Photocatalytic Reduction of CO$_2$ into Fuels: A Short Review

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Abstract: The photocatalytic reduction of CO$_2$ with water vapour and catalysts under UV irradiation to yield hydrocarbons is a potential way of decreasing greenhouse gas and it represents an attractive alternative energy source to fossil fuels. However, this process still has to overcome several hurdles, because it involves the activation of two stable molecules, H$_2$O and CO$_2$, and simultaneous conversion through a multi-step electron transfer reaction.

The problem of CO$_2$ emission and the possibility of exploiting CO$_2$ as a raw material reaction is first reported in this short review. Subsequently, the fundamentals of photocatalysis are described. Finally, TiO$_2$-based photocatalysts are reviewed, taking into consideration the optimization methods that can be adopted to improve performances. The information gained from this analysis will help to contribute towards a better understanding of the main parameters that affect the activity of photocatalysts and will ultimately lead to the optimized synthesis of more efficient photocatalytic material for the photocatalytic reduction of CO$_2$ to fuels.

Keywords: CO$_2$ conversion, Solar fuels, Photocatalyst, TiO$_2$.

1. INTRODUCTION

The use of fossil fuels results in a dilemma for society. On one hand, the combustion of coal, natural gas and oil satisfies about 90 per cent of our current energy needs. However, it produces, and releases into the atmosphere, more than 3.5 t of carbon dioxide (CO$_2$) for each 1 t of equivalent carbon burned [1].

Moreover, the Earth's surface temperature has risen by approximately 0.6 K over the past century, with particularly significant increases over the past 20 years.

There are many reasons why fossil fuels remain so popular: they are accessible, in different forms, in almost all of the world; humans have learned how to use them effectively to provide energy for a variety of applications; they are relatively cheap and easily transportable.

It is clear that, in our current global energy economy, a higher standard of living means increasing energy consumption [2].

This situation is shown in Figure **1**, where the human development index (HDI) is plotted against the per capita energy consumption, with energy expressed in units of kilogram equivalents of oil.

The current approaches towards the reduction of CO$_2$ emissions are mainly focused on carbon capture

and storage (CCS). Carbon capture refers to the removal of CO$_2$ from flue gas, by means of gas separation, before it is released into the atmosphere, while carbon sequestration (storage) refers to the isolation of CO$_2$ from the atmosphere.
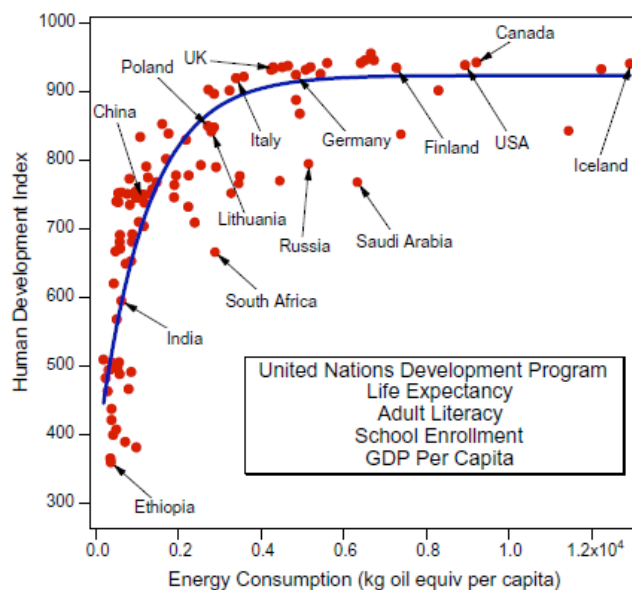

Figure 1: The Human Development Index, a measure of the quality of life developed by the United Nations Development Program, is plotted against the per capita energy consumption of 103 of the world's most populous nations, representing a total of 5.763 billion people. The data refer to 2004 [2].

At present, the most commonly used technologies for the capture of CO$_2$ are gas absorption into chemical solvents, permeation through membranes, gas adsorption into a solid sorbent and cryogenic distillation, but none of these are economically convenient.

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A reduction in CO_2 emissions can be achieved through three approaches: post combustion capturing, pre-combustion capturing and oxy fuel combustion [3].

A fourth option, which is the topic of this work, is to use captured CO_2 to synthesize sustainable hydrocarbon fuels [4].

The great advantage of liquid fuels (*e.g.* petroleum, diesel and others) is their intrinsic chemical energy content and the easiness by which they are stored and transported.

It is possible to reduce CO_2 with hydrogen or even electricity, to synthesize sustainable fuels, but the renewable source that has to be used as the vector to transform CO_2 into fuels would not contribute to the net CO_2 emissions.

An idealized energy cycle is shown in Figure **2**, where CO_2 is transformed into carbon neutral liquid fuels and sustainable or renewable electricity is used to produce hydrogen and the resulting Fischer-Tropsch process liquid hydrocarbon fuels [5].

The energy requirements for the production of such renewable fuels depend on the methods that are used to capture CO_2 and to produce hydrogen.

In a recent survey of their work, Olah *et al*. have stated: "Carbon dioxide can be chemically transformed from a detrimental greenhouse gas causing global warming into a valuable, renewable and inexhaustible carbon source of the future allowing environmentally neutral use of carbon fuels and derived hydrocarbon products" [6].

Therefore, the aim throughout the world is to improve capture and storage technologies; this will allow large amount of CO_2 to be obtained, which will then become available as feedstock for innovative conversion to synthetic fuels.

CO_2 is a highly stable molecule. Therefore, for the chemical conversion of carbon dioxide to a synthetic
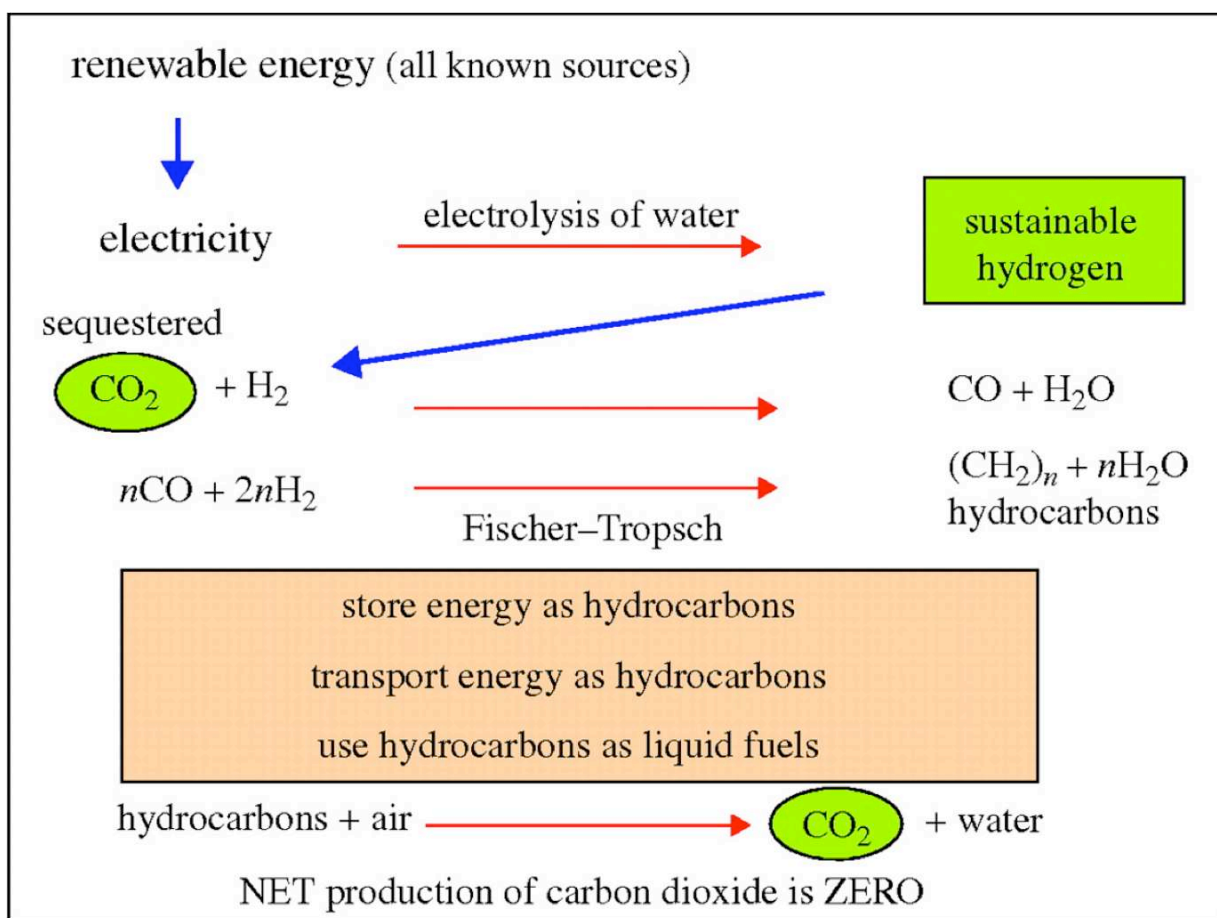

Figure 2: A generic energy cycle using captured or sequestered CO_2 and sustainable or renewable hydrogen to yield carbon-neutral or renewable carbonaceous fuels [5].
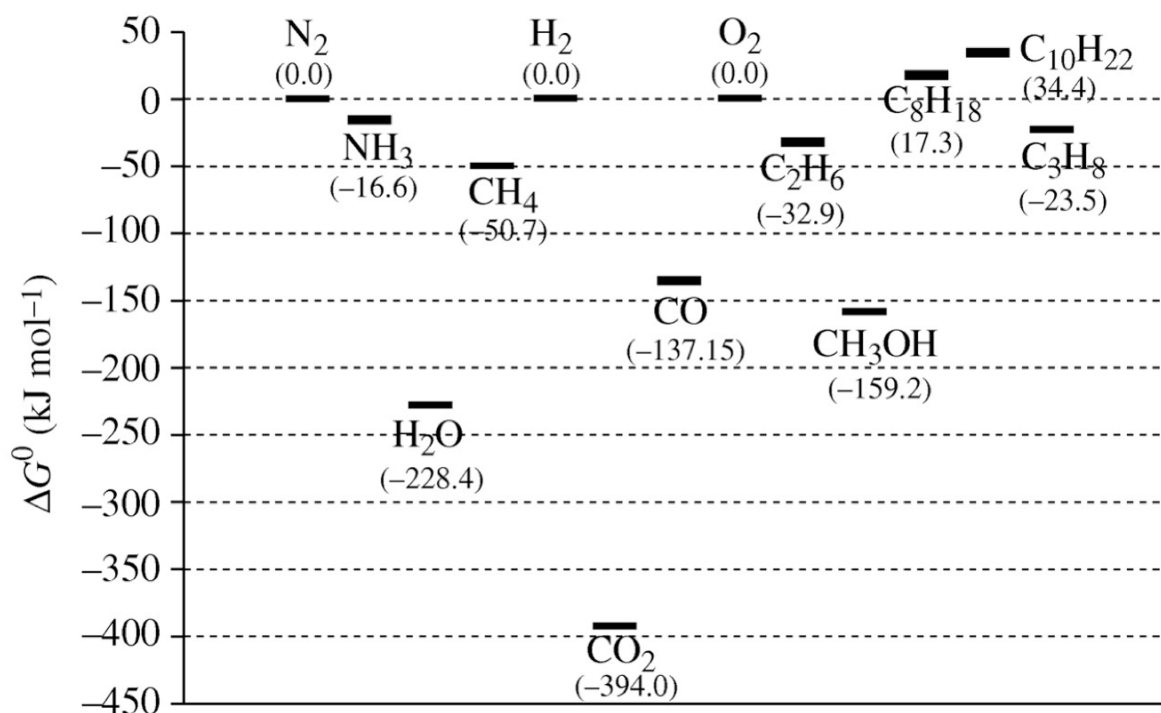
Figure 3: Gibbs free energy of formation for selected chemicals (data compiled and calculated from the NIST database, http://webbook.nist.gov/chemistry/name-ser.html). Here, the ΔG^0 of the constituent elements is taken as the reference point [5].

fuel, it is necessary to assure a high energy input, optimized reaction conditions and very active catalysts. A key aspect of the thermodynamics of any possible CO_2 conversion is illustrated in Figure **3**.

However, it is important that any chemical reaction is driven by the differences in Gibbs free energy between the reactants and the products of a chemical reaction, as can be seen from the Gibbs-Helmotz relationship:

$$\Delta G^0 = \Delta H^0 + T\Delta S^0 \qquad (1)$$

Neither term (ΔH^0 or $T\Delta S^0$) of Gibbs free energy is favourable for the conversion of CO_2 into other molecules [7].

Owing to the strong carbon-oxygen bond, a considerable amount of energy must be provided to obtain the carbon reduction.

Although the entropy term makes little or no contribution to the thermodynamic driving force for any reaction involving CO_2, the enthalpy term should be taken as an initial point to assess the thermodynamic stability and feasibility of any CO_2 conversion. According to Freund and Roberts, the use of CO_2 as a reactant will only emerge with the employment of novel catalytic chemistry [7].

However, ΔG^0 only provides information on the yield of the products at equilibrium through the relationship $\Delta G^0 = -RTlnK$, and the kinetics of such a process might be favourable.

Thus, if the kinetics are favourable, a CO_2 reduction to CO may also be possible on the metal surface, or some other catalytic material, *e.g.* nanoscale metal particles encapsulated in nanoporous or mesoporous hosts [8, 9].

Endothermic chemical reactions are the basis of a large number of industrial-scale chemical manufacturing processes. Steam reforming of hydrocarbons to syngas is the classic example:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad (2)$$

$$\Delta H^0 = +206.3 \ kJmol^{-1} \qquad (3)$$

This highly endothermic reaction is used worldwide for the high-volume production of hydrogen in the gas, food and fertilizer industries.

Dry reforming instead shows the reaction of CO_2 with a hydrocarbon, CH_4. This reaction is important to understand the mechanisms that are involved in the conversion of CO_2 in flue gas to produce chemical fuels:

$$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2 \tag{4}$$

$$\Delta H^0 = +247.3 \text{ kJmol}^{-1} \tag{5}$$

It is important to note that these two reactions give rise to syngas with different H_2/CO molar ratios. Both are useful for the formation of syngas for an eventual production of liquid fuel [5].

The enthalpy contributions that point out the importance of the chemical reactions to convert CO_2 are shown in Figure **4**. Thermodynamically speaking, the conversion of CO_2 is easier if it is used as a co-reactant with other substances that have higher Gibbs free energy, *e.g.* H_2 or CH_4.

These hydrogen-bearing energy carriers give up their intrinsic chemical energy to promote the conversion of CO_2 [5].

Thus, the reaction heats for the production of CO from CO_2 as a single reactant or with CO_2 as a co-reactant are particularly significant. It is important to compare the energetics of the thermal dissociation of CO_2,

$$CO_2 \rightarrow CO + 0.5\,O_2 \tag{6}$$

$$\Delta H^0 = +293.0 \text{ kJmol}^{-1} \tag{7}$$

with that of the reaction of CO_2 with H_2,

$$CO_2 + H_2 \leftrightarrow CO + H_2O \tag{8}$$

$$\Delta H^0 = +51.0 \text{ kJmol}^{-1} \tag{9}$$

Similarly, increasing the amount of oxygen in the dry reforming reaction leads to a decrease in the enthalpy of the reaction.

2. PHOTOCHEMICAL PRODUCTION OF SYNTHETIC FUELS

As previously mentioned, CO_2 reduction is a highly endothermic process, therefore the sustainable utilization of CO_2 is only possible if renewable energy, such as solar, wave, wind or nuclear energy, is used as an energy source.

The solar photocatalytic reduction of CO_2 has the potential of being a means of recycling CO_2 and of storing intermittent solar energy in synthetic carbon-neutral fuels that are suitable for storage and use in the residential, industrial and transportation sectors.

For this reason, an increase in the efficiency of the photoreduction of the CO_2 process is one of the most challenging tasks of environmental catalysis.
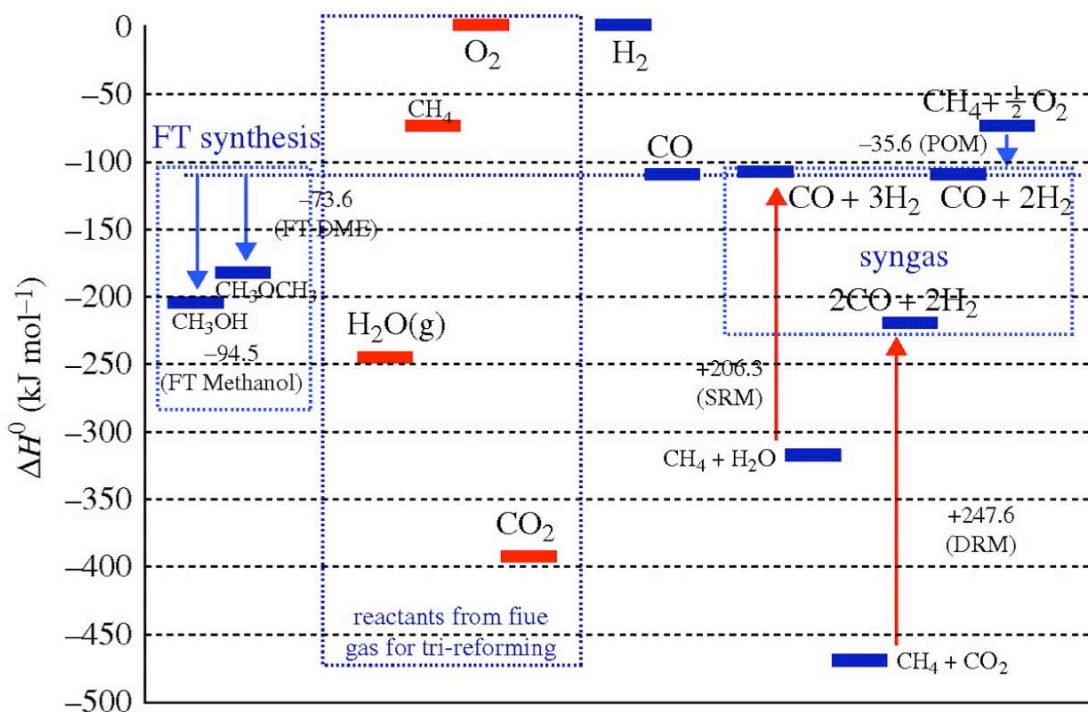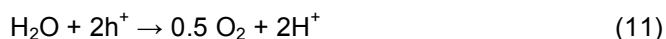

Figure 4: Gibbs free energy of formation for selected chemicals. The ΔH^0 of the constituent elements is taken as the reference point [5].

The study of photocatalysis started during the seventies. This phenomenon was discovered in 1972 by Fujishima and Honda who split water using solar energy (photo-electrolysis), in the same way as happens with the photosynthesis of the chlorophyll [10].

For this purpose, they modelled an electrochemical circuit made up of two electrodes immersed in water: a single crystal of TiO_2 and an electrode of Pt. After illumination of the TiO_2 surface, using radiation with a lower wavelength than 415 nm, they noted a flow of current from the Pt electrode to the TiO_2 electrode through an external circuit.

From the direction of the flow of the current, they deduced that an oxidation reaction occurs on the TiO_2 electrode while, a reduction reaction occurs on the Pt electrode.

In this way, Fujishima and Honda proved that water can be split into oxygen and hydrogen using UV-visible light, according to the following mechanism:

$$TiO_2 + 2hv \rightarrow 2e^- + 2h^+ \qquad (10)$$

$$H_2O + 2h^+ \rightarrow 0.5\ O_2 + 2H^+ \qquad (11)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (12)$$

The overall reaction is:

$$H_2O + 2hv \rightarrow 0.5\ O_2 + H_2 \qquad (13)$$

The reaction took place, in the presence of titanium dioxide (TiO_2), under UV irradiation, at room temperature.

Heterogeneous photocatalysis is defined as: "a catalytic process during which one or more reaction steps occur by means of electron-hole pairs photo-generated onto the surface of semiconducting materials illuminated by light with suitable energy" [11].

The first steps of the photocatalytic reduction of CO_2 are the absorption of photons by a photocatalytic material and the conversion of these photons into electron-hole pairs that have to be spatially separated to obtain chemical reduction and oxidation half-reactions at the semiconductor-electrolyte interface.

As far as CO_2 photoreduction using water as the co-reactant is concerned, water oxidation and CO_2 reduction have to occur simultaneously.

However, the current CO_2 photoreduction catalysts are not sufficiently effective enough, because of the inefficient absorption of solar energy, the fast recombination of the photoexcited electron-hole pairs and the backward redox reactions.

2.1. Principles and Mechanism

Photocatalysis is a process by which a catalyst is activated by photons. This process involves a catalyst, generally a semiconductor, absorbing photon energy to promote an electron transfer from the valence band (VB) to the conduction band (CB).

The energy difference (ΔE_g) between the valence band and the conduction band is called energy band gap; its value for a semiconductor is considered to be equal to or less than 4 eV (Figure **5**).
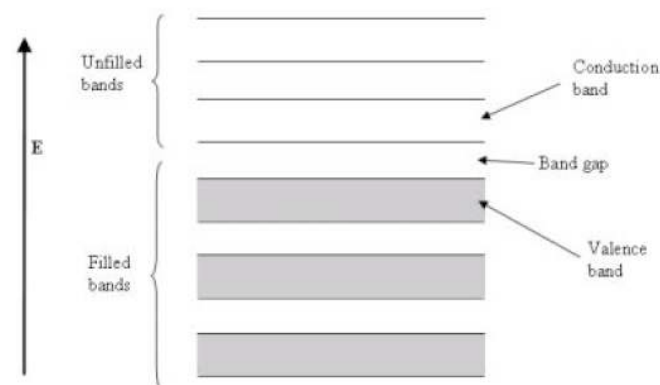

Figure 5: Band structure in a semiconductor.

According to the band gap model [12], VB electrons can be transferred to the CB when the semiconductor is illuminated by photons with energy equal to or higher than the band gap (minimum energy that the light has to have to make the material electrically conductive). In this way, a hole forms in the valence band and a negative charge (electron) forms in the conduction band. This system is known as an electron-hole pairs. After migration to the semiconductor surface [13], electron-hole pairs may induce a redox reaction through adsorbates with a suitable redox potential [14].

As shown in Figure **6**, a catalyst performs as both an electron donor (route A) and an acceptor (route B).

When the semiconductor is in contact with water, these holes (h^+) can produce hydroxyl radicals (OH·), while the electrons (e^-) can produce a super-oxide anion (O_2^-). These two highly reactive species are able to decompose adsorbed substances [10].

From a thermodynamic point of view, if the redox potential of the VB is more positive than that of the adsorbates, holes can oxidize adsorbed compounds.

Instead, if the redox potential of the VB has a more negative redox potential than the adsorbates, CB electrons can reduce adsorbed species. At the same time, electron-hole pair recombination occurs with the release of thermal energy and/or light [16].
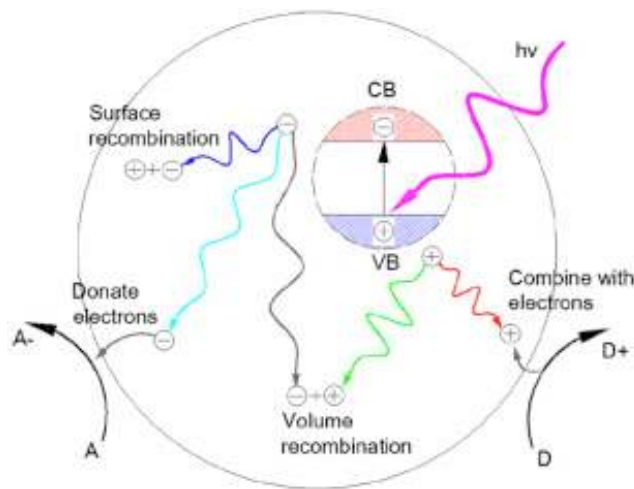

Figure 6: Light excitation effect on a generic semiconductor material: electron and hole pairs formation [15].

The photocatalytic process rate depends above all on the type of semiconductor and on the type of electromagnetic radiation [30].

A good catalyst should have the following characteristics:

- The hole redox potential should be sufficiently positive to allow the donor function;

- The electron redox potential should be sufficiently negative to allow the acceptor function;

- Good stability, with no release of toxic photo-products.

- Other factors, that can influence a photocatalytic reaction, are:

- The pH of the medium, with which the semiconductor is in contact, which influences the semiconductor charge;

- The concentration of the substrate, which influences the reaction kinetics;

- The temperature.

Several semiconductors are used as photocatalysts: TiO_2, ZnO, CdS and Fe_2O_3. Of these semiconductors,

hematite shows a lower photocatalytic activity than TiO_2, even though it absorbs in the visible range; ZnO and CdS, besides being less photoactive than TiO_2, also have the disadvantages of releasing, Cd^{2+} and Zn^{2+} ions into the solution [17].

TiO_2 seems to be the ideal photocatalyst as it is:

- Not expensive;

- Available in nature;

- Not harmful;

- Strongly oxidising.

Moreover, the photogenerated electrons are sufficiently reducing to produce the superoxide anion of the oxygen [18].

Several oxidation reactions occur in an irradiated semiconductor, but the most interesting are:

$$semiconductor + hv \rightarrow e^- + h^+ \tag{14}$$

$$e^- + h^+ \rightarrow heat \tag{15}$$

$$e^- + O_2 \rightarrow \cdot O_2^- \tag{16}$$
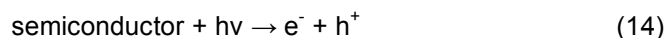
The generation of a superoxide radical is followed by:

$$O_2^- + H_2O \rightarrow HO_2\cdot + OH^- \tag{17}$$

$$HO_2\cdot + e^- \rightarrow HO_2^- \tag{18}$$

Finally, hydroxyl radicals are generated through the following reaction:

$$OH^- + h^+ \rightarrow OH\cdot \tag{19}$$

Equation 14 refers to the formation of an electron-hole pair in the semiconductor, after solar irradiation; equation 15 is relative to the recombination of the electron-hole pair on the particle surface.

In order to boost the activity of a photocatalyst, it is necessary to suppress, or at least to reduce, reaction 15, so as to promote reactions 16 and 19. In this way, the formed radical will attach adsorbed organic substrate, and the photo-oxidation process will be started.

The species that form are strongly oxidizing: with the exception of fluorine, hydroxyl radicals are the strongest oxidizers present in nature.

The photocatalytic reactions that occur between a photocatalyst and the adsorbed species follow Langmuir-Hinshelwood kinetics, where the rates of reaction, R, are proportional to the extent of the covering of the adsorbed species, according to this equation:

$$R = -dC/dt = k_r\theta = k_rKC/1+KC \qquad (20)$$

where k_r is the reaction constant, K is the adsorption coefficient of the reactant and C is the reactant concentration [19]. When the concentration of the organic substances (reactant) is low, the KC term is negligible and, equation 20 can be approximated to a pseudo-first-order reaction.

2.2. Mechanism of CO_2 Photo-Catalytic Reduction with TiO_2

The photocatalytic conversion of CO_2 into useful products, mainly CH_4 and other inorganic and organic substances such as: CO, HCOOH, HCHO, CH_3OH, has been studied for a long time [20-24]. Even though knowledge is still limited, the reaction mechanisms proposed until now are based on the observed charge transfer and reaction orders that have been acquired from macroscopic electrochemical testing [25]. According to the published literature, CO_2 photochemical reduction follows different reaction pathways, depending on the used catalyst and on the experimental conditions. The mechanism represented in Figure **7**, for the photocatalytic conversion of CO_2 with TiO_2 using water as the reductant, was proposed by Tan *et al* [26].

When UV light with sufficient photonic energy (hv) and an appropriate wavelength are used, photon-generated electrons and holes are formed on the TiO_2 catalyst surface. The holes first react with the H_2O vapour adsorbed on the catalyst, and hydroxyl radicals ($\cdot$OH) and hydrogen ions (H^+) are produced. The water is then oxidized by the $\cdot$OH radicals, and oxygen and H^+ are formed. In the meantime, CO_2 molecules are reduced to carbon radicals ($\cdot$C), with CO as a byproduct. At the end, the carbon radicals react with H^+ to produce CH_4. The eventual presence of CO in the gaseous product mixture is due to an incomplete CO_2 reduction, which in turn could be due to different reasons (for example: insufficient H^+ amount, or the recombination of $\cdot$C radicals and oxygen on the catalyst surface).

2.3. TiO_2 Based Catalysts

Semiconductor materials, such as TiO_2, ZnO, ZrO_2, CdS, ZnS, Fe_2O_3, SiC, WO_3, and various combinations have been applied for photocatalytic purposes. Considering their commercial availability, as well as their suitable optical/electronic qualities and chemical stability, TiO_2 nano-materials appear to be promising candidates [25]. Titanium dioxide can be used for many applications, because of its unique characteristics. Such a material can be employed to develop easy to clean surfaces and self-cleaning surfaces, because it is super hydrophilic. Moreover, TiO_2 is known for its capability to generate high mobility electrons and holes when exposed to light, which are able to promote chemicals reactions. Its unique photocatalytic properties make titanium dioxide a good catalyst for the degradation reaction of many wastes [27]. Kinetic studies have shown that the photocatalytic activity of TiO_2 depends on the crystalline form, and controversial
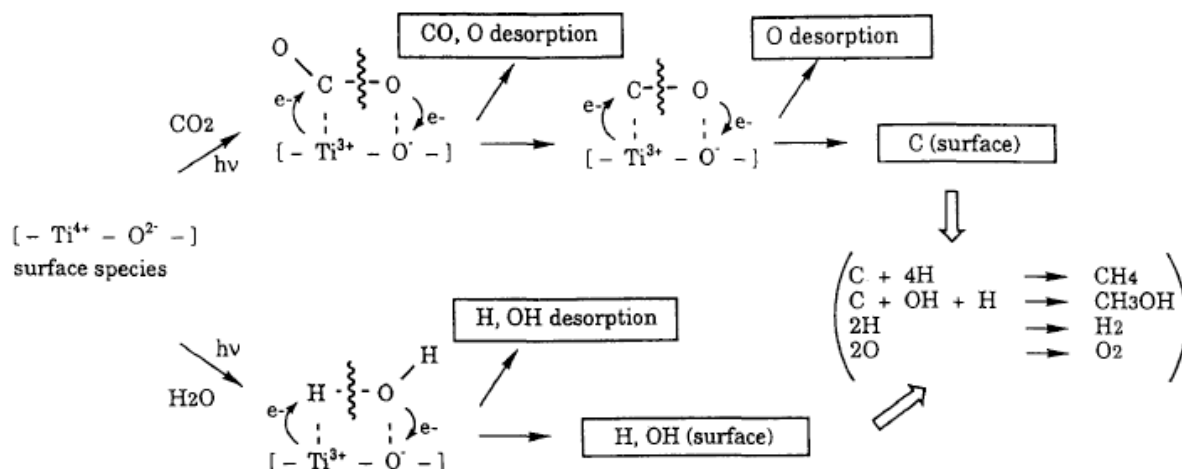

Figure 7: Schematic representation of the photocatalytic reduction of CO_2 with H_2O on the anchored titanium oxide [26].

results have been reported in the literature. Some authors have in fact stated that anatase is more reactive than rutile [28, 29]. Others have found that rutile works better [30-32], while some others have detected synergistic effects in the photocatalytic activity when both phases are used together [33-35]. Since the photocatalytic reduction of CO_2 over TiO_2 under UV light was first discovered, many techniques have been applied to investigate suitable sensitizers for visible-light adsorption and to increase the activity of the reaction. Titanium dioxide, used as a catalyst for UV irradiation, is considered the best oxide for this purpose, and it has adequate band-gap values (of around 3.0 and 3.2 eV for rutile and anatase, respectively). Moreover, titanium oxide is reasonably cheap, photo-stable and non-toxic, making it a perfect candidate for the photocatalytic process [26], and thus satisfies the thermodynamic requirements needed for the occurrence of the investigated photocatalytic reactions. Despite extensive research and the progress that has been made, the photocatalytic conversion of CO_2 by TiO_2 is still far from the practical application stage, due to the low product yields [25]. Its efficiency in reducing carbon dioxide is in fact still very low. The reasons for this low reduction rate are not obvious and not fully understood. One of the main objectives of this study is to obtain a better understanding of the fundamental mechanisms behind the photocatalytic reduction reaction of CO_2. One of the challenges for the application of these semiconductor photocatalysts is the fast recombination of photo induced holes (h^+) and electrons (e^-). Another challenge is the requirement of UV light excitation, due to the wide band gap of TiO_2 [36]. Titanium oxide can only be excited by high energy UV irradiation with a shorter wavelength than 387.5 nm [27]. As a result, the efficiency of CO_2 conversion to fuels is generally low. Many attempts have been made to improve its productivity, and some important characteristics of this material have been changed. Some examples, found in literature, are reported hereafter:

- Shape. TiO_2 can be produced in powder, pellet [26] and film [37] form. Moreover, many advanced nano-architectures have been engineered, such as: nanoparticles [38], nanotubes [39] nanorods and nanoribbons [40]. The smaller the material dimension, the higher the specific surface area, and the reduction efficiency increases. Detailed studies on TiO_2 powders, in which their dimensions have been changed, have shown that the highest methane production is reached for a grain size of 14 nm [41]. The band gap of TiO_2 semiconductor becomes larger for decreasing nanoscale particle sizes and the surface area increases. The specific surface area determines the active sites available for the reaction to take place. Smaller TiO_2 particles absorb more photoenergy; higher yields of methane and methanol are obtained, especially with nanoparticles with diameters of 29 to 14 nm. When the particle size is further reduced to 4.5 nm, the CO_2 reduction rate instead decreases, probably due to the change in optical and electronic properties of the nanometer crystals [42].

- Noble metal, transition metal and rare earth element loading. Nobel metal and transition metal loading plays an important role in TiO_2 photocatalysis, and its effect is remarkable in CO_2 photoreduction. The modification of TiO_2 with metal (*e.g.* Pt [43], Ag [44] or Cu [45]) particles or clusters has been reported to suppress charge recombination, because the loaded co-catalysts serve as electron traps [46, 47]. Photocatalytic activity is therefore improved. However, too high concentrations of metal dopants may lead to the formation of recombination centers that, in turn, lead to reduced catalyst efficiency. While metal modifications on TiO_2 apparently enhance charge separation, they make a limited contribution to extending the photo response to the visible light region [47]. Even rare earth elements, such as Ru [48], have been used to improve catalyst properties.

- Non-metal doping. It has been widely reported that doping or co-doping TiO_2 with non-metals (*e.g.* C, N, S, P, etc.) results in a significant band gap narrowing, which, in turn, leads to high photocatalytic efficiency under visible light irradiation [47].

- Dispersion of Ti or TiO_2 species in a support material. Another way of increasing the CO_2 reduction efficiency of titanium oxide is to disperse it in a carrier material, such as mesoporous zeolite [49], glass or mesoporous materials [50]. The anchoring method allows a good spreading of the Ti species, which act as active sites for carbon dioxide reduction, in the carrier material pores. Mesoporous frameworks have unique characteristics, such as nanoscale

pores, unusual internal surface topologies, and other particular features that endures a unique local structure and high selectivity in photoreduction to the catalyst prepared within. These kinds of materials have a greater efficiency than titanium oxide.

3. CONCLUSION

One of the most promising technologies for the production of solar fuels from renewable energy sources is the photocatalytic reduction of CO_2 in the presence of water vapour. However, the greatest challenge of this technology is the development of efficient photocatalysts that are able to overcome the high over-potential required to perform the CO_2 reduction reaction, which is responsible for the slow kinetics of such a photo-catalytic process. The structures and properties of TiO_2-based catalysts have been reviewed in this paper. This review clearly shows that while a significant improvement in the development of TiO_2-based photocatalyst has been made, there is still considerable room for further improvement. The main parameters that affect the activity of the TiO_2-based photocatalysts discussed in this review could be a good basis for further development of high performance photocatalytic reactors.

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