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Atmospheric CO_2 mitigation technologies: carbon capture utilization and storage

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Recently, the utilization of carbon dioxide has gained in consideration as it may contribute to improve the economics of CO_2 capture process by producing added value goods and is now considered a valid alternative to geological CO_2 storage. Nowadays, the scientific community considers the integrated carbon capture, utilization and storage an important mitigation technology that involves the carbon dioxide sequestration from fuel combustion or industrial processes, its transport (*via* ship or pipeline) and conversion into valuable products or its per- manent storage deep underground in geological formations. Noteworthy, CCS is functional to a linear economy, whereas utilization of carbon dioxide is at the hearth of a circular economy and its strategic role will grow in the future. In this mini review, the current state of the art in the field of capture, disposal, and reuse of CO_2 as technologies for its overall reduction in the atmosphere will be discussed.

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Introduction

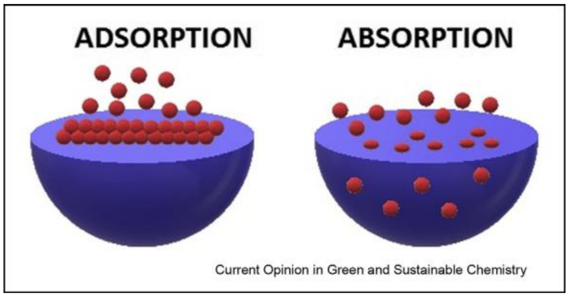
Recent alert on rapid climate change are emphasizing risks for ecosystems and heavy impacts on human life. The accumulation of anthropogenic greenhouse gases in the atmosphere, including methane, nitrogen oxide and carbon dioxide (the latter represent about 77% of greenhouse gases), has received widespread attention. So far, the carbon dioxide utilization market potential was around 200 $MtCO_2/y$ (300 in the best case) [1], compared with about 14,000 $MtCO_2/y$ emitted from large point sources [2]. The market for CO_2 use remains relatively small in an economy based on fossil carbon. Conversely, the conversion of carbon dioxide into chemicals, materials and fuels may increase to much higher levels (>>Gt/y) [3] if perennial energies are used as primary energy sources for powering processes. The CO_2 emission from power plants or combustion processes in general has caused in the last 50 years an increase of the atmospheric concentration from 325 ppm [4] to 408 ppm [5] and is supposed to contribute to more than 60% of global warming, thus pushing the scientific community to find solutions that may reduce the emission to avoid the increase of the global temperature of more than 2 °C. Despite the direct corre- lation, ‘CO_2 concentration in the atmosphere/increase of temperature’ is still questioned [6], to reduce CO_2 emission is positive as it means to preserve fossil carbon resources and reduce the high temperature heat transfer into the atmosphere due to the inefficient (*ca* 30%) conversion of chemical energy into other forms of energy.

CO_2 capture

Because of the large size, CO_2 capture requires highly efficient, selective and cost-effective technologies that are easily usable and have low environmental impact. Although, capture is practiced since a few decades at Mt/y scale, there is room for improvement. As a matter of fact, most procedures on stream are based on absorption into amine solutions that can operate under a range of gas compositions, achieving high levels of CO_2 removal [7e9] with some disadvantages related to high costs [10], corrosion of plants [11] and slight degradation of amines. Most recent approaches are based on physical absorption or chemical adsorption [12] (Figure 1) using different substrates such as activated carbon functionalized with amines, metal oxides, alkali metals and ionic liquids [13e16] characterized by fast adsorption and desorption kinetics, low energy consumption (effective reduction of 2 MJ/kg CO_2), simple usage operations [17] and low energy demand for their regeneration.

In addition, polymeric membranes, prepared using green technologies [18], and ceramics are widely used because of their low capital cost, low energy penalty and operational simplicity relative to other competitive technologies [19], leveraging the interactions between surfaces and interfaces. In such a system, natural gas, before combustion or after combustion, flows through the membrane with different mechanisms such as solution/diffusion, adsorption/diffusion, molecular sieve and ionic transport.

Figure 1



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Adsorption and absorption of molecules on an active substrate.

For example, in the case of gas separation membranes, preferential permeation is achieved through pores, whereas for gas adsorption membranes, microporous solid membranes are used as contacting device between the gas and liquid flow. When the membrane material has higher affinity to one particular component of the flue gas, this affinitive component is preferentially adsorbed on the membrane surface and then the adsorbed gas molecules move along the pore surface to the permeate side until desorbing to the permeate gas [20,21].

Conversely, agents such as metal-organic frame- works [22] find reduced application because of their preferential affinity to water. Even cryogenic [23] (condensation and desublimation in a cryogenic chamber, where gaseous CO_2 is liquefied under triple point conditions, whereas N_2 remains in the gas phase) or enzyme [24] technologies are not yet economically attractive and will not be discussed in this mini review.

Materials and technologies in CO_2 capture

In the field of activated carbon and porous organic polymers, particular interest is arousing the study of microporous systems in which the amount of absorbed CO_2 is strictly dependent on the surface area and pore size, permitting the modulation of the efficiency at different pressure and temperature. The microporous/ mesoporous carbons provide at room temperature CO_2 uptakes of 32-33 mmol g^{-1} CO_2 at 30 bar and 44-49 mmol g^{-1} CO_2 at 50 bar. At low pressure, the uptake decreases at pressure very close to CO_2 partial pressure in flue gas (4.2-4.5 mmol CO_2 g^{-1} at 1 bar and 1.1- 1.4 mmol CO_2 g^{-1} at 0.15 bar) [25,26]. The use of sorbent samples having differing textural properties and morphologies allowed us to elucidate structure/sorption relationships: high microporosity, rather than large overall surface area, is of primary importance for good CO_2 capture performance. For example, two porous carbon materials with near identical high surface area (w2700 m^2/g) and very high pore volume (w10 cm^3/g), but with different microporosity and pore size distributions, led to dramatically different CO_2 capture performance. Overall, large pore volumes obtained from distinct mesopores were found to significantly impact adsorption performance [27]. Nitrogen incorporation on porous carbons (NPCs) can ensure efficient CO_2 capture while simultaneously raising CO_2/N_2 selectivity because of the improved surface polarity of the porous carbons that induces an enhanced CO_2 adsorption by acid-base force and dipole-quadrupole interaction. On the other hand, NPCs are commonly prepared from high-cost N-containing polymers, sometimes using expensive catalysts or under drastic conditions [28,29]. One way to keep costs relatively low is the use of monomers such as pyrazole, benzimidazole [30] or triazine-based covalent organic polymers [31] that are prepared with a very simple procedure [32] from low-cost reactants with plentiful N, under mild conditions and without catalysts. They can be used as precursors for fabrication of NPCs under KOH-assisted carbonization. It is important to observe that CO_2 uptake is proportional to Brunauer- Emmett-Teller (BET) surface area and total volume. For the same precursor polymer, increasing the carbonization temperature from 500 to 700 °C, the CO_2 uptake first increases and then decreases: the material obtained at a carbonization temperature of 600 °C has the highest CO_2 uptake (4.7 mmol/g at 0 °C and 1 bar). At 0 °C and 0.15 bar, the sample with BET surface area of 798 m^2/g and N content of 9.05 wt% has the largest CO_2 uptake (1.68 mmol/g), whereas that with a surface area of 1873 m^2/g and a N content of 5.56 wt% shows the lowest CO_2 uptake (1.02 mmol/g). This result suggests that the N content is a predominant factor governing CO_2 adsorption at a low pressure (0.15 bar).

Considering that the flue gas temperature is usually in the range of 150e400 °C, the use of moderate temperature sorbents becomes necessary on these conditions. Sorbents containing alkali or alkaline-earth metals such as Na_2CO_3, K_2CO_3 and Cs_2CO_3-doped MgO have attracted increasing attention because they can be operated at moderate temperatures (100e400 °C) and are applicable to both post-combustion and pre-combustion capture. MgO coupled with other oxides like Al_2O_3 or TiO_2 results a good sorbent at temperature lower than 200 °C [33e35].

Porous polymers were synthesized by emulsion polymerization of divinylbenzene and 2-ethylhexyl methacrilate used as a novel support for the wet impregnation of polyethylenimine (PEI), thus resulting in the poly-high-internal-phase emulsion (HIPE)/PEI adsorbent. It has been observed that tuning the PEI loading from 0 to 60 wt% results in increasing the CO_2 sorption capacity from 1.5 to 4 mmol/g, but further increase reduces the CO_2 sorption capacity because of the reduced accessibility of amine groups from PEI agglomeration [36]. Sorption capacity is also affected by the temperature. It increases with temperature in the range of 25-70 °C, suggesting that beyond adsorption thermodynamics; higher temperature may overcome the kinetic barrier as well as facilitate mass transfer of CO_2 into the bulk polymer and causes the expansion of PEI aggregates on the surface and within pores of adsorbent, thus providing more accessible active sites for adsorption. Nevertheless, at 80 °C, the equilibrium sorption capacity, as expected, decreases. Another aspect considered is the moisture content, in fact the CO_2/amine reactions are different in wet and dry conditions. Dry conditions promote the formation of ammonium carbamates requiring two amine groups per CO_2 moiety, whereas wet conditions favour the formation of ammonium bicarbonates implying one amine, water and CO_2: so addition up to 3% v/v moisture increased CO_2 sorption capacity from 2.8 mmol/g to 4 mmol/g but a higher load acts negatively probably because of the competition of water molecules with CO_2 for available adsorption sites. From the point of view of kinetics and thermo- dynamics of the adsorption, the activation energies for CO_2 adsorption and desorption of poly-HIPE/PEI are 13.74 kJ/mol and 36.12 kJ/mol, respectively. These data indicate that CO_2 desorption using poly-HIPE/PEI has the potential to reduce CO_2 capture cost because of the low activation energy and high CO_2 desorption rate. As such, poly-HIPE/PEI constitutes an advantageous alternative to traditional methods in CO_2 capture from gas mixtures.

Mesoporous silica materials (Figure 2) [37,38] of various shapes appear to show interesting properties.

For example, SBA-15 [39] and MCM-41 [40] exhibit a very good combination of high surface area, adjustable pores with narrow pore size distribution, and high pore volume. Such supports behave well towards functionalization with amines both for physical loading of monomeric and polymeric amines (i.e., amine impregnation) *via* weak interactions between the amine and the support and through covalent tethering of amino- silanes (i.e., amine grafting) to the support showing significant CO_2 uptake at low CO_2 levels, fast CO_2 absorption kinetics and good thermal stability. Large pore size and/or high interwall pore volume of the support improve the adsorptive properties *via* enhanced amine accessibility. This fact has permitted different triamine functionalization through dry and wet grafting observing that large-pore supports exhibit the highest surface density of amine groups (up to 35 mmol/m^2), highest CO_2 uptakes (up to 1.88 mmol CO_2/g) and CO_2/N ratio (up to 0.33 mol CO_2/mol N), and fastest adsorption kinetics. In the case of intrawall, pore volume decreased by 53% for samples with identical pore sizes, with lower CO_2 uptakes (up to 63%) and CO_2/N ratios (up to 62%), whereas slower adsorption kinetics were observed, particularly for the lowest adsorption temperature (25 °C). Large pore supports also allowed higher surface amine density to be achieved because of reduced steric hindrance between grafted triamine species [41].

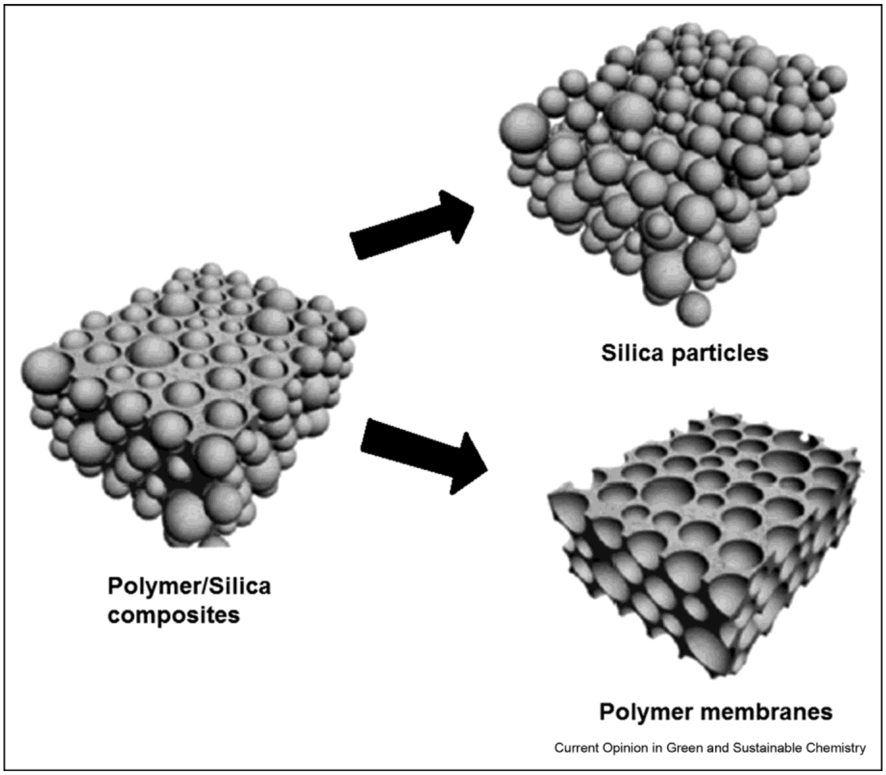

Figure 2. Mesoporous silica polymer [38].

Membrane technology [42] attracts special attention for CO_2 capture thanks to the easy use combined with good performance: the only disadvantage is related to loss of performance over time because of limited long-term stability and fouling [43,44]. Membranes are made of very thin selective layers, typically in the range of 0.1e 2 mm, of different materials, both organic and inorganic [45]: polymers have been more successful because of their high selectivity. Owing to the low permeation capacity of CO_2, the most important parameter to consider in these systems is permeability. Generally, the permeance is inversely proportional to the thickness of the membrane, so thin membranes with sub-microscale selective layers are required. The thin film composite membrane consists of an ultrathin polymer highly selective layer and a porous support for excellent permeation. The thickness of the support is strongly influenced by the viscosity of the polymer solution used: the greater fluidity of the latter on the one hand allows us to use thin layers but on the other hand can partially cover the pores of the support reducing selectivity. The addition of a highly permeable polymer between the support and the selective layer can improve membrane performance [46]. In some cases, nanoporous support as amino functional polyhedral oligomeric silsesquioxanes impregnated with low-molecular-weight polymers (polyethylene glycol dimethylether) are synthesized with excellent results both in terms of permeability and CO_2 uptake [47]. Ultrathin, ethylenediamine- functionalized graphene oxide hollow fibre membranes were deposited on the inner surface of polyethersulfone: an excellent CO_2 separation performance with CO_2 permeance of 660 GPU and CO_2/N_2 selectivity of > 500 at 75 °C was obtained [48].

CO_2 transport and disposal

The processes immediately after the CO_2 capture, involve CO_2 disposal or utilization. In general, CO_2 needs to be transported from the production site (power industrial plants) to the storage or utilization site. However, one can suppose that CO_2 separated from chemical plants can be converted on site into other chemicals as the site has the facilities. If not converted on site, CO_2 can be transported using pipelines or shipped and stored underground, in depleted oil and gas fields [49], deep saline aquifer formations [50], and deep unminable coal seams [51] that are widely distributed throughout the globe in all sedimentary basins and are typically located several kilometers below the earth's surface. Mineral carbonation [52] represents a storage approach in which CO_2 gas is converted into stable carbonates in presence of divalent metal oxide or silicates such as Mg or Ca minerals (peridotite) which have a carbonation capacity of more than 100 trillion tons of CO_2 [53].

So far, only a few (5e7) millions of tonnes per year of CO_2 have been stored underground (mostly *via* enhanced oil recovery) and the process is still under deep investigation as it has been made clear that it is not without risks to humans and the environment. For example, gradual leakage of CO_2 or large-scale leakage caused by catastrophic failure of the system could remove the benefits of capturing CO_2 and the pressure underground may also lead to small seismic events. In addition, many studies are highlighting the multiple interactions that may occur with the organic/inorganic substances present on the site, such as different carboxylic acid that strongly affect the water wetness of the rock [54] influencing the storage capacity and containment security. Studies are being carried out on the efficiency of storage regimes by depleted shale tanks because of their extremely narrow pore space that can act either as a storage tank and a garrison, with an additional advantage of a large number of wells that can be easily converted into CO_2 injectors [55].

CO_2 utilization

Although underground storage is the fastest and large- scale solution in a linear economy, a link to a circular carbon economy [6], is represented by CO_2 use and conversion into materials, chemicals and energy products (Figure 3).

However, it must be considered that despite the large applications currently in place (over 200 Mt/y), they are vastly insufficient compared with global CO_2 production (37 000 Mt/y). Large volume conversion can be achieved only in cases where CO_2 utilization processes are coupled with renewable energy sources. Nature has always removed CO_2 from the atmosphere through photosynthesis, where crops and other plants naturally consume CO_2 and sunlight and release oxygen [56], but the recent rapid industrial and social development made the natural system insufficient to use anthropogenic CO_2 [57]. Among natural systems, microalgae have the best capability of CO_2 capture and conversion into biomass and are considered for fast-enhanced CO_2 fixation.

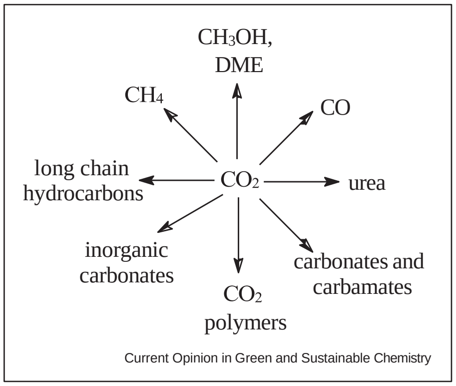

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Figure 3. Main CO2 conversion into materials, chemicals and energy products

Different species of microalgae could convert CO_2 or its derived forms such as bicarbonate/carbonate [58], and their potential can be exploited using several technologies such as thinner semipermeable liquid-liquid membrane [59], photobioreactor [60,61] also adding small amounts of sugars that increase the photoautotrophic growth [62]. It is important, however, to consider that if flue gas is used directly, the content of gases such as SOx and NOx, potentially harmful to algae metabolism, must be kept below the threshold level that varies according to the organism. From the point of view of chemical conversion, there are thermodynamic and kinetic barriers to CO_2 conversion due to its (high stability ($\Delta G^\circ w$—394 kJ/mol). The use of a energy rich reaction partner [3] (amines, olefins, alkynes, dienes, *etc*) and appropriate catalysts are needed to promote the conversion of CO_2 as co-reagent into different chemicals as linear and cyclic carbamates, isocyanate and ureas (C-N bond), linear and cyclic carbonates (C-O bond) and acids and esters (C-C bond).

Use of CO_2 in the formation of C–N bond

The largest amount of CO2 used today is in the forma tion of CeN bonds in the industrial synthesis of urea. Noteworthy, carbamates, isocyanates and ureas (symmetrical and asymmetrical) are high-added-value products used as pharmaceuticals, agrochemicals, fuel additives and polymers. Today, they are still prepared using highly toxic phosgene [63], but phosgene-less routes are based on CO2 and amines (ureas) [64] and CO2, amines and alcohols (carbamates, Eq. (1)), over coming thermodynamic limits by shifting the reaction by-products removal [65,66]. It is possible to build integrated processes that produce two or more chemicals using the same reaction. In fact, primary amines can be treated with CO2 gas to form the resulting carbamic acids that in situ can be dehydrated under Mitsunobu conditions to yield the intermediate isocyanates, which can be condensed with the same amines to form the desired ureas [67]. The direct reaction of amines with CO2 to afford urea derivatives [68] generally requires high pressure (14e140 atm) and high temperature (130-170 C) but a series of N,N0-diaryl, dialkyl and alkyl-aryl ureas were synthesized with high yield starting from silylamines and CO2 in toluene [69].

$$\mathrm{RNH2 + CO2 + R'OH \rightarrow RNHC(O)OR' + H2O}$$

Use of CO2 in the formation of C–O bond (1)

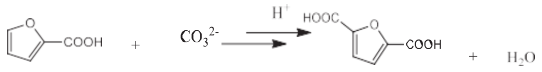
Organic carbonates both linear and cyclic, are generally non-toxic compounds that are widely used for the syn thesis of important industrial chemicals including monomers, polymers, surfactants, plasticizers and also used as fuel additives. At the same manner of carbamates, the use of CO2 in their reaction with alcohols with specific catalysts (Eqs. (2) and (3)), avoids the use of phosgene or carbon monoxide. Chemicals such as aromatic phosgene-free polycarbonates or aliphatic polycarbonates like polypropylene carbonate, poly ethylene carbonate, polylimonene carbonate and poly urethanes are produced starting from CO2 [70,71]. Heterogeneous catalysts based on metal oxides or mixed oxides are highly wished because of the easy recover ability and cheapness. CeO2-based systems are very active catalysts for the synthesis of dimethyl carbonate from CO2 and CH3OH [72,73], as well as for the reaction of CO2 with polyols affording polycarbonates [74,75]. Polyhedral MgO can work as solid base catalyst for the synthesis of propylene carbonate from CO2 and propene oxide [76]. Water elimination is a key factor for shifting the equilibrium to the right and for catalyst preservation [77]. Attention on product separation at the end of the ethanoleCO2 reaction on Ni/Cu-based catalysts has been more recently put using membrane reactors based on zeolites: water or other compounds formed in the reaction may condense or adsorb in the pores of the zeolite, preventing other species permeating through the membrane [78]. One way to improve the responsiveness of biphasic gas-liquid systems and those that re-relive CO2 is to use continuous flow processes thanks to a higher catalytic surface-to-volume ratio of reagents and rapid mixing [79]

$$\mathrm{2\ ROH + CO_2 \longrightarrow ROC(O)OR + H_2O} \quad (2)$$

$$\mathrm{HOCH_2CH_2OH + CO_2 \longrightarrow \overline{OCH_2CH_2O}C(O)} \quad (3)$$

Use of CO2 in the formation of C–C bond

In cases seen so far, CO2 reacts with nucleophile O or N. For the formation of C-C bonds for carboxylic acid preparation (Eq. (4)), carbanions are required. Many organometallic reagents and related substrates have a strongly nucleophilic carbanionic-type functionality, which usually reacts more or less easily with CO2 to give the corresponding carboxylic acid salt [80]. CO2 is used as direct and indirect carboxylating reagent, in fact high amount are used to produce inorganic carbonates that can be used in the synthesis of dicarboxylic acids [81]. The most important application of dicarboxylic acids is in the polymer industry, where they are used both as monomers and additives. Interestingly, photo-carboxylation of organic substrates has been achieved using semiconductors either bare or supported on graphene oxide [82,83].



Photocatalytic CO_2 reduction

Photocatalytic CO_2 reduction can directly convert CO_2 and water into hydrocarbon solar fuel [6], syngas [84] and polymers [85] is attracting much attention. CO_2 can be reduced into different high energetic species as HCOOH, HCHO, CH_3OH, and CH_4. During the multistep photocatalytic CO_2 reduction reactions, the light-excitation attributes, band structure, and separation efficiency of photogenerated charge carriers are three important factors for influencing the photo- generated electrons in catalytic CO_2 reduction reactions, which can regulate the product selectivity. Abundant and cheap metal systems are tested to produce a multielectron catalyst also if the real limit is that the excited state deactivates quickly because of low-lying d-d excited state. Cu(I) complexes are attracting attention [86]. AgeMgOeTiO_2 composite materials exhibits extended visible light absorption owing to the surface plasmon resonance effect of the Ag NPs. Deposition of MgO NPs, as basic sites, could facilitate the adsorption of CO_2 molecules. The synergetic effects of Ag and MgO as a bi-cocatalyst contribute to enhanced photo- catalytic activity and CH_4 selectivity for CO_2 reduction [87].

CO_2 conversion *via* hydrogenation

Catalytic hydrogenation represents another way to convert CO_2 into added value chemicals or fuels [88]. Methanol synthesis is carried out using supported organic systems [89] or metal oxide nanoparticles catalysts [90] that ensure the recoverability and reuse of catalytic species; hydrocarbons preparation has the drawback of water formation that can be solved using hydrophilic membranes [91] or the formation of CO intermediate that can decrease the selectivity [92] and olefins through the methanol route using zeolite, or directly [93]. These approaches are strictly related to hydrogen production and to consider the sustainability of the total route, hydrogen production should be based on renewable source.

Coupling catalysis and biotechnology for CO_2 conversion

Enzymes are an example of how catalysis can be achieved with biotechnology exploiting different reactive mechanisms conducted through the use of micro- organisms [94]. Both enzymes and full microorganisms can be used for CO_2 conversion. Bio-electrochemical systems are interesting systems [95]. In addition to microalgae, afore mentioned, fermentation systems are used to convert CO_2 into CH_4 or other photosynthetic products. Synthetic natural gas generally is produced chemically by catalyzed gasification and syngas conversion to methane [96], suffering high energy consumption and high costs. Recently, processes have been developed in which biomass gasification is conducted through bacterial strains that can ensure good selectivity at moderate costs [97]. Studies have also been conducted to improve plant aspects through process modelling [98]. Gas solubility, gas hold-up and gas contact time with microorganisms are important operational parameters for efficient consumption of the main substrates which are in the gas form. It is known that large amounts of CO_2 are obtained from the processing of sewage sludge. Good results are being achieved by coupling anaerobic digesters and bio-electrochemical systems to guide CO_2 reduction (dissolved in a watery medium) into biomethane. This technique uses electroactive microorganisms, already used in the treatment of wastewater, with the production of electricity (microbial fuel cells), hydrogen (microbial electrolysis cells) or other chemicals (microbial electrosynthesis cells) [99].

The last approach considered in this mini review for CO_2 conversion is the so-called artificial photosynthetic systems trying to mimic the activity of photosynthetic systems in plants. As a matter of fact, this approach should be better named ‘Solar Chemistry’ as it consists in ‘water splitting’: a photoanodic-type semiconductor captures solar photons for water splitting (H_2O oxidation with electron releasing) coupled with a p-type semiconductor cathode (or a supported catalyst) for CO_2 reduction (electron consumption) in a saturated $NaHCO_3$ solution. An interesting recent application is the use of proton membranes for the production of syngas from CO_2 and H_2O with an efficiency of con- version of solar-to-syngas energy up to 13.6% [100,101], performing much better than natural systems.

Biotechnological approaches are also very useful to obtain monomers such as lactic acid or succinic acid used to obtain polylactic acid or polybutylene succinate [102]. Polyhydroxyalkanoates can also be obtained directly from CO_2 though fermentation process [103].

Conclusions

The carbon capture, utilization and storage can be considered a strategy that, combined with a more intelligent use of fossil carbon, may assure the avail- ability of the future generation. Significant advances have been achieved, from both academic and industrial research, to reduce as much as possible CO_2 emissions in the atmosphere. Nonetheless, the mentioned technologies do not have the same potential in terms of CO_2 emission mitigation. In particular, owing to energy limitation, the CO_2 conversion into carbonates, carbamates, ureas or carboxylates can be today exploited at small scale. An interesting approach towards the con- version of large volumes of CO_2 is the use of bio- technologies or integrated systems, that may have an important role in the conversion of ‘exhaust’ carbon into ‘working’ carbon by reducing CO_2 into energy, materials and fuels.

Conflict of interest statement

Nothing declared.

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