

Applications of supercritical technologies to CO₂ capture and utilization

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Abstract

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1. Introduction

There is an increasing global concern about the negative effects of climate change, which are related to the increasing concentration of greenhouse gases in the atmosphere, and in particular CO₂, due to the use of fossil fuels. The recent Paris Agreement, set in 2015, has as its main objective the reduction of CO₂ emissions in order to avoid a global temperature increase higher than 2°C. To attain this objective, it is necessary to gradually replace fossil fuels by renewable energies with zero CO₂ emissions, but it can be expected that fossil fuels will remain as the main energy source for many years, particularly for production of electricity and as fuels for vehicles. Therefore, other solutions such as carbon capture and storage (CCS) technologies must be considered, because they would enable a significant reduction of the CO₂ emissions of thermal power plants or chemical industries such as the industries of production of ammonia, hydrogen and cement [1].

Different CO₂ capture technologies have been researched. Among them, the most developed technology at industrial level is the absorption using aqueous solutions of alkanolamines, a method that has been used since the 30s to remove CO₂ and other acid gases from natural gas [2]. Alkanolamines such as monoethanolamine (MEA), diethanolamine (DEA) and

methyldiethanolamine (MDEA) selectively and reversibly react with CO_2 forming carbamates, and can capture 0.5-0.7 mol CO_2 /mol amine [3,4]. However, the heat of absorption is high, implying that the amine regeneration step, which is carried out by desorption at temperatures of 100 – 150°C, has high energy consumption. Alternative absorption processes for CO_2 capture processes have been developed, such as the “Chilled Ammonia” process presented by the French company Alstrom [5]. This method uses an aqueous ammonia solution at low temperature (2-10°C), where CO_2 is absorbed as ammonia carbonate, bicarbonate and carbamate. Typically, 0.33-0.67 mol CO_2 /mol NH_3 can be absorbed. As in the case of amines, regeneration is carried out by desorption at temperatures of 100-150°C and pressures of 2-136 bar. Compared to the case of amines, the heat of desorption from the ammonia solution is much lower, which implies that the energy costs of the regeneration also are lower. The disadvantage of this method is the need of big amounts of refrigeration water. For this reason, in general this method is only considered for facilities located near the sea.

Besides these absorption methods, other CO_2 capture technologies are being developed, such as adsorption of membrane separation [6]. In general, all these processes are costly, because in addition to the cost of the CO_2 separation process, the cost of compressing and transporting CO_2 to the storage site is also high. In fact, it has been estimated that even employing favorable technologies for CO_2 separation such as oxy-fuel combustion, the incorporation of a CO_2 capture and storage unit in a thermal power plant implies a significant penalty on the global efficiency of the plant, which is estimated as 2 – 3 % of the global efficiency of the power plant [7], a penalty that is assumed estimating that the benefits of reduced CO_2 emissions outweigh it.

Therefore, it can be concluded that CO_2 capture is a complex and costly process, which justifies the general appreciation of CO_2 as a problematic residue that causes considerable economic problems and environmental harms. In contrast, looking into nature, carbon dioxide is the basic chemical resource used by plants. By transforming it into chemical fuels, they store

surplus solar energy for periods of need. By converting it into complex organic compounds, they obtain the building blocks that they need to grow and live. A similar approach can be followed in the industry, converting CO₂ in valuable compounds that can generate a profit instead of simply storing it [8]. Furthermore, it must be considered that fossil fuels not only provide most of the energy we use, but also are the main raw material used by the chemical industry. Therefore, it is necessary to find an alternative of base compounds for the chemical industry that can gradually replace the compounds obtained from fossil fuels as they run out. CO₂ utilization technologies can also contribute to this purpose, because they can produce important platform chemicals such as formic acid or methanol, and CO₂ is a widespread resource that can contribute to the creation of a novel decentralized industrial structure that produces “just enough” [9].

Following this approach, different Carbon Capture and Utilization (CCU) technologies are being researched [10]. Among other options, four key CO₂ conversion technologies are being intensively studied: (1) catalytic copolymerization of CO₂, particularly with highly reactive epoxides for the synthesis of polycarbonates [11]; (2) thermo-catalytic CO₂ conversion processes [12, 13]; (3) CO₂ fixation in photo-bioreactors [14]; and (4) photocatalytic CO₂ conversion processes, also known as “artificial photosynthesis” methods [15]. The application of supercritical fluids can contribute to the development of these technologies in several aspects such as materials design, process intensification and reaction engineering. The objective of this article is to present an overview of the recent progress and the perspectives in the application of supercritical fluids in carbon dioxide utilization technologies. Since the copolymerization of CO₂ is discussed in another article of this special issue, this application will not be considered in this article.

2. Catalysts for Artificial Photosynthesis

The origin of “artificial photosynthesis” systems is usually tracked back to the seminal work of Fujishima and Honda, who in 1972 demonstrated the photoelectrochemical splitting of

water using a single-crystal TiO₂ photoanode and a Pt cathode with an external electrical bias [16]. Following this work, a considerable work has been carried out in the development of photoelectrochemical and photocatalytic CO₂ conversion systems, and particularly in the development of suitable photocatalysts, which are an essential element of these systems.

The photocatalysts employed are materials that are able to absorb light energy, generating free electrons (e⁻) and holes (h⁺), as shown in Figure 1 [17]. Some of the most employed materials are TiO₂ and other semiconductors. The photo-induced electron-hole pairs produced in these materials can initiate the redox reactions required to convert CO₂. Therefore, a fundamental aspect determining the photocatalytic activity of the material is the efficiency of stabilization of the charge separation induced by light excitation. Charge separation can be enhanced adding metal co-catalysts to the material, such as Pt, that actuate as sinks for the free electrons produced. Such semiconductor-cocatalyst systems are some of the most promising photocatalytic materials for water splitting and CO₂ reduction available today [18]. Charge separation can also be stabilized by geometrical factors, producing catalysts with appropriate and controlled (nano) sizes and shapes [19]. Following this approach, different (and, in some cases, patented) designs describe nano-structured materials with a high aspect ratio (e.g. fibers or rods), including: TiO₂ nanofibers [20], TiO₂-coated ZnO nanorods deposited over a silicon substrate [21], or a double-layer structure, formed by Si nanowires vertically disposed over the two sides of a PEM membrane [22] (Figure 2). Moreover, the range of light wavelengths in which the photocatalytic material is active is an extremely important property. Ideally, the material should have a maximum activity in the visible light range, but commonly used semiconductor photocatalysts, such as commercial TiO₂, show their maximum activity in the UV range. The development of photocatalysts suitable for light absorption in a wide wavelength range is extremely challenging, because light absorption depends on many factors, including the chemical composition, the crystalline structure and type and density of defects, the particle size, or the interactions at the interface between the photocatalyst and the co-

catalyst. It is therefore necessary to develop a method for production of the catalyst that can control all these aspects. Considering the possibilities of supercritical fluid technologies for the development of such materials with tailored properties, several researchers have studied the production of photocatalysts in supercritical media.

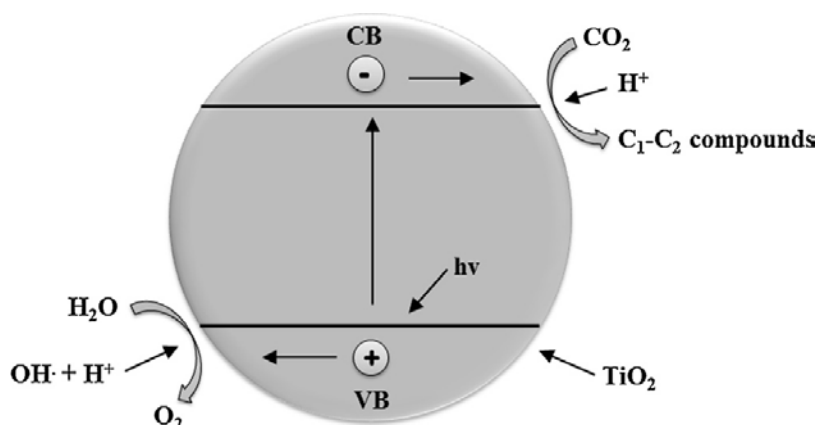


Figure 1: Schematic representation of the reaction mechanism of the photocatalytic CO_2 reduction over a semiconductor particle. Reproduced from [17] with permission.

As previously described, semiconductor-cocatalyst photocatalytic systems are frequently used as particles of appropriate size, generally in the nanometer range. Different supercritical fluid processes can be used to produce such metal nanoparticles with controlled and narrow particle size distribution [23]. A first alternative is the synthesis in supercritical CO_2 media by thermolysis of an organometallic precursor. In order to apply this method, a suitable precursor with a high solubility in supercritical CO_2 must be available. The first step of the process is the dissolution of this precursor in CO_2 . If the deposition of the produced particles over a scaffold is desired, the supercritical dissolution is put into contact with the scaffold during this step, with the objective of adding the precursor to the scaffold by adsorption or physical deposition. After this, the supercritical dissolution is heated up, causing the decomposition of the organic part of the organometallic precursor. Metal particles are thus produced, generally as metal oxides. Employing this method, Alonso et al. [24] researched the synthesis of TiO_2 nanoparticles in supercritical CO_2 and evaluated the influence of synthesis conditions on the photocatalytic activity of the material. In this work, TiO_2 anatase nanoparticles were obtained

by thermohydrolysis of DIPBAT (diisopropoxititanium bis acetylacetonate) in supercritical carbon dioxide with different alcohols (ethanol and isopropylalcohol). Moreover, the photocatalytic activity of the material was tested considering the degradation of aqueous solutions of methyl orange as model reaction. It was found that the crystallinity was a fundamental parameter on the photocatalytic activity of the material. The crystallinity could be tailored modifying the operation temperature. The operation range was 200°C – 300°C, and higher crystallinity was obtained at higher temperatures, leading to a higher photocatalytic activity. In contrast, other operating parameters such as the operating pressure did not have a significant effect on the photocatalytic activity. The activity also showed some variation when the alcohol employed in the thermohydrolysis was changed, with higher activity in the case of particles obtained with isopropanol. According to authors, this result could be related to the density of surface hydroxyl groups in the particles. Figure 2 presents a SEM image of the TiO₂ particles produced.

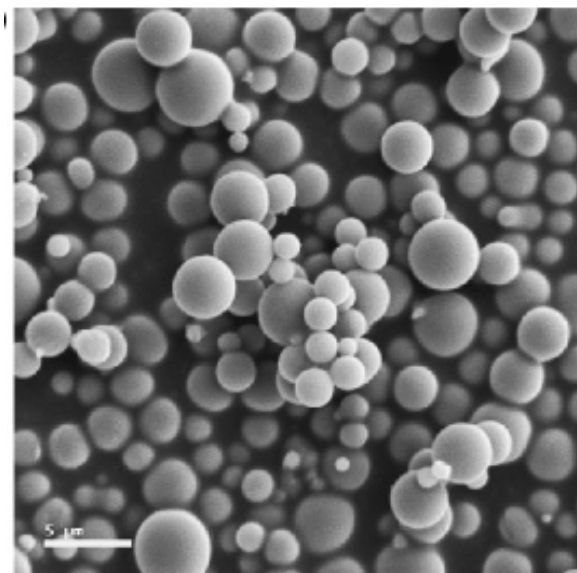


Figure 2: TiO₂ microparticles synthesized in supercritical CO₂. Adapted from [24] with permission.

Camarillo et al. [25] applied TiO₂ nanoparticles synthesized in supercritical CO₂ with a similar procedure to the photocatalytic reduction of CO₂, comparing them with commercial Degussa

P-25 TiO₂ particles (Evonik). They characterized the light absorption properties of the TiO₂ particles, finding that particles synthesized from supercritical CO₂ exhibited a higher light absorption in the visible range than the commercial particles. This is a major improvement of the properties of the catalyst, since TiO₂ catalysts are generally limited to operation in the UV range and show poor light absorption in the visible range. In connection with this result, particles synthesized in supercritical media also showed lower band gap energy than commercial catalysts, a result that also indicates a more efficient light absorption. Authors suggested that this result could be due to the existence of surface oxygen vacancies in the materials synthesized in supercritical fluids, which effectively harvest visible light and create a color center [26]. Indeed, as presented in Figure 3, it could be observed by a simple visual inspection that while commercial particles showed a bright white color, particles synthesized in supercritical fluids presented darker grey or green colors, a clear indication of light absorption in the visible range. Camarillo et al. [25] also assessed the stabilization of the charge separation attained with the different materials. X-ray diffraction (XRD) assays showed that the particles produced in supercritical fluid had smaller crystallite sizes than commercial particles, a property that is favorable for the stabilization of charge separation, because the crystalline fractures and the contact surfaces between crystallites slow down the recombination of free electrons and holes. However, while commercial particles consisted of a mixture of anatase and rutile crystalline phases, CO₂-synthesized particles consisted exclusively of anatase, as also observed by Alonso et al. [24], which in this case is an unfavorable property because the presence of different crystalline phases can also slow down charge recombination. As a result of the combination of these properties, particles synthesized in supercritical CO₂ showed a higher photocatalytic activity in the reduction of CO₂, enabling the production of CH₄ and CO with reaction rates that were 22 and 1.7 times higher, respectively, than the rates obtained with commercial TiO₂ particles.

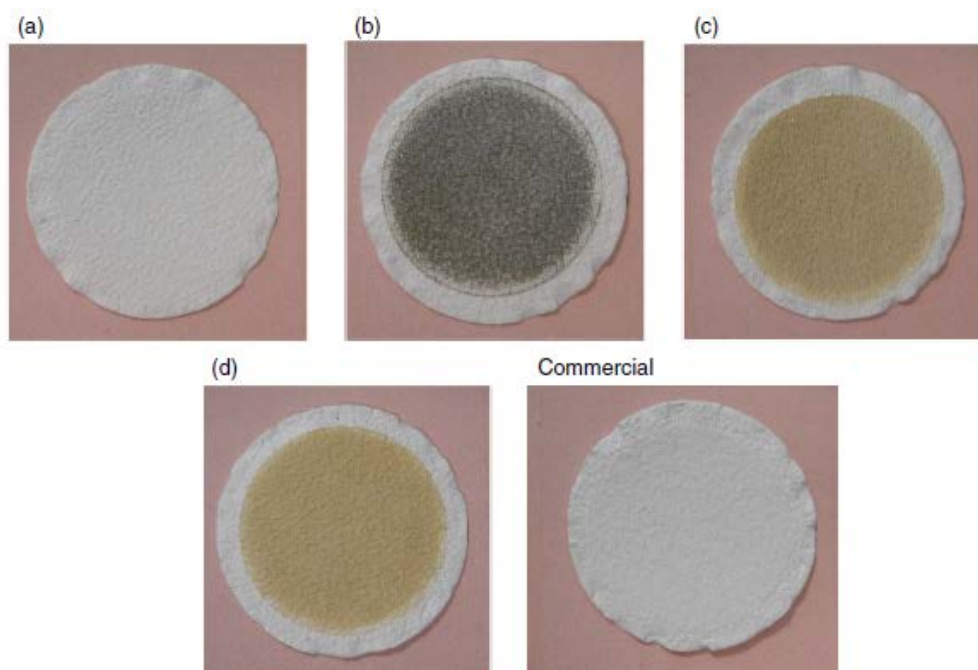


Figure 3: TiO₂ particles synthesized by Camarillo et al. [25] after photocatalytic experiments, prepared from different Ti precursors and solvents: (a) TTIP-isopropyl alcohol; (b) TTIP-ethanol; (c) DIPBAT-isopropyl alcohol; (d) DIPBAT-ethanol. Reproduced from [25] with permission

The synthesis procedure in supercritical CO₂ can also be used to obtain composite TiO₂ – metal cocatalyst particles. In further works, S. Tostón et al. [27] and Camarillo et al. [28] investigated the application of TiO₂ particles doped with Cu or Pt. TiO₂/Pt catalysts, obtained by simultaneous thermohydrolysis of TiO₂ and Pt precursors (titanium tetraisopropoxide or diisopropoxititanium bis acetylacetonate, and palladium acetyl acetonate, respectively). As in previous cases, XRD assays showed a high crystallinity of the TiO₂ particles produced, composed exclusively of anatase phase, but in this case diffraction peaks that could correspond to PdO phases could also be observed, indicating that a fraction of Pd was not well dispersed in the TiO₂ matrix. As in the previous work, a shift in the light absorption range to the visible range was observed in UV-VIS diffuse reflectance assays, which is favorable for the application of the catalysts with natural sunlight. CO₂ reduction experiments showed the production of CO, methane and ethane, and the rates of formation were 3-22 times higher

than the rates observed with commercial, undoped TiO₂ particles. Comparing with the results of their previous works, authors observed that the addition of Pd enhanced the selectivity toward methane. The best results were obtained with the catalysts with the highest Pd load (3 wt%), indicating that the presence of segregated PdO phases observed in XRD assays did not have a detrimental effect on the photocatalytic activity.

Another method for the synthesis of metal and semiconductor nanoparticles is the hydrothermal synthesis under supercritical conditions [29]. The process consists of mixing an aqueous solution of a metal precursor with a stream of water at near-critical or supercritical conditions, which causes the degradation of the organic part of the precursor and the formation of metal oxide nanoparticles. The mixing kinetics between the precursor solution and the supercritical water are a crucial parameter for the successful synthesis of the nanoparticles. With an appropriate design of this mixer, the process can be carried out continuously. Chowdhury et al. [30] tested the photocatalytic activity of TiO₂ particles synthesized with this method in the visible light range. The synthesis was carried out using water-ethanol solvent mixtures, at operating temperatures ranging from 200°C to 400°C. Particles with anatase crystalline structure were obtained, with sizes that ranged from 10 nm at 250°C to 100 nm at 400°C. The most interesting result of the work was the nano-twinned structure of the particles, which is a favorable property for the photocatalytic activity of the material because the changes of orientation of the crystal at twin crystal surfaces enhance charge separation. In this work, the photocatalytic activity of the material was tested considering the degradation of methylene blue as model reaction. A high photocatalytic activity was observed even working under visible light, which is a promising result for the application of this material in CO₂ reduction reactions.

The results of these works show that TiO₂ micro/nano particles produced with supercritical fluids show promising photocatalytic properties. However, the handling of micro/nano particles in real applications can be problematic, as in flow reactors they are prone to

problems of agglomeration and washing-up. Therefore, incorporation of these particles in a suitable support that prevents these problems can be a suitable solution. Among other options, aerogels produced by supercritical CO₂ or supercritical alcohol drying of gels offer a combination of convenient properties for photocatalytic applications: besides the high surface area and high porosity that make aerogels excellent supports for catalytic materials, as shown in Figure 4 silica aerogels show high transparency and therefore they do not interfere with the light absorption of photocatalytic materials. Navarrete et al. [31] have applied this property employing silica aerogels as supports of a photocatalytic material in a flow reactor. In this case, the photocatalyst was a combination of ZnO nanorods and Cu nanoparticles, which was incorporated in the silica aerogel during the gelation phase. The aerogel-supported catalyst showed a high photocatalytic activity in the visible light range by a plasmonic effect promoted by the small particle size, with a maximum in light absorption at 498 nm, corresponding to green light. The material was effective for the photocatalysis of the conversion of CO₂ by a reverse water gas shift reaction, attaining reaction rates at near-ambient temperature that were comparable to rates observed in previous works at temperatures of 200°C.



Figure 4: (A) Transparency makes aerogels suitable catalyst supports for photocatalytic applications. (B) Silica aerogels functionalized with ZnO-Cu photocatalysts by Navarrete et al.

[31]

Besides being a support to stabilize photocatalytic particles, aerogels of semiconductor materials can be themselves active photocatalytic materials. Indeed, TiO₂ aerogels produced

by supercritical CO₂ drying have been applied as photocatalysts. Yao et al [32] investigated the photocatalytic activity of SiO₂-TiO₂ aerogels. They found an unexpectedly high activity, estimated as 15 times higher than the activity of TiO₂ nanoparticles. This high activity could be related to the morphology of the material, which as shown in Figure 5 showed an ordered mesoporous structure with pores of 2 – 20 nm. This is a very interesting result, because this structure is spontaneously formed by self-assembly. Thus, aerogels produced by this method are nano-structured materials with comparable properties as the structured materials previously described [19-22], but they can be produced at a much lower cost than these materials.

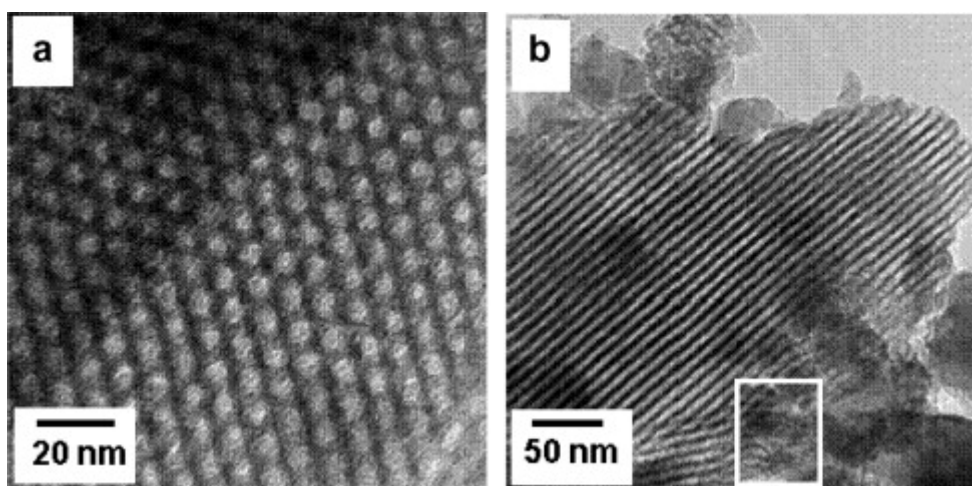


Figure 5: Ordered pore structure of SiO₂-TiO₂ aerogels. Reproduced from [32] with permission

Another method to increase the absorption of light in the visible range is to employ materials dyed with similar pigments as those used by plants to capture light. Such materials have been employed as catalysts in dye-sensitized solar cells (DSSCs), which are photovoltaic or photocatalytic systems that are already commercially available, although in general they have the disadvantage relying on ruthenium complexes as light sensitizer dyes, which are rather expensive and difficult to manufacture [33]. Aerogels can also be impregnated with these dyes, as shown by Iwai et al. [34], who impregnated a TiO₂ aerogel with a commercial ruthenium-based dye (N-719). Comparing the impregnation of the dye in commercial TiO₂ films and in aerogel films prepared by supercritical drying, these authors found that the amount of dye

adsorbed increased when the surface area of the film was higher, and therefore was significantly higher in TiO₂ aerogels than in commercial films, as a result of the high surface areas that characterize aerogels. As a result, the current-voltage performance achieved using the dyed aerogels in the solar cell was also higher than the performance of DSSCs with commercial TiO₂.

To finish this section, it is worth noting that supercritical fluid processes have also been applied to prepare catalysts for alternative, non-photocatalytic CO₂ conversion processes. An example is the catalyst for the electrochemical reduction of CO₂ presented by Jiménez et al. [35], which consists in Pt particles deposited over carbon nanotubes by a supercritical impregnation method.

3. Intensification of CO₂ reduction processes

As discussed in the previous section, the catalyst is an essential element of CO₂ conversion processes, but it is not the only element that determines their performance. Indeed, despite their potential and the promising results already achieved, CO₂ conversion processes also face important criticisms, that usually highlight not only the cost and the complexity of the catalysts required, but also the low productivities that are typically achieved. To some extent, these appreciations are due to the reactor configurations used by many researchers, that following the original work of Fujishima and Honda [16] often consist of batch, multiphasic (gas-liquid) photo(electro)chemical cells with physically separated electrodes. Undoubtedly, these devices are very important and useful for research, but they have the disadvantage of having a small contact area with the catalyst and operating with dilute solutions, which lead to the formation of correspondingly dilute products. For these reasons, these devices cannot be transferred to an industrial environment. Therefore, alternative scalable –and, preferably, single-phase, continuous-flow- reactors must be designed.

Several continuous flow reactor designs for the photocatalytic conversion of CO₂ have been proposed [17]. Some alternatives include the slurry reactor design with top illumination, the

optical fiber reactor design with side illumination and the internally illuminated reactor with top illumination, as shown in Figure 6. Additionally, the intensification of the energy delivery to the catalyst must also be considered [36]. For this purpose, catalyst activation by microwaves and plasma can be considered as alternatives to the light activation of the catalyst.

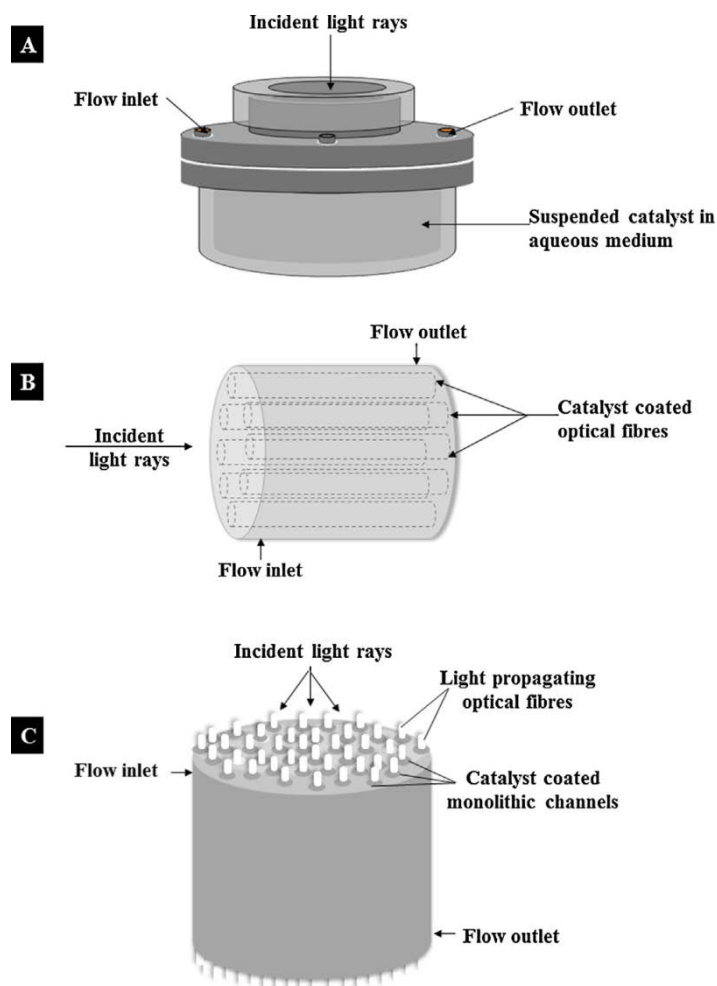


Figure 6: Schematic diagram of (A) slurry reactor design with top illumination, (B) optical fiber reactor design with side illumination and (C) internally illuminated reactor with top illumination. Reproduced from [17] with permission.

Another option for intensification of the reaction is the operation at high pressures. Operation at moderate pressures enables an increase in the concentration of reagents, and operation at near-critical and supercritical phases can allow operating in a single phase region, thus eliminating the mass transfer resistance associated to phase interfaces. Several authors have researched the influence of pressure in photocatalytic CO₂ conversion reactions [17]. In

biphasic gas-water systems, an improved selectivity toward methane and an increased reaction rate has been reported when the reaction is carried out at a higher pressure, due to the higher solubility of CO₂ in the liquid phase [37]. Kaneco et al. [38] also investigated the effect of pressure using TiO₂ suspended in isopropyl alcohol. They observed that the production of methane increased when pressure was increased from 0.2 to 2.8 MPa, while pressure inhibited the formation of formic acid. In a subsequent work, Kaneco et al. [39] investigated the photocatalytic reduction of CO₂ in supercritical conditions (35°C, 9 MPa) employing TiO₂ powders. The authors applied a two-step process, in which the catalyst was first put into contact with CO₂ and irradiated with light, causing the formation of ·CO₂⁻ radicals adsorbed on the catalyst surface, and water was then added to the system as proton donor, completing the process of formation of formic acid. Authors highlighted that this method avoided the limitation of the extremely low concentrations of CO₂ in aqueous solution at ambient pressure, which are a major cause of the low productivities of conversion reactors operating at these conditions, and thus showed favorable prospects for scale-up. Mizuno et al. [40] researched the effect of pressure on the photocatalytic reduction of CO₂, in this case employing aqueous suspensions of TiO₂, i.e., with simultaneous addition of CO₂ and water to the reactor. These authors observed that as pressure was increased, the amounts of methane, ethane and ethylene in the gas phase drastically increased. They suggested that increasing the pressure increases the CO₂ availability on the CO₂ surfaces, as the adsorbed species shift from hydrogen species at low pressures to carbon species at higher formation, thus promoting the formation of the lower hydrocarbons as gaseous products.

Although in these works the application of high pressure has been investigated in batch reactors, it can also bring benefits to continuous flow reactors. The reduction of CO₂ in continuous flow microreactors has already been studied [41], but in these studies ambient pressure is generally applied. As discussed, operation at higher pressures can improve the performance of these reactors due to the increase of reagents concentration and the

possibility to operate in single phase in a wider range of CO₂-H₂O mixture compositions. As a proof of this concept, Navarrete et al. [31] have performed the photocatalytic CO₂ conversion by reverse water gas shift reaction at moderate pressures, operating in single gas phase conditions in a continuous flow microreactor.

However, even at moderate or high pressures, the solubility of water in gaseous or supercritical CO₂ is low. This solubility limit can be further reduced if temperature is also increased. Following this idea, Kometani et al. [42] have studied the photocatalytic reduction of CO₂ at high pressure and temperature, up to 400°C and 30 MPa. Pt-loaded TiO₂ was used as catalyst. Authors observed that upon reaching supercritical conditions, with a single CO₂-H₂O phase, a drastic increase in the reaction yield is produced, with formation of CO, methane, hydroxymethane and formic acid. In contrast, the yield of H₂ production by water splitting showed a monotonous increase when temperature is increased, as of course this reaction does not require contact between CO₂ and H₂O and it is not limited by interphase mass transfer. This result indicates that the control of fluid phase conditions is an essential element for enhancing the performance of CO₂ photocatalytic conversions.

4. Hydrothermal CO₂ reduction

An alternative method to overcome the high chemical stability of CO₂ and convert it into valuable chemicals is the operation at hydrothermal conditions. In fact, it is considered that hydrothermal reactions played an important role in the formation of organic compounds in Earth, including the formation of fossil fuels as well as the abiogenic formation of hydrocarbons from inorganic compounds such as CO₂. Traditionally, it has been thought that these processes take place over extremely long times, at geological scales. However, more recently it has been possible to replicate these reactions at laboratory conditions at considerably shorter reaction times, in the order of 50 – 100 h [43]. Therefore, if these natural hydrothermal conversion processes can be replicated at industrial scale and at sufficiently short times, they would be suitable to efficiently convert CO₂ and biomass residues in valuable

chemical compounds and fuels [44]. The conversion of several biomass or organic residues in hydrothermal media has already been demonstrated, by hydrolysis with or without catalysts [45, 46] or by gasification [47]. These processes have even achieved an incipient commercialization. Renmatix [48] has commercialized the production of sugars in hydrothermal conditions, while Hydromethan AG [49] applies the catalytic gasification of organic residues in supercritical water to the production of methane.

Following these results, the reduction of CO₂ in hydrothermal media has raised a considerable interest because it can overcome one of the main difficulties of other CO₂ conversion methods: the production of H₂ by a cheap and a simple method. Indeed, it has been proven that in hydrothermal reactors, hydrogen can be produced in-situ by oxidation of zero-valent metals. Therefore, in this method water acts simultaneously as environmentally friendly solvent and as hydrogen source. Moreover, the in-situ production of hydrogen also enhances the rate of the reduction reaction of CO₂, probably due to the participation of radical intermediates or of adsorbed species in the reaction [50]. Figure 7 presents a schematic representation of the reactions involved in the hydrothermal conversion of CO₂ with metal reductants.

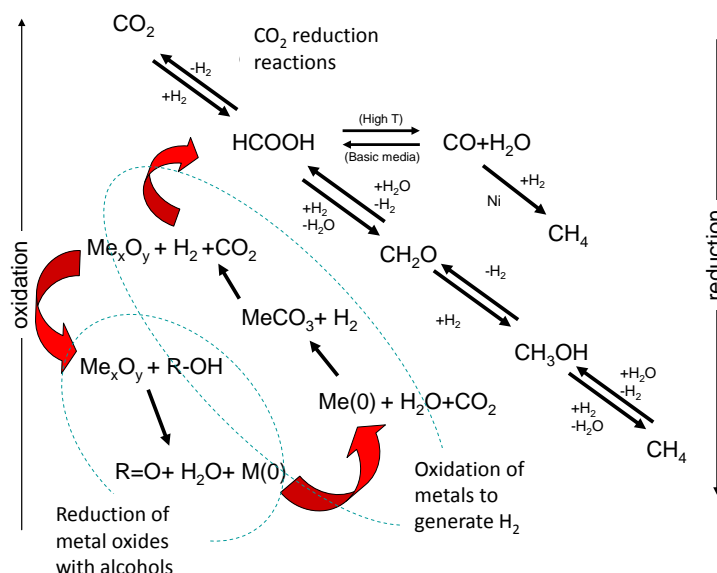


Figure 7: Schematic diagram of the mechanism of conversion of CO₂ by hydrothermal reduction with metal reductants

The reduction of CO₂ in hydrothermal media has been proved employing different metals as reductants and/or catalysts, forming formic acid. The most frequently studied combination is Fe as reductant, with Ni [50] or Cu [51] as catalyst. With these materials, yields of conversion to formic acid higher than 75% have been achieved operating at temperatures of 200°C – 350 °C with residence times of 1 – 2 h. Other authors have proved that the reduction can be carried out employing only Fe, without catalysts, but in this case reaction times increased up to 75 h [51, 52, 53].

Besides Fe, other metals have been used as reductants, including Mg, Mn, Zn and Al. The most promising results have been obtained using Zn or Al, obtaining yields up to 60% without using another metal as catalyst [50]. In the case of Zn, conversion to formic acid with a yield of 60% has been achieved operating at 325°C with a residence time of only 10 min, while at longer operating times methane traces are formed [54]. In this process, Zn acts as reductant, and the ZnO thus formed acts as catalyst. In further studies of the same authors it has been reported that employing Cu as catalyst and Zn as reductant, the formic acid initially obtained by hydrothermal conversion of CO₂ is further converted to methanol [55].

Usually, formic acid is the main product obtained with this process [50, 51], although some authors have obtained phenol [53], methane [52] or methanol [55] by a similar process. Although the precise mechanism of the reaction is unknown, the results so far obtained suggest that formic acid is the first product of CO₂ reduction, which is then converted to formaldehyde, methanol and finally methane [43]. In fact, these products are observed when reaction times are increased [52, 53, 55]. Experimental results indicate that the selectivity toward formic acid is favored by operation in basic pH conditions, which stabilize formate as a anion in aqueous solution. For this reason, experiments are usually carried out using bicarbonate as CO₂ source, or adding NaOH to the medium if CO₂ is supplied as a gas in order to dissolve it as bicarbonate [56]. Moreover, changes in the catalyst employed or its concentration can lead to the production of different compounds. For example, when Ni is

used as catalyst, methanol production is favored at high Ni concentrations, while the use of Fe favors the formation of formic acid, and the use of Fe_3O_4 increases the formation of methanol [56].

As it can be observed, a drawback of this method is that the metal used as reductant is consumed during the process, forming a metal oxide. In order to recover the metal, the photocatalytic reduction of the metal has been proposed [54]. Another alternative is adding another reductant to the hydrothermal medium suitable for reducing the metal oxide, thus enabling the operation in a closed cycle with respect to the metal. In particular, biomass residues, glycerin [50] or residues of Sulphur-containing polymers have been used to reduce the metal and reutilize it in the process [56]. Additionally, some authors have proved that CO_2 reduction can be carried out in hydrothermal media by oxidation of an alcohol, without addition of any metals [57].

5. Conclusions and perspectives

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