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Abstract: Carbon dioxide (CO_2) is considered one of the main contributors to the greenhouse effect and is currently a key challenge throughout the world. Therefore, the CO_2 complications associated with the environment have in particular been focused on in this review, and various strategies regarding CO_2 mitigation, or the utilization of different technologies to produce renewable fuels or useful chemicals to overcome the energy crisis, have been considered together with the recent developments in the photocatalytic reduction of CO_2 by means of different titania photocatalysts to produce various energy-bearing products. The problems, progress and future prospects regarding CO_2 utilization are presented. This present review indicates that the devolvement of efficient active photocatalysts for this technology is still under way and that better efficiency of the desired products could be accomplished. It is also shown that this technique is still at an embryonic stage, due to a lack of proficiency, and that the yield discrimination is very low. It can therefore be concluded that further research efforts are needed to boost this process towards commercialization in the near future.

Keywords: CO_2; greenhouse gas; titania; photocatalysis; renewable energy

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Acknowledgements

1 Introduction

Carbon dioxide is considered to be one of the main greenhouse gasses. The others are Methane (CH_4), Chlorofluocarbon (CFC) and Nitrous Oxide (N_2O). CO_2 plays a significant role in the global warming, due to its important contribution to the greenhouse effect (CO_2-55%, CFCs-24%, CH_4-15%, and N_2O-6%), and is currently considered a key challenge for the world [1, 2]. The Special Report of the Intergovernmental Panel on Climate Change (IPCC) on Emission Scenarios (SRES, 2000) projects an increase in the global greenhouse gases (GHG) emissions from 25 to 90% CO_2 between 2000 and 2030 [3].

On one hand, the main emission sources of CO_2 are mainly due to the burning of fossil fuels, such as oil, natural gas, coal etc., which accelerate the greenhouse effect. Human activities generate about 37 billion tons of CO_2 emissions each year, with about 30 gigatons (Gt) of this coming from the energy-related emissions. It has been reported that about 98% of the carbon emissions result from the combustion of the fossil fuels (coal, oil, and natural gas) [4]. On the other hand, the depletion of the fossil fuels throughout the world is dramatically increasing every year because of the ever increasing energy demands of humans as well as because of the increased global population. It has been estimated that these emission in CO_2 concentrations will have increased temperature on average, by 1.4 - 5.8 °C towards the end of this century. Consequently, to fulfil the energy demand for the future generations and to prevent the globe from being over-heated, CO_2 should be used as a raw feedstock to promote energy bearing products in a positive way for overcoming the energy crisis [5]. It can roughly be estimated that about 5–10% of the total CO_2 emissions could be suitable for the production of fuels and chemicals, that is, about one order of magnitude higher than actual use of CO_2 in industry [6]. Therefore, in order to minimize the CO_2 greenhouse effect and in the research of alternative sources of renewable energy, various technologies have been adopted for the capturing of CO_2 from the atmosphere: CCS (Carbon Capture and Storage), DAC (Direct Air Capture), SCPP (Solar Chimney Power Plants), etc. All of these are supposed to be long-term technologies; however, low stability is still a major challenge. In addition, other methods have also been used to capture CO_2, such as post combustion, pre-combustion and oxy-combustions, but unfortunately these are not yet economically feasible technologies [7].

Although CO_2 capture technologies are now widely being accepted by researcher as a pathway toward declining the growth rate of CO_2, overall, society is currently aware of the CO_2 utilization too. Indeed, CO_2 reuse is being considered as one of the main contributors to a low-carbon economy. Nevertheless, catalytic technologies for CO_2 conversion are still at an embryonic stage. In order to move towards such objective, it is necessary a more efficient use of resources and energy as well as the development of novel and effective technologies that employ renewable energy sources. Furthermore, an increase in the scientific efforts is essential, not only to develop new routes but also to efficiently assess problems associated with innovation ideas. Along with this increase in efforts, both public and private funds will be necessary to reach this goal. From this perspective, the SPIRE initiative [8] states that the CO_2 utilization is one of the most important pillars to boost sustainability, and to make the chemical industry competitive.

At the moment, a great deal of research has been carried out on exploring new ways of reducing CO_2, for example, electrochemical CO_2 reduction [9], photovoltaic processes [10], electrochronic display devices [11, 12], thermal CO_2 photocatalytic reduction [13], biological reduction by plants [14], and photoelectrochemical reduction of CO_2, as previously reported by Halmann et al. [15], using an electrochemical cell. Unfortunately, the use of an electrochemical cell for CO_2 conversion leads to certain disadvantages because of its very slow kinetics and its very high-energy demand [16]. On another hand, the photocatalytic reduction of CO_2 in aqueous form was firstly reported by Inoue et al. [17]. Later on, this field led to interest in both liquid and gas phases for the production of valuable chemicals such as CH_4, methanol (CH_3OH), carbon monoxide (CO), formic acid (HCOOH), formaldehyde (HCHO), etc. [18-23]. This technique is still at a developing stage, because of its low efficiency towards fuels formation, but in the meantime, the possibilities of take advantage of a green process for the production of fuels and chemicals while decreasing the CO_2 level in atmosphere makes

it an interesting method to be analysed and developed.

This review is focused on the issues that arise from the CO_2 emissions to the environment, on various strategies regarding CO_2 mitigation and on its utilization through different technologies to produce renewable fuels or useful chemicals for overcoming the energy crisis. In particular, the attention is concentrated on the recent developments in the field of the photocatalytic reduction of CO_2 by means of different titania photocatalysts to produce various energy-bearing products. Finally, future prospects regarding an efficient CO_2 utilization are also presented.

2 Environmental issues regarding CO_2 and recent strategies for alternative fuels

The increasing level of CO_2 in the atmosphere is not only considered a challenging problem throughout the world, but has also made it necessary for many scientists, investigators and researchers to explore various approaches in order to find a better solution for the energy crisis. The French scientist Jean Baptiste Fourier first observed the effect of greenhouse gases in 1827. This effect is caused by the greenhouse gasses, in particular by, CO_2, water vapour, ozone (O_3), CH_4 and N_2O. The increase in the greenhouse effect constitutes about 70% of CO_2, 24% CH_4 and about 6% of N_2O. This increased concentration of CO_2 in the atmosphere is mainly due to the burning of fossil fuels, such as oil, coal and natural gas. Land-use changes, cement manufacturing and deforestation contribute to this increase and there is an overall release of about 6 Gt of carbon into the atmosphere each year. The global average surface temperature has been estimated, through a climate change simulation [24], to have increased by about 0.6 °C over the 20th century. On the other hand, IPCC has stated that the global GHG emissions should be reduced by 50 to 80% by the year 2050 [3]. Moreover, there has been a slight alteration in the release of CO_2 into the atmosphere over the 1000 year period up to the 20th century. It has been reported that the concentration in Antarctica ice core of CO_2 increased slowly from 280 to 295 ppmv between years 1000 AD to 1900 AD [25]. This analysis is statistics based. From the year 1958 AD to 2004 AD, the CO_2 on the atmospheric air increased sharply from 315 to 377 ppmv [26] and such values are still gradually increasing. The recent data indicate that since October 2011up to June 2016, the CO_2 concentration has increased from 388.96 to 406.81 ppmv, respectively [27]. On the other hand, the depletion of the energy sources is mainly due to the rapid increase in the world's population, the rise in public transportation, and the construction of a larger and larger number of industries, which release toxic substances into the atmosphere, thus causing health as well as environmental problems [28].

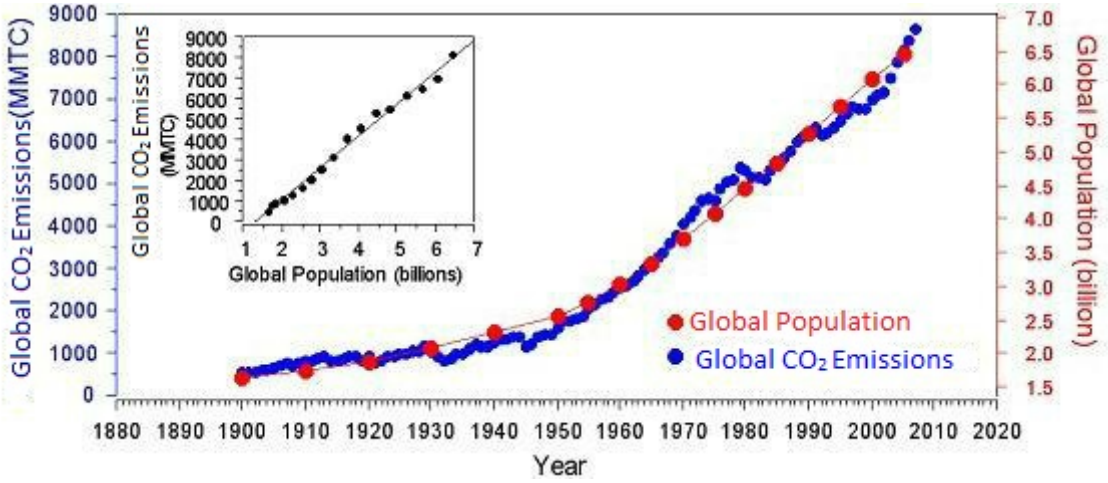


Figure 1.The correlation between CO_2 emissions and the world's population. Adapted from [29].

In addition, another key fact is the use of large amounts of CO_2 at an industrial scale. CO_2 is currently being used in a variety of applications, for example, in the metal industry, for the food and beverages, for the pulp, paper and electronics purposes, for the health care and laboratory analyses as well as chemical production. At present, the Earth's energy requirements are estimated at 14 TW/y.

Considering the economic development, the high consumption of fuel and constantly increasing number of people in the world, it is estimated that the energy demand in 2050 will be between to 28-30 TW/y. It is also estimated that in the case of the continued use of the traditional energy sources, the CO_2 levels will rise to 40 billion Mg per year by 2030 [29]. The correlation between the CO_2 emissions and the world's population is shown in Figure 1.

The presence of CO_2 in the atmosphere has two aspects, one of which is very crucial for the existence of life, *i.e.* for the photosynthesis of plants, for the carbon cycle and for many useful industrial applications, while the other aspect involves some drawbacks, for instance, global warming. The later issue has currently become a challenging topic for the scientists, investigators, researchers, etc. To tackle this problem, many investigations have been carried out over the last few decades by applying different technologies to control the CO_2 emissions and/or convert them into valuable energy products. Various possible strategies for the conversion of CO_2, such as the physicochemical approaches, the sustainable (or renewable) methanol synthesis and the production of syngas (CO/H_2) derived from the flue gases, which are produced from coal, gas or oil-fired electric power stations, in addition to the photochemical production of synthetic fuel [30], are of great interest. In order to prevent the global warming problems, the scientists involved in the study of the atmosphere have suggested that there should be a reduction in our current level of CO_2 emissions by about 60%, which would have a great impact on the climate changes [31]. It has been estimated that the total CO_2 emissions from fossil fuels is about 35.9 Gt /year all over the world [27]. The primarily sources of these emissions are connected to the production of electricity for public use and the production of heat, which release almost 35% of CO_2, along with the public transport, which is responsible for 24%. Another 41% of the CO_2 emissions are due to manufacturing, industrial energy use, auto producers and other sectors (see Figure 2) [32].

Photo-technology is considered one of the most encouraging ways of CO_2 conversion into value added products. The high concentration of CO_2 in the atmosphere could be captured and stored by means of various technologies [33]. Currently, different modes are being applied to capture CO_2, such as chemical and physical adsorption [34], cryogenic processes [35] and membrane separation [36]. The most recent way of capturing CO_2 is known as “ammonia scrubbing” [37] which is the first step toward using CO_2 as the feedstock in different technologies to produce value added products

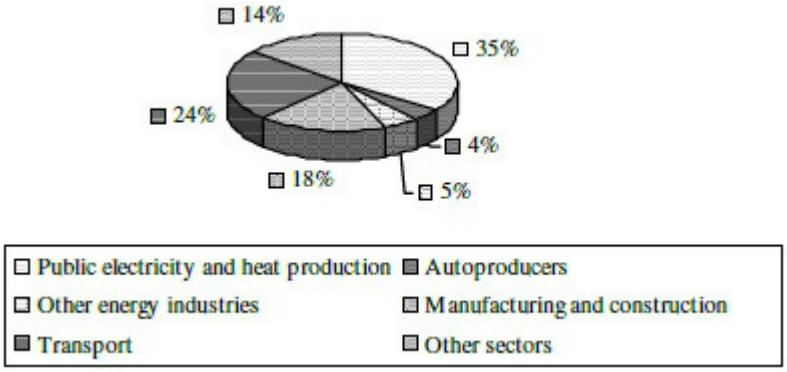


Figure 2.Sources of CO_2 emission from fossil fuel combustion. Adapted from [32]

3 CO_2 utilization technologies for renewable fuel formation

The increasing level of CO_2 in the atmosphere has not only threatened global warming, but has also raised various questions on how to control or reduce the CO_2 emissions to some extent. Therefore, much more attention has been paid by a number of researchers to gather CO_2 and convert it into valuable chemicals or fuels.

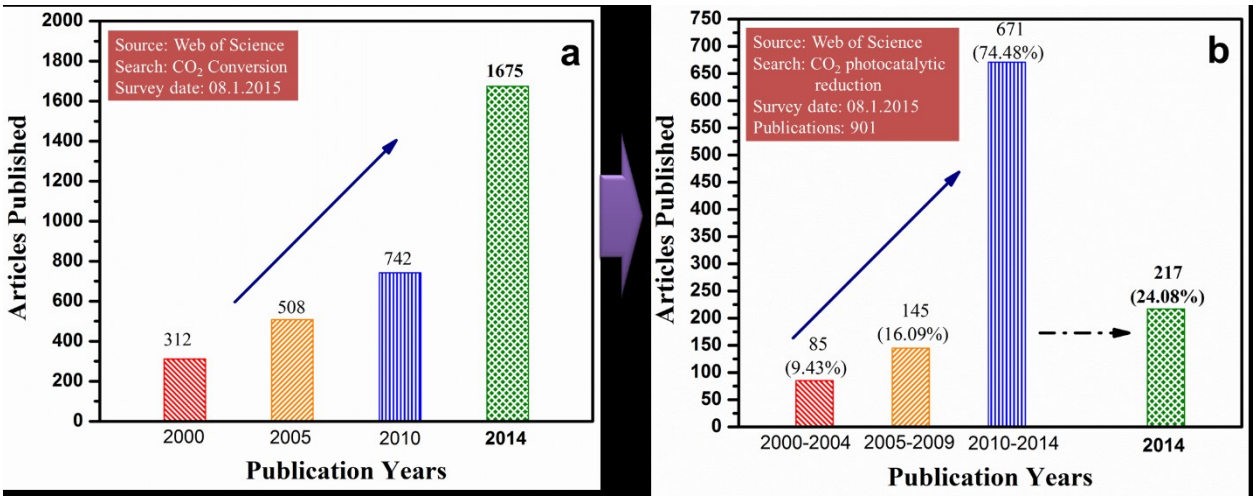


Figure 3. Publication trend of CO_2 conversion vs. CO_2 photocatalytic reduction.

Figure 3 shows the research trend pertaining to the CO_2 utilization, which has increased significantly in recent years. Observing the topic 'CO_2 conversion' shown in Figure 3a, it can be seen that the publications in the 2000 period (publications including books, journals, reviews, patents etc.) rose to over 320, a number that increased even more to 1675 at the end of 2014. Similarly, the five-year publication trend regarding 'CO_2 photocatalytic reduction' shown in Figure 3b, and in particular for the year 2014, indicates the recent profound interest in this area.

Moreover, the chemical utilization of CO_2 has increased over the last few years, and because of this increasing tendency, chemical industries are now taking part in the conversion of CO_2 to produce even higher energy density compounds such as fuel products. Additionally, recycling and reuse of CO_2 not only address the balance of atmospheric CO_2, but also represent valuable carbon sources renewable fuels formation. Recently, various studies have also been carried out, from the economic point of view, for the future of the chemical industry [38].

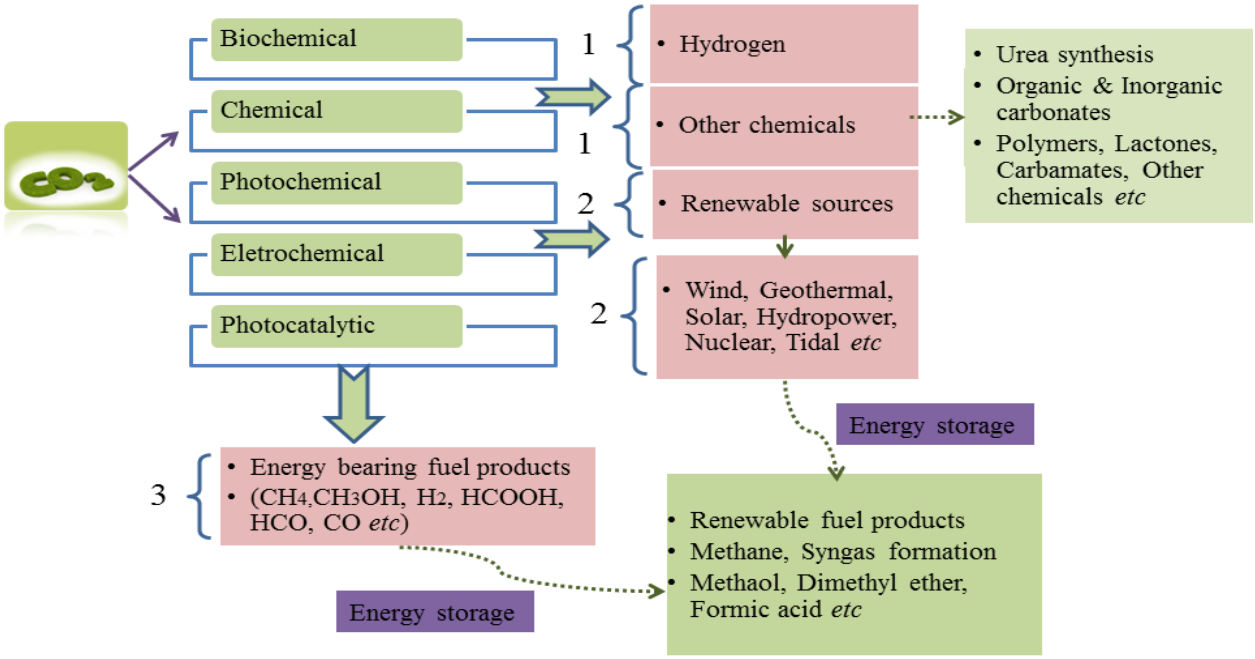


Figure 4.CO_2 utilization pathways.

The main products of the CO_2 conversion should be fuels to reduce the net CO_2 emissions significantly and to generate the renewable products of high economic value, such as those shown in Figure 4. Various options have been adopted for the CO_2 conversion, such as the hydrogenation of

CO_2 to form oxygenates; besides, hydrocarbons are the most intensively investigated products of the CO_2 conversion. Methanol synthesis from CO_2 and H_2 has been proposed, and another possibility is the production of dimethyl ether (DME), which is considered a "clean" burning fuel. Moreover, the photocatalytic reduction of CO_2 to a fuel by means of semiconductor catalysts is one of the most important techniques to obtain energy-bearing products. It has been reported that photocatalysis is a 'green' technology with promising applications over a wide assortment of chemical and environmental technologies [39]. Therefore, there are various possibilities of activating and of converting CO_2, but it is first necessary to overcome a thermodynamic barrier. For this reason, providing sufficient energy for the reaction is the critical aspect that should be considered when evaluating the alternative routes for the CO_2 conversion. For such a conversion of CO_2 to chemicals, reducing agents as well as intermediates species are needed to complete the reaction, for instance, the production of methanol by electrochemical CO_2 hydrogenation requires the use of protons (H^+) and electrons (e^-) consecutively [40-42]. Another possible route is the conversion of CO_2 to syngas (CO/H_2), which can be then converted into other chemicals or clean fuels [43] Generally, there are several approaches that can be considered for the CO_2 conversion to meet the energy demands [44], and the starting materials should be energy rich, unsaturated, and organometallic compounds.

3.1 Economic aspects of CO_2 for chemical production

CO_2 purification and recovery remain the main problems in terms of cost. However, these problems are not critical as there are many sources of rather pure CO_2 in the refinery and from chemical processes for the production of; ammonia, H_2, ethylene oxides, liquefied natural gas, Fisher-Tropsch coal, as well as it is a product from bio refineries, fermentation process, etc. [45]. It has been estimated that around 500 million tons of low cost (US $ 20/ton) and high concentration CO_2 is obtainable globally as a by-product from fertilizer plants, industrial sources and from natural sources. Diluted CO_2 is emitted at a higher cost, which could be captured from the power, cement and steel plants, etc. It is hoped that by introducing the limitation on the emission of CO_2 all around the world, the cost of the captured CO_2 and the market price of CO_2 will decrease in the near future [46].

3.2 CO_2 utilization technologies

By using different technologies different derivatives can be produced from CO_2 (see Figure .5). Several technologies have recently been explored and are reported in literature [28, 46] for the efficient utilization of CO_2 for useful products. These technologies are based on hydrogenation, electrochemical, thermochemical or biocatalytic processes, and photocatalytic reduction, which are further summarized and compared in this section of this review report.

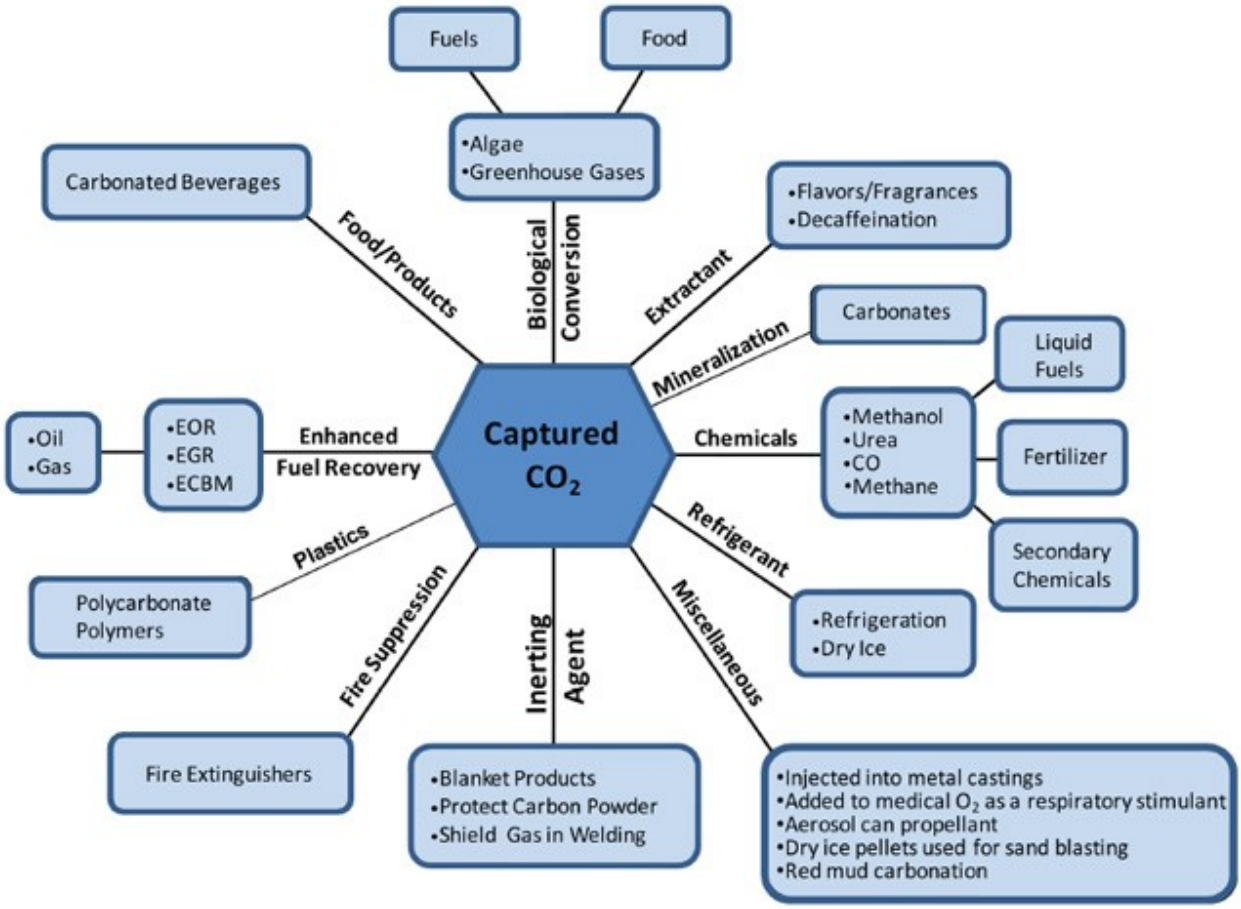


Figure 5. CO_2 derivatives using different technologies. Adapted from [47].

3.2.1. Thermodynamics of CO_2 conversion reactions

In order to convert CO_2 to other products, substantial input of energy and active catalysts are required due to the stability of this molecule that has a rather low energy content (ΔG_{f0} = –394 kJ/mol in gas phase). In Table 1 the free energy changes and other redox parameters for standard reduction reaction at pH = 0 are mentioned. Based on these tabulated data and on the fact that these reactions are reduction protonation and not hydrogenation, the variation of the redox potential with temperature can be calculated by the Gibbs- Helmholtz relationship:

$$E(T) = \frac{-\Delta G}{nF} = -\frac{(\Delta H(T) - T\Delta S(T))}{nF}$$

where *G* is Gibbs free energy, *H* is enthalpy and *S* is entropy.

Based on this formula, temperature can be pointed out as an effective parameter for the outcome of the reaction. Indeed, at room temperature, the entropy contribution, through the term (–*T*Δ*S*) is negligible with respect to the thermodynamic driving force for the CO_2 reaction; thus, the change of enthalpy (Δ*H*) during the reaction is a good guide to its thermodynamic feasibility [47]. For example, at low temperatures, CO production is less favored electrochemically rather than formation of other products like formaldehyde [48].

From Table 1, it is clear that the multielectron CO_2 reduction reactions require comparable potentials to that necessary for the H_2 evolution reaction ($H^+ + 2e^- \rightarrow H_2$, E^o = -0.41V at pH=7), while the single-electron reduction potential of CO_2 to form CO_2^- radical exhibit a much higher value. CO_2^- radical has been identified as an intermediate for the production of CO, formic acid and even methane [49, 50]. Figure 6 reports a proposed mechanism of CO_2 reduction in aqueous solution, under basic and acidic conditions. It have been reported that in acidic solution the CO_2 reduction to either CO or HCOOH is nonspontaneous compare to H_2 redox couple, instead reduction to methane is spontaneous [48]. Indeed, the reduction potential of CO_2 to CH_4 and CH_3OH is thermodinamically

more feasible than that required to reduce protons to H_2. Nevertheless, despite the thermodynamic feasibility to reduce CO_2, there are kinetic barriers for accomplishing the multielectron reduction processes that cause high overpotentials and limit such reactions. Thus, reduction of CO_2 in aqueous solutions is expected to be accompanied, or eventually replaced, by the kinetically more favored H_2 evolution.

Table 1.The standard ΔG° (25°C; pH = 7) and the corresponding E° values

Reaction	ΔG^0 (kJ mol^{-1})	E^0 (Volts vs. NHE)
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	11.68	-0.53
$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH$	24.63	-0.61
$CO_2 + 4H^+ + 4e^- \rightarrow H_2CO + H_2O$	148.85	-0.48
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	-139	-0.38
$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	-17.42	-0.24
$CO_2 + e^- \rightarrow CO_2^{\cdot -}$	183.32	-1.9

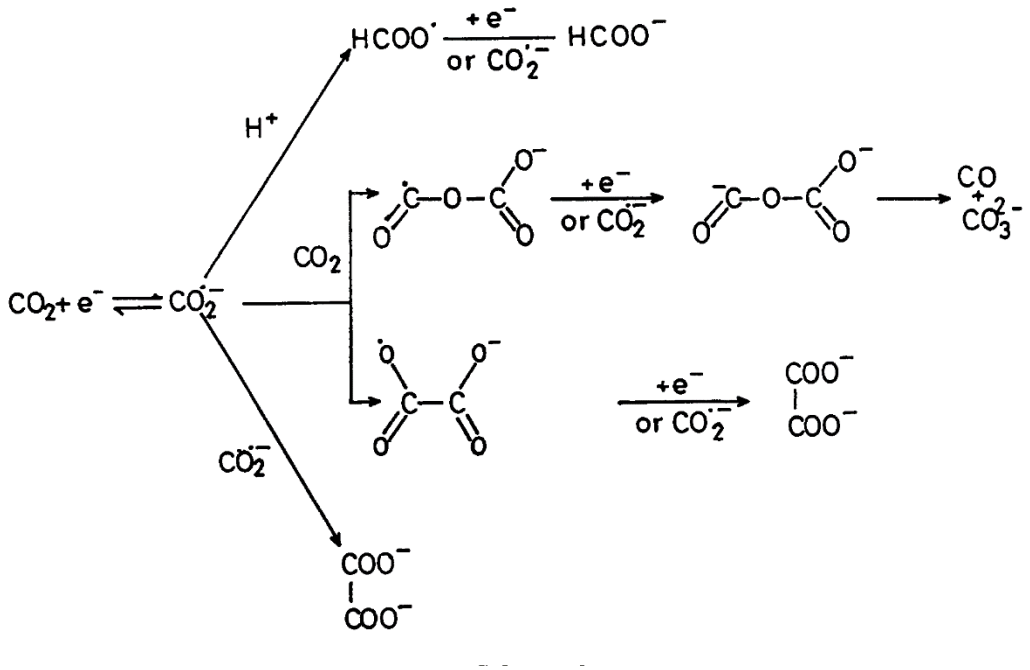


Figure 6. Reaction mechanism of CO_2 reduction. Adapted from [49]

3.2.2. Hydrogenation of CO_2

The hydrogenation of CO_2 over catalytic beds at elevated temperatures and pressures to produce hydrocarbons such as methane, or oxygenated hydrocarbons such as dimethyl ether and methanol, is a viable approach only if the hydrogen is produced from water electrolysis; by employing renewables energy sources (*i.e.* electrical energy from sunlight, wind, etc.) [51]. The hydrogenation of CO_2 to lower carbon products, for example (CH_4, CH_3OH), as well as to obtain higher molecular weight alkanes and alcohols through C–C bond formation, is possible [52]. A variety of products, such as methanol, dimethyl ether (DME) and other carboxylic acids (formic and acetic acids), can be produced with this technique. Moreover, various homogeneous and heterogeneous catalysts have been used for CO_2 hydrogenation, which involves multi-step routes. For instance, H_2 can be produced by electro or photocatalytic water splitting processes and, then, it can be used to hydrogenate the CO_2. Moreover, the reverse water-gas shift (RWGS) reaction is very important in the catalytic hydrogenation of CO_2, since it can be used to subsequently form methanol or dimethyl ether [16]. This reaction is considered a mildly endothermic reaction with an enthalpy change of $\Delta H_{298\ K}$ = 41.2 kJ/mol and Gibbs free energy change of $\Delta G_{298\ K}$ = 28.6 kJ/mol. The RWGS reaction is the primary step in CO_2 hydrogenation for fuel production:

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

Iron-chromium catalysts are considered very active at 400˚C or at higher temperatures, but a significant problem arises as a high equilibrium constant is necessary to drive the RWGS reaction towards right side. The equilibrium can be shifted to the right by increasing the CO_2 concentration, and a high H_2 concentration is able to increase the CO_2 consumption. The removal of water vapour from the reactor also drives the reaction to the right side. Different catalysts have been studied for the RWGS reaction [53]. Copper-based catalysts, particularly in CuO/ZnO oxides modified by alumina, zirconia, titania and/or silica [54], as well as iron or cerium-based catalysts, require a temperature above 400 ˚C to achieve an appreciable CO_2 conversion; therefore, these catalysts are not suitable for the RWGS reaction. The CO produced by means of the RWGS reaction could also be used for hydrogenation and methanol formation, or methanol could be synthesized from a feed of CO_2 and H_2 under feasible conditions. A book has recently been published, by the Nobel Laureate Olah [55], called 'The Methanol Economy', which deals with the production of methanol or dimethyl ether. Many studies have indicated that CO_2 is a better feed component for methanol formation than CO for the hydrogenation process, as indicated by the following reaction:

$$CO_2 + 3H_2 \rightleftharpoons CH_3OH + H_2O$$

The RWGS reaction causes a rapid conversion of H_2 and CO_2 to CO and H_2O. However, water acts as an inhibitor on the catalyst and causes the slowing down of the consecutive methanol formation step. Therefore, to overcome this critical issue, some improved catalysts have been used for CO_2 hydrogenation for methanol production[56]. In addition, multicomponent catalytic systems (*e.g.* $Cu/ZnO/ZrO_2/Al_2O_3/SiO_2$) have shown good performances and stable productivity, as well, the use of different precipitating agents have been found to significantly affects the physicochemical properties of such multi-functional catalysts and their catalytic performance [57]. Another aspect that affect the productivity is the feed. Usually, productivity is 3–10 times lower when a pure CO_2 feed is used instead of a CO/CO_2 feed, because of the higher oxidation power of CO_2 and its more negative effect on the catalyst than that of CO.

Dimethyl ether, which is a clean burning alternative to diesel, could be produced from methanol dehydration over an acidic catalyst:

$$2CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O$$

However, there are two another possibilities for the production of DME:

$$2CO + 4H_2 \rightleftharpoons CH_3OCH_3 + H_2O$$

$$3CO + 3H_2 \rightleftharpoons CH_3OCH_3 + CO_2$$

The synthesis of DME is more favourable from syngas than from methanol. As methanol synthesis and methanol dehydration are both limited by reaction equilibrium, the equilibrium constraint of methanol formation may be avoided by continuous removal of methanol through its conversion to DME directly from syngas [58]. The thermochemical process involves the direct decomposition of CO_2 to carbon monoxide and oxygen:

$$CO_2 + energy \longrightarrow CO + 1/2\ O_2$$

The reaction is endothermic, and it involves a free energy change (ΔG^0) of 257 kJ/mol. For a 100% conversion of CO_2, the reaction should be carried out at a minimum temperature of about 3075 °C, at which ΔG^0 becomes zero. However, in principle, the CO yield can be as high as 30% at temperatures near 2400 °C, but unfortunately the yield is low and a backward reaction may occur. The methanol fuel produced from CO_2/H_2 is a renewable energy source, as recognized by the Renewable Energy Directives of the European Union. However, renewable energy sources must be used for the methanol synthesis, e.g. either electrolysis or bio-routes, using semiconductor photocatalysts. Methanol formation offers more advantages over the other solutions (such as FT hydrocarbon synthesis). Its benefits include a very simple synthesis process with higher selectivity and flexibility and reduced transport costs. Methanol could also be used as a raw material in the process industry for the synthesis of olefins, etc. Owing to its low emission rate, and higher output

power, some pilot units have proved that using methanol fuel decreases NOx emission by around 30% compared to that of CH_4 usage as a fuel [59]. Another benefit of the use of methanol is that the small water content in the methanol causes a further reduction in the NOx emission. Furthermore, methanol can also be used for many other purposes, such as in chemicals, power generation and in transportation.

On another hand, urea can be synthesized from ammonia and CO_2, a process that is well established at a large scale. An urea boosting technology has shown that the capturing of fossil fuel CO_2 for urea production not only could solve the problem of the reduction of GHG emissions, but can also be used in an integrated ammonia-urea manufacturing plant that uses natural gas as a feedstock in the reforming process to produce CO_2 and NH_3. A large amount of NH_3 can be produced by using the surplus CH_4. Generally, ammonia is synthesized from hydrogen (from natural gas) as well as nitrogen (from the air). Firstly, natural gas is converted into hydrogen:

$$CH_4 + H_2O \rightleftharpoons 3H_2 + CO$$

$$CH_4 + 2H_2O \rightleftharpoons 4H_2 + CO_2$$

Then, air is mixed in the gas stream to obtain a H_2:N_2 ratio of 3:1. Furthermore, hydrogen and nitrogen are treated at higher temperatures/pressures in the presence of iron catalyst to produce ammonia, which is a very crucial component in the synthesis of urea:

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

The ammonia and carbon dioxide are fed into the reactor at higher temperatures and pressures to produce urea, which is produced in two steps. In the first step, ammonium carbamate, an intermediate product, is formed and then it further dehydrates to produce urea, as indicated below.

Ammonium carbamate formation:

$$2NH_3 + CO_2 \rightleftharpoons H_2NCOONH_4$$

Urea formation:

$$H_2NCOONH_4 \rightleftharpoons H_2NCONH_2 + H_2O$$

Urea is used as a fertilizer because of its rich nitrogen component. Therefore, it is of great importance in the field of agriculture and is also used in the manufacturing of resins for timber processing as well as in the yeast manufacturing process. Additionally, the synthesis of substituted urea is also attracting a great deal of attention at an industrial scale [60] and is being applied in various fields, such as in the refinery process, in pharmaceuticals, in agrochemicals and also in petrochemical industries.

3.2.3. Electrochemical conversion

The electrochemical conversion of CO_2 was first reported in 1978 by Halmann, who used p-GaP under UV light illumination [15]. Later on, the mechanism behind the electrochemical conversion of CO_2 was first described by Bockris et al. in 1989 [61] as:

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

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

In such a way, a high potential is required to form the CO_2^- radical [62, 63]. In addition, a great deal of work has to be done on the use of electrocatalysts to split the dissolved CO_2 into liquids. Various products, such as the simplest form of CO to very complex, oxygenated hydrocarbons of high-energy content, can be synthesized directly. This technology offers some positive aspects because of its compatibility with the well-established water electrolysis technology, and the possibility of using photovoltaic derived electricity. In aqueous electrolytes, such as $NaHCO_3$ and $KHCO_3$, water and carbon dioxide reduction processes take place simultaneously at the cathode, due to the proximity of their reduction potentials (H^+/H_2O potential is – 0.41 V *vs.* NHE whereas CO/CO_2 potential is – 0.53 V *vs.* NHE at pH = 7). One of the many challenges in electrochemical CO_2 reduction chemistry has to do with the interaction between CO_2 and water. When dissolved CO_2 is introduced to electrochemical conditions a set of reversible reaction can happens, as shown in Figure

7, which needs to be considered in function of the solution pH and the used electrocatalysts [64]. However, a wide range of hydrocarbons can be produced from the co-electrolysis of water and carbon dioxide. It has been observed that more hydrogen than hydrocarbons are produced when some metal electrodes, for instance, Ni, Pt, Co, Rh, and Fe, are used, because of their low hydrogen over-potential and high CO adsorption [65, 66]. Some other metals, for instance Cd, Pb, Hg, Bi, Sn and In, first produce formate ions and then undergo splitting of CO_2 [67]. Some noble metals and some other metals, such as Au, Ag, Pd, Ga and Cu result in a reasonable hydrogen production, but show low CO_2 adsorption. Among the different electrolytes that are available, copper has been considered as one of the most suitable materials for the production of hydrocarbons and oxygenated hydrocarbons in aqueous solutions [68]. In Table 2 a list of some used catalysts for electrochemical CO_2 reduction and their products is shown.

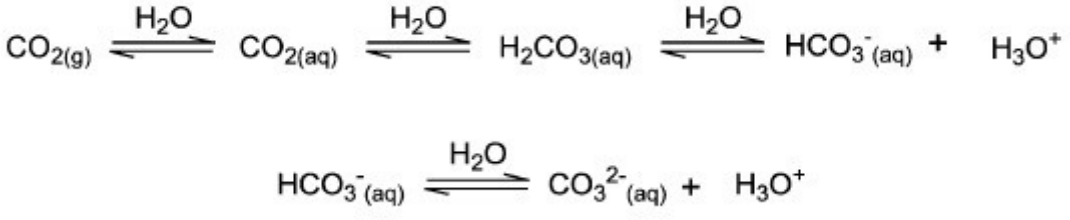


Figure 7.Equilibrium reactions of CO_2 and water. Adapted from [65]
Table 2.Electrochemical reduction of CO_2 and their product

3.2.4. Thermochemical splitting of CO_2

The capturing of CO_2 from the atmosphere can be obtained through various capturing technologies. The capturing and conversion of CO_2 are high intensive energy processes. However, the direct reduction of carbon dioxide using concentrated sunlight with thermochemical cycles is one of the most encouraging approaches for the production of hydrocarbons from CO_2 reduction with H_2O. The thermochemical process involves the direct decomposition of CO_2 to carbon monoxide and oxygen:

$$CO_2 + energy \longrightarrow CO + \frac{1}{2}O_2$$

The reaction is highly endothermic, with a free energy change (ΔG^o) of 257 kJ/mol. Similarly, for a 100% conversion of CO_2, the reaction should be carried out at a minimum temperature of about 3075 °C, with zero ΔG^o. In theory, the CO yield can be as high as 30% at temperatures close to 2400 °C, but it is much lower because of backward reactions. Galvez *et. al.* carried out a second law thermodynamic analysis of Zn/ZnO and FeO/Fe_3O_4 cycles [86].

$ZnO \Leftrightarrow Zn + ½\ O_2$ 1

$\Delta H^o 25^oC = +350.5\ kJ/mol$

$Zn + CO_2 \Leftrightarrow ZnO + CO$ 2

$\Delta H^o 25^oC = -67.5\ kJ/mol$

The reaction in Eq. (1) is highly endothermic and requires a temperature of about 1700 °C to form gas phase zinc and oxygen. The overall reaction is net production of O_2, which is sum of Eq. (1) and Eq. (2). A temperature between 425 and 725 °C is suggested to operate these reactions with 39% of efficiency under concentrated solar radiation.

The Sandia National Laboratory (SNL) is working on a two-step FeO/Fe_3O_4 thermochemical process, the so-called 'Sunshine-to-Petrol' process, to assimilate CO_2 and H_2O splitting processes in order to directly form diesel, gasoline or jet fuel as end products [87]. This process utilizes the concept of a thermochemical 'heat engine', called Counter- Rotating Ring Receiver Reactor Recuperator (CR-

5), to convert concentrated solar energy into thermal energy [87]. However, the feasibility of thermochemical CO_2 splitting has yet to be proved.

3.2.5. Biocatalytic processes

CO_2 utilization plays a significant role in the biocatalytic industry and provides a variety of opportunities for the synthesis of chemicals. For instance, Evonik is pursuing an acetone fermentation process using CO_2, the so called COOBAF project. In this process, industrial waste gas streams containing CO, H_2 and CO_2, as well as genetic modified acetogenic microorganisms, such as Clostridium ljungdahlii, Clostridium carboxidivorans and Clostridium aceticum, are used for acetone synthesis. In addition, an Escherichia coli (E. coli) strain has been developed specifically to produce succinic acid along with wheat-derived glucose, which is used as a substrate. Moreover, longer chain alcohols could be produced by means of the metabolic pathway of smart engineered bacteria (e.g. genetically modified E. coli) through the conversion of CO_2. For instance, isobutanol formation is being carried out by means of modified cyanobacterium [88]. Additionally, another CO_2 conversion possibility is a non-natural metabolic pathway. In this process, branched chain amino acids are protracted to produce long-chain abiotic keto acids as well as alcohols (carbon chain 5 to 8) in the presence of 2-isoproplylmalate synthase and other enzymes [88]. The optimization of this technique was made during the synthesis of 6-carbon alcohol, *i.e.* (S)-3-methyl-l-pentanol.

The biosynthesis route for the CO_2 utilization through the syngas fermentation is another interesting approach that is widely acceptable at an industrial scale, for which CO/H_2 is used rather than pure CO_2. In this process, Carbon Monoxide Dehydrogenase (CODH) enzyme from clostridium thermoaceticum is utilized to catalyze the reversible oxidation of CO to CO_2 using an iron (Fe) and nickel (Ni) containing metalloenzyme. This enzyme can also be coupled with a semiconductor catalyst such as TiO_2 (since its conduction band has good reducing ability), which produces the electrons necessary for the reduction process. In addition, TiO_2 nanoparticles, after the modification with CODH, and a photosensitizer under the illumination of visible light on specific reaction conditions, produce CO ($250\mu mol\ g\text{-}TiO_2^{-1}/h^{-1}$) [89-91]. The formation of fuels and chemicals through syngas fermentation offers a great advantage over the metal catalytic conversion, because of the higher specificity of the biocatalyst, the lower energy costs, the greater resistance to catalyst poisoning, and the independence of a fixed H_2:CO ratio. On the other hand, the biocatalysts are very costly. However, numerous microorganisms, such as acetogens, including Clostridium ljungdahlii, Clostridium autoethanogenum, Eurobacterium limosum etc., have been reported to be able to produce fuels and chemicals through syngas utilization [92].

Another feasible approach for the CO_2 conversion through biomass is the production of biofuels and, thus, several feedstocks have been used for such purpose [93]. The use of microalgae appears the most promising route for biofuels production. The oil content of algae is significantly higher than that of crops. Similarly, many algal species have a dry weight oil content of more than 30%; as well, the oil content can be as high as 80% in some strains, such as Schizochytrium sp. and Botryococcus braunii [94]. Algae itself fixes carbon dioxide and facilitates carbon recycling without any assistance. Moreover, bioethanol is commonly produced from sugar or starchy crops, such as sugar cane, and plant cellulose, using fermentation processes. Similarly, biodiesel is currently being produced from oil crops, for example, corn, soybean, canola, coconut, oil palm, in the presence of microalgae. In this transesterification biodiesel production process, triglyceride oil reacts with methanol in the presence of catalysts, such as sodium hydroxide or potassium hydroxide. Then, biodiesel can be used in the combustion process when it is blended with petro diesels. The biodiesel produced from microalgae is considered a significant source of global energy. The world's fuel production from biomass is rapidly increasing, while the sunlight-to-fuel energy conversion efficiency of photosynthesis is approximately 1%. It appears that biofuels will be a part of the future energy infrastructure, but they are unlikely to play a decisive role.

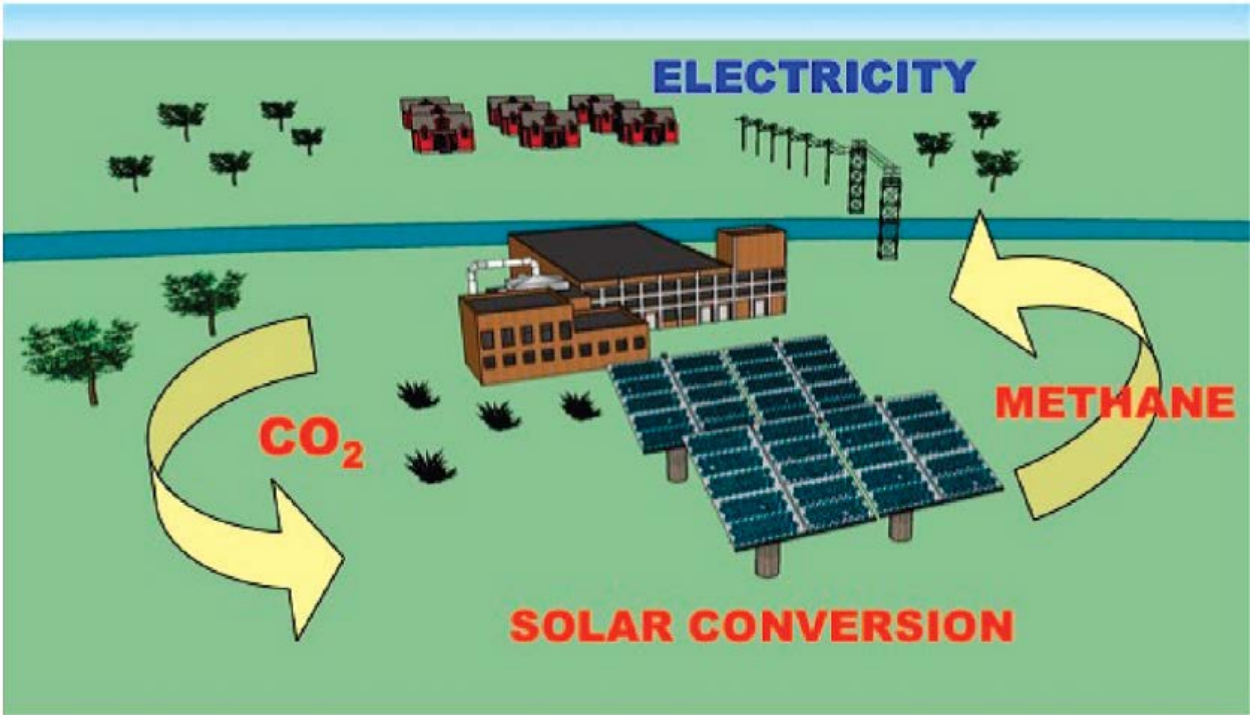


Figure 8. Solar fuels system for CO_2 conversion with H_2O to fuel. The fuels can be stored, transported or recycled with CO_2 passing through a photocatalytic process to again fuel formation. Adapted from [95].

Over the last few years, there has been a great deal of curiosity in the utilization of CO_2 through new approaches, which involve the use of homogeneous photocatalysts. For instance, methane or methanol can be produced from the CO_2 conversion with hydrosilanes under zirconium phenoxide borane complexs, or N-heterocyclic carbenes as catalysts [96, 97].

3.2.6. Photocatalytic reduction

The photocatalytic reduction of CO_2 to a fuel has been an attractive approach in the last few decades, because of the benefits it offers over other technologies. CO_2 is readily available as a feedstock and can be used infinitely for many fuels syntheses. The reactions can be carried out at mild conditions to obtain short-chain hydrocarbon photocatalytic products from CO_2 reduction that can help to solve the problem of the energy crisis and help to protect the environment. This technology would be more favourable to replace fossil fuels with CO_2 as a carbon source (energy) in the chemical industry. The pioneering work by Fujishima and Honda in 1972, which is known as the 'Honda-Fujishima effect', on the photocatalytic splitting of water by TiO_2 electrodes, opened the door for future generations in the field of photocatalysis [98]. After this discovery, attention in this research field has been focused not only on a specific area, but also on different applications from a laboratory to an industrial scale by using semiconductors, such as TiO_2. Moreover, Blajeni et al. later on used single-crystal p-GaP and p-GaAs photoanodes to produce methanol as well as formic acid and formaldehyde [99]. In a subsequent work, Halmann et al. introduced the use of titanate catalyst powder suspended in an aqueous solution, through which CO_2 was bubbled in the presence of natural sunlight to produce formic acid, formaldehyde, and methanol [100]. The Fujiwara group studied ZnS nanocrystal photocatalysts and their visible light response. They reported that a high content of metal ions improved the photocatalytic activity for CO_2 reduction as the result of a shift in the materials band gap [101]. Such strategy is based on the incorporation of metal dopants in substitutional or interstitial positions in semiconductors structure, which can generates trap levels within the band gap. Such trap levels can form narrow bands that are located below the minimum edge of the conduction band. Consequently, electrons can be excited at these levels, exploiting lower-energy photons than such required to excite the pristine material, to become trapped, with the holes having enough lifetime for water oxidation; electrons-holes recombination is moreover suppressed, thus increasing the overall process efficiency [87, 102]. Another strategy consists on the used of co-catalysts, such as the

case of Barton and coworkers who have used a catalyzed p-GaP based photoelectrochemical cell for the reduction of CO_2 to methanol [63].

In the following sections, emphasis will be made on describing the basic mechanisms and recent developments on TiO_2-based photocatalysts, aimed to enhance their CO_2 conversion photoactivity.

4 Photocatalytic reduction of CO_2 with titania-based materials

The photocatalytic reduction of CO_2 to sustainable fuels is a challenging and promising application, because it offers many advantages, for instance:

- CO_2 photo-catalytic reduction can be carried out in moderately mild condition, e.g. at room temperature and pressure;
- CO_2 is readily available as a key carbon source, which can be used infinitely to produce clean solar energy;
- Short-chain hydrocarbon can be obtained as photocatalytic products from the CO_2 reduction process, thus helping to overcome the energy crisis problem to a certain extent;
- This technology could favourably be used to replace fossil fuels with CO_2 as a C source in the chemical industry.

In recent years, a great deal of effort has been directed towards the conversion of CO_2 to hydrocarbons or renewable fuels in both liquid or gaseous phases [19, 112-125], using various semiconductor photocatalysts, mostly under UV light sources to simultaneously overcome the global heat problems and to fulfil the future energy demands. After the pioneer work of Fujishima and Honda on water photo-splitting over TiO_2 [98], attention on photocatalysis approaches have not only been developed on that specific era, but different applications from a laboratory to an industrial scale have emerged by using different semiconductor materials.

As mentioned briefly above, one of the first works on photocatalytic reduction of CO_2 in an aqueous solution was carried out by Inoue et al. [17]. In such work, different semiconductors, e.g. TiO_2, WO_3, ZnO, CdS, GaP and SiC were used to produce energy bearing products such as formaldehyde (HCHO), formic acid (HCOOH), methyl alcohol (CH_3OH), trace amounts of methane (CH_4) and carbon monoxide (CO), under xenon and mercury-lamps illumination. Subsequently, numerous investigators have tried to boost the photocatalytic technology by using CO_2 as a reducing agent in presence of H_2O vapour and other solvents [32, 103-111].

Subsequently, various photocatalyst oxides and non-oxides, such as TiO_2, CdS, ZnS, SiC, WO_3, Fe_2O_3, ZrO_2, Ga_2O_3, ZnO, and MgO_2, have been used extensively for photocatalytic reduction [1, 125]. However, some of these catalysts suffer from certain limitations, e.g. ZnO is highly unstable as it dissolves immediately in water to form $Zn(OH)_2$, which causes the catalyst inactivation. In addition, Fe_2O_3, and WO_3 have conduction band edges below the reversible hydrogen potential, thus an external electrical bias is needed to complete the splitting of H_2O for H_2 production [126]. Therefore, the major criterion for an efficient semiconductor photocatalyst is that the redox potential of the e^-/h^+ should lie within the band gap domain of the photocatalyst in order to obtain a better efficiency of the CO_2 reduction. Of all these above-mentioned materials, TiO_2 is one of the few catalysts able to satisfy all of the requirements that a good photocatalyst should have. TiO_2 is a widely used semiconductor, due to its adequate reduction potential value for CO_2 (-0.24V) towards methane formation [20]. Moreover, its holes are strongly oxidizing and redox selective. In addition, TiO_2 is an environmentally friendly material, which shows a good oxidation power, strong resistance to chemicals and photo corrosion, non-toxicity, superior charge transport properties, a low operational temperature, low cost, and significantly low energy consumption. Over the last few years, TiO_2 has drawn the attention of many scientists, due to its different potential applications.

In particular, for which regard the photoreduction of CO_2 over TiO_2 based materials, such trend is dramatically increasing every year because of the unique aforementioned properties of the TiO_2 and its easy availability. TiO_2 can be used in its pure form (bare), or doped with different metals and non-metals, or even in a highly dispersed form within mesoporous silica, zeolites or carbon materials to enhance its photoactivity, as shown in Table 3. It is evident that to date, many investigations have

been focused on this area, in order to obtain good productivity and selectivity for specific products, but this approach is still far from being able to offer the desired efficiency. The development of new technological approaches [127], application of innovative synthesis methods for the formation of high surface area nanostructured catalysts [128], as well as investigation on new co-catalysts to be coupled to the TiO_2 might be some of the ways of enhancing the photocatalytic activity. Moreover, research activities on this field should have the objective of not only establishing robust technologies and materials that can be used for this application, but also of developing cost effective ones [104, 105, 129-131].

Table 3. Photocatalytic reduction of CO_2 on bare, doped and highly dispersed TiO_2 based materials

Photocatalysts	**Reductants**	**Light source**	**Products**	**References**
TiO_2	H_2O	450 Xe lamp	CH_4, C_2H_4	Adachi et al. (1994) [132]
TiO_2	H_2O	75 W high-pressure Hg	CH_4, CH_3OH, CO	Anpo et al. (1995) [129]
TiO_2	H_2O	75 W high-pressure	CH_4, CH_3OH, CO	Yamashita et al. (1995) [104]
TiO_2	H_2O, 0.2M, NaOH solution	4.5kW Xe lamp	HCOOH, CH_3OH, CH_4, C_2H_6OH, C_2H_4, C_2H_2	Mizuno et al. (1996) [130]
TiO_2	H_2O, liquid CO_2	990W Xe lamp	HCOOH	Kaneco et al. (1997) [131]
Pt-TiO_2/Y zeolite	H_2O	75 W high-pressure Hg lamp λ> 280 nm,	CH_4, CH_3OH	Anpo et al. (1997) [105]
TiO_2 nanocrystals SiO_2 matrices	1M 2-propanol, solution	500W high-pressure Hg arc lamp	$HCOO^-$, CO	Liu et al. (1997) [133]
TiO_2 (P25)	Isopropyl alcohol	4.2 Kw Xe lamp	CH_4, HCOOH	Kaneco et al. (1998) [134]
Ti-MCM-41, Ti-MCM-48	H_2O vapor	High-pressure Hg lamp, λ> 280 nm	CH_4, CH_3OH	Anpo et al. (1998) [131]
Rh/TiO_2	H_2	Ultra high pressure Hg lamp λ = 290-450	CH_4	Kohno et al. (1999) [135]
TiO_2	Methanol, ethanol 2-propanol, nitric, hydrochloric, and phosphoric acid	0.96wK Xe lamp	HCOOH	Kaneco et al. (1999) [136]
TiO_2/SiO_2, Ti-MCM-41	H_2O	100W high-pressure Hg lamp	CH_4, CH_3OH	Ikeue et al. (2002) [137]
Ti/Si hexagonal and cubic	H_2O	100W high-pressure Hg lamp	CH_3OH CH_4	Shioya et al. (2003) [138]
Ti-SBA-15	H_2O	Mercury lamp	CH_4, CH_3OH	Hwang et al. (2004) [139]
TiO_2 suspension	H_2O	λ=350nm	CH_4	Dey et al. (2004) [140]

Cu/TiO_2	H_2O	UV light	CH_3OH	Wu et al. (2005) [141]
TiO_2	H_2O	UV light	CH_4	Tan et al. (2006) [108]
TiO_2(P25)	H_2O, H_2	15W UVA λ= 365nm	CH_4, CO, C_2H_6	Lo et al. (2007) [113]
TiO_2 pellets	H_2O vapors	UVC 253.7nm	CH_4, CO, H_2	Tan et al. (2007) [112]
TiO_2	H_2O	15W UVA lamp, λ=365nm	CH_4, C_2H_6OH, HCOOH	Xia et al. (2007) [109]
TiO_2	H_2O vapor	200W Hg/Xe lamps	H_2, CH_4	Tan et al. (2008) [142]
Pure TiO_2 anatase	H_2O	8W Hg lamp, λ=254nm	CH_4, CH_3OH	Koci et al. (2009) [20]
Cu/TiO_2-SiO_2	H_2O	Xe lamp	CO, CH_4	Li et al. (2010) [141]
Ag/TiO_2	H_2O	8W Hg lamp, λ=l254nm	CH_4, CH_3OH	Koci et al. (2010) [144]
TiO_2	H_2O	UV light	CO	Dimitrijevic et al. (2011) [145]
Ti-SBA-15	H_2O vapor	120W high pressure Hg lamp	CH_4, C_2H_4, C_2H_6	Yang et al. (2011) [121]
Bulk TiO_2, Ti Oxide	H_2O	UV lamp	CH_4, CH_3OH	Mori et al. (2012) [124]
$Cu(I)/TiO_{2-x}$	H_2O vapor	150W solar simulator	CO	Liu et at. (2012) [146]
$Cu\text{-}I/TiO_2$	H_2O vapor	UV light	CO, CH_4, CH_3Cl	Zhang et al. (2012) [147]
Pt/TiO_2	H_2O vapor	100W high pressure Hg lamp	CH_4	Uner and Oymak (2012) [148]
Ce/TiO_2 SBA-15	H_2O vapor	UV Xe lamp	CO, CH_4	Zhao et al. (2012) [149]
R/TiO_2 modified A/TiO_2 nanorods	H_2O vapor	UV Hg lamp	CH_4, CH_3OH, H_2, CO	Wang et al. (2012) [150]
Ti-KIT-6	H_2O vapor	UV 300W	CH_4, CH_3OH	Hussain et al. (2013) [19]
Au/Ti/SBA	H_2O	200W Hg lamp	CH_4	Mei et al. (2013) [151]
Montmorillonite/TiO_2	H_2O vapor	200 W Hg lamp	CH_4, CO	Tahir et al. (2013) [152]
Ti-KIT-6	H_2O vapor	UV light	CH_4, CH_3OH, H_2, CO	Akhter et al. (2014) [18]
GaP/TiO_2 Pt- GaP/TiO_2 Pd- GaP/TiO_2	H_2O vapor	Visible light	CH_4	Marcì et al. (2014) [153]
Ni/TiO_2	H_2O vapor	UV/Visible light	H_2,CH_3OH, CH_3CH_2OH, CH_3CHO	Ola et al. (2014) [154]

Ce/TiO_2	100ml H_2O + 0.2 mol/l NaOH	UV 8 W Hg lamp	CH_4, H_2	Matejová et al. (2014) [155]
Au/TiO_2	75 mL of aqueous suspension containing 25 vol.% methanol in water	UV Source	H_2	Ortega et al. (2014) [156]
$Ag\text{-}Au\text{-}Pd/TiO_2$	Thermostated water	UV-vis irradiation (1000 W Xenon lamp)	CH_4	Cybula et al. (2015) [157]
Noble metal-doped graphene oxide/TiO_2 ternary composites	H_2O vapor	15 W energy-saving daylight bulb	CH_4	Tan et al. (2015) [158]
TiO_2/InP	$[EMIM]BF_4$	0.15 W 532 nm laser	CO	Zeng et. al. (2015) [159]
Ag-TiO_2 nanocomposites	DI water	Visible light	CH_4	Feng et. al.(2015)[158]
N-doped TiO_2	H_2	UV source (100W Hg reflector lamp)	CH_4 , CO	Tahir et. al. (2015) [160]
ReP–TiO_2 hybrid	5:1 DMF/TEOA	UV-filtered simulated solar light (100lmW cm_{-2}, λ>420 nm)	CO	Windle et. al. (2015) [162]
Au/Cu alloy - $SrTiO_3/TiO_2$	hydrous hydrazine ($N_2H_4{\cdot}H_2O$)	UV/Vis light	CH_4, C_2H_6, C_2H_4, and C_3H_6	Kang et. al. (2015) [163]
$Pt/SrTiO_3$–Rh/Pt/CuAlGaO4 WO3	AM 1.5G	2MmM $FeCl_2/FeCl_3$	CH_3OH, H_2,O_2	Cheng et. al. (2015) [164]
Ni–TiO_2	H_2O	6 (3W/cm2) UV lamps	CH_4	Kwak et. al. (2015) [165]
N–TiO_2/spirulina	H_2O	13 W lamp	CH_4, C_2H_6, C_2H_4, ,C_3H_6 and H_2	Phongamwong et. al. (2015)[166]

Two major types of ‘Heterogeneous photocatalysis’ have been studied extensively over the last few years: one is the bulk semiconductor photocatalyst and the other is the matrix dispersed photocatalyst [167-169]. Both types have been used for their potential to help solve environmental problems, as well as those related to energy generation and the synthesis of organic materials (methane, methanol, carbon monoxide, formic acid, formaldehyde, and other hydrocarbons etc.,). The modification of photocatalysts with various species that can enhance its performance is considered a vital step. Different approaches have been used by various researchers on the modification of titania, as summarized in Figure 9 and discussed in the following sub-sections of this review.

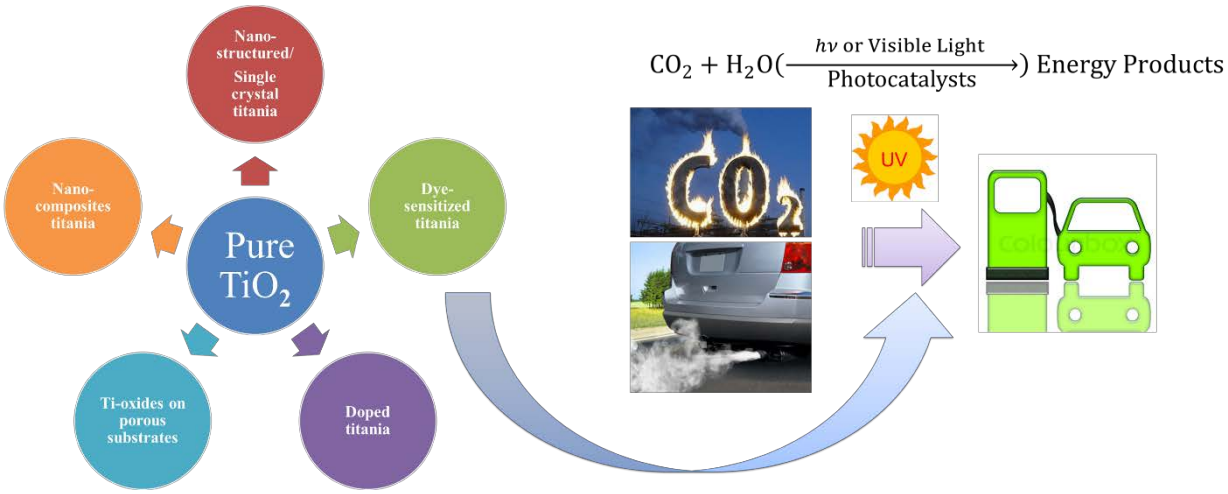


Figure 9.Various routes for TiO_2 modification for the enhanced photocatalytic conversion of CO_2 to fuels.

4.1 Molecular interactions of CO_2 on titania photocatalysts

As mentioned before, titania has become one of the favoured photocatalysts for CO_2 reduction because of its stability, low cost, non-toxicity and its superior charge transport. Despite all the advantages of titania as a photocatalyst the conversion efficiency of CO_2 is still too low for industrial applications. Further progress requires a well knowledge of CO_2 interactions at atomic level with titania at its exposed surfaces.

Titania exist in three crystalline form: anatase, brookite and rutile. The rutile and anatase phases are the more extensively studied, with anatase being regarded as the more photocatalytically active phase [170]. As discussed previously, it is believed that formation of the radical anion CO_2^- is the first step toward CO_2 reduction. He *et. al.* [171] reported that CO_2^- radicals can be formed on the surface of titania anatase. They used first-principle calculations to determine the binding configuration of CO_2 and CO_2^- radicals on perfect and oxygen-deficient anatase (101) surfaces by using both cluster and periodic models. They concluded that the reduction potential of adsorbed CO_2 on a (101) surface is lower by 0.24 V than the reduction potential of a CO_2 molecule, both in aqueous solution, due to the formation of hybridized orbitals, which facilitates charge transfer to CO_2 [171].

Further density functional theory (DFT) calculations on brookite (210) and anatase (101) surfaces demonstrated that the brookite (210) surface has the same building blocks as the anatase (101) one [172]. However, in a more recent work, Andino *et. al.* [173] demonstrated by computational DFT calculations that an unmodified brookite (210) surface will not result in charge transfer to CO_2 by itself and, at the same time, presence of oxygen vacancies within the brookite (210) surface will enhance the interaction and charge transfer to CO_2 molecule.

A comparison of the most stable sites of anatase titania, i.e. (001) and (101) surfaces, for CO_2 molecular interactions has been reported by Ferrari *et. al.* [174]. As shown in Figure 10, their results of DFT calculations and simulations demonstrate that a high activity of (001) surface can be due to a stronger basicity of the surface oxygen sites; as a result, carbonate and bicarbonate formation occurs in this site. On the other hand, in the most stable (101) surface site, CO_2 is less adsorbed and retains its molecular properties.

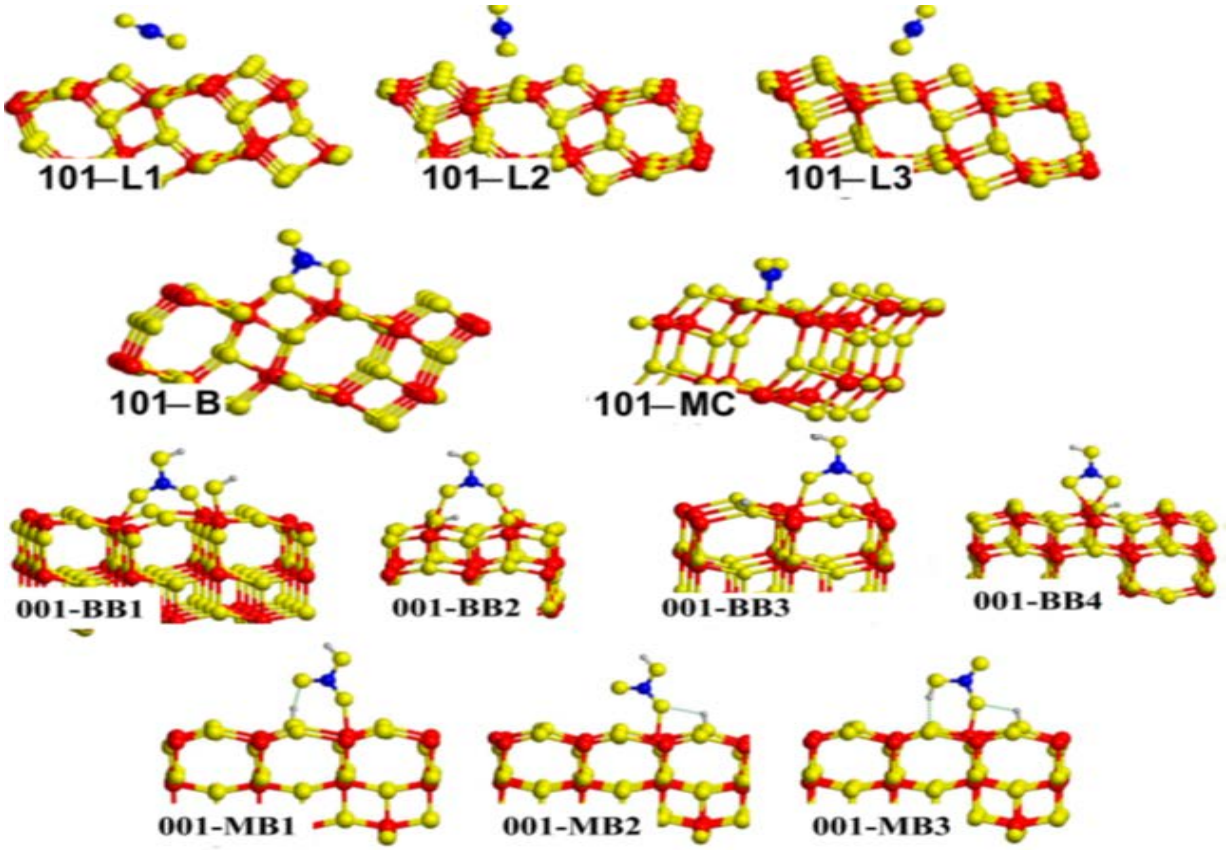


Figure 10. Investigated bicarbonates on the anatase (101) and anatase (001) surface. Oxygen, titanium, carbon, and hydrogen atoms are represented in yellow, red, blue, and gray, respectively. Adapted from [174].

4.2 Pure/bulk titania photocatalysts

In heterogeneous photocatalysis, two or more phases are used in the photocatalytic reaction: 1) a light source with semiconductor material is used to initiate the photoreaction, 2) a catalyst is used to carry out substrate oxidation or reduction reactions. Bulk semiconductor photocatalysts include metal oxides, sulphides, nitrides, oxynitrides and titanium dioxides, the latter being the most frequently used photocatalysts in CO_2 photoreduction. As shown in Figure 11-A, in the case of bulk TiO_2 materials, upon UV irradiation, the absorption of photons with equal or greater energy than the band gap energy of the semiconductor (3.2 eV for anatase) produces e^-/h^+ pairs, as shown in Eq. (4.1).

$$TiO_2 \ (\xrightarrow{h\nu})e^- cb\ (TiO2) + \ h^+ vb(TiO2) \qquad 4.1$$

This leads to the promotion of electrons towards CB and to the holes being left behind in the VB. Consequently, the TiO_2 particle can act as either an electron donor or acceptor for the molecules in the surrounding medium. Thus, the overall efficiency of the photocatalytic activity and product selectivity of the bulk titania is low, because of some limitations of the bulk TiO_2, for example, the chance of charge recombination is higher and the lifetime of the photogenerated e^-/h^+ pairs is very short (nanoseconds), both of which could have adverse effects on CO_2 photocatalytic activity.

The reduction of CO_2 with H_2O often results in the formation of CH_4, CH_3OH, HCHO and CO (see Figure 11-A). The yields of these products are increased through an increase in the duration of the UV light, which is a clear indication that their formation from the CO_2 reduction with H_2O vapour takes place in a solid-gas phase system with powdered TiO_2.

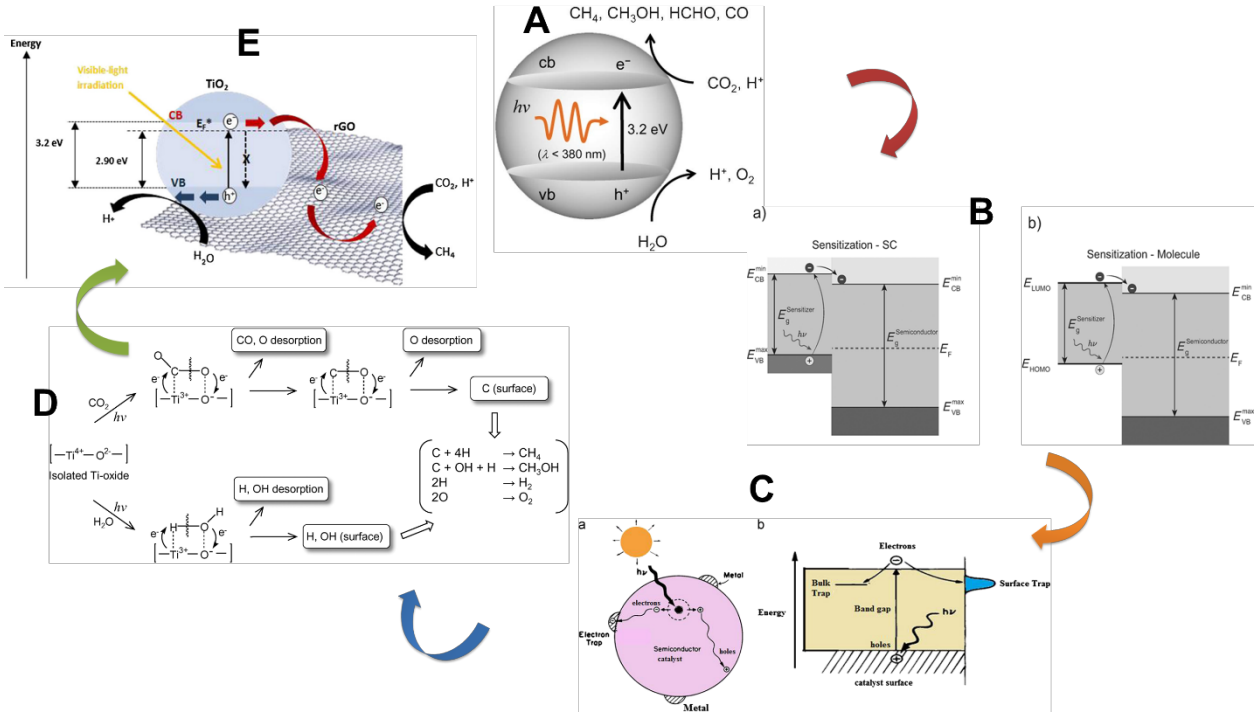


Figure 11.. Reaction schemes for the photocatalytic reduction of CO_2 with H_2O on (A) bulk TiO_2 [124]; (B) sensitization of a wide band gap semiconductor (B-a) narrow band gap with an aligned conduction band, (B-b) a dye that absorbs in the visible region [175]; (C-a) doping of a semiconductor photocatalyst with metals for electron trapping, (C-b) surface and bulk electron carrier trappings[176]; (D) the isolated titanium oxide species proposed by Anpo et al.[124], (E) reduced graphene oxide-TiO_2 nanocomposites [177].

4.3 Nanostructured titania and single crystal titania photocatalysts

Nanostructured TiO_2 has been explored in various shapes, including nanospheres (zero dimensional) [178-180], nanofibers (one dimensional) [178, 180-184], nanotubes (one dimensional) [185-187], nanorods (one dimensional) [140, 188, 189], nanosheets (two dimensional) [179, 190-195] and TiO_2 interconnected architectures (three dimensional) [19, 196-201], etc., all of which have been used for photocatalysis applications.

The photocatalytic reduction of CO_2 with H_2O on rutile-type single crystal TiO_2 (100) and TiO_2(110) surfaces was performed by Yamashita et al. [202], who found that selectivity of the photocatalytic reactions depends to a great extent on the type of TiO_2 crystal surface. UV-irradiation of a TiO_2(100) single crystal catalyst in the presence of a mixture of CO_2 and H_2O produced hydrocarbons, CH_4 and CH_3OH with 3.5 and 2.4μmol h^{-1} g-cat^{-1} yields, respectively, but a limitation for a TiO_2 (110) single crystal (only 0.84μmol h^{-1} g-cat^{-1} CH_3OH and no CH_4 formation). However, the photo-generated electrons that localize on the surface sites of excited TiO_2 participate with CO_2 molecules to form intermediate and surface Ti atoms, which act as reductive sites. Consequently, a TiO_2 (100) single crystal has shown more photocatalytic activity towards hydrocarbon formation [202].

In more recent work, He *et. al.* [203] used anatase TiO_2 catalysts with various morphologies, such as nanoparticle, nanotube, and nanosheet, which were synthesized through a hydrothermal method. The main products of photocatalytic reduction of CO_2 in aqueous TiO_2 suspensions were found to be methane, methanol, formaldehyde, carbon monoxide, and H_2. In such work TiO_2 sheets showed to be more active due to high-energy exposed (001) facets, which facilitates the oxidative reaction of H_2O with photogenerated holes, leaving more photogenerated electrons available for the reduction of CO_2 on the (101) facets [203].

4.4 Dye sensitization and doped titania photocatalysts

Narrow-band semiconductors or visible-light-active molecules (dyes) are generally used as sensitizing agents, as can be seen in Figure 11-B. Sensitization with dyes is a commonly used technique in solar and photoelectrochemical cells, and a large number of inorganic or organic dyes have been adopted. Similarly, coupled semiconductors, for instance, CdS and TiO_2, or CdSe and ZnO, have been used to enhance the efficiency, through the extension of the absorption range, and to improve the charges separation [204]. The LUMO of the dye has to be higher in energy than the conduction band edge of the semiconductor for electron transfer to occur [205].

The dye sensitization process is only limited because of a narrow band gap. If these approaches are not introduced, the visible or solar light is insufficient, and this causes the reduction of photoactivity. Wu J.C.S. [206] found that the CH_4 production from the CO_2 reduction over N3-dye–Cu (0.5wt%)–Fe(0.5 wt%)/TiO_2-P25 increased when moving from a solar to artificial light response. Thus, the used light source and its intensity have an effect, *i.e.* 0.617 μmol CH_4/g-cat h and 0.84 μmol CH_4/g-cat h were produced with an average concentrated sunlight intensity of 60 mW/cm^2 and 225 mW/cm^2, respectively, employing artificial light in the 320–500 nm range.

Moreover, Yang et al. [207] have described the possibility of a contamination effect by residual C in the catalyst. They demonstrated that carbon residues present on the catalyst surface were involved in the photocatalytic reduction of CO_2 to CO. It was observed that these carbon residue, which are mainly originated by Ti alkoxides and polyethylene glycol (PEG) during the TiO_2 synthesis, can be effectively removed by prolonged exposure of the catalyst surface to UV irradiation in the presence of H_2O vapor, other than by another methods like thermal treatment in air. Due to observation of adsorbed ^{12}CO as the main product rather than ^{13}CO over Cu(I)/TiO_2, it was concluded that ^{12}C originating from carbon residues was the predominant carbon source. By Isotopic labelling of Ag, Au and Pd–TiO_2 samples tested for CO_2 reduction, it was confirmed that the formation of CH_4 was due to organic impurities present on the catalysts and not to $^{13}CO_2$ [157].

The main barrier to the photocatalytic activity of a titania catalyst is the higher rate of recombination of e^- and h^+ pairs. The best way of overcoming this problem and of preventing the recombination of e^- and h^+ pairs, is to load the photocatalysts with metals and noble metals, which function as charge-carrier traps, or to induce the activity with isolated Ti-species. The surface defects sites and inequalities that are present on the catalyst surface, as well as in the bulk, participate as charge carrier traps and suppress the recombination of electrons and holes, as can be seen in Figure 11-C. However, different studies on CO_2 reduction with H_2O have been carried out in order to improve photoactivity. Some modified titania, doped with metals such as Cu with loadings from 0.3 to 1.0 wt%, reduced the CH_4 production, but promote the CH_3OH formation [208]. It was then suggested that a further increase in the Cu load on TiO_2 would increase the CH_3OH yield significantly. 3wt% Cu/TiO_2 was found to be optimized with maximum of three times higher activity for methanol production than the original TiO_2 [209]

In another work by Wu *et. al.*, it was observed that the maximum methanol yield (0.45 μ mole/g-cat·h) was obtained by using 1.2 wt% Cu/TiO_2 that was tested under increasing light intensities from 1 to 6 W/cm^2 [141].

In a recent work, Fang *et. al.* [210] used Hierarchical CuO−TiO_2 hollow microspheres for photodriven reduction of CO_2 to CH_4. As a result, the CuO-incorporated TiO_2 hollow microsphere catalyst demonstrates much higher photocatalytic activity toward the photoreduction of CO_2 with H_2O into CH_4 compared with commercial Degussa P25 TiO_2 (see Figure 12) [210]. Similarly, Pt/TiO_2 can favour the production of CH_4, which has been shown to increase remarkably as Pt loading is increased from 0.1 to 1.0 % on titania [129].

Non-metal dopants effectively redshift the TiO_2 photocatalyst system and lead to a narrowing of the band gap. Various studies have been reported on non-metal substitution with N, C, F, P, and S, but N-doping has been found to be more effective and to lead to better photocatalytic activity than

the other non-metals [211]. Sathish *et. al.* also reported higher photocatalytic activity for a N-TiO_2 system, and found that the photocatalytic activity of N-TiO_2 to visible light was higher than pure TiO_2 and P25 [212]. The photocatalytic reduction of CO_2 with H_2O vapour using nitrogen doped TiO_2 nanotube arrays, co-catalyzed with copper and/or Pt nanoparticles, has been investigated by Varghese et al. [115]. Methane was obtained as the main product with a yield of 160 μL/gh; however, some other hydrocarbons were also produced in the presence of natural sunlight. In addition, another study on N-doped TiO_2 has recently been carried out by Michalkiewicz *et. al.* [213] and, in such case, methanol was found as the main CO_2 reduction product. In general, it has been observed that the TiO_2 photocatalytic efficiency depends mainly on the employed synthesis route, the high surface area and the composition of its crystal phase.

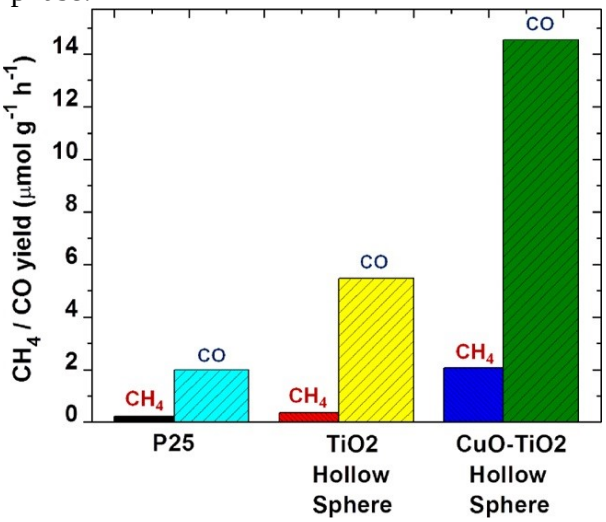


Figure 12. A comparison for CH_4 and CO production by photoreduction of CO_2 with P25, TiO_2 hollow spheres and CuO-TiO_2 hollow spheres. Adapted from [210]

4.5 Ti–oxide anchored on porous silica glass, zeolite, and mesoporous molecular sieve materials

In another type of heterogeneous photocatalyst, the isolated species, which are entrapped in an inert matrix with a large surface area, have a good adsorption property of the reactants and light, and have enhanced photoactivity towards fuel formation. In addition, in isolated Ti-highly dispersed species, photogenerated charges e^-/h^+ pairs are very close to each other, which play a very significant role in the photocatalysis process of CO_2 reduction.

In such a way, isolated and tetrahedrally coordinated Ti–oxide species, under light irradiation, transfers an electron from the oxygen O^{2-} to the Ti^{4+} ions, and this results in the transit state formation of pairs of trapped hole centers $O^-$and electron centers Ti^{3+}, which are located quite near to each other, compared to the electron and hole produced in bulk titania photocatalysts [124]:

$$[Ti^{4+} - O^{2-}] \xrightarrow{h\nu} [Ti^{3+} - O^-] \qquad (4.2)$$

Moreover, because of this unique property, Ti-isolated species play a significant role in different photocatalytic reactions. The reaction mechanism of CO_2 reduction and H_2O oxidation is elucidated in isolated Ti-species, as can be seen in Figure 11-D. Currently, these procedures are used extensively in the CO_2 reduction process, as the photocatalytic productivity and selectivity towards valuable fuel products is higher in isolated titania than in bulk titania.

The anchoring of Ti–oxide catalysts has led to the evolution of CH_4, CH_3OH and CO from the CO_2 reduction with H_2O at 323 K. The total yield was larger under UV-irradiation at 323 K than at 275 K. The efficiency of the photocatalytic reaction depends to a great extent on the H_2O/CO_2 ratio, and its activity increases when the H_2O/CO_2 ratio is increased, but an excess amount of H_2O suppresses the reaction. Hence, an optimum H_2O/CO_2 should also be considered to obtain the highest photocatalytic activity. Sasirekha *et. al.* [107] investigated the yield of CH_4, which was shown to

increase significantly as a result of a photocatalytic reduction of CO_2 with H_2O when titania was doped on a SiO_2 support material.

In the same way than powdered TiO_2, Ti–oxide anchored onto zeolites, e.g. Y-zeolite, have been used for the CO_2 reduction in presence of H_2O under UV-irradiation and have led to the evolution of CH_4 and CH_3OH at 328 K, while a certain number of lower hydrocarbons, such as C_2H_4 and C_2H_6, have also been observed [41]. As shown in the Figure 13, Ti-oxide species with a tetrahedral coordination anchored by ion-exchange on Y-zeolite (*i.e.* sample ex-Ti–oxide/Y-zeolite) exhibit high activity and selectivity for the formation of CH_3OH; while the formation of CH_4 is dominant on both bulk TiO_2 and TiO_2 prepared by impregnation onto Y-zeolite (*i.e.* sample imp-Ti–oxide/Y-zeolite). In addition, improved photocatalytic activity towards CH_4 (12 μmol g^{-1} TiO_2-h^{-1}) has been observed, following the deposition of Pt, but the CH_3OH selectivity has been significantly decreased. Thus, the results indicate that Ti-oxides tetrahedral coordinated species serve as active photocatalysts for CO_2 reduction with H_2O, and that their selectivity towards CH_4 formation can increase by doping with metals [124].

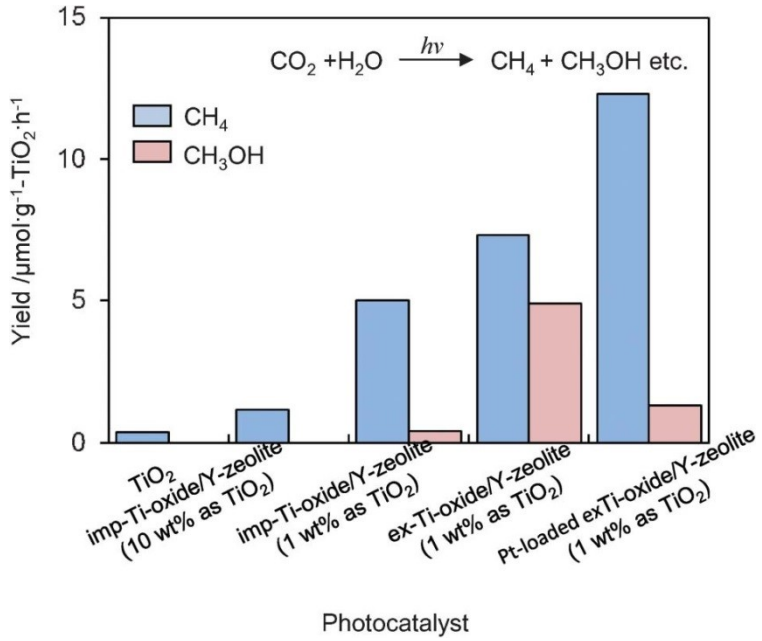


Figure 13.Photocatalytic reduction of CO_2 with H_2O on anatase TiO_2 powder, Ti-oxide anchored on Y-zeolite prepared by different preparation methods (i.e. imp: impregnation and ex: ion exchange) with various titania wt% loadings. Adapted from [124]

The CH_4 and CH_3OH yields for the photocatalytic reduction of CO_2 and H_2O on Ti-oxides supported on various porous materials are shown in Figure 14, The relationship between the selectivity for the formation of CH_3OH and the number of surface OH groups on the porous materials with respect to its effect on the reactivity of the Ti-oxide has been investigated. It has been found that the highest apparent photocatalytic reactivity for the formation of CH_3OH is achieved on a thin transparent film catalyst with a hexagonal mesopore structure (*i.e.* Ti-PS, h, 50). Even though, the selectivity for the formation of CH_3OH was the highest on the film with a cubic mesopore structure (i.e. Ti-PS, c, 50) and with the lowest number of surface OH groups [214]. With such a thin transparent film catalyst, the number of photons absorbed by the Ti-oxide catalysts was obtained by subtracting the number of outlet photons from the number of incident photons. As a result, it was possible to determine the real quantum yield for the photocatalytic reduction of CO_2 with H_2O on tetrahedrally-coordinated Ti-oxides constructed within porous silica materials to be 0.3% at room temperature (at 25 ºC), by dividing the total number of photo-formed products (such as CH_4 and CH_3OH, etc.) by the number of photons absorbed by the catalysts.

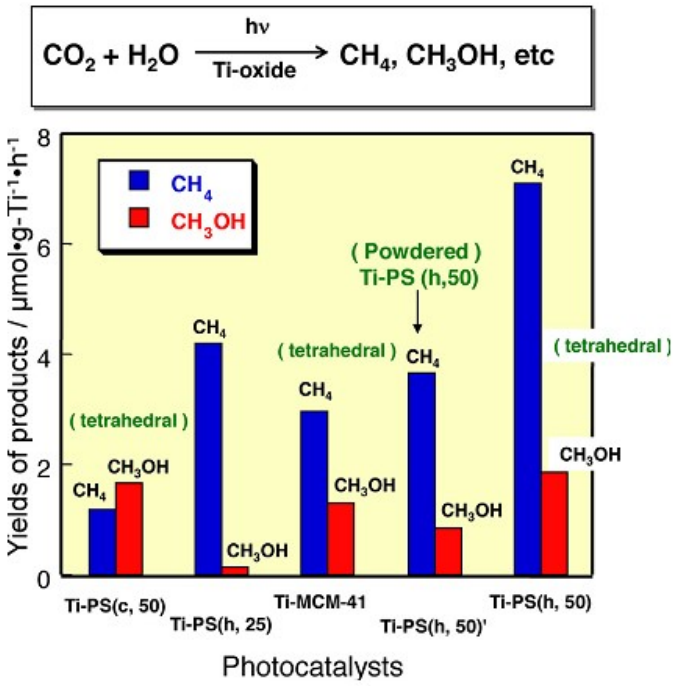


Figure 14. CH_4 and CH_3OH yields for the photocatalytic reduction of CO_2 with H_2O on Ti-PS(h 25), Ti-PS(c, 50), Ti-MCM-41, the powdered form of Ti-PS(h, 50) and Ti-PS(h, 50) potocatalysts at 295 K. Intensity of the irradiated light: 265 mW cm-2. Adapted from [203].

The Ti–oxide species within mesoporous silica have been shown to have a distinctive structure and high selectivity in the oxidation of organic substances with hydrogen peroxide [215]. However, Ti-containing zeolites, such as TS-1, Ti–Beta and mesoporous molecular sieves Ti–MCM, Ti–HMS, Ti–FSM, as shown in the Figure 15, have better photocatalytic activity for CH_4 and CH_3OH formation.

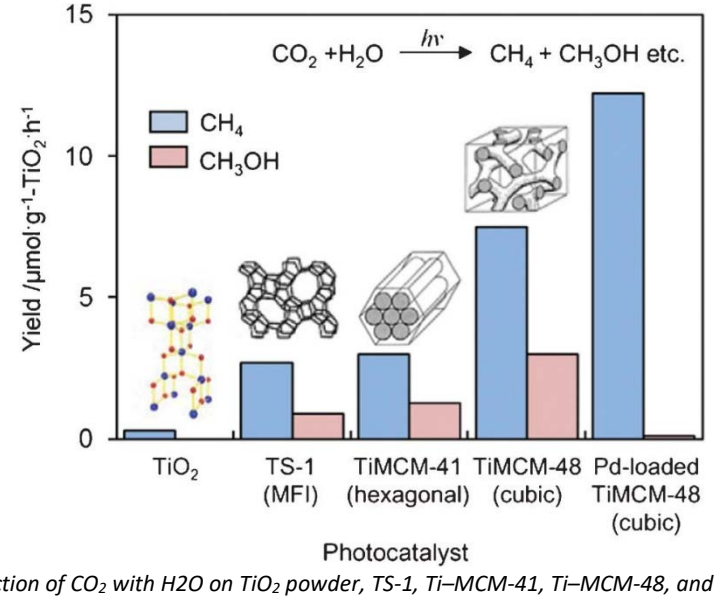


Figure 15. Photocatalytic reduction of CO_2 with H2O on TiO_2 powder, TS-1, Ti–MCM-41, Ti–MCM-48, and the Pt-loaded Ti–MCM-48 catalysts towards CH_4 and CH_3OH formation. Adapted from [124]

Ti-oxide in the mesoporous molecular sieve can be highly dispersed, which is able to improve hydrocarbons formation. For instance, CH_4 formation was shown to be higher in a metal-doped mesoporous molecular sieves (more than 13 $\mu mol.g^{-1}TiO_2.h^{-1}$), while the selectivity of CH_3OH formation was higher in Ti-MCM 48 (almost 3 $\mu mol.g^{-1}TiO_2.h^{-1}$) because of its 3-D pore structure as well as its larger pores size. Hence, a 3D pore structure facilitates not only good dispersion of the active sites [200], but also a good diffusion of the reactant and products, and hence an improved photocatalytic reduction of CO_2 towards different fuels.

4.6 Nanocomposites or supported titania photocatalysts

Ti/Si binary oxide catalysts, in the presence of a gaseous mixture of CO_2 and H_2O, form CH_4 and CH_3OH as the main products. A greater photocatalytic reduction of CO_2 has been observed for hydrocarbon formation. The high photocatalytic activity for the binary oxides is closely associated with the formation of the charge transfer excited complex due to the highly dispersed tetrahedral Ti–oxide species. Ti–oxide species maintain a tetrahedral geometry until the TiO_2 content reaches approximately 20 wt%. Accordingly, Ti/Si binary oxides with such a high Ti content can be successfully utilized as active photocatalysts for the efficient reduction of CO_2 with H_2O in solid-gas systems. However, Wu J.C.S. *et. al.* [206] noticed that methane formation increased for the loading of mixed oxides with metal components, such as Cu and Fe. They -acac, showed a higher production rate with a Cu(0.5wt%)-Fe(0.5wt%)/TiO_2–SiO_2 catalysts (~ 0.279 μmol/g-cat.h) than with the undoped mixed oxide, *i.e.* TiO_2–SiO_2 (~ 0.177 μmol/g-cat.h).

Hussain et al. [216] have recently introduced TiO_2/Mesoporous silica (KIT-6) systems that can be used to photocatalytically convert CO_2 to tunable energy products. Different TiO_2 loadings on 3-D mesoporous silica, which produced CH_4, CH_3OH (hydrocarbons) and CO, H_2 (similar to syngas), were explored. The 3-D ordered pore structure of the KIT-6 support was a convenient source for less recombination of the produced electron-hole pairs. This support was also helpful in the adsorption and transportation of reactants and products.

Recently, interesting results have been obtained also by employing titania composites with carbon nanomaterials, that is, carbon nanotubes (CNTs) and graphene. Overall, only a few studies have been conducted on carbon-based composite materials for the photocatalytic reduction of CO_2. It has been reported that the photo-oxidation of organic compounds increases when CNTs and graphene are added to TiO_2 [217]. In such a way, electrons are fast transferred from TiO_2 to the CNTs or graphene sheet, which results in an enhancement of the photocatalytic activity response [116] and can leads to the promotion of the TiO_2/C-based composite response to visible light. A narrowing of the band gap of graphene/TiO_2 photocatalysts have been observed, as shown in Figure 11-E [177]. However, presence of defects in the graphene have shown a negative enhancing effect on the recombination rate of photogenerated e^-/h^+ pairs.

Multiwalled carbon nanotube (MWCNT) supported anatase and rutile TiO_2 have also been explored recently in the context of photocatalytically converting CO_2 to produce different products, for instance C_2H_5OH and HCOOH [105]. MWCNT supports help to mitigate the TiO_2 agglomeration and less recombination of electrons and holes by their efficient charges transport along the MWCNT. L.-L. Tan *et. al.* [158] have recently also reported noble metal modified reduced graphene oxide/TiO_2 ternary nanostructures for the visible-light-driven photoreduction of carbon dioxide into methane. Shown and compared in Figure 16, the three-component nanocomposites, in particular Pt-GT, exhibit enhanced photocatalytic activities towards the photoreduction of CO_2 to CH_4 gas under the irradiation of normal light bulbs. However, the yield of the system is still not sufficient and further studies, aimed to explore more efficient systems for commercialization, are already needed.

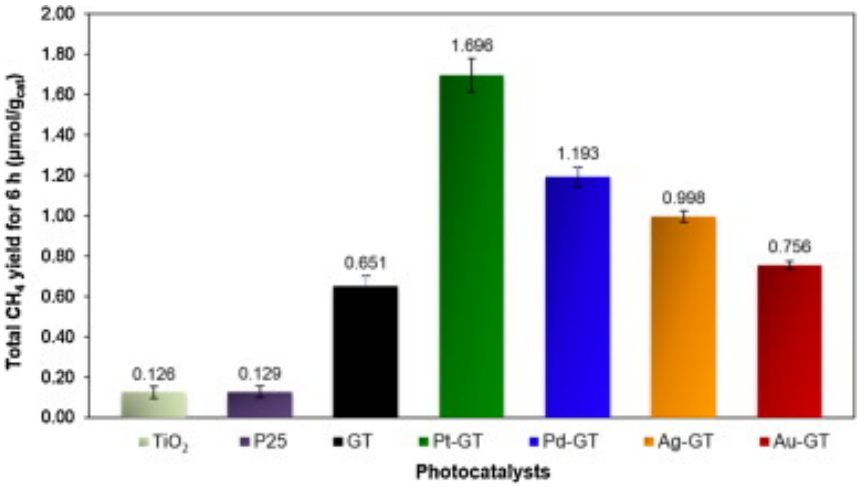


Figure 16. Noble metal modified reduced graphene oxide/TiO_2 (GT) ternary nanostructures for the visible-light-driven photoreduction of carbon dioxide into methane (yield after 6h). Adapted from [158].

Many other materials have been reported in a recent review [218] as supports for TiO_2-based photocatalysts, with which the photocatalytic conversion of CO_2 has been shown to vary according to the kind of support. Moreover, different support materials could result in different morphologies as well as in different particle sizes of TiO_2, or in different interactions between TiO_2 and the supports, which change activity and selectivity for the production of different compounds.

5 Summary: issues, progress and prospects

CO_2 plays a significant role in global warming, due to its important contribution to the greenhouse effect, and it is therefore currently considered a key challenge for the world. On the other hand, the depletion of fossil fuels throughout the world is dramatically increasing every year, because of the increasing energy demands of humans as well as the increased global population. Therefore, in this scenario, much more attention should be paid to limit CO_2 emissions as well as to convert it into valuable chemicals and energy-bearing products, and in particular to the formation of fuels for the future generations.

The possible technologies for the conversion of CO_2 to valuable products include: CO_2 hydrogenation; urea synthesis; the electrochemical conversion of CO_2; the thermochemical conversion of CO_2; the utilization of CO_2 through biotechnological routes; the utilization of CO_2 through biomass, and the photocatalytic reduction of CO_2 to renewable fuels. However, of all these alternatives, the photocatalytic reduction of CO_2 to renewable fuels is the most promising to solve the problem of the energy crisis as well as to simultaneously protect the environment to some extent.

A proper selection of the photocatalyst is the first step towards enhancing photoactivity. Many photocatalysts, including oxides and non-oxides, e.g. TiO_2, ZnO, Fe_2O_3, ZrO_2, SnO_2, $BiWO_3$, Ti-MCM-41, CdS, TNTs, ZnS, GaN, SiC, etc., have been explored extensively in this process to produce valuable fuel products. Of all the above mentioned photocatalysts, TiO_2 has proved to be the best, from all the different points of view, to fulfil the requirements of an ideal photocatalyst. Unfortunately, pure bulk titania also shows a lower efficiency towards fuel formation, due to the greater chance of recombination of e^-/h^+ pairs and to the short lifetime of the photogenerated charges (in the nanoseconds scale).

Therefore, many efforts have been made, including the synthesis of nanostructured titania, single crystal titania, titania doped with metals or non-metals, dye sensitized titania, etc, in order to be able to utilize these materials more effectively to convert CO_2 into renewable energy products. However, most of these techniques are complex as well as costly.

On the other hand, isolated Ti-oxide species are more active and beneficial than pure bulk titania, due to the localized photogenerated e^-/h^+ pairs, which play a significant role in the photocatalytic reduction of CO_2. Moreover, there are fewer e^-/h^+ pair recombination as well as a longer lifetime of

photogenerated e^-/h^+ pairs (in the microseconds scale) compared to bulk TiO_2. However, it is difficult to obtain abundant isolated sites dispersed on the porous support material and, moreover, they are more active under UV illumination.

Nanocomposites or supported TiO_2 systems have opened up new possibilities and have recently achieved promising results under UV as well as visible or solar light, but their low efficiency is still a key challenge for their commercialization. Therefore, the devolvement of efficient active photocatalysts for this technology is still an ongoing quest.

A massive amount of scientific research on the photocatalytic reduction of CO_2 to enviable chemicals has revealed that better efficiency towards the desired products could be accomplished, but this technique is still at an embryonic stage, due to the lack of proficiency; moreover, the yield discrimination is very low for commercialization purposes. Therefore, although the photocatalytic reduction of CO_2 is still at an embryonic stage, it appears promising for the future. Further improvements and modifications to this technique are needed to boost this process in the near future.

Finally, the key points that need to be considered for future improvements in the photocatalytic reduction of CO_2 to fuel are:

- The development of novel photocatalyst materials, not only in bare form (i.e. TiO_2), but also doped/coupled with metals, non-metals or composites with other supporting materials as well as the testing of novel ternary mixed oxides. The main focus should be on enhancing the properties of high band gap semiconductors by exploiting the visible part of the solar light, as well as by increasing the transport of photogenerated e^-/h^+ pairs and reducing its recombination rate.
- More detailed studies are recommended regarding the rate limiting step of CO_2 reduction photocatalysis, in order to understand the reaction kinetic of CO_2 adsorption and product desorption so as to enhance the overall efficiency of this process.
- The low photocatalytic efficiency of the CO_2 reduction process could be increased through in-depth optimization studies on all the key factors (*i.e.* on reaction mechanisms, catalysts activity, etc) or on the operational parameters that have an important influence on the activity (i.e. temperature, pressure, light concentration, etc.).
- The stability, since deactivation and regeneration phenomena in CO_2 photocatalytic reduction are still unclear, and in-depth studies are required to investigate all the involved factors as well as to understand the causes of the low efficiency of CO_2 reduction towards high valuable products.

Acknowledgements

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