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CONVERSION OF CARBON DIOXIDE TO SYNTHETIC ORGANIC FUELS THROUGH PHOTOCATALYSIS - A REVIEW

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ABSTRACT

The combustion of fossil fuel resources releases large amount of carbon dioxide (CO_2) into the atmosphere leading to various environmental concerns including the problem of climate change and consequent global warming. It is still a great challenge to manage the emitted CO_2 in view of the enormous cost and technicalities required in modern day CO_2 disposal technologies. Photocatalytic conversion of CO_2 into gaseous and liquid organic fuels, using solar energy is an attractive process to address the problem of managing excess amount of CO_2 that could have entered the troposphere. This process relies on a renewable energy source, the sun, and photocatalysts, which are readily prepared, to convert CO_2 into useful products, such as formaldehyde, methanol, formic acid, acetic acid, methane, etc, which are synthetic fuel sources. The products depend on the photocatalyst and the reaction medium. This paper reviewed the selected approaches that used CO_2 as feedstock for the photocatalytic production of synthetic organic fuels and other useful products. The reaction mechanism as proposed by different researchers including different methods of achieving light absorption, electron-hole separation, and energy gap matching for reduction of CO_2 to different products are considered. The study may be helpful in harnessing solar energy in the context of climate change mitigation and energy generation.

Key words: Carbon dioxide, climate change, fuel, global warming, photocatalysts

INTRODUCTION

Power plants, automobiles, and many other sources release large quantities of greenhouse gases into the atmosphere each year. Among the greenhouse gases are water vapour, carbon dioxide, methane, oxides of Nitrogen (NOx), ozone (O_3) and chlorofluorocarbons (CFCs). A major greenhouse gas is carbon dioxide. The amount of carbon dioxide produced is increasing as many sources produce copious amounts of it. Activities such as burning of fossil fuels and manufacturing of cement from limestone ($CaCO_3$) increase the amount of carbon dioxide in the air [1]. Excessive amount of CO_2 is particularly harmful because it can linger in the atmosphere for tens of thousands of years [2]. The atmosphere contains 0.05% carbon dioxide [3]. In a particular area, CO_2 concentration in the pre-industrial era was only 250 ppm whereas currently it is at 380ppm [4]. Carbon dioxide plays an important role in determining the temperature of the planet earth. This is because the gas absorbs sunlight and infra red radiation, preventing a portion of the heat from radiating back into space [1]. The undue amounts of carbon dioxide could cause the earth to heat up significantly and exacerbate global warming with its negative consequences as were recorded in the twentieth century. The climate change is commonly linked to a situation when too much heat is getting into the troposphere (0-20km) and also too much heat is prevented from escaping. An increase of these greenhouse gases in the atmosphere will trap too much heat nearer the Earth's surface, less heat escapes back into space, leading to a rise in global temperatures, known as global warming.

For example, there was Hurricane Mitch in 1998 in which heavy rain caused flooding that cost the lives of over 10,000 people in Central America. In 1999, two cyclones hit India's eastern coastline which left over 9,000 people dead. Apart from the rampant effects of flooding, other problems associated with climate change within the period included water-borne diseases, drought, choking smoke, sweltering heatwave, soil erosion and food shortages [5].

A lot of research and investments have been involved towards finding immediate solutions to lower CO_2 atmospheric level. One common method is by CO_2 sequestration. This process entails capturing and storing CO_2 in safe places, like, in deep sea. It is reckoned to be an immediate option to mitigate the global warming problem [6]. However, it is considerably expensive and has become a burden for those countries, which are practicing this process. Besides, most of the associated processes require extraneous energy input, which may result in the net growth of CO_2 emission. Furthermore, there are many concerns on the effects of long-term underground storage of CO_2. It is more expensive and technically demanding to keep using this CO_2 disposal technology. Another approach was the Kyoto protocol agreement of 1997 which was aimed at reducing CO_2 emission by countries. So far, the compliance is feeble and more CO_2 is pushed into the air.

The idea of capturing CO_2 from any source-power plants, automobile emissions, atmosphere, etc- and converting it to fuels using sunlight, instead of disposing it, is a very attractive field of study. It directly contributes to the mitigation of CO_2 related global warming consequence while simultaneously solving the problem of sustainable and renewable energy shortage.

In this paper, synthesis of organic fuels including methanol, acetic acid, formaldehyde, formic acid, etc., from CO_2, using solar energy with various photocatalysts are reviewed and summarized by citing all the relevant references.

PHOTOCATALYTIC REDUCTION OF CO_2

Solar energy can be harnessed to drive CO_2 conversion by different methods such as biochemical, radiochemical, thermochemical, photochemical and electrochemical processes [7]. We focus here on the photochemical method requiring the use of photocatalysts.

Artificial photosynthesis

Natural plants demonstrate the most direct strategy for CO_2 and renewable energy production, as carbon dioxide is converted to energy-rich sugars by photosynthesis. The equation for natural photosynthesis is as given below:

$$6CO_2 + 6H_20 \xleftrightarrow{hv} C_6H_{12}0_6 + O_2$$

In this process, specialized pigments (e.g. chloroplast) in plants absorb sunlight and initiate chemical reactions which results in the reduction of CO_2 and the synthesis of carbohydrates. Other products like protein are formed in the plant cytoplasm [8].

In the photocatalytic reduction of CO_2, artificial photosynthesis is applied. Here, CO_2 can be reduced to useful compounds by irradiating it with UV light at room temperature and ambient pressure. The use of photocatalysts for the conversion of CO_2 into a high-energy-content fuel via renewable solar energy mimics the natural photosynthesis. To realize a practical, efficient and artificial photosynthetic system, the process involves only water, carbon dioxide, sunlight and photocatalyst (catalysts, activated with sunlight), equivalent to chlorophyll in natural photosynthesis. The equation resembles that of the natural photosynthesis:

$$CO_2 + 2H_20 \xrightarrow{hv} \begin{array}{l} CH_3OH + 3/2O_2 \\ CH_3COOH \\ ETC. \end{array}$$

Energy gap matching and generation of electron-hole pairs

Photocatalysis is described as a change in the rate of a chemical reaction or its initiation under the action of ultraviolet, visible or infrared radiation in the presence of a substance — the photocatalyst — that absorbs light and is involved in the chemical transformation of the reaction partners [9].

The development of efficient photocatalysts requires understanding of CO_2- catalyst interactions and electron transfer pathways. The photocatalysts should achieve visible light responsiveness and facilitate charge separation. Electrons need to absorb energy for excitation from the valence band to the conduction band. This energy is delivered by absorption of a photon having energy equal to or greater than the band gap energy of semiconductors. Electrons are released from crystallic bonds and excited to the conduction band after absorption of a photon. At the same time, positive holes are generated as well. This whole process is called the generation of electron–hole pairs [10]. Once promoted, the electrons could theoretically conduct through the material and interact with any species that is embedded on the material's surface. Usually, photons in the ultraviolet spectrum have enough energy to induce semiconductor behavior in photocatalytic materials [11].

Photocatalysts semiconductor materials are used because their valence and conduction bands are separated by a band gap. Semiconductors are the most suitable photocatalysts for CO_2 reduction because they are best able to reduce CO_2 into fuels such as methane or methanol. The equation below shows the reduction of CO_2 into methanol and oxygen.

$$CO_2 + 2H_2O \xrightarrow{\text{Light}} CH_3OH + O_2$$

There are different types of photocatalyst and whilst they are all activated by light, some are activated by the UV spectrum of light and some are activated by visible light.

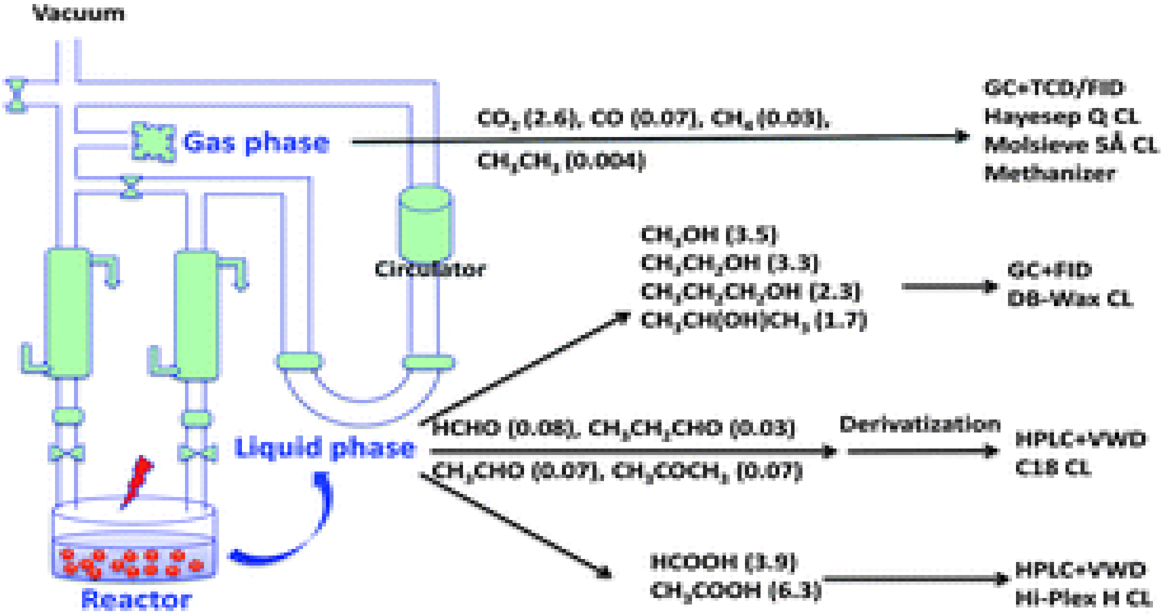
Two groups of catalysts for consideration are the heterogeneous (semiconductor) and the homogeneous (coordination compound) catalysts. Heterogeneous catalysts are where the catalysts are in a different phase to the reactants. Homogeneous catalysts are where catalysts and reactants are in the same phase.

As reported [12], most common heterogeneous photocatalyts are transition metal oxides and semiconductors, which have unique characteristics. Unlike the metals which have a continuum of electronic states, semiconductors possess a void energy region where no energy levels are available to promote recombination of an electron and hole produced by photoactivation in the solid. The void region, which extends from the top of the filled valence band to the bottom of the vacant conduction band, is called the band gap. When a photon with energy equal to or greater than the materials band gap is absorbed by the semiconductor, an electron is excited from the valence band to the conduction band, generating a positive hole in the valence band. The ultimate goal of the process is to have a reaction between the excited electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reductant to produce an oxidized product. Due to the generation of positive holes and electrons, oxidation-reduction reactions take place at the surface of semiconductors. In the oxidative reaction, the positive holes react with the moisture present on the surface and produce a hydroxyl radical. The activity of the photocatalyst can be enhanced by metal ‘doping’, which means that a metal is added to the surface of the catalyst to change its properties very slightly.

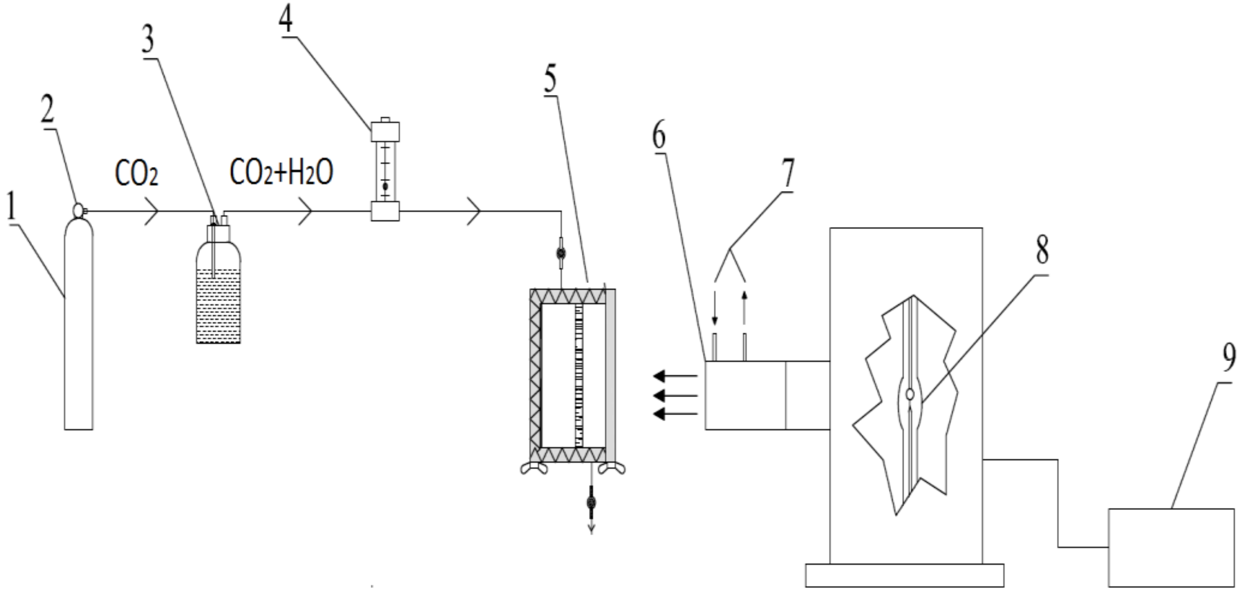
In a solar photovoltaic cell, photogenerated electron-hole pairs are driven efficiently in opposite directions by an electric field existing at the boundary (junction) of n- and p-type semiconductors (or at semiconductor/metal junctions).

Qin *et al* [13] reported that when photocatalyst titanium dioxide (TiO_2) absorbs ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), it will produce pairs of electrons and holes. The electron of the valence band of titanium dioxide becomes excited when illuminated by light. The excess energy of this excited electron promote the electron to the conduction band of titanium dioxide therefore creating the negative-electron (e^-) and positive-hole (h^+) pair. This stage is referred as the semiconductor's ' photo-excitation ' state. The energy difference between the valence band and the conduction band is known as the ' Band Gap '. Wavelength of the light necessary for photo-excitation is: 1240 (Planck's constant, *h)* / 3.2 ev (band gap energy) = 388 nm. The positive-hole of titanium dioxide breaks apart the water molecule to form hydrogen gas and hydroxyl radical. The negative-electron reacts with oxygen molecule to form super oxide anion. This cycle continues when light is available. The photo-excited electrons can reduce CO_2 to form CO, formic acid, methanol, and methane.

A typical schematic [14] for photocatalytic reduction of CO_2 is given below:



Also another illustration by Cybula [15] gives a typical set up:



Schematic illustration of the batch reactor system for the CO_2 photoreduction test: 1) cylinder of CO_2; 2) gas cylinder valve; 3) water bubbler; 4) gas flow meter; 5) photoreactor equipped with a quartz window; 6) water filter; 7) inlet and outlet cooling water; 8) xenon lamp; 9) feeder

The products of a photocatalytic reduction of CO_2 depend on the photocatalysts and on the reaction medium [15, 16].

Reli *et al* [10] proposed the reaction scheme for the photocatalytic reduction of CO_2 by H_2O on ZnS in the presence of Na_2SO_3. Photoexcited electrons (e^-) and positive holes (h^+) are produced when incident photons are absorbed in ZnS (Eq. 1, 2). Photoexcited positive holes can be converted by H_2O to H^+. At the same time, CO_2 molecules adsorbed on the surface of ZnS gained electrons and were reduced to CH_4, CH_3OH and CO (Eq. 4-6)

$$\mathrm{ZnS} \xrightarrow{hv} e^- (\mathrm{ZnS}) + h^+ (\mathrm{ZnS}) \qquad (1)$$

$$e^- (\mathrm{ZnS}) + h^+ (\mathrm{ZnS}) \xrightarrow{hv} \text{heat} \qquad (2)$$

$$2\ H_2O + 4\ h^+ \xrightarrow{hv} O_2 + 4\ H^+ \qquad (3)$$

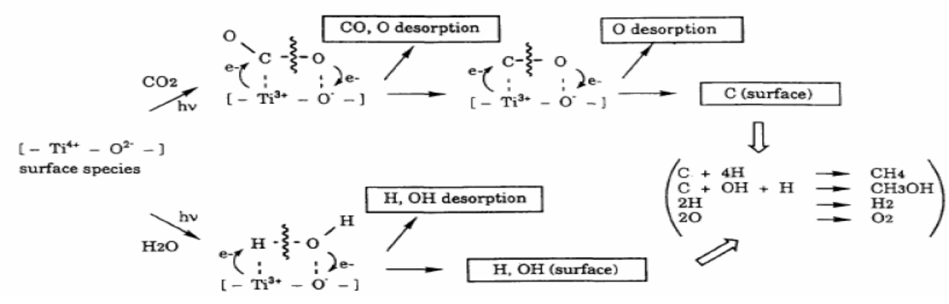
$$CO_2\ (aq) + 8\ H^+ + 8e^- \xrightarrow{hv} CH_4 + 2\ H_2O \qquad (4)$$

$$CO_2\ (aq) + 2\ H^+ + 6e^- \xrightarrow{hv} CH_3OH + H_2O \qquad (5)$$

$$CO_2\ (aq) + 2H^+ + 2e^- \xrightarrow{hv} CO + H_2O \qquad (6)$$

PRODUCTS OF CO_2 REDUCTION WITH DIFFERENT PHOTOCATALYSTS

It has been shown that CO_2 could be transformed into hydrocarbons when it is in contact with water vapour and catalysts under UV irradiation. This is depicted by Anpo *et al* [17] as shown below:



Photocatalytic reduction of CO_2 with H_20 on the anchored titanium oxide

Many types of semiconductor photocatalysts, such as titanium dioxide (TiO_2) [18], ZrO_2 [19], CdS [20], and combinations thereof [21] have been widely studied for the purpose of CO_2 conversion. TiO_2 was extensively studied as a photocatalyst [22-24] because of its high photocatalytic activity, long-term chemical stability, non-toxicity and low cost [13]. In the past few years, carbon-based TiO_2 photocatalysts have attracted cosmic interest for improved photocatalytic performance [25, 26].

TiO_2 suspensions in metals such as Pd, Rh, Pt, Au. Cu, or Ru may be used for CO_2 reduction. Other metals such as Hg, Cd, Pb, Tl, In, Sn, Pt, Ni, Fe, Ti, Au, Ag and Zn can effect CO_2 reduction. ZnS, CdS, zeolites, transition metal complexes such as ruthenium and cobalt have been employed with much success [27, 28].

In an experiment, CO_2, mixed with water vapour in saturation state, was discharged into a quartz reactor containing porous TiO_2 pellets and illuminated by various UV lamps of different wavelengths for 48 h continuously. The gaseous products extracted were identified using gas chromatography. The results confirmed that CO_2 could be reformed in the presence of water vapour and TiO_2 pellets into CH_4 under continuous UV irradiation at room conditions. CO and H_2 were also detected [29].

Although the efficiencies of present titanium dioxide based photocatalysts are low, the incorporation of carbon based nanostructures such as carbon nanotubes [30] and metallic nanoparticles [31] have been shown to enhance the efficiency of these photocatalysts.

In the presence of water, carbon dioxide was converted into methane in the technique by Tan *et al* [29].

Izumi [16] reported about the metal-loaded TiO_2 photocatalysts in which an aqueous suspension of TiO_2, Rh/TiO_2, or Rh/WO3-TiO_2 at 333K was bubbled with a CO_2 flow and illuminated by a xenon lamp, and the exit gas was trapped at 273 K and analyzed. The major product was formaldehyde. Minor amounts of methanol formic acid were also detected.

Sun *et al* [32] tested Metalorganic frameworks (MOFs), a new class of porous materials comprised of metal ions or metal clusters connected by organic ligands, as alternative photocatalysts due to their high porosity, structure diversity and tunable optical properties. Their study revealed that MOFs are of great potential as a new generation of photocatalysts for CO_2 reduction as amino functionalized NH_2-MIL-125(Ti) was photoactive for converting CO_2 to HCOO- under visible light in the presence of triethanolamine (TEOA) as sacrificial agent.

Shie *et al* [33] used Ag/TiO_2 and Cu/TiO_2 made by impregnation method at 254 nm wavelength of UV irradiation to reduce CO_2. The major product in the Na_2CO_3 solution was methanol and the gas product was methane.

Nazimek and Czech [34] studies of modified TiO_2 catalysts supported on Al_2O_3 were conducted in a self-designed circulated photocatalytic reaction system at room temperature and under constant pressure. Their experimental results indicated that the highest yield of the photoreduction of CO_2 with H_2O was obtained using TiO_2 with the active anatase phase modified by Ru and WO_3 addition. The conversion was very high – almost 97% of CO_2 was transformed mainly into methanol (14% vol.) and into small amount of formic, acetic acid and ester.

Iranian researchers succeeded in the simultaneous conversion of carbon dioxide and methane to useful chemicals at low temperature through photocatalytic reaction by using titanium dioxide nanoparticles deposited on stainless net [35].

Ahmed *et al* [36] synthesized ordered layered double hydroxides (LDHs) consisting of zinc and/or copper hydroxides and combined with aluminum or gallium. These LDH compounds were then applied as photocatalysts to convert gaseous CO_2 (2.3 kPa) to methanol or CO under UV–visible light using hydrogen. ZnAAl LDH was the most active for CO_2 photoreduction and the major product was CO. Methanol was the major product formed by the inclusion of Cu in the LDH photocatalysts.

Izumi [16] compiled a number of investigations which reported CO_2 photoreduction catalysts, reaction conditions, and the formation rates in water/with moisture using semiconductor photocatalysts other than TiO_2. The photocatalysts included ZnO, CdS, GaP, SiC, Cu-p-SiC, $BiWO_6$, $InNbO_4$, Pt-$NaNbO_3$, RuO_2-Zn_2GeO_4 and Ag-CaLa4Ti_4O_{15}. The range of the amounts was between 0.02g-1g. The reactants were CO_2 and H_2O, while the light source varied between Light, 300 W Xe arc, 400 W HP Hg and 500 W Xe/HP Hg. The major products were acetaldehyde, CO, ethanol, methane, methanol and formic acid.

Lin [37] results showed that different reaction conditions influence the products just as different catalysts do. TiO_2 photocatalytically produced methane in aqueous solutions; formic acid, formaldehyde, and methanol were also produced. When TiO_2 was atomically dispersed in zeolites or ordered mesoporous SiO_2 and doped with Pt, Cu, N, I, CdSe, or PbS, the methane and CO formation rates were greater. As for semiconductors other than TiO_2, CdS, SiC, $InNbO_4$, HNb_3O_8, Bi_2WO_6, promoted $NaNbO_3$, and promoted Zn_2GeO_4 produced methane or methanol.

Promoted $A^{II}La_4Ti_4O_{15}$ produced CO. ZnO and GaP formed formaldehyde and methanol. The photocatalytic reduction of CO_2 was also surveyed with hydrogen, because hydrogen can be obtained from water photosplitting by utilizing natural light. CO was formed using TiO_2, ZrO_2, MgO, and Ga_2O_3, whereas both CO and methanol were formed using layered-double hydroxides consisting of Zn, Cu, Al, and Ga.

The effect of reaction medium on CO_2 photocatalytic reduction yields over ZnS nanoparticles deposited on montmorillonite (ZnS-MMT) was investigated by Reli *et al* [10]. Four different reaction media, such as NaOH, $NaOH^+Na_2SO_3$ (1:1), NH4OH, $NH4OH^+Na_2SO_3$ (1:1), were tested. The pure sodium hydroxide was better than ammonium hydroxide for the yields of the both gas phase (CH_4 and CO) and liquid phase (CH_3OH). The addition of Na_2SO_3 improved methanol yields due to the oxidation prevention of incipient methanol to carbon dioxide. The gas phase yields were decreased by the Na_2SO_3 addition.

CONCLUSION

The recent literature on photochemical reductions of CO_2 is reviewed. The approaches that employed photocatalyst materials with readily available solar energy from sunlight were dwelt on. Synthetic fuels derived by photocatalytic reduction of carbon dioxide will not add even a single molecule of carbon dioxide in the environment. The fuels obtainable depend on the photocatalyst employed and the reaction conditions. The photocatalytic reduction of CO_2 is safer, less expensive, and simpler than current approaches of CO_2 sequestration. In view of the poor implementation of the Kyoto Protocol of 1997, which was an agreement by world leaders to cut greenhouse gas emissions, the photocatalytic reduction of CO_2 may be the alternative to mitigate global warming.

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