9 Photocatalytic Reduction of Carbon Dioxide by Water: A Step Towards Formation of Fuels and Chemicals

9.1 INTRODUCTION

9.1.1 Heterogeneous Photo Catalysis

The rigorous study of photo-catalytic reactions is continuous from 1970. The concept and the term 'heterogeneous photo-catalysis' were introduced and developed in Lyon to describe the partial oxidation of alkanes and olefinic hydrocarbons. The reactions took place at ambient temperature in the presence of a photo-catalyst conventionally titanium dioxide (TiO_2, anatase) under UV irradiation. Heterogeneous photo-catalysis is defined as "catalytic process during which one or more reaction steps occur by the involvement of electronhole pairs, photo-generated on the surface of semiconducting materials illuminated by light of suitable energy". This pathway differs from the usual thermal reaction sequence and leads to reaction product selectivity patterns different from those observed with the thermal catalyzed reactions.

9.2 PRINCIPLES OF PHOTO-CATALYSIS

The band gap is one of the characteristic parameters for the electronic structure of any semiconductor and is defined as the energy interval (ΔE_g) between the valence band (VB) and the conduction band (CB). VB is defined as the highest energy band in which all or most of the energy levels are occupied by electrons, whereas CB is the lowest energy band whose energy states will be unoccupied or partially occupied with electrons. The band gap model proposed by Demeestere et al. [1] is shown in Scheme.1.

Electrons from VB are transferred to the CB when the semiconductor is illuminated with photons having energy content equal to or higher than the value of the band gap, creating electronhole pairs (1). After migration to the
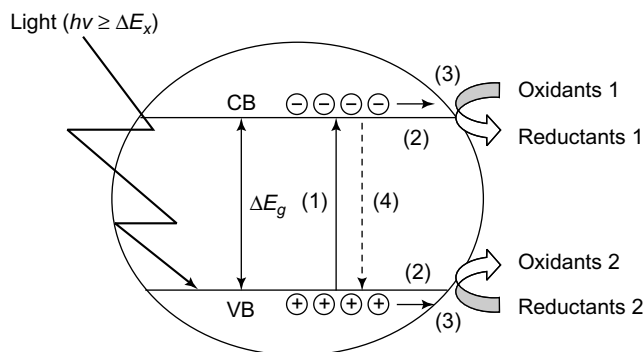
Figure 9.1   *Scheme 1. Pictorial representation of the "band gap model.": (1) Photo induced electron hole pair creation; (2) charge migration to the surface; (3) redox reactions; (4) recombination. VB and CB represent valence band and conduction band, respectively.*

semiconductor surface (2), electronhole pairs may induce redox reactions with adsorbates having suitable redox potentials (3). From a thermodynamic point of view, VB holes can oxidize adsorbed compounds if the redox potential of the holes/electrons of the VB is more positive than that of the adsorbates. Similarly, CB electrons can reduce adsorbed species if they have a more negative redox potential than that of the adsorbates. In a sense the energy of the top of the valence band denotes the oxidising power and the energy of the bottom of the conduction band denotes the reducing capacity of the semi-conductor. In the absence of suitable adsorbates, electronhole pair recombination occurs with release of thermal energy and/or light (4).

The rate of a photo catalytic reaction depends on the type of the photo-catalytic semi-conductor and on the light radiation used [2]. Other factors that influence a photo-catalytic reactions are:

- pH of the medium with which the semiconductor surface is in contact;
- concentration of the substrate influencing the reaction kinetics;
- stream of photons, as oversupply of light accelerates electronhole recombination;
- temperature, higher temperatures usually cause frequent collision between the semiconductor and the substrate

9.3   APPLICATIONS

A variety of applications ranging from anti-fogging, anti-microbial and self cleaning surfaces, through to water (conisdered in a separate chapter) and air purification, disinfection of water and solar induced hydrogen production (dealt with in separate chpater), have been developed and many of these

have made their way into commercial products. However, extensive research continues to further optimise this technology and to widen the spectrum of potential applications, especially in the following areas:

- Conversion of water to hydrogen gas by photo-catalytic water splitting: The ultimate target of water splitting is to provide clean hyrogen fuel through the utilization of solar energy. Efficiencies of differing magnitudes for solar water splitting have been reported for the photo-voltaicphotoelectrolytic device of Khaselev and Turner and for the photovoltaicelectrolytic device of Licht [3]. [see for a detailed consideration in another chapter]

- Conversion of carbon dioxide into hydrocarbons in the presence of water: In this case, Photo-catalysis provides a way to mimic photosynthesis by employing a semiconductor catalyst to absorb and utilize solar energy to convert chemicals into other forms.

- The application of illuminated semiconductors for the remediation of contaminants has been used successfully for a wide variety of compounds such as alkanes, aliphatic alcohols, aliphatic Conversion of carbon dioxide into hydrocarbons in the presence of water:

   In this case, Photo-catalysis provides a way to mimic photosynthesis by employing a semiconductor catalyst to absorb and utilize solar energy to convert chemicals into other forms.

- The application of illuminated semiconductors for the remediation of contaminants has been used successfully for a wide variety of compounds such as alkanes, aliphatic alcohols, aliphatic carboxylic acids, alkenes, phenols, aromatic carboxylic acids, dyes, Polychlorinated biphenyls (PCB), simple aromatics, halogenated alkanes and alkenes, surfactants, and pesticides as well as for the reductive deposition of heavy metals (e.g., Pt^{4+}, Au^{3+}, Rh^{3+}, Cr(VI)) from aqueous solution to surfaces [4]. Some of the aspects of this application will be dealt with in a separate chapter.

- Use of titanium dioxide in self-cleaning surfaces: Free radicals generated from TiO_2 can oxidize organic matter.
   Photo-catalytic surfaces have the potential to act against a variety of air pollutants and odours. This process can be used to remove microbes, oxidize volatile organic carbons (VOC), formaldehyde, ammonia and inorganic gaseous substances such as nitrogen- or sulphur-oxides (NO_X, SO_X).

9.4   COMPONENTS OF A PHOTO CATALYST

In addition to the photo catalyst, whose primary function is to absorb light energy, several other components can be added to modify the photo-catalyst
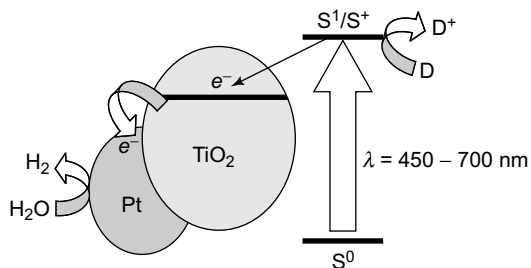
Figure 9.2   *Scheme.2. Pictorial representation of the operation of the photo-catalytic system for the release of hydrogen from water based on metalsemiconductor and a dyesensitizer. Legend: S0, S1, and S+. are the sensitizer in the ground, excited, and one electron oxidized states of the dye, respectively [5].*

system based on their specific application and for improving the overall efficiency of the process [5].

9.4.1   Photo-catalytic Systems Based on Semiconductors and Sensitizers

The large group of the light-sensitive materials that have been investigated as photo-catalysts includes fairly wide-band semiconductors, mostly elemental semicondcutors, metal oxides and sulphides (a listing is given in another place) that absorb UV light. One method of extending their light sensitivity to the visible region of the spectrum is the use of colored substances or sensitizers. In systems with sensitizers, the dyes absorb visible light and in the excited state inject electrons into the semiconductor.

9.4.2   Photo-catalytic Systems Based on Semiconductor Hetero-structures

In binary systems based on narrow-band and wide-band semiconductors the absorption of visible light by the narrow-band component leads to the injection of an electron into the wide-band semiconductor. The hole remains spatially separated from the electron and interacts with the electron donor.

9.4.3   Photo-catalyst Systems Based on Semiconductors Doped with Metal Cations

The doping of wide-band semiconductors with transition metals creates local energy states in the forbidden gap. The excitation of electrons from those local energy states by visible light leads to the transfer of electrons into the conduction band.
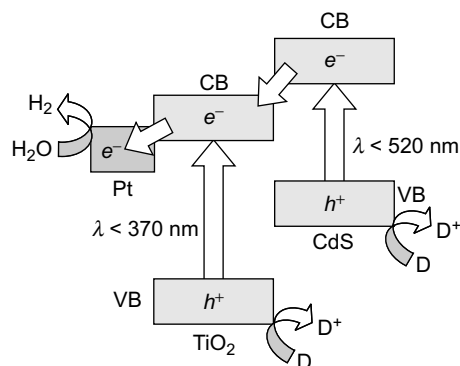
Figure 9.3   *Scheme 3. Simplified pictorial diagram for the spatial separation of the photo-generated charges in the CdS/TiO2 hetero structures and the formation of hydrogen from water during the action of visible light [5]*
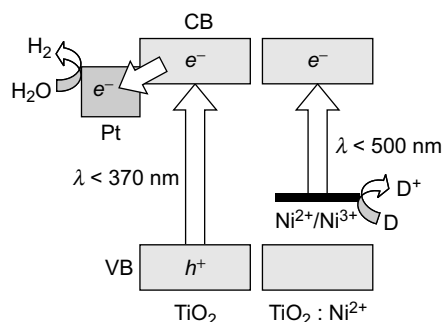

Figure 9.4   *Schematic diagram of the operation of the Photo-catalytic system for the release of hydrogen from an aqueous solution of electron donor D with the participation of titanium dioxide doped with Ni^{2+} (TiO_2:Ni^{2+})[5].*

9.4.3 Photo Catalyst Systems Based on Semiconductors Doped with Anions

One of the approaches for decreasing the forbidden band gap in oxide semiconductors is partial substitution of the oxygen by other elements especially nitrogen, carbon, and sulfur since their p wave functions will have energy and symmetry close to that of the wave functions of the valence band. This type of substitution makes it possible to realize "band design," i.e., intentional shift of the position of the valence band of the photocatalyst since the p orbitals of the so called substitutional atoms are expected to be situated in the top of the valence band above the p orbitals of the oxygen, thereby narrowing the forbidden band without substantially altering the bottom of the

conduction band. The energy band scheme for such a substituted system (for example nitrogen substituted system is shown in Scheme 5.
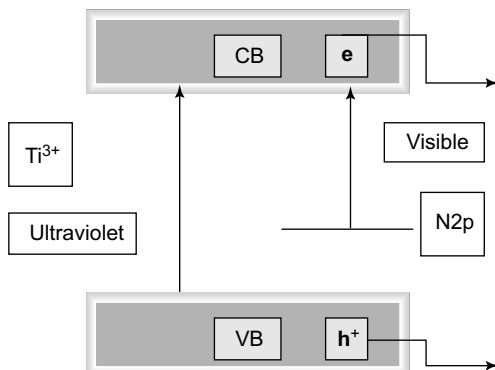
Figure 9.5   *Scheme 5. Schematic energy level diagram for nitrogen substituted TiO2 [Bare semiconductor absorbs UV radiation while the localized energy levels of nitrogen above valence band facilitates the visible light absorption] [5].*

9.5   CO$_2$ MANAGEMENT - PHOTO-CATALYSIS FOR CO$_2$ MITIGATION

CO$_2$ is a colorless and odorless gas. The molecule is linear with a double bond between the carbon and oxygen atoms (O=C=O). CO$_2$ occurs in nature and serves as source of carbon for photosynthesis by plants and crops. It is present in atmosphere with a volumetric concentration of 0.039 % (389 parts per million by volume, ppmv). Other characteristics of CO$_2$ are given in Table 9.11 together with that of CO and COCl$_2$.

Table 9.1   *Comparion of properties of Various C$_1$ building blocks*

Factors	CO	COCl$_2$	CO$_2$
MAK Value	30 ppm	0.1 ppm	5000 ppm
Toxicology	Affinity for Hemoglobin 210 times that of oxygen	War gas	Danger of asphysiation at 10 vol% in air
Environmental Hazard	Yes	High	Negative
Flammability	12-74%	No	No
Boiling point	81K	291 K	195 K (sublime)
Storage	Only at less than 5 Mpa	Difficult	No problem
Transport	Gas bottles or tanks in kg 'quantities	possible	Gas bottles or tanks

The emission of carbon dioxide into the atmosphere, released mainly by the burning of fossil fuels is one of the most serious problems with regard to the greenhouse effect [6]. All human activity generates about 37 billion tons (37 Gt) of CO_2 emissions each year, with about 30 Gt of this coming from energy-related emissions.

Total emissions were less than 25 Gt, twenty years ago, and under business as usual scenarios, emissions are projected to rise to over 50 Gt in twenty years from now. Burning 1 t of carbon in fossil fuels releases more than 3.5 t of carbon dioxide [7]. The Earths surface temperature has risen by approximately 0.6 K in the past century, with particularly significant warming trends over the past two decades. Hence CO_2 reduction/management (capture, storage and sequestration) have become key issues in controlling global warming.

9.6 REDUCTION OF CO_2 EMISSIONS

The reduction of CO_2 emissions can be achieved by three approaches [8]:

(1) Efficient use of carbon-based energy sources,

(2) Use of alternative or carbon-free energy sources,

(3) Use of a post treatment carbon-capture technology.

Carbon capture refers to the removal of CO_2 from industrial flue gas by a gas separation process prior to release to the atmosphere.

9.6.1 Sequestration

Carbon sequestration (storage) is the isolation of carbon dioxide (CO_2) from the earth's atmosphere. Sequestration can play a significant role in preventing continued CO_2 build-up in the atmosphere.

Geological sequestration involves storing CO_2 underground in rock formations that can retain large quantities of CO_2 for long periods of time. The CO_2 would be held in small pore spaces inherent in rocks. It is possible that CO_2 injection into coal seams and mature oil fields could assist in the extraction of coal bed methane or oil that would otherwise be left in the ground, which could help offset the costs of sequestration.

### 9.6.2 Other Carbon Capture Technologies

Currently, technologies such as gas absorption into chemical solvents, permeation through membranes, cryogenic distillation, and gas adsorption onto a solid sorbent are available for the capture of CO_2 from flue gas. However these are not economically feasible [8].

9.6.3 CO_2 Conversion

CO_2 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 CO_2 conversion techniques are under investigation [9] which include chemical reduction by metals which takes place at relatively high temperatures.
$2Mg + CO_2 \rightarrow 2MgO + C$

$Sn + CO_2 \rightarrow SnO_2 + 2CO$

$2Na + 2CO_2 \rightarrow Na_2C_2O_4$
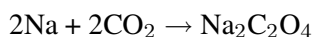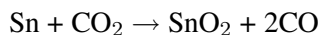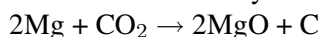
Thermochemical conversion in presence Ce^{4+} and temperatures higher than 1173 K

$CO_2 \longrightarrow CO + (1/2)O_2$

Radio-chemical Method using gamma radiation

$CO_2 \longrightarrow HCOOH, HCHO$

Photo-chemical Conversion in presence radiation

$CO_2 \longrightarrow CO, HCOOH, HCHO$

Bio-chemical conversion in presence of bacteria

$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$
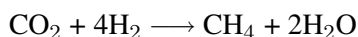
The bacteria Methanobacterium thermoautotrophicum can be immobilized in a fixed bed or on hollow fibres, and feeding stoichiometric ratios for the reaction attains 80% of the theoretical yield.

Electro-chemical conversion (eV)

$CO_2 + xe^- + xH^+ \longrightarrow CO, HCOOH, (COOH)_2$
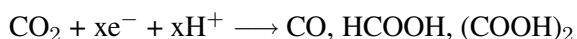
Bio-photochemical Conversion

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

CO2 + Oxoglutaric acid $\longrightarrow$ isocitirc acid Electro-photo-chemical conversion (radiation and eV) $CO_2 + 2e^- + 2H^+ \longrightarrow CO + 2H_2O$ Conventional catalytic reduction of CO_2 to chemicals (formic acid, methanol, methane etc.) with external hydrogen is feasible [10] but hydrogen has to be produced via renewable resources to render it viable and sustainable.

9.6.4 Photo-catalytic CO_2 Reduction

The CO_2 reduction process is thermodynamically uphill as illustrated by its standard free energy of formation (G = -394.359 kJ/mol) [11]. Economical CO_2 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 to yield hydrogen and hence requires similar combination of activation steps. The most ideal and desirable process would then be the simultaneous reduction of CO_2 and water to yield hydrocarbons, which essentially works out to artificial photosynthesis.

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 and easy to construct. Photo-catalytic process occurs via the direct absorption of photons with energy greater than or equal to the band gap of the photo-catalyst to generate 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.

9.6.5 Thermodynamics

There are two conceptual routes to produce renewable carbon containing fuels using solar energy [11].

- Direct photo-reduction of CO_2 using water as a reductant.
- Photolysis of water to generate hydrogen and further reaction of this hydrogen with carbon dioxide forming C_1C_2 fuels.

Water splitting and carbon dioxide reduction take place simultaneously on the photo–catalyst/co-catalyst surface, and thermodynamic requirements of these processes put constraints on the band gap of the materials used as photo-catalysts. 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 CO_2 are 257 and 283 kJ/mol at 298 K (1atm). Hence, the minimum energy required for water and CO_2 splitting processes are, respectively, 1.229 and 1.33 eV (per photon). In theory, the band gap of a photo-catalyst used for co-splitting of CO_2 and water should be at least 1.33 eV [11]. One, two, four, six and eight electron reduction potentials (vs. NHE) for CO_2 reduction and H_2O oxidation at pH 7 and 298 K assuming unit activities for all gaseous and aqueous species are given below [11].

From the above scheme it is clear that CO_2 photo- reduction is not a single-step reaction. Upon transfer of one electron, the structure changes from linear to bent structure which results in irreversible reduction [9]. Additionally,

Reaction	E^0_{redox} V vs NHE
$2H^+ + 2e^- \longrightarrow H_2$	-0.41
$H_2O \longrightarrow 1/2\ O_2 + 2H^+ + 2e^-$	0.82
$CO_2 + e^- \longrightarrow CO^{2-}$	-1.9
$CO_2 + H^+ + e^- \longrightarrow HCO_2$	-0.49
$CO_2 + 2H^+ + 2e^- \longrightarrow CO + H_2O$	-0.53
$CO_2 + 4H^+ + 4e^- \longrightarrow HCHO + H_2O$	-0.48
$CO_2 + 6H^+ + 6e^- \longrightarrow CH_3OH + H_2O$	-0.38
$CO_2 + 8H^+ + 8e^- \longrightarrow CH_4 + 2H_2O$	-0.24

single electron transfer to CO_2 is highly endergonic, because of the negative adiabatic electron affinity of CO_2. The initial step in the photo-catalytic reduction of CO_2 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. The time scale of this electron-hole recombination is two to three orders of magnitude faster than other electron transfer processes. Therefore, any process which inhibits electron-hole recombination would greatly increase the efficiency and improve the rates of CO_2 photo-reduction. The kinetics of CO_2 photo reduction are also dependent upon many other factors such as intensity of incident light, fraction of the incident light absorbed by the photo-catalyst, the specific surface area of the photo-catalyst absorbing the light, etc.

### 9.6.6   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 the excited state, corresponds to the minimal photon energy and depends on the band-gap energy, e.g. for TiO_2 anatase with band gap energy of 3.2 eV corresponds to 387.5 nm [2].

The wavelength of light influences the yield of CO_2 photo-catalytic reduction products; irradiation using the light with shorter wavelength (254 nm) is significantly more effective for the CO_2 reduction using TiO_2 than that with the wavelength of 350 nm [12].

Electron excited states are produced via electronic transitions, the probability of which depends on the light intensity. At low light intensities, the CO_2 reduction rate increases linearly with the light intensity, at mid-range light intensities, the photo-catalytic reaction rate is dependent on the square root of light intensity; and at high light intensities the rate is independent of the light intensity [2].

Large-band-gap semiconductors are the most suitable photo-catalysts for CO_2 reduction, because they provide sufficient negative and positive redox potentials in conductance and valence bands, respectively. The disadvantage of using wide band-gap semiconductors is the requirement for high energy input [13].

Even though some of the semiconductors have smaller band gap values, only some of them are catalytically active since the energy levels of either the conduction band or valence band are not appropriate for CO_2 reduction or water decomposition. Some of these semiconductors also undergo photocorrosion as well.
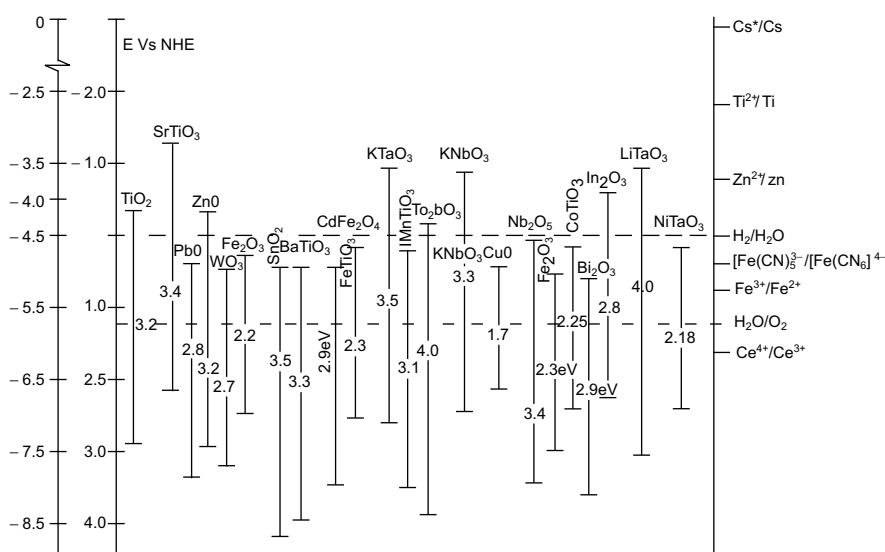
Figure 9.6   *Conduction band and valence band potentials of semiconductor photocatalysts relative to energy levels of the redox couples [13]*
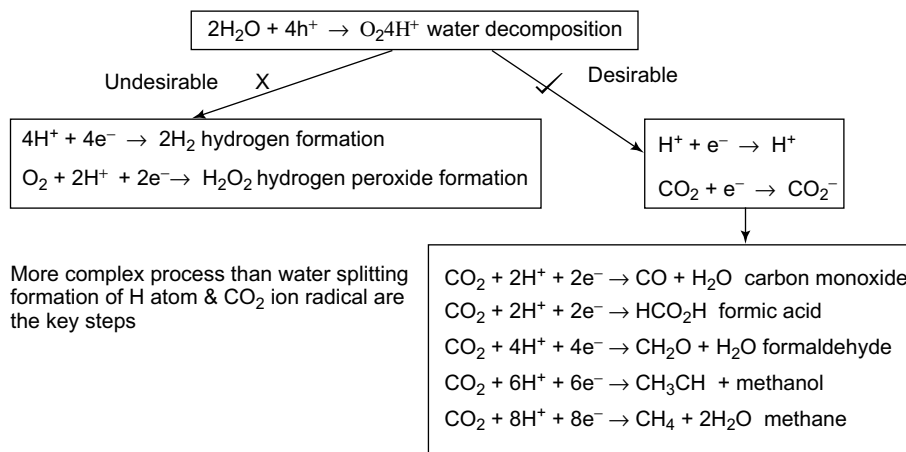
9.6.7   Photocatalytic Reduction of CO_2 with Water: State of the Art

The possible photo-catlytic reaction pathways are shown in Figure 9.2.

The state of art in this possibility can be summarized as follows:

1. Primary criterion for catalysts for hydrogen evolution from water by activation by photon.
2. Majority of investigations pertain to titania based catalyst with varying characteristics.
3. Titania is the preferred catalyst in various crystalline, morphological and nanostructural (tubes, sheets, films and foams) forms modified by doping with metals and anions coupled with various semiconductor oxides and sensitizers have been investigated extensively.

$2H_2O + 4h^+ \rightarrow O_2 4H^+$ water decomposition

Undesirable   X   Desirable

$4H^+ + 4e^- \rightarrow 2H_2$ hydrogen formation

$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$ hydrogen peroxide formation

$H^+ + e^- \rightarrow H^+$

$CO_2 + e^- \rightarrow CO_2^-$

More complex process than water splitting formation of H atom & CO_2 ion radical are the key steps

$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$ carbon monoxide

$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$ formic acid

$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O$ formaldehyde

$CO_2 + 6H^+ + 6e^- \rightarrow CH_3CH$ + methanol

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

Figure 9.7   *The Possible $CO_2 + H_2O$ photo catalytic pathways*

4. Doping with metals and non-metls to extend the light absorption range and achieve charge separation.

5. Pt,Cu, Ru and Ag are the metals used to improve hydrocarbon yields.

6. Maximum yield of methanol is 2655 micro moles on 3% Cu/TiO_2 catalyst at 333K under UV light, 2450 ν W/cm^2 after 6 hrs, slurry phase, 0.3 g catalyst in 300 ml water;QE- 19 %- Slamet et.al., Catalysis Communications 6 (2005) 313319.

7. Maximum methane to HC yield was 200 ppm, Pt-Cu on N doped TiO_2 nano tube arrays, sunlight, 100 mW/cm^2 low pressure static reactor using CO_2 and water vapor.

8. Alkali metal and alkaline earth tantalates, titanates and bi-metallics-could be viable options.

Inoue et al., [14] have reported the photocatalytic reduciton of CO_2 in aqueous solutions to produce a mixture of formaldehyde, formic acid, methanol and methane using various wide-band gap semiconductors such as tungsten trioxide (WO_3), titanium dioxide (TiO_2), zinc oxide (ZnO), cadmium sulfide (CdS), gallium phosphide (GaP), and silicon carbide (SiC). These semiconductors were activated by both xenon and mercury lamp irradiation. The formaldehyde and methyl alcohol yield was highest in the presence of SiC, a behavior attributed to the relative position of the SiC conduction band with respect to the $HCHO/H_2CO_3$ redox potential. The SiC conduction band edge lies at a higher position (more negative) than the HCHO/ H_2CO_3 redox potential, which is believed to be responsible for the high rates of product formation. The absence of methyl alcohol when WO_3 was used as catalyst, with a conduction band at a position lower than the $HCHO/H_2CO_3$

redox potential, further indicates the influence of band-edge positions on CO_2 reduction.

Investigations related to the photosynthesis reaction of CO_2 with water vapor to form CH_4 over metal-loaded $SrTiO_3$ have also been conducted. Due to its higher conduction band edge position compared to the redox potential of CH_3OH/H_2CO_3, strontium titanate could effectively reduce carbon dioxide dissolved in an aqueous electrolyte [15,16]. The effect of doping transition and noble metals such as Ru, V, Cr on TiO_2 has also been studied. It has been found that the production rate of organic compounds such as formic acid, formaldehyde and methanol increased when TiO_2 was doped with RuO_2 . The highest initial energy conversion obtained was found to be 0.04%.

Anpo et al.,[6] studied the photo-catalytic reduction of CO_2 with water on various titanium oxide catalysts. The anatase phase of the catalyst with large band gap with sufficient surfaceOH groups showed good efficiency for the formation of methane. The yields depended on the ratio of CO_2 to water, the reaction temperature. They observed that the best mole ratio of H_2O /CO_2 for the conversion of carbon dioxide is 5. Addition of Pt to the TiO_2 led to an increased methane yield compared to methanol formation. In another report Anpo et al., [17] reported the use of highly dispersed titanium oxide on glass for the photo catalytic reduction of carbon dioxide. From the direct detection of intermediate species, they proposed that methane formation resulted from the reaction between carbon radicals and atomic hydrogen.

The use of Cu as a co-catalyst was reported by Adachi et al [18] in which Cu-loaded TiO_2 powder was suspended in a CO_2 pressurized solution at ambient temperature, with methane and ethylene produced under Xe lamp illumination. Tseng et al (2004) also studied the effect of copper loading on titania. The methanol yield of 2.0 wt.% Cu/TiO_2 was 118 νmol/g following 6 h of UV illumination. The yield was higher than those of solgel TiO_2 and Degussa P25. The redistribution of the electric charge and the Schottky barrier of Cu and TiO_2 facilitates electron trapping via supported Cu. The photocatalytic efficiency of Cu/TiO_2 was markedly increased because of the lowering of the re-combination probability for holeelectron pairs. The highest quantum and energy efficiencies achieved were 10 and 2.5%, respectively. Slamet et al [19] suggested that CuO may be the most active dopant compared to the other copper species. Because Cu_2O has the highest positive value of redox potential Cu^+, Cu_2O dopant should effectively act as an electron trap to prohibit electronhole recombination. However, owing to the relatively strong interaction between TiO_2 and the dopant particle implanted in the vacant sites of TiO_2 , the dopant with more positive potential redox exceedingly catches electron from conduction band edge. Consequently the dopant-trapped electrons are more difficult to be transformed to the adsorbed species on

catalyst surface and hence it may play a role as a center of electronhole recombination.

Guan et al.,[20] studied the reduction of CO_2 with water over a hybrid catalyst, in which a Pt-loaded $K_2Ti_6O_{13}$ photo-catalyst was combined with a Fe-based catalyst supported on a dealuminated Y-type zeolite (Fe-Cu-K/DAY). In this reaction system, $Pt/K_2Ti_6O_{13}$ catalyst decomposes water to produce H_2 and the Fe-Cu-K/DAY catalyst reduces CO_2 with the resulting H_2 incorporated into organic compounds. When the reaction temperature is increased from room temperature to 600K by concentrating the solar irradiation, the product yield of hydrogen increased from 13.7 νmol/g-h to 20.5 νmol/g-h. Also additionally formic acid, methanol and ethanol were obtained. Guan et al., [21] also reported the use of Pt-loaded $K_2Ti_6O_{13}$ photo catalyst combined with a CO_2 hydrogenation catalyst Cu/ZnO. When the composite catalyst was used under concentrated sunlight, CH_3OH was successfully formed in addition to the above products. Guan et al., [22] also investigated the reduction of CO_2 over zero-valent Fe0 and Fe0-based composites in an aqueous solution at room temperature. It was found that H_2 can be effectively evolved from water over zero-valent Fe0 in the presence of gaseous CO_2 together with a small amount of hydrocarbons. When Fe0 was combined with Cu, K, and Al components, hydrocarbons such as CH_4 and C_3H_8 and alcohols such as CH_3OH and C_2H_5OH were also effectively produced. The XPS, XRD, and photoemission yield measurements revealed that the Fe0 surface as well as the bulk was oxidized to Fe_3O_4 and other possible oxides during the reaction. This corrosion process is promoted by the dissolution of CO_2 in water and the resultant protons oxidize Fe0 to evolve H_2. Moreover, the evolved H_2 serves as the reactant for the CO_2 hydrogenation on the active site of Fe0, especially for the Fe0KAl and Fe0CuKAl composites.

Kaneco et al., [23] studied the CO_2 photoreduction using TiO_2 powders in liquid CO_2 medium. Carbon dioxide has limited solubility in water. Also reduction of CO_2 is competitive with hydrogen formation via water. To overcome this disadvantage, liquid CO_2 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., [24] studied the photo-catalytic reduction of carbon dioxide using TiO_2 pellets. Pellet increased the contact areas and adsorption capacity. The yield was significant when compared to the system generated using thin film coating technique.

Koci et al., [25] studied the effect of TiO_2 particle size on photo catalytic reduction of carbon dioxide. As the particle size decreased, higher yields of methanol and methane over the TiO_2 nano particles under the illumination of light were obtained. The optimum particle size corresponding to the highest

yields of both products was 14 nm. For crystal sizes smaller than 14 nm the catalyst activity dropped probably due to the changes in optical and electronic properties of the nanometer crystal. The observed optimum particle size was a result of competing effects of specific surface area, chargecarrier dynamics and light absorption efficiency. Liuet al., [26] have studies the photo catalytic reduction of CO_2 on sol gel derived titania supported CoPC system. The nano particles of cobalt phthalocyanine loaded on titania showed eficient CO_2 reduction activity. This has been attributed to the effective electron transfer to titania surface and also the reduction of the recombination of electron and hole. Lo et al., [27] studied the photo-reduction of carbon dioxide with H_2 and H_2O over TiO_2 and ZrO_2 in a circulated photo -catalytic reactor. Experimental results indicated that the highest yield for the photo-reduction of CO_2 was obtained using TiO_2 with $H_2 + H_2O$ and ZrO_2 with H_2. Photo-reduction of CO_2 over TiO_2 with $H_2 + H_2O$ formed CH_4, CO, and C_2H_6 with the yield of 8.21, 0.28, and 0.20 mmol/g, respectively, while the photo- reduction of CO_2 over ZrO_2 with H_2 formed CO at a yield of 1.24 mmol/g. The detected reaction products supported the proposition of two reaction pathways for the photo reduction of CO_2 over TiO_2 and ZrO_2 with H_2 and H_2O, respectively. A one-site LangmuirHinshelwood (LH) kinetic model was applied to simulate the photo-reduction rate of CO_2.

Koci et al., [28] studied the influence of reactor geometry on photoreduction of carbon dioxide using two annular batch reactors. The dependence of products yields on the reactor diameter and on the volume of the liquid phase confirmed the fact that the requirement of perfect mixing is difficult to fulfill in 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.

Wu et al., [29] applied an optical fibre reactor to the photo reduction of CO_2 with H_2O using TiO_2, Cu/TiO_2, Ag/TiO_2, $CuFe/TiO_2SiO_2$ and dye-sensitized CuFe/P25 coated optical fibers. Compared with a traditional packed-bed reactor, an optical fiber provides a medium to transmit light uniformly throughout a reactor. 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. Ulagappan et al., [30] used Ti-silicalite molecular sieves as a catalyst for 266 nm UV laser radiation induced reduction of CO_2 and H_2O gas mixtures, obtaining HCOOH, CO, and $HCOOCH_3$. Product origins were studied by IR spectroscopy, indicating that CO originated from the secondary photolysis of HCOOH, while $HCOOCH_3$ was the result of spontaneous Tishchenko reaction of $CH_2=O$.

Anpo et al. [31] carried out the CO_2 photo reduction using Ti-MCM-41 and Ti-MCM-48 mesoporous zeolite catalysts. Photo-catalysts prepared within the zeolite cavity and frame-work have unique local structure and high selectivity in photo-reduction. The titanium oxide species included within the zeolite framework have been found to exist as isolated tetrahedral titanium oxide species. These Ti-containing zeolite catalysts exhibited high photo-catalytic efficiency and selectivity for the formation of methanol.

Some researchers have attempted to replace water with other reductants. This provides a high reaction yield and high selectivity to desired products by changing the mechanism. Liu et al. [32] 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 because these radicals are not well dissolved in 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. Subsequently, the carbon atom of the radical tends to react with a proton to produce formic acid. Dey [33] 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 formation of methane.

Titania per se is active for photo-catalytic reduction of CO_2 with H_2O, but the rates are extremely low since its conduction band edge is not suitable for water and CO_2 reduction, though it can readily oxidize water [34]. Promotion with co-catalysts like Pt [35], Ru [36], Rh [37], Ni [38] and Ag [39] vastly enhance the rate in several ways, like, charge separation, retarding re-combination and trapping of charge carriers, besides activation of CO_2 and water reduction and facilitating further surface transformations leading to hydrocarbon products.

Effect of bimetallics on TiO_2 was also studied. Luo et al. [40] studied the CO_2 reduction on Copper and Cerium Co-Doped Titanium dioxide. Photo-catalysts copper and cerium co-doped titanium dioxide were prepared via the equivalent-volume incipient wetness impregnation method. The methanol yield could reach up to 180.3 νmol/g-cat rapidly. Ce atoms activated water and CO_2 molecules, while Cu atoms act as the channel of photo-electrons in real time and prevent the recombination of electrons and holes. Xia et al. [41] studied the reduction of CO_2 with water using multi-walled carbon nanotube supported [MWCNT] TiO_2. The catalysts were prepared by both sol-gel and hydrothermal method. In using the solgel method, the MWCNTs were coated

with anatase TiO_2 nanoparticles, and by the hydrothermal method, rutile TiO_2 nanorods were uniformly deposited on the MWCNTs. The composite catalysts prepared by the solgel method lead to the main formation of ethanol, while HCOOH is found to be the major product on the sample prepared by the hydrothermal method.

When CO_2 present in the atmosphere dissolves in water it is mostly present in the form of carbonate. Many of them have studied photo-catalytic reduction of carbonate to form various chemicals. Ku et al. [42] studied the photo-catalytic reduction of carbonate in aqueous solution by the UV/TiO_2 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/TiO_2 reduction process were found to be methanol and methane. A LangmuirHinshelwood type kinetic equation was developed for modeling the photo catalytic reduction of carbonate.

Sayama et al. [43] investigated the effect of carbonate salt addition on the photo catalytic decomposition of liquid water over PtTiO$_2$ 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 H_2 and O_2. 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 photo-decomposition of water. The carbonate ion affects both the Pt particles and the TiO_2 surface. The Pt was covered with some titanium hydroxide compounds and therefore, the rate of the back reaction (H_2O formation from H_2 and O_2) on the Pt was suppressed effectively in the presence of carbonate ions. On the other hand, the TiO_2 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.

A significant breakthrough in the photocatalytic reduction of gas phase CO_2 by solar radiation has recently been achieved by Varghese and co-workers [34], using nitrogen doped TiO_2 nanotube arrays co-catalyzed with copper and/or Pt nanoparticles, in which water vapor saturated carbon dioxide was reduced to methane and other hydrocarbons under natural sunlight. The yield of methane was reported to be 160 νL/gh.The high rate of carbon dioxide conversion can be attributed to the high surface area and nanoscale wall thickness of the nanotubes, enabling the surface species to readily receive both charge carriers generated near the surface due to the wave function overlap and those generated deep inside the wall via diffusion. The quantum efficiency was found to be 0.74 %.

Many researchers have studied the Photocatalytic reduction of CO_2 using external hydrogen. Tsuneok et al. [44] performed this over MgO, CaO, ZrO_2, Ga_2O_3, and Al_2O_3. Ga_2O_3 exhibited the highest photo-catalytic activity in

this process, and CO gas was selectively generated at room temperature and atmospheric pressure. The amount of CO gas evolved depended not only on the amount of CO_2 but also on the amount of H_2 adsorbed on Ga_2O_3. The chemisorbed CO_2 species involved in the photo catalytic reduction of CO2 over Ga_2O_3 was not the bidentate bicarbonate species but the mono dentate bicarbonate species. The dissociatively adsorbed hydrogen on Ga_2O_3 reduced the mono dentate bicarbonate to the bi-dentate formate under photo irradiation. The bi dentate formate, which was an intermediate in the photocatalytic reduction, decomposed to CO. They proposed that photo-catalytic reduction of CO_2 over Ga_2O_3 takes place via a Langmuir-Hinshelwood-type mechanism, which is not the case for ZrO_2 or MgO. Teramura et al. [45] carried out the Photo-catalytic reduction of CO_2 using H_2 as reductant over $ATaO_3$ photo-catalysts [A = Li, Na, K]. Only CO gas was generated over all samples under photo- irradiation. The photo-catalytic activity was higher in the order corresponding to $LiTaO_3$ ¿ $NaTaO_3$ ¿ $KTaO_3$. The order of the photo catalytic activities was consistent with that of the E_g [optical band gap] values. The amount of evolved CO gas almost strongly depends on the amount of chemisorbed CO_2 in the case of $ATaO_3$ [A = Li, Na, K]. In addition, the photo-catalytic activity increased with increasing the calcination temperature of $LiTaO_3$. This means that a smooth charge separation in a $LiTaO_3$ photo-catalyst and chemisorption of CO_2 on the surface contribute to effective reduction of CO_2 in the presence of H_2.

Catalyst systems other than TiO_2 were also intensively studied. Watanabe et al. [46] studied the Photosynthesis of methanol and methane from CO_2 and water molecules on a ZnO surface. The photochemical synthesis of methanol and methane from CO_2 and water molecules was observed at 278 K by irradiating ZnO powder with visible light under high pressures of 25 to 35 kg/cm^2 of CO_2 gas. The best conversion efficiency was found to be about 6% with respect to reactant water molecules using a 75 W Xe lamp. Kanemoto et al. [47] studied the photo-reduction of Carbon dioxide over ZnS Quantum Crystallites. The dissolution of CO_2 in water gives an aqueous solution of pH 3.7 under a pressure of 1 atm. ZnS is unstable under acidic conditions, decomposing into H_2S and Zn^{2+} by the reaction with acid. Freshly prepared colloidal ZnS suspensions effectively catalyze photo-reduction of CO_2 in water at pH 7 with NaH_2PO_2 in the coexistence of Na_2S under UV irradiation. Wang et al. [48] carried out the Photocatalytic hydrogen evolution from water in the presence of Carbon dioxide over $NiO/Ca_2Fe_2O_5$. The catalyst $NiO/Ca_2Fe_2O_5$ was studied in the photo catalytic splitting of water in the presence of carbon dioxide. It is believed that CO_2 may react with water to form $HCO_3{}^-$ and $CO_3{}^{2-}$, which promote the scavenging of holes by OH,

and thus enhance the photo-catalytic activity. At the same time, a portion of CO_2 is photo-catalytically reduced to formic acid.

Ahmed et al. [49] studied the Photocatalytic conversion of carbon dioxide into methanol using zinccopperM [III] [M = aluminum, gallium] layered double hydroxides. These LDH compounds were applied as photo catalysts to convert gaseous CO_2 [2.3 kPa] to methanol or CO under UVvisible light using hydrogen. Zn Al LDH was the most active for CO_2 photo-reduction and the major product was CO formed at a rate of 620 nmol $h^{-1}g^{-1}$ cat, whereas methanol was the major product formed by the inclusion of Cu in the LDH photo-catalysts, e.g., at a formation rate of 170 nmol $h^{-1}g^{-1}$ cat using Zn-Cu-Ga photo-catalyst. Yan et al. [50] studied the CO_2 photo reduction using meso porous $ZnGa_2O_4$. A reactive templating route to prepare meso porous $ZnGa_2O_4$ at room temperature has been reported. By using RuO_2 as co-catalyst, the as-prepared meso porous $ZnGa_2O_4$ shows high photo catalytic activity for converting CO_2 into CH_4 under light irradiation, because of strong gas adsorption and large specific surface area of the mesoporous photo-catalyst.

In short the state of art and challenges in this area are as follows:

1. The reaction rate is slow and the yields obtained are also low.
2. The catalysts are often deactivated and arresting the deactivation has to be attempted.
3. The quantum efficiency of the process is often very low
4. For economic viability one has to prepare catalysts which will be active in the visible region and also will give more than 10% quantum efficiency.
5. One has to generate catalyst systems which will be able to harness light energy effectively and possibly one can generate systems containing macro cyclic ligands like porphrins and Phthalocyanins.

The current situation on the selection of photo-catalytic materials for water splitting has been depicted pictorially by D. Payne Department of Chemistry, University of oxford from Osterloph, 2008. This representation reproduced in Figure 9.3 clearly shows that one has to develop photo-catalytic materials which will be active in the wavelength region 400 nm and also should be capable of providing quantum efficiencies greater than 10%.

9.6.8   Future Directions

As described earlier, 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. The process has the potential to become a viable and sustainable alternative energy source to fossil fuels.
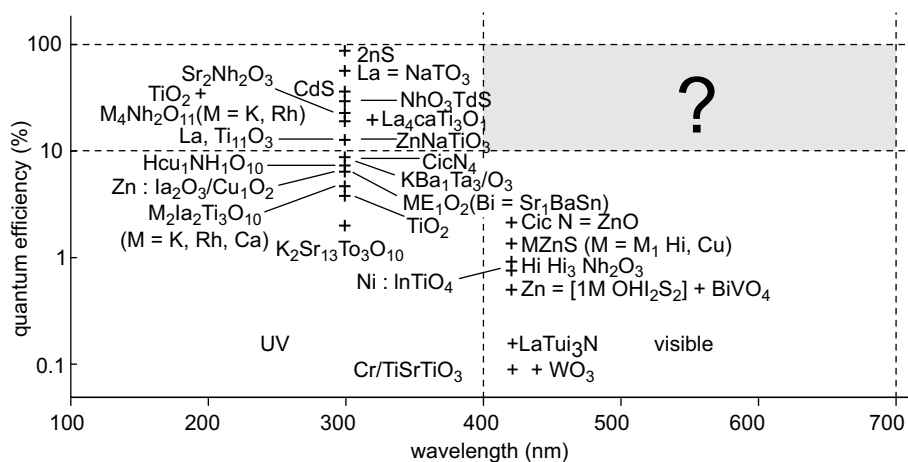
Figure 9.8 *The pictorial representation of the known and exploited semiconductors and their efficiencies for water splitting reaction. (reproduced from Phil. Trans. R. Soc., 368,3343 (2010).)*

However, it has thrown up several tough challenges to the scientists and technologists, namely,

- The process centers around the activation of two thermodynamically most stable molecules, CO_2 and water
- Conversions achieved so far are extremely small, less than 1%, occurring at very slow rate
- Catalysts tend to get deactivated over short period.
- CO_2 photo reduction process is highly complex, involving mult-electron transfer and non- selective, leading to a range $(C_1\text{-}C_3)$ of hydrocarbon products
- Design of catalysts, consisting of photo catalysts and co-catalysts aided by metal ion / anion doping and light harvesting components/sensitizers, 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 are thermodynamically not favourable. Since the second step involves multi-electron transfer,the rates are small relative to the first. These two steps are to be synchronized to achieve higher yields of hydrocarbons.

Nevertheless, research efforts on these fronts are being pursued with full vigour by many laboratories round the globe. Design of efficient catalyst systems and achieving higher yield of desired products are the two key issues being pursued by the researchers. Though titania continues to be the most extensively studied photocatalyst [51-54], efforts to develop alternative catalysts, based on various semiconducting metal oxides/sulfides/nitrides/phosphides, layered titanates, binary and ternary oxides of Nb, Ta, Ga and In in conjunction with alkaline, alkaline earth and rare earth oxides and with a host of co-catalysts and sensitizers, are in full swing [55-59].

REFERENCES

1. Demeestere, K., J. Dewulf and H. V. and Langenhove (2007) Heterogeneous Photo-catalysis as an Advanced Oxidation Process for the Abatement of Chlorinated, Monocyclic Aromatic and Sulfurous Volatile Organic Compounds in Air: State of the Art. Critical Rev. in Environmental Science and Technology, 37, 489-538.

2. Ko, K., L. Obalov, and Z. Lacn (2008) Photocatalytic reduction of CO_2 over TiO_2 based catalysts. Chemical Papers, 62, 19.

3. Fujishimaa, A., X. Zhang, Donald, and A. Tryk (2007) Heterogeneous photocatalysis: Fromwater photolysis to applications in environmental cleanup. Int. J. Hydrogen Energy, 32, 2664 2672.

4. Hoffmann, M., R., S. T. Martin, W. Choi, and D. W. Bahnemann (1995). Environmental Applications of Semiconductor Photocatalysis. Chem. Rev., 95, 69-96.

5. Stroyuk, L., A. I. Kryukov, S. Y. Kuchmii, and V. D. Pokhodenko (2009). Semiconductor Photocatalytic systems for the Production of Hydrogen by the action of visible light. Theoretical and Experimental Chem., 45, 209-233.

6. Anpo, M., H. Yamashita, Y. Ichihashi, and S. Ehara, (1995) Photocatalytic reduction of CO_2 with water on various Titanium Oxide catalysts. J. Electroanal. Chem., 396 ,21-26.

7. Maginn, E. J, (2010) What to Do with CO_2 J. Phy. Chem. Lett., 1, 34783479.

8. Usubharatana, P., D. McMartin, A. Veawab, and P. Tontiwachwuthikul, (2006) Photocatalytic Process for CO_2 Emission Reduction from Industrial Flue Gas Streams. Ind Eng. Chem. Res, 45, 2558-2568.

9. Scibioh, M. A., and B. Viswanathan, (2004) Electrochemical Reduction of Carbon dioxide: A Status Report. Proc Indian National Science Academy, 70A, 407-462.

10. Nam, S. S., H. Kim, G. Kishan, M. J. Choi, and K W. Lee, (1999) Catalytic conversion of CO_2 to hydrocarbons over rare earth promoted iron catalysts supported on KY Zeolite. Appl. Catal. A. Gen., 179, 155-159.

11. Indrakanti, V. P., J. D. Kubickib and H. H. Schobert (2009) A Photoinduced activation of CO_2 on Ti-based heterogeneous catalysts: Current state, chemical physics-based insights and outlook. Energy Environmental Science, 2, 745758.

12. Matthews, R. W., and S. R. McEvoy, (1992) A comparison of 254 nm and 350 nm excitation of TiO_2 in simple photocatalytic reactors. J. Photochem. Photobiol. A: Chem, 66, 355366.

13. Roy, S. C, O. K. Varghese, M. Paulose, and C. A. Grimes (2010) Toward Solar Fuels: Photocatalytic Conversion of Carbon Dioxide to Hydrocarbons. Am. Chem. Soc. Nano letters, 4, 12591278.

14. Inoue, T., A. Fujishima, S. Konishi, and Honda, K.,(1979).Photoelectrocatalytic Reduction of Carbon-Dioxide in Aqueous Suspensions of Semiconductor Powders. Nature, 277, 637638.

15. Halmann, M., M. Ulman, and B. A. Blajeni, (1983) Photochemical Solar Collector for the Photoassisted Reduction of Aqueous Carbon-Dioxide. Sol.Energy, 31, 429431.

16. Halmann, M., V. Katzir, E. Borgarello and J. Kiwi (1984) Photoassisted Carbon dioxide Reduction on Aqueous Suspensions of Titanium Dioxide. Sol. Energy Mater., 10, 85-91.

17. Anpo, M., and K. Chiba, (1992) Photocatalytic Reduction of CO_2 on Anchored Titanium-Oxide Catalysts. J. Mol. Catal., 74, 207212.

18. Adachi, K., K. Ohta, and T. Mijuma,(1994) Photocatalytic Reduction of Carbon-Dioxide to Hydrocarbon Using Copper-Loaded Titanium-Dioxide. Solar Energy, 53, 187190.

19. Slamet, H. W. Nasution , E. Purnama , S. Kosela, and J. Gunlazuardi,(2005) Photocatalytic reduction of CO_2 on copper-doped Titania catalysts prepared by improved-impregnation method. Catal. Commun., 6, 313319.

20. Guan, G., T. Kida, T. Harada, M. Isayama, and A. Yoshida (2003). Photoreduction of carbon dioxide with water over $K_2Ti_6O_{13}$ Photocatalyst combined with Cu/ZnO catalyst under concentrated sunlight. App. Catal. A: General, 249, 1118.

21. Guan, G., T. Kida, and A. Yoshida, (2003) Reduction of Carbon Dioxide with Water under Concentrated Sunlight Using Photocatalyst combined with Fe-Based Catalyst. App. Catal., B, 41, 387396.

22. Guan, G., T. Kida, T. Ma, K. Kimura, E. Abe and A. Yoshida, (2003). Reduction of aqueous CO_2 at ambient temperature using zero-valent iron-based composites. Green Chem., 5, 630634.

23. Kaneco, S., H. Kurimoto, K. Ohta, T. Mizuno, and Akira,(1997) Photocatalytic reduction of CO_2 using TiO_2 powders in liquid CO_2 medium. J. Photochem. Photobiol. A: Chemistry , 109, 59-63.

24. Tan, S. S., L. Zou, and E. Hu,(2006) Photocatalytic reduction of carbon dioxide into gaseous hydrocarbon using TiO_2 pellets. Catal. Today, 115, 269273.

25. K. Koci, L. Obalova, L. Matejova, D. Placha, Z. Lacny, J. Jirkovsky, O. Solcova (2009). Effect of TiO_2 particle size on the photocatalytic reduction of CO_2 Applied Catalysis B: Environmental 89, 494502.

26. Liu, S., Z. Zhao and Z. Wang (2007) Photocatalytic reduction of carbon dioxide using solgel derived titania-supported CoPc catalysts. Photochem. Photobiol. Sciences, 6, 695700.

27. Lo, C.C., C. H. Hung, C. S. Yuan, and J. F Wu (2007) Photoreduction of carbon dioxide with H_2 and H_2O over TiO_2 and ZrO_2 in a circulated photocatalytic reactor. Sol. Energy Mater. Sol. Cells, 91, 17651774.

28. Koc, K., MartinReli, O. Kozk, Z. Lacny, DanielaPlach, PetrPraus, and LucieObalov (2010) Influence of reactor geometry on the yield of CO_2 Photocatalytic reduction. Catal. Today doi:10.1016/j.cattod.2010.12.054

29. Wu, J. C. S., T.-H. Wu, T. Chu, H. Huang, and D. Tsai, (2008) Application of Optical-Fiber Photoreactor for CO_2 Photocatalytic Reduction. Topic in Catalysis, 47, 131136.

30. Ulagappan, N., and H. Frei,(2000) Mechanistic Study of CO_2 Photoreduction in Ti Silicalite Molecular Sieve by FT-IR Spectroscopy. J. Phy. Chem.A, 104, 78347839.

31. Anpo, M., H. Yamashita, Y. Ichihashi, Y. Fujii, and M. Honda,(1998). Photocatalytic Reduction of CO_2 with H_2O on Titanium Oxides Anchored within Micropores of zeolites: Effects of the Structure of the Active Sites and the Addition of Pt. J. Phys. Chem. B, 101, 26322636.

32. Liu, B.-J., T. Torimoto, and H. Yoneyama,(1998) Photocatalytic reduction of CO_2 using surface-modified CdS photocatalysts in organic solvent. J. Photochem.Photobiol. A: Chem., 113, 93-96.

33. Dey G. R., (2007) Chemical Reduction of CO_2 to different Products during Photo Catalytic Reaction on TiO_2 under Diverse Conditions: an Overview J. Natural Gas Chem., 16, 217226.

34. Varghese, O.K, M. Paulose and T. J. Latempa,(2009) High-Rate Solar Photocatalytic conversion of CO_2 and Water Vapor to Hydrocarbon Fuels. Nanoletters, 9, 731-737.

35. Zhang Q.H., W.D. Han, Y.J. Hong and J.G. Yu,(2009) Photocatalytic reduction of CO_2 with H_2O on Pt-loaded TiO_2 catalyst. Catal. Today, 148, 335-340.

36. Sasirekha, N., Basha, S.J.S., and Shanthi, K.,(2006) Photocatalytic performance of Ru doped anatase mounted on silica for reduction of carbon dioxide. Appl. Cataly, B, 62, 169180.

37. Kohno, Y., H. Hayashi, S. Takenaka, T. Tanaka, T. Funabiki, and S. Yoshida, (1999) Photocatalytic reaction of H_2O+CO_2 over pure and doped Rh/TiO_2. J. Photochem. Photobiol. A: Chem., 126, 117-123.

38. Fan, J., E-Z. Liu, L. Tian, X-Y. Hu, Qi He, and T. Sun (2010) Study on Synergistic Effect of N and Ni^{2+} on Nano Titania in Photocatalytic Reduction of CO_2. Am. Soc. Civil Engineers. doi:10.1061/(ASCE)EE. 1943-7870.0000311.

39. Koci. K., K. Mateju, L. Obalova, S. Krejcikova, Z. Lacny, D. Placha, L.Capek, A. Hospodkova, and O. Solcova,(2010) Effect of silver doping on the TiO_2 for Photocatalytic reduction of CO_2. Appl Catal B: Environmental, 96, 239244.

40. Luo, D., Y. Bi, W. Kan, N. Zhang, and S. Hong, (2011) Copper and Cerium Co-Doped Titanium dioxide on Catalytic Photo reduction of Carbon dioxide withWater: experimental and theoretical studies. J. Mol. Structure,doi: .1016/j.molstruc.2011.03.044

41. Xia X-H ., Z-J. Jia, Y. Yu, Y. Liang, Z. Wang, and L-L. Ma, (2007) Preparation of multi-walled carbon nanotube supported TiO_2 and its Photocatalytic activity in the reduction of CO_2 with H_2O. Carbon, 45, 717721.

42. Ku, Y., W-H Lee, and W-Y Wang, (2004) Photocatalytic reduction of carbonate in aqueous solution by UV/TiO_2 process. J. Mol Catal. A: Chemical, 212, 191196.

43. Sayama, K., and H. Arakawa, (1997) Effect of carbonate salt addition on the photocatalytic decomposition of liquid water over $PtTiO_2$ catalyst. J. Chem. Soc. Faraday T rans. 93, 1647-1654.

44. Tsuneoka, H., K. Teramura, T. Shishido, and T. Tanaka (2010) Adsorbed Species of CO_2 and H_2 on Ga_2O_3 for the Photocatalytic Reduction of CO_2 J.Phy. Chem. C, 114, 88928898.

45. Teramura, K., S-i Okuokab, H. Tsuneokab, T. Shishidob, and T. Tanaka (2010) Photocatalytic reduction of CO_2 using H_2 as reductant over $ATaO_3$ photocatalysts (A = Li, Na, K). Appl. Catal. B: Environmental, 96, 565568.

46. Watanabe, M., (1992) Photosynthesis of methanol and methane from CO_2 and H_2O molecules on a ZnO surface. Surface Science Lett., 279, 236-242.

47. Kanemoto, M., T. Shiragami, C. Pac, and S. Yanagida (1992) Effective Photoreduction of Carbon Dioxide Catalyzed by ZnS Quantum Crystallites with Low Density of Surface Defects. J. Phy. Chem., C, 96, 3521-3526.

48. Wang, Y., Y. Wang, and Y. Gao (2010) Photocatalytic H_2 evolution from water in the presence of Carbon dioxide over $NiO/Ca_2Fe_2O_5$ Reaction Kinetics Mechanics Cataly., 99, 485491.

49. Ahmed, N., Y. Shibata , T. Taniguchi, and Y. Izumi (2011), Photocatalytic conversion of carbon dioxide into methanol using zinccopperM(III) (M = aluminum, gallium) layered double hydroxides. J. Catal.,doi:10.1016/j.jcat.2011.01.004.

50. nYan, S C., S. X. Ouyang, J. Gao, M. Yang, J. Y. Feng, X. X. Fan, L. J.Wan, Z. S. Li, J. H. Ye, Y. Zhou, and Z. G. Zou (2010) A Room Temperature Reactive - Template Route to Mesoporous $ZnGa_2O_4$ with Improved Photocatalytic Activity in Reduction of CO_2. Angew. Chem. Int. Ed., 49, 64006404.

51. Fujishima, T. N. Rao, and D. A. Tryk, Titanium dioxide Photocatalysis, Journal of Photochemistry and Photobiology C: Photochemistry Reviews,Vol. 1, no. 1, pp. 1-21, 2000.

52. Carp, C. L. Huisman and A. Reller, Photoinduced reactivity of titanium dioxide, Progress in Solid State Chemistry, vol. 32, no. 1-2, pp. 33-177, 2004.

53. Fujishima, X. Zhang, Titanium dioxide photocatalysis: Present situation and future approaches,ComptesRendusChimie, vol. 9, no. 5-6, 750-760, 2006.

54. Fujishima, X. Zhang, D.A. Tryk, Heterogeneous photocatalysis: From water photolysis to applications in environmental cleanup, International Journal of Hydrogen Energy, vol. 32, no. 14, pp. 2664-2672, 2007.

55. F. E. Osterloh, Inorganic Materials as Catalysts for Photochemical Splitting of Water, Chemistry of Materials, vol. 20, no.1, pp. 35-54, 2008.

56. G. Palmisano, E. Garca-Lo pez, G. Marc, V.Loddo, S. Yurdakal, V. Augugliaro and L. Palmisano, Advances in selective conversions by heterogeneous photocatalysis, Chemical Communications, vol. 46, no. 38, pp. 7074-7089, 2010.

57. Z. Jiang, T. Xiao, V. L. Kuznetsov and P. P. Edwards, Turning carbon dioxide into fuel Phil. Trans. R. Soc. Vol.A368 3343-3364 (2010).

58. K. Li, D. Martin and J. Tang, Conversion of Solar Energy to Fuels by Inorganic Heterogeneous Systems Chinese Journal of Catalysis, vol.32, 879-890, 2011.

59. N.M. Dimitrijevic, B. K.Vijayan,O. G. Poluektov, T. Rajh, K. A. Gray, H. He and P. Zapol Role of water and carbonates in photocatalytic transformation of CO_2 to CH_4 on titania Journal of American Chemical Society, vol.133, 3964, 2011.