailed low temperature ESR measurements on TiO₂ nano particles dispersed in aqueous alkaline solutions, have indicated the formation of H atoms and OH radicals in addition to methyl (.CH₃) and methoxy (.CH₃O) radicals on the surface. However the formation of surface formate species is proposed as the initial step according to the Scheme. 4 below:

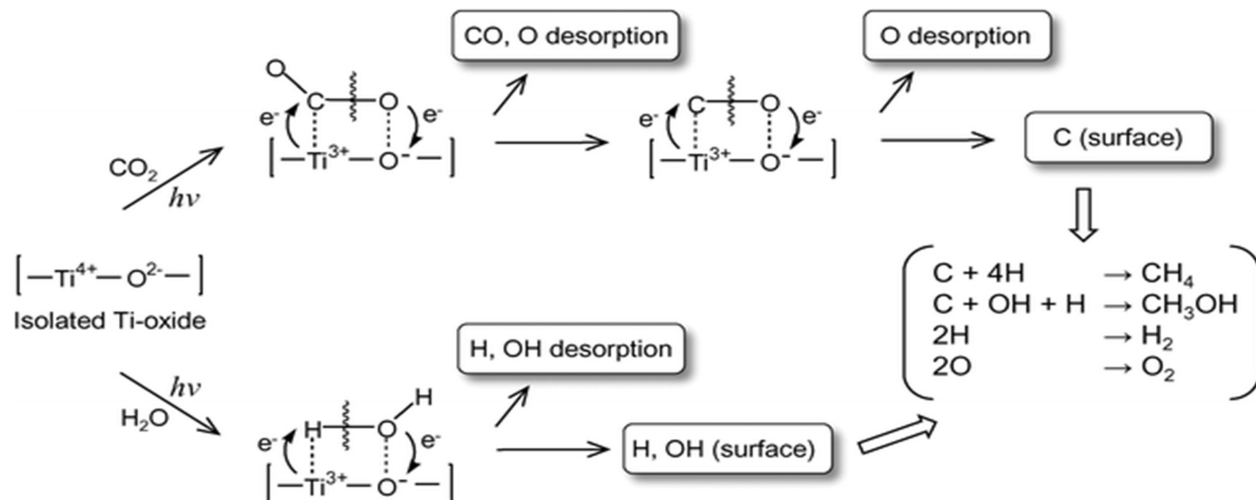


Scheme 4 Proposed mechanism of photo catalytic transformation of CO₂ to methoxy radical over TiO₂ in the presence of dissociated/ bound water [246]

Ulagappan and Frei [145] carried out a mechanistic study of the reaction with methanol as electron donor on Ti silicalite using in-situ FT-IR spectroscopy and traced the reaction pathway using isotopic labelling studies with C¹⁸O₂, ¹³CO₂ and ¹³CH₃OH. HCOOH was identified as the primary product, which on pyrolysis gives CO. In the absence of methanol, water was confirmed as the electron donor.

Koci et al. studied kinetic model for CO₂ photo reduction with respect to the formaldehyde pathway [247] the result shows that the formation of methane did not correspond to the consecutive reduction of formic acid and methanol. Hence they have proposed carbene pathway for CO₂ photo reduction shown in Fig. 1.9 b, in this pathway, anion radical bind through carbon

on the semiconductor surface, formation of CO and O occur in the first step. Then adsorbed CO reduced with two electrons to form carbon residue on the semiconductor surface, which further combines with .H to form carbene and methyl radicals and finally CH₄. Formation of different transient surface species and their transformations on TiO₂ during photo catalytic reduction of CO₂ by water was traced by Anpo et al [43, 248] using ESR, EXAFS and other spectroscopic techniques. Ti³⁺, H, C and CH₃ radicals were detected by ESR studies carried out at 77K. The charge transfer excited state, (Ti³⁺-O)^{3*} with Ti in tetrahedral co-ordination, formed by absorption of light energy, was proposed as the active site on which CO₂ gets reduced to CO and C, which on addition of active surface hydrogen forms hydrocarbons. Further mechanistic pathways in this case, have been elucidated in Scheme. 5.



Scheme. 5. Schematic representation of the photo catalytic reduction of CO₂ with H₂O on anchored titanium dioxide [43, 248]

A recent publication by Yang et al [249] on the photo catalytic reduction of CO₂ using Ti-SBA-15 deals with the investigations on the effects of varying feed composition on the product patterns, with a view to understand the reaction mechanism. In particular, addition of CO, H₂ in the place of H₂O, methanol and formaldehyde was studied in detail. While CH₄, C₂H₄ and C₂H₆ could be observed with CO + H₂O with reasonable rates, with CO+H₂ mixture, the reaction rates were very low. It was concluded that H₂O was a more efficient reductant with CO₂ or CO than H₂. CH₃OH was not a significant product and when added with the feed and it did not increase

the reaction rate. Similarly added formic acid also did not enhance product formation. These observations rule out methanol or formic acid as intermediates in the formation of hydrocarbons on Ti-SBA-15. However, added formaldehyde underwent facile conversion to hydrocarbon products. Based on the detailed analysis of the products it was proposed that CO₂ photo reduction proceeds through the formation of CO in the initial stages followed by its conversion to formaldehyde, which in turn gets converted to other hydrocarbon products. Ti-OH site, which on photo activation gets converted to [Ti (III)-O]* is considered as the active site [145].

Yang mechanism ?

Kinetic models for photo catalytic reduction of CO₂ with water on titania have been reported by Lo et al. [168] and Tan et al. [250]. Both authors have applied single site Langmuir-Hinshelwood [L-H] type kinetic model to simulate the process. Lo et al.[168] could successfully validate their model with the experimental data with a pseudo first order reaction rate equation. Tan et.al [250] adopted the reaction scheme involving the formation of surface carbon radicals as proposed by Anpo et al. [43, 248] and could predict rates of formation of methane and hydrogen. Koci et al. [247] while applying the L-H model have checked the suitability of the two reaction mechanisms proposed, i.e., one by Anpo [43, 248] and the other by Wu [67] and observed that their model supports Anpo's mechanism wherein CO is proposed as the primary intermediate. Hence carbene reaction pathway is a more plausible reaction pathway for CO₂ reduction.

Shkrob et al [245, 251, 252] have proposed Glyoxal reaction pathway for CO₂ photo reduction by adopting EPR study, which includes both oxidation and reduction reactions. In the previous reaction pathway authors were interested in reduction reactions (electrons), but highly oxidative holes are also present in the system. The formation of oxidized products from formaldehyde and methanol is more favorable compared to reduce product form it. Hence Shkrob et al proposed C₂ complex reaction pathway shown in Fig. 1.9c, in which dimerization of formyl radical to gives glyoxal, further reduced to form acetaldehyde through vinoxyl radical. CH₃CHO easily oxidized to form unstable acetyl radical which further undergoes decarbonylation to form methyl radical, and then combine with .H to form CH₄.

While the formation of C₁ hydrocarbons could be explained to a reasonable level of acceptability, the understanding on the pathways leading to the formation of C₂ and >C₂ hydrocarbons was not clear. Dimerization of surface C₁ species was proposed as the possible route for the formation of C₂ hydrocarbon products [253], though direct experimental evidence to

this effect was lacking.

Yang et al. [249] observe that the backward reaction ie, oxidation of hydrocarbons back to CO₂ and water, proceeds to a significant extent. This implies that the oxygen produced by the splitting of water, which is responsible for the backward reaction, has to be removed effectively to increase hydrocarbon yields. Means of separating physically the oxidation and reduction sites would be crucial in this respect. It is clear that the reaction mechanism is quite complex and depends on the type of the catalysts/active sites.

1.9 Deactivation of photo catalysts

In some cases [146, 89, 133, 135, 151] the catalysts reported for photo reduction of CO₂ tend to get deactivated within short period, while in few cases activity beyond 20 hrs. has been reported. Transformation of photo activated CO₂ to hydrocarbons proceeds through several hydrocarbon intermediates, whose identity or nature is yet to be established. Accumulation of these intermediates on the catalyst surface and blocking of the active sites is one of the major reasons for the catalyst deactivation. In the case of catalyst nano particles dispersed in liquid media, coagulation and reduction in light absorption power [146] and changes in the oxidation state of metal ions [133] may lead to catalyst deactivation. Regeneration with air helps in restoring the activity. However the phenomenon of catalyst deactivation in this process needs further study, especially when large scale applications of this process are desired.

An in-depth understanding of the reaction mechanism and the fast deactivation of the photo catalyst would be helpful in the development of superior catalysts for this process that has the potential to emerge as a sustainable route for the production of fuels and chemicals.

1.10. Future trends and research directions

Photo catalytic reduction of carbon dioxide with water to fuels/chemicals (methane, methanol, etc.,) is an emerging area of research towards utilizing the abundant sunlight. Though the process has the potential to become a viable and sustainable alternative energy source to fossil fuels, it has thrown up several tough challenges to the scientists and technologists, which are yet to be tackled, namely,

- Facilitating the activation of two thermodynamically most stable molecules, CO₂ and H₂O
- Conversions achieved so far are extremely small, < 1 %, occurring at very slow rate

- Catalysts tend to get deactivated over short period which needs further studies
- CO₂ photo reduction process is highly complex, involving multi electron transfer and non-selective, leading to a range (C1-C3) of hydrocarbon products- reaction pathways have not been established yet
- Design of catalysts consisting of photo active phase/support and co-catalysts aided by metal ion and /or anion doping and light harvesting components/sensitizers, as a functionally integrated composite, is equally complex.
- Ideal catalysts are expected to display maximum efficiency towards solar energy absorption and possess requisite band energy level characteristics to drive the redox reactions.
- The process involves two steps, spitting of water and reduction of carbon dioxide, which is thermodynamically more favourable. Since the second step involves multi-electron transfer, the rates are very slow relative to the first. These two steps are to be synchronized to achieve higher yields of hydrocarbons.
- Multiple and complex surface reaction pathways that involve several carbon containing ion radicals, render the selective formation of methane or methanol a difficult task.
- Further decomposition of the products and promotion of backward reactions also contribute towards lower yields.
- Catalyst deactivation proceeds through the formation of carbonaceous species on the surface. This implies that the metal function responsible for the hydrogenation of carbonaceous species needs to be improved though availability of hydrogen via water splitting may not be the issue.
- Titania, subjected to a wide range of modifications, in the form of titania based composites and in different morphological forms has been explored to enhance the activity for photocatalytic reduction of CO₂ with water with respect to pristine titania. Primary objectives behind the modifications, namely, promoting visible light activity, retarding the recombination of charge carriers by effective physical separation (by doping with metals, anions & cations), facilitating their transport through titania surface, isolation of titania sites by dispersion on high surface area supports and incorporation of suitable active elements to bring out required redox reactions, have been realized to a significant extent. However, the expected improvement in activity has been moderate, an increase by 2-4 times, which is too low for any possible practical applications.

- In-depth investigations on the surface reaction pathways by *in-situ* spectroscopic methods, supported by sound theoretical studies on the activation and surface transformations of CO₂ and other aspects for investigation, as detailed in the earlier section, would be helpful in controlling deactivation and achieving higher conversions.

Nevertheless, research efforts on these fronts are being pursued with the objectives of designing of efficient catalyst systems to achieve higher yields of desired products and improving catalyst life. Efforts in future have to be towards the development of alternative catalysts, based on various semiconducting metal oxides/sulfides/nitrides/phosphides, layered titanates, binary and ternary oxides of Nb, Ta, Ga & In in conjunction with alkaline, alkaline earth and rare earth oxides and with a host of co-catalysts and sensitizers.[9, 10, 74-244, 254, 255]

Especially, the following areas/aspects are worth exploring further:

- A number of binary and ternary oxides of Bi, V, Nb & Ta with Gr IIIA elements like, Al, Ga & In are known to be efficient catalysts for photo catalytic splitting of water in the visible region [256, 257]. These systems with suitable co-catalysts like NiO could be excellent catalysts for CO₂ photo reduction
- Most of these oxides are synthesized by high temperature solid state reaction with very low surface area. Soft chemistry routes could be explored to get high surface area samples. However, in such cases, the contribution due to residual carbon on the catalysts is to be accounted for.
- These compounds possess well-defined crystal structure and hence their solid state and photo-physical properties could be fine-tuned to derive maximum performance
- Performance of such photo catalysts could be improved further by forming composites with advanced materials like CNT, graphene [258-261] and Nafion [262] which facilitate free and fast transfer of charge carriers could be another way to improve performance.
- Studies on modes of adsorption and activation of CO₂ on metals, metal oxides, which act as co-catalysts- experimental as well as theoretical approaches are to be pursued.
- Use of different co-catalysts, single as well as bi-component systems
- Elucidation of the mechanistic pathways for the transformation of transient surface species and formation of C₂ and higher carbon number products
- Modes of deactivation of catalysts and possibilities for regeneration

It is expected that the use of photo electrochemical cells (PEC) for conversion of CO₂ to methanol [263-266] would add another dimension to the process, to get improved yields of hydrocarbons. Additionally, development of novel and more efficient catalyst systems and prevention of re-oxidation of products could help in improving the efficiency of the process.

1.11 Scope of the present investigation

CO₂ is one of the cheapest and most abundant carbon containing raw material in the earth. But the usage of CO₂ as raw material is thermodynamically unfavorable due its stability and chemically inert nature. Hence thermodynamically uphill reactions can be solved by developing a good catalyst system. The production of fossil fuels from green house gas CO₂ and abundantly available water in the presence of natural sunlight is an attractive research, because it will give remedy to both energy and environmental issues which we are facing day today life. There is some relief from green house effect by using CO₂ as reactant and also getting fossil fuel (energy) from natural source such as solar light and water. The challenge is to activate thermodynamically most stable molecules CO₂ and H₂O. Photo catalytic reduction with water has the potential to emerge as a viable process. Since, photo catalysst can convert solar energy into chemical energy and also have the ability to promote non-spontaneous reactions ($\Delta G > 0$). Hence design of photo catalysts is an important and challenging task.

The primary objective of the present investigation is to design novel photo catalysts for CO₂ reduction. Detailed literature survey on different types of catalysts investigated so far reveal that two perovskite type catalysts, NaTaO₃ and Sr₃Ti₂O₇, which display significant activity for splitting of water and possess conduction and valance band energy levels suitable for CO₂ photo reduction have not been exploited so far. Both oxides, being wide band gap semi-conductors, are to be suitably modified to enable visible light absorption. Attempts have been made to modify these oxides and explore their activity for CO₂ photo reduction. Besides, meso-porous character of the photo catalysts is known to improve the activity (Ref). In order to explore this aspect, a comparative study of standard titania P-25 and a lab-made mesoporous titania in pristine and doped (N,S & Fe) forms have been investigated. Accordingly, investigations covering several other aspects, as detailed below, around these three main catalyst systems (TiO₂, La-NaTaO₃ and Sr₃Ti₂O₇) have been planned:

- Studies on titania based catalysts:

- Comparison of mesoporous titanium dioxide with standard P-25 titania
- Influence of doping/co-doping with N,S & Fe
- Effect of supporting N, S &Fe co-doped TiO₂ samples on sepiolite
- Studies on La modified NaTaO₃ based photo catalysts:
 - Influence of different co-catalysts: Ag, Au, Pt, Pd, NiO, CuO and RuO₂ and bi-metallic co-catalysts, Pt-CuO & Pt-NiO
 - Effect of metal–non metal (Fe,N) co- doping
 - Sensitization with Cobalt tetra phenyl porphyrin (CoTPP)
 - Effect of addition of basic component, MgO
- Studies on layered perovskite type titanates based on Sr₃Ti₂O₇ as photo catalysts:
 - Comparison of strontium titanates- SrTiO₃, Sr₃Ti₂O₇ and Sr₄Ti₃O₁₀
 - Effect of doping/co-doping Sr₃Ti₂O₇ with N,S & Fe

Hydrothermal and polymer complex methods have been adopted for the preparation of the tantalates and titanates. All catalysts have been subjected to comprehensive characterization studies, using XRD, DRS-UV, photo luminescence, SEM, TEM, XPS, Raman spectroscopic techniques and surface area analysis. Photo catalytic efficiency of the prepared catalysts for CO₂ reduction with water has been studied in a lab-made photo reactor, with UV-visible radiation. Observed activity patterns have been rationalized in terms of structural, morphological, electronic and photo-physical properties of the catalysts, so as to arrive at a basis for the design of effective photo catalysts for this application.

1.12. Organization of the thesis

Chapter 1. Introduction

Chapter 2. Experimental methods

Chapter 3. Studies on titania based catalysts

Chapter 4. Studies on La modified sodium tantalite based catalysts

Chapter 5. Studies on strontium titanate based catalysts

Chapter 6. Summary and Conclusions

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