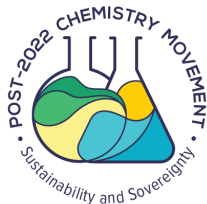


Trends in Carbon Dioxide Capture and Conversion

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Carbon dioxide capture and conversion is gaining increased attention due to climate change issues. The direct air capture of CO₂ may be accomplished with functionalized adsorbents that can work at atmospheric pressure and room temperature. The captured CO₂ may be converted into fuels and chemicals. CO₂ can be hydrogenated to methanol, which is a commodity used in the fuel and chemical sectors, over Cu.ZnO-based catalysts. Improvements to catalyst formulation are still needed to operate at lower temperatures. Dimethyl ether can be directly produced from CO₂ and H₂ through the use of bifunctional catalysts. Organic carbonates appear as promising compounds of wide use in the chemical sector. Cyclic carbonates may be produced from CO₂ and epoxides with the use of Lewis acids catalyst. Zeolites impregnated with metal halides appear to be a promising system to achieve high conversion and selectivity. Aliphatic organic carbonates can be produced from CO₂ and alcohols, but the reaction presents thermodynamic limitations. The role of oxygen vacancies on CeO₂-based catalysts and use of dehydrating agents in the production of dimethyl carbonate will be discussed in this account. The challenges and future perspectives for the direct air CO₂ capture and conversion into fuels and chemicals will be addressed.

**Keywords:** CO₂, CCU, methanol, DME, organic carbonates, chitosan

1. Introduction

The industrial revolution was based on the use of fossil fuels to run the machines that changed the world.¹ No one can deny the benefits of the industrial era to our society. The world is now a giant metropolis; travel between countries can take several hours instead of several months with the development of jet airplanes. Food and goods became accessible to the population after the development of synthetic fertilizers and plastics. Life expectancy significantly increased upon the discovery of new drugs to treat diseases. Therefore, life in the 21st century is healthy, wealthy, and more comfortable than it was in the 18th century, in the early stages of the industrial revolution.

Nevertheless, all these accomplishments came with the increase of the CO₂ emissions to the atmosphere, together with the devastation of major forest areas in the world.

Hence, Earth is facing fast climate changes that may impact life in the planet, jeopardizing all the benefits brought to the society by the industrial revolution. The nations around the globe are concerned with this situation and many climate agreements have been signed since the end of the 20th century. Today, it is consensual that an increase of up to 1.5 or 2 °C in the average temperature of the planet must be pursued until the end of the century. This target implies that we must change our energy matrix in the forthcoming years, replacing fossil to renewable energy sources and drastically reducing the carbon emissions.

The recent report of the Intergovernmental Panel on Climate Change (IPCC)² has drawn five possible scenarios or shared socioeconomic pathways (SSP) for the CO₂ emissions until the end of the century. SSP1 denotes a sustainable pathway (1). SSP1a also denotes a sustainable pathway, but with higher level of radiative forcing by 2100. SSP2 denotes an intermediate pathway (2), with emissions decreasing throughout the years, but not reaching zero by 2100. SSP3 and SSP5 refer to unsustainable pathways

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(3 or 5), with fossil sources still sharing important parts of the world's energy matrix. Radiative forcing is defined as the difference between the solar radiation absorbed and radiated to space by Earth in W m^{-2} . A positive number means that the Earth receives more energy from the sun than it radiates to the space. For the sustainable pathways, the projected radiated forcing by 2100 is within 1.9 and 2.6, whereas for the unsustainable pathways the projected value can be as high as 8.5.

One can see from Figure 1 that only with sustainable pathways (SSP1 or SSP1a) the world would meet negative CO_2 emissions before the end of the century, with high probability of keeping the increase of temperature within 1.5 to 2 °C relative to the preindustrial era. The intermediate pathway (SSP2) will lead to an estimated increase of at least 2.7 °C, whereas following the unsustainable pathways (SSP3 and SSP5) the temperature of the planet may increase in 3.6 and 4.4 °C, respectively, considering the most favorable estimates. Therefore, it is urgent to act and start decreasing the anthropogenic CO_2 emissions during this decade.

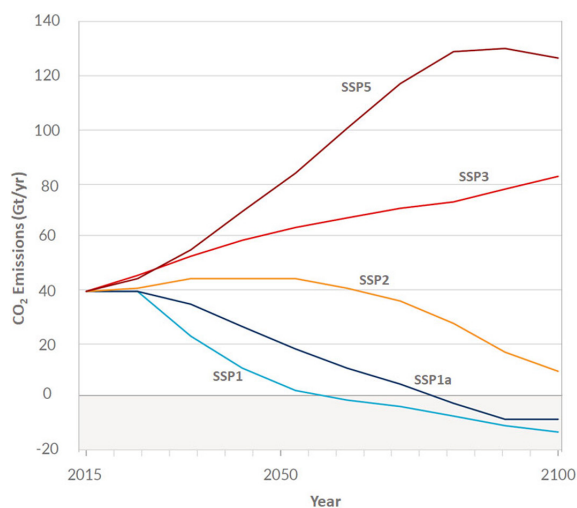


Figure 1. Projected scenarios for the future CO_2 emissions (adapted from reference 2).

All organic-derived fuels were originated from photosynthesis, with CO_2 and water as feedstocks. Figure 2 depicts the cycles of fossil and bio-derived fuels. Oil and coal were produced upon the geological transformation of organisms that lived on Earth millions of years ago. Time and conditions led to energy-dense molecules like hydrocarbons. The biofuel cycle takes few months, leading to more oxidized, less energy-dense, molecules like sugars and triglycerides. The fossil cycle is beyond the human lifetime. Thus, depletion of the present reserves will lead to shortage of fossil fuels and accumulation of CO_2 in the atmosphere. On the other hand, the biofuel cycle is within

the human time frame, but yields less energetic molecules and may induce competition for food, which may lead to social problems. Therefore, an anthropogenic fuel cycle must be idealized to circumvent the time frame of the fossil cycle and the energy density and food competition that may be present in the biofuel cycle. This cycle may involve CO_2 direct air capture (DAC) for the synthesis of energy-rich molecules. In addition, the cycle must be completed within the time frame of couple of hours (Figure 2).

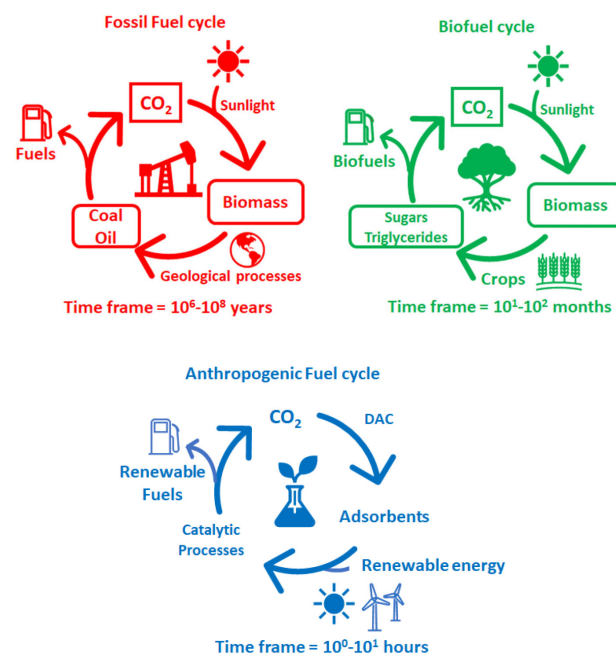


Figure 2. Fossil, bio and anthropogenic fuel cycles.

Carbon dioxide is a linear molecule with zero dipole moment. The CO_2 molecule has acidic properties and is considered the anhydride of the carbonic acid. The enthalpy of formation is $-94 \text{ kcal mol}^{-1}$, making CO_2 highly stable from the thermodynamic point of view. Figure 3 shows two axes to be considered when CO_2 conversion is concerned.^{3,4} Reduction of the oxidation state of the carbon atom requires energy input. Therefore, to go from CO_2 (the highest oxidation state) to CH_4 (the lowest oxidation state) a significant energy input is required, as methane has an enthalpy of formation around $-18 \text{ kcal mol}^{-1}$. On the other hand, keeping the same oxidation state of the carbon atom, the process may present thermodynamic limitations. Hence, production of organic carbonates, urethanes and urea-derivatives may involve equilibrium issues that must be circumvented in order to achieve high yields. The diagonal axle shows molecules, such as higher hydrocarbons and alcohol, in which the synthesis from CO_2 will involve some degree of energy input as well as thermodynamic concerns.

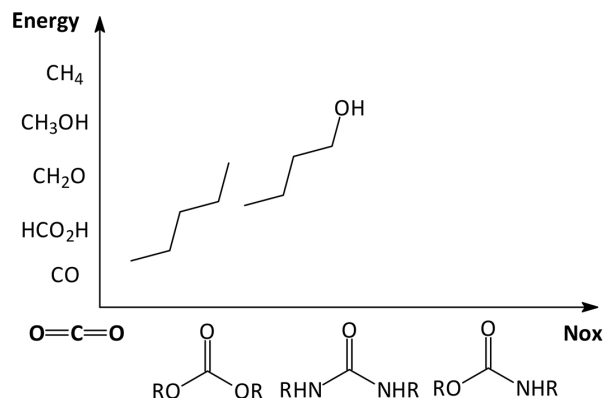


Figure 3. Representation of the energy-oxidation relationship in CO_2 transformations (adapted from references 3 and 4).

In this account, we wish to show the recent advances and trends in CO_2 capture and conversion. The aim is to focus on functionalized adsorbents, capable of directly capturing CO_2 from the air, and converting it to fuels, like methanol and dimethyl ether (DME), as well as chemicals, such as organic carbonates.

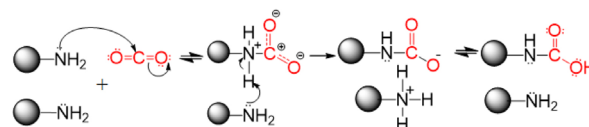
2. CO_2 Capture by Functionalized Adsorbents

The direct air capture of CO_2 (DAC) is an excellent option for achieving negative emissions in the forthcoming years.⁵ It is dissociated in space and time from existing power plants that capture the CO_2 emitted upon the burning of fossil fuels.⁶ The development of materials for capturing CO_2 from the air dates back from the 1930.⁷ However, the contextualization in scenarios of climate changes was only considered at the end of the last century. In the last two decades, DAC has grown in importance with the development of functionalized materials that can selectively capture CO_2 , by chemisorption, from diluted gas streams.⁸ The CO_2 adsorption on non-functionalized materials, such as carbons, zeolites and metal-organic frameworks (MOFs), involves physisorption. Thus, less energy is required for releasing the gas from the surface. Nevertheless, as physisorption is not specific, these materials present low CO_2 uptake at concentrations similar to atmospheric air, limiting their use in DAC processes.⁹

To deal with these challenges, surface functionalization of porous materials with amino groups has emerged as a viable alternative for DAC.¹⁰ Materials such as silica,¹¹ polymers,¹² resins,¹³ and nanomaterials¹⁴ have been chemically or physically modified with linear, branched, or polymeric amines. These adsorbents combine the advantage of high specific area with high affinity for the CO_2 molecule, resulting in higher adsorption/desorption rates and selectivity. Therefore, they have been considered the most promising materials for DAC.

Amino-functionalized materials capture CO_2 through acid-base reactions. Figure 4 illustrates two proposed mechanisms. In anhydrous conditions, primary and secondary amines can react directly with CO_2 leading to the formation of ammonium carbamates or carbamic acid derivatives.¹⁵ The reaction scheme usually requires two amino groups *per* CO_2 molecule. In wet conditions, tertiary amines catalyze the formation of bicarbonate and carbonate.¹⁶ The stoichiometry involves 1 mol of CO_2 for each mol of amino group to afford ammonium bicarbonate and carbonate salts.

(a) Anhydrous conditions



(b) Wet conditions

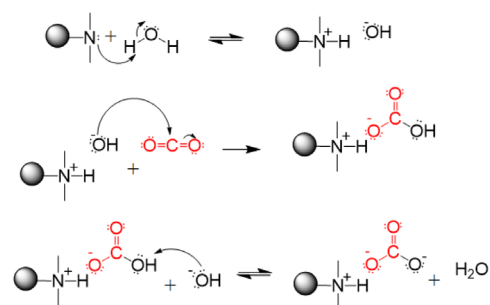


Figure 4. Proposed mechanism of CO_2 adsorption on amino-functionalized materials at: (a) anhydrous and (b) wet conditions.

The amino groups have been incorporated on the surface of the solid materials through impregnation, covalent tethering via grafting or covalent tethering via *in situ* polymerization.¹¹ In the impregnation procedure, an amine solution is deposited on the support and the excess of solvent is removed upon drying.¹⁷ In covalent tethering procedures, the amines are covalently anchored on the support via grafting with an amino-siloxane reagent or other reactions that lead to polymerization.¹⁸ Figure 5 shows the three main methods for preparing amino-functionalized adsorbents for application in DAC processes.

Several amino compounds, such as monoethanolamine (MEA), tetraethylenepentamine (TEPA), and pentaethylenehexamine (PEHA) have been impregnated on porous supports (Figure 6). Although impregnated solids present high adsorption capacities at low concentrations of CO_2 , the weak interaction between the support and the amino compounds can result in loss of functionalization during the adsorption/desorption cycles, which involves temperature and pressure swing. Branched polyethyleneimine (PEI)

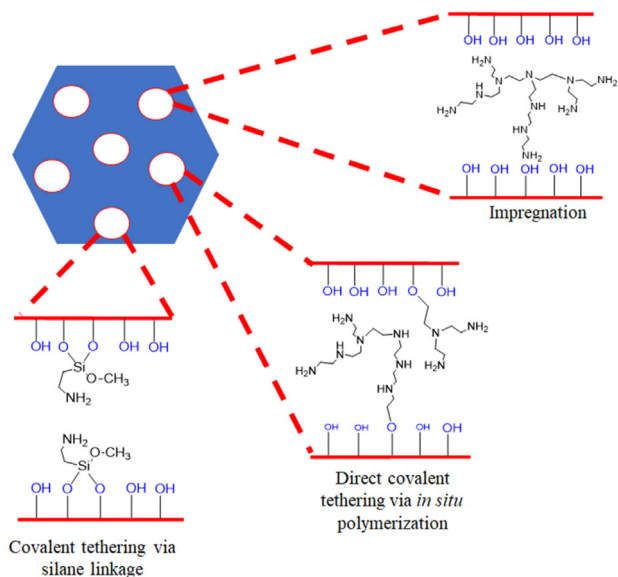


Figure 5. Pictorial representation of different amino functionalization procedures of materials.

has often been used in DAC processes because of its high density of amino functionalization and low vapor pressure under the adsorption/desorption conditions.

Choi *et al.*¹⁹ were the first to report the use of commercial silica impregnated with PEI to capture CO₂ from the air. The functionalized silica showed CO₂ adsorption capacity of 2.36 mmol g⁻¹ under simulated ambient air conditions. However, the adsorption capacity is reduced to 30% of the initial value after four cycles.

Goeppert *et al.*²⁰ used PEI-impregnated fumed silica for DAC simulated conditions. Impregnation with 33 and 50% of PEI produced materials with CO₂ uptakes of 1.18

and 1.71 mmol g⁻¹ at 25 °C, respectively. These materials presented improved adsorption kinetics in dry and wet conditions, being superior to zeolites, which have poor performance in humid conditions. Wang *et al.*²¹ studied SBA-15 (Santa Barbara amorphous-15) impregnated with 50% of PEI for simulated DAC process. They observed CO₂ uptake of 0.51 mmol g⁻¹. Other supports such as alumina²² and silica fiber²³ can also be used for PEI impregnation, but usually show lower CO₂ adsorption capacities. The main benefit is the high stability in humid and anhydrous conditions.

Amino-impregnated mesoporous supports present some limitations. These materials may present pore restrictions that prevent high loadings of the amine. Another point is associated with the gas transport process, considering that the pore size and amine loading limit the diffusional kinetics. To address these drawbacks, materials with bimodal pore systems are promising candidates. Recently, Kwon *et al.*²⁴ synthesized a hierarchical silica structure impregnated with PEI, using a double template method, and evaluated the performance under DAC conditions. The adsorption capacity was 2.6 mmol g⁻¹ under anhydrous condition and 3.4 mmol g⁻¹ under humid conditions.

Aminopropyl siloxanes (APS) and diethylenetriamine (DT) (Figure 7) are the most used feedstocks for grafting amino functionality on porous materials, such as MCM-41 (Mobil composition of matter No. 41). The main advantage is the high stability during several adsorption/desorption cycles, but the major drawback is the lower adsorption capacity compared with the impregnated materials.²⁵ Belmabkhout *et al.*²⁶ investigated MCM-41 materials

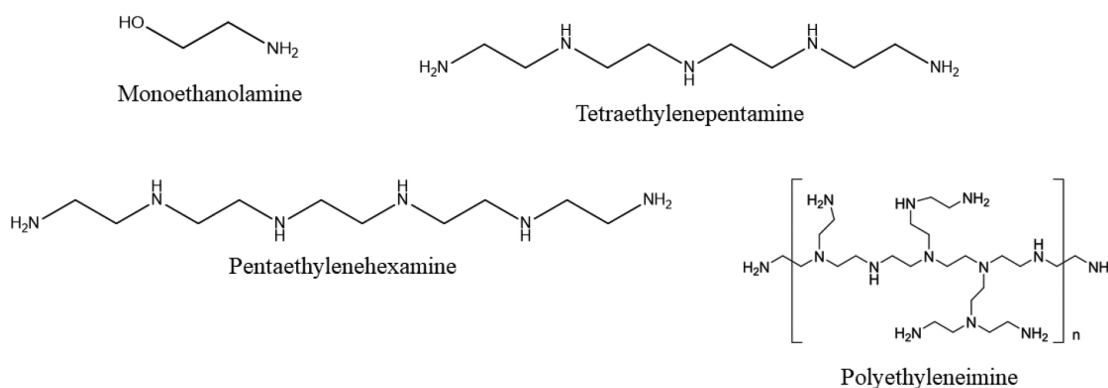


Figure 6. Structures of the most common amines used in the functionalization of solid supports for direct air capture.

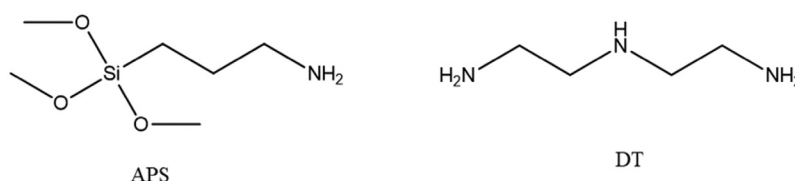


Figure 7. Structure of APS and DT amino-compounds used for functionalization of porous materials.

functionalized with DT for DAC simulated processes, observing a CO₂ adsorption capacity of 0.98 mmol g⁻¹ at 25 °C, with high selectivity.

A new class of amino-functionalized materials, described as hyperbranched amino silica (HAS), can be produced by *in situ* polymerization on SBA-15.²⁷ These materials have adsorption capacities in the range of 0.2 to 1.5 mmol g⁻¹ and exhibit excellent stability during adsorption/desorption cycles. Other materials such as polymers, ion exchange resins, and carbons have been functionalized with amino groups and studied in the direct air capture of CO₂. Lu *et al.*²⁸ developed amino-functionalized porous polymers with specific area of 4023 m² g⁻¹ and CO₂ adsorption capacity of 1.04 mmol g⁻¹ under DAC conditions. PEI impregnated ion-exchange resin presents CO₂ adsorption of 2.26 mmol g⁻¹ at 25 °C.²⁹

Ethylenediamine-functionalized MOFs have also been studied for CO₂ direct air capture.³⁰ Adsorption capacities as high as 3.89 mmol g⁻¹ under DAC conditions have been observed,³¹ but the main problem is the stability of the materials during various adsorption/desorption cycles. Nanomaterials are another potential class of functionalized adsorbents for DAC processes. Cellulose nanofibers modified with phthalimide showed CO₂ uptake of 5.2 mmol g⁻¹ under DAC conditions.³² Assessments of other properties that may affect the capture process are still needed, such as performance under real conditions and detailed analysis of the kinetic process associated with adsorption/desorption cycles.

Our group has focused on a different approach for obtaining functionalized materials for CO₂ capture. We have exploited the hydrothermal carbonization of chitosan, a natural nitrogen-containing polysaccharide.³³ Table 1 shows the nitrogen content, surface area and CO₂ uptake of different carbonized chitosan materials. One can see that upon hydrothermal carbonization the nitrogen content and surface area does not change, but the uptake of pure CO₂ at 1 bar and 25 °C increased by more than four folds relative to the parent chitosan. The combination of chitosan hydrothermal carbonization followed by calcination in the presence of K₂CO₃ significantly increases the surface area,

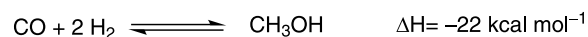
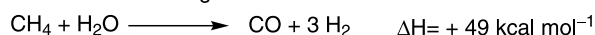
while maintaining a high degree of functionalization of the material. The CO₂ uptake was increased by 10 folds, showing the potential of these functionalized materials for DAC, although the adsorption kinetics is significant slower, probably due to the lower concentration of adsorption sites *per* surface area.

3. Hydrogenation to Methanol and DME

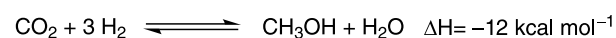
Methanol is an important commodity mostly used in the manufacture of resins, plastics, adhesives, and paints, as well as in the production of biodiesel.³⁴ The so-called “Methanol Economy” was proposed by Olah *et al.*³⁵ as a sustainable alternative to replace fossil fuels, when produced from CO₂ and H₂ obtained from renewable sources.

The main current process of methanol synthesis involves natural gas reforming, followed by reaction of the produced syngas over Cu.ZnO.Al₂O₃ catalysts. The overall process is energy-intensive, being endothermic by 27 kcal mol⁻¹ (Scheme 1). The CO₂ hydrogenation to methanol is exothermic but requires an additional hydrogen molecule and produces water as byproduct.³⁶ Although there is a commercial plant in Iceland that produces methanol using this route,³⁷ the process is still incipient and there are still many challenges to be overcome. Besides CO₂ capture, the source of hydrogen and improved catalyst formulations³⁸ are among the main issues to be addressed for the widespread use of this process.

Route from natural gas



Route from CO₂



Scheme 1. Pathways from natural gas and CO₂ for the synthesis of methanol.

The traditional Cu.ZnO.Al₂O₃ catalyst is active in the hydrogenation of CO₂ to methanol.⁴ However, the best

Table 1. Functionalization, surface area and CO₂ uptake of chitosan-derived materials

Material	N / wt. %	Area / (m ² g ⁻¹)	CO ₂ uptake ^a / (mmol g ⁻¹)	Kinetic constant ^b / (g mmol ⁻¹ min ⁻¹)
Chitosan	7.3	2.2	0.1	15.3
CHIT-HTC-24 ^c	7.3	1.8	0.3	3.7
CHIT-HTC-48 ^c	7.5	2.6	0.45	3.2
CHIT-HTC-48-CO3-700 ^d	5.6	2262	4.5	0.2

^aMeasured at 1 bar of CO₂ at 25 °C; ^b2nd order kinetic constant (k) taken from the adsorption isotherm at 1 bar of CO₂ at 25 °C; ^chydrothermal carbonized chitosan, number denotes time in h; ^dhydrothermal carbonized chitosan subjected further to calcination with K₂CO₃, number denotes temperature of calcination.

performance is observed at 270 °C, where the equilibrium of the reaction is less favorable (Figure 8). At lower temperatures, the methanol yield is significantly below the thermodynamic threshold due to the activity of the catalyst. Above 270 °C, reverse water gas shift becomes important, and affects the methanol yield. Thus, the design of new catalyst formulation, able to work near the thermodynamic limits at lower temperatures, is highly desired.

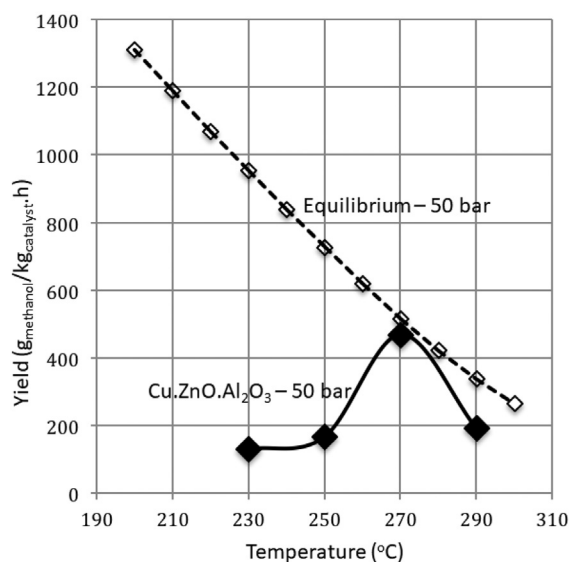


Figure 8. Methanol yield on the hydrogenation of CO₂ over Cu.ZnO.Al₂O₃ catalyst at different temperatures.

Many metal oxides, such as chromium, rare earth elements, gallium, and zirconium can be used together or replacing Al₂O₃ in the traditional Cu.ZnO catalyst.³⁹ ZrO₂ is one of the main promoters of the methanol synthesis catalysts and may improve the thermal stability, minimizing the sintering of the Cu particles.⁴⁰ Lanthanum oxide can increase the Cu surface area.⁴¹ There are also studies on the use of different families of catalysts for CO₂ hydrogenation. For instance, catalytic systems using In₂O₃ have shown high activity and selectivity for CO₂ hydrogenation to methanol.⁴² The creation of oxygen vacancies seems to be important, and it is possible to increase the number of active vacancies using ZrO₂ as promoter of In₂O₃ catalysts. The main drawback for the widespread use of In₂O₃ as catalyst in the hydrogenation of CO₂ to methanol is its limited availability. Indium is an endangered element,⁴³ with mineral reserves being scarce all over the world.

The preparation of the catalyst precursor is of prime importance to produce a good Cu.ZnO methanol catalyst. It has been reported⁴⁴ that formation of zincian malachite phase during the aging process is crucial to prepare a high-active catalyst. We have studied the aging of different Cu.ZnO catalyst formulations, trying to establish the best

conditions to form zincian malachite phases, as shown from the XRD patterns (Figure 9). Promotion with ZrO₂ and MgO led to the formation of the malachite phase at the same aging conditions used for Al₂O₃ promotion. On the other hand, CaO and BaO promoters did not lead to formation of zincian malachite phases at same aging conditions. As a direct consequence, the textural properties of these two catalyst formulations were significantly worse (Table 2). Therefore, optimizing the aging conditions is of prime importance to prepare good catalysts for methanol synthesis from CO₂ and H₂.

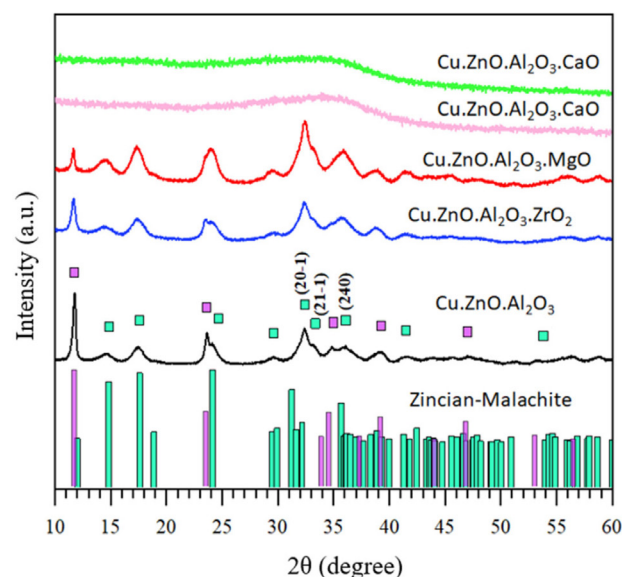


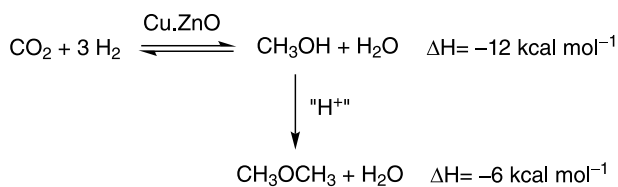
Figure 9. XRD patterns of the catalyst precursors with the different promoters after aging at 60 °C and 100 min.

Table 2. Textural properties of different catalyst precursors after aging at 60 °C and 100 min

Catalyst precursor after aging	Area / (m ² g ⁻¹)
Cu.ZnO.Al ₂ O ₃	92
Cu.ZnO.Al ₂ O ₃ .ZrO ₂	118
Cu.ZnO.Al ₂ O ₃ .MgO	119
Cu.ZnO.Al ₂ O ₃ .CaO	29
Cu.ZnO.Al ₂ O ₃ .BaO	30

DME is considered a clean fuel, which can burn without emitting particulate matters and sulfur, used to replace diesel in compression ignition engines due to its high cetane number.⁴⁵ It can be produced by dehydration of methanol over acidic catalysts in the temperature range of 250 to 400 °C and pressures above 18 bar.⁴⁶ Zeolites, alumina, and mixed metal oxides are among the most traditional acid catalysts used. Tuning the catalyst acidity is important to avoid side reactions, especially formation of hydrocarbons.

A direct route to DME, from CO₂ and H₂, can also be envisaged, being a good option to shift the equilibrium of the CO₂ hydrogenation, as the methanol formed may be converted to DME (Scheme 2). The process involves bifunctional catalysts, containing a metallic component, usually Cu.ZnO, supported over an acidic material.⁴⁷ We have studied⁴⁸ the use of alumina and niobium oxide as support for the direct synthesis of DME from CO₂. Higher selectivity to DME can be observed with Al₂O₃ as support of the Cu.ZnO methanol catalyst, because of its higher acidity compared with niobium oxide. The selectivity to DME can be further improved by modifying the alumina with (NH₄)₂SiF₆.⁴⁹ This procedure introduces silicon atoms on the alumina surface producing sites of higher acid strength.



Scheme 2. Direct route of DME production from CO₂ using bifunctional catalysts.

There is no industrial plant that produces DME directly from syngas or CO₂. Although many academic studies have been reported in the literature, the process requires improvements on catalyst formulation to control hydrogenation and dehydration. Both reactions are exothermic, but the water formed may affect the dispersion of the Cu particles and the acidity of the support. Thus, improvements on catalyst formulations are still necessary to turn the direct route feasible.

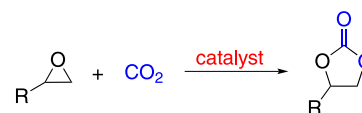
4. Production of Organic Carbonates

The conversion of CO₂ to organic carbonates has been extensively investigated as a sustainable alternative to produce valuable chemicals. Organic carbonates have wide applications, including monomers for polycarbonates, polar aprotic solvents of low toxicity, electrolytes in lithium ion batteries, green alkylating agents and fuel additives.⁵⁰

Cyclic organic carbonates are generally produced from the reaction of CO₂ with epoxides using homogeneous catalytic systems, but the use of heterogeneous systems is gaining importance.⁵¹ On the other hand, reaction of CO₂ with alcohols to afford aliphatic organic carbonate presents thermodynamic limitations. Hence, besides developing active and selective heterogeneous catalytic systems, it is important to find sustainable solutions to shift equilibrium and achieve high yields of the aliphatic carbonate.

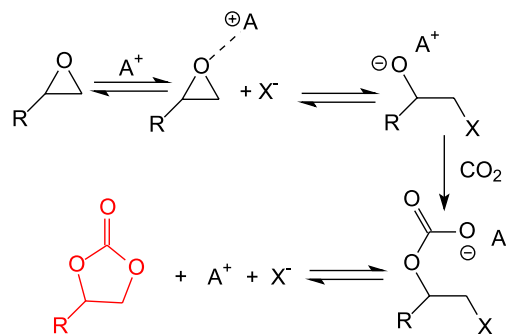
4.1. Cyclic organic carbonates

The reaction of CO₂ with epoxides to afford cyclic organic carbonates does not produce byproducts (Scheme 3). Depending on the experimental conditions, the formed cyclic organic carbonate can undergo *in situ* polymerization, but this can be kept to a minimum extent if the polycarbonate is not the primary goal. Furthermore, the epoxide is highly reactive compared to other ethers due to the ring tension. The cycloaddition of CO₂ to ethylene oxide (EO) is thermodynamically favorable and exothermic ($\Delta H = -34 \text{ kcal mol}^{-1}$), affording ethylene carbonate, a commercially important cyclic organic carbonate.



Scheme 3. Cycloaddition of CO₂ to epoxide.

Scheme 4 shows the most acceptable mechanistic pathway of the acid-catalyzed reaction of CO₂ with epoxides. The ring oxygen atom is firstly activated through interaction with a Lewis acid (A⁺). Then, a nucleophile (X⁻), usually a halide, opens the activated epoxide ring to yield a halodrin intermediate, which then reacts with CO₂ to afford a carboxylate. In the last step, occurs an intramolecular nucleophilic attack, leaving the halide and yielding the cyclic organic carbonate.



Scheme 4. Mechanistic pathway of the synthesis of cyclic organic carbonates with a Lewis acid (A⁺) as catalyst and a nucleophile (X⁻) as a co-catalyst.

Most of the catalytic systems used in this reaction are homogeneous. The Lewis acid is usually a metal complex, such as metalloporphyrins,⁵² salen metal complexes,⁵³ among others. The nucleophile or co-catalysts normally involve quaternary ammonium salts.⁵⁴ The industrial production of cyclic organic carbonates occurs through homogeneous catalysis, with metal halides being the probable catalyst.⁵⁵ Nevertheless, reusing the catalyst is difficult and has motivated the search for active and

selective heterogeneous systems. Zeolites,⁵⁶ MOF,⁵⁷ silica-based⁵⁸ and metal oxides⁵⁹ have been studied as promising heterogeneous catalysts for the production of cyclic organic carbonates. All present advantages and disadvantages that impair their commercial use up to now.

Our group⁶⁰ has focused on the use of zeolite Y impregnated with metal iodides, as heterogeneous catalysts in the reaction of styrene oxide and CO₂ to afford styrene carbonate. The results indicated that KI impregnated on potassium-exchanged zeolite Y (KI/KY) is more active than pure KI, although presenting significantly higher epoxide/iodide molar ratios. The conversion and selectivity to styrene carbonate (SC) depends on the amount of iodide impregnated on the zeolite (Table 3). Styrene glycol (SG) is formed as byproduct, probably from hydrolysis of styrene epoxide by some remaining water in the medium.

Table 3. Conversion and selectivity in the reaction of styrene oxide with CO₂ over different catalysts. Reaction conditions: 100 °C, 50 bar, 12 h

Catalyst	Epoxide/I ⁻ molar ratio	Conversion / %	Selectivity	
			SC ^a	SG ^b
KI	15	13	100	
KI(5)/KY ^c	220	80	87	13
KI(10)/KY ^c	110	94	95	5
KI(13)/KY ^c	86	95	98	2

^aStyrene carbonate; ^bstyrene glycol; ^cKI impregnated on potassium-exchanged zeolite Y, the number in parenthesis stands for the wt.% of iodide on the zeolite.

Periodic DFT (density functional theory) calculations, using ethylene oxide as model for the epoxide and LiI/LiY as model of the zeolite system, corroborated the experimental results, indicating that the rate-determining step is the iodide attack to the epoxide ring. Calculations also indicated the enzyme-like behavior of the zeolites in this reaction. The transition state is perfectly fitted within the pores, upon the participation of two opposing framework aluminum sites. Whereas one site interacts with the impregnated KI, the other activates the epoxide ring, which becomes perfectly aligned with the KI cluster for the opening of the ring (Figure 10).

4.2. Aliphatic carbonates

Dimethyl carbonate (DMC) is the most important aliphatic organic carbonate.⁶¹ The main market for DMC

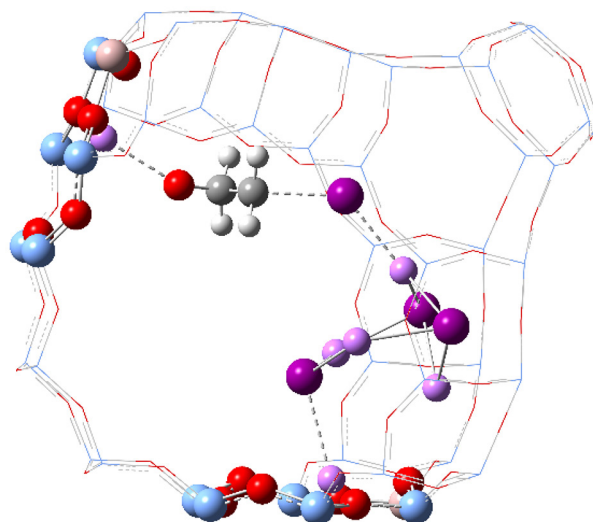
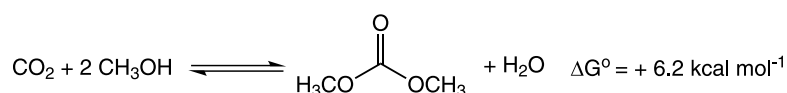


Figure 10. Calculated transition state for the opening of the epoxide ring of ethylene oxide on LiI/LiY catalytic system, at periodic boundary conditions with Perdew-Burke-Ernzerhof (PBE) correlation functional.

is Asia, predominantly China and Japan, where DMC is used in the production of polycarbonates. In India, the pharmaceutical industry is responsible for most of the DMC consumption.

Many routes can be used to produce DMC.⁶²⁻⁶⁴ The current commercial processes are: (i) oxidative carbonylation of methanol over copper-based catalysts; (ii) methylnitrite carbonylation and (iii) transesterification of methanol with ethylene carbonate.⁶⁵ However, they are cost-intensive, also involving hazardous (CO) or explosive (pure O₂) reagents and, therefore, they cannot be considered completely green or sustainable. On the other hand, direct synthesis from CO₂ and methanol has been investigated and considered the most sustainable one (Scheme 5). Nevertheless, it is not favored by thermodynamics and equilibrium must be shifted in order to achieve reasonable yields of DMC.

Many heterogeneous catalysts have been investigated for this reaction, particularly metal oxides. The general, most acceptable, mechanistic scheme involves the adsorption of methanol on acidic sites (A) of the catalyst, followed by interaction with the strong adjacent basic sites (B) to afford adsorbed methoxide (CH₃O⁻) and H⁺ (Figure 11).⁶⁶ Although there is some agreement in the literature about the first step, different proposals have evolved for the next steps, especially the formation of the hemi-carbonate intermediate. Many authors suggest that the



Scheme 5. Direct synthesis of DMC from CO₂ and methanol.

hemi-carbonate is formed from the reaction of CO_2 with adsorbed methoxy species, through the general Eley-Rideal catalysis mechanism.⁶⁷

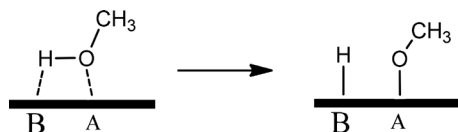


Figure 11. Schematic representation of the formation of methoxy species on the direct synthesis of DMC from CO_2 and methanol.

Wada *et al.*⁶⁸ showed that the presence of oxygen vacancies on CeO_2 -type catalysts improves the yield of DMC. The authors proposed a mechanism involving formation of oxygen vacancies on the CeO_2 surface, upon reduction with H_2 , as the first step. Then, the CO_2 molecule is adsorbed on these vacancies probably yielding a carbonate intermediate. Methanol is adsorbed on the acid-base sites, as previously discussed, producing the methoxide intermediate. Thus, according to this mechanistic route, at least two adsorbed species are involved.

As CeO_2 -based catalysts receive considerable interest in the production of DMC from CO_2 and methanol, the role of the oxygen vacancies has been continuously studied.⁶⁹ The vacancies present strong basic properties,⁷⁰ and may adsorb CO_2 to yield carbonate and bicarbonate species. Thus, some authors⁷¹ believe that the rate-determining step is the adsorption and activation of CO_2 on the catalyst surface to generate bidentate carbonate.

We recently carried out⁷² a periodical DFT study on the formation of oxygen vacancies as a function of the exposed CeO_2 plane, and their role on CO_2 adsorption (Figure 12). The results indicated that the exposed (110) plane is more prone to form the vacancies. In addition, it was the only plane that affords carbonate intermediates upon CO_2 adsorption. The theoretical results were fully confirmed by experiments with nanostructured CeO_2 catalysts.

The direct synthesis of DMC from CO_2 and methanol is limited by thermodynamic ($\Delta G^\circ = +6.2 \text{ kcal mol}^{-1}$). The reaction is exothermic and increasing temperature does not favor equilibrium toward the products. Hence, to achieve high yields of DMC is necessary to shift equilibrium, which is normally carried out by removal of the water from the medium.

Many non-reactive and reactive dehydrating agents have already been studied. The most common non-reactive agents are membranes⁷³ and molecular sieves.⁷⁴ Nevertheless, since the reaction is usually carried out above 100°C and at high pressures, the non-reactive agents are poorly effective in removing water from the medium and shifting equilibrium. On the other hand, reactive dehydrating agents are capable of undergoing hydrolysis with the water produced as byproduct, shifting the chemical equilibrium toward higher DMC yields.

The combination of CeO_2 as catalyst and 2-cyanopyridine as dehydrating agent has been reported⁷⁵ to be particularly relevant to achieve high yields of DMC. However, the

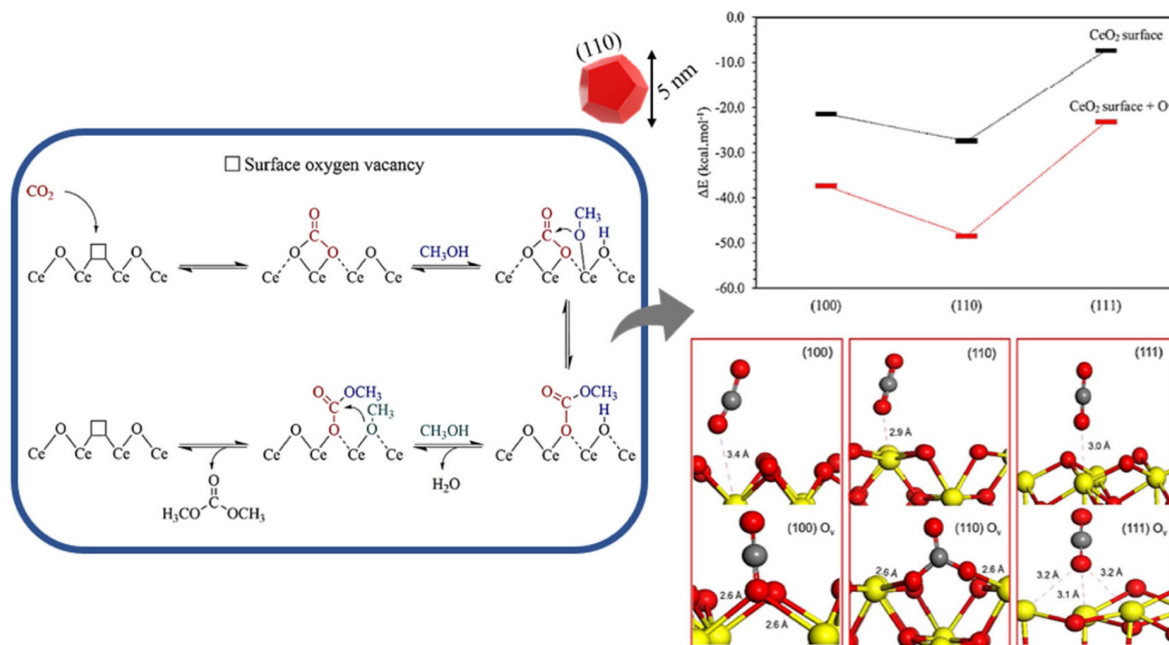
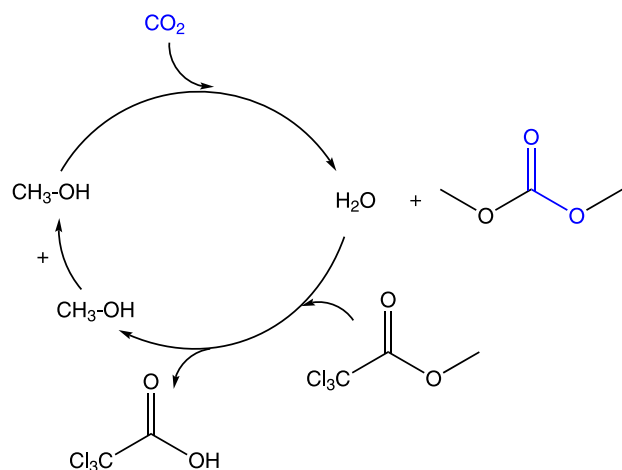


Figure 12. Schematic pathway of DMC synthesis from CO_2 and methanol on CeO_2 nanoparticle and DFT results showing the CO_2 adsorption energy on CeO_2 (100), (110) and (111) surface planes with and without oxygen vacancies. Yellow spheres: cerium atoms; red: oxygen atoms and gray: carbon atoms (reproduced from reference 72 with copyright permission from Elsevier).

hydrolysis of 2-cyanopyridine produces 2-picolinamide and other useless byproducts, making the process unsustainable, because transformation of these side products in the original nitrile is not straightforward. Alternatively, we have used methyl trichloroacetate^{69,76} as a sustainable dehydrating agent (Scheme 6). The ester is hydrolyzed faster than DMC in the reaction medium, producing trichloroacetic acid, which can be further separated and transformed back into the ester, being virtually recycled to the medium.



Scheme 6. Use of methyl trichloroacetate as dehydrating agent in the synthesis of DMC from CO₂ and methanol. Potential recycling of the trichloroacetic acid.

It also produces higher yields of DMC compared with 2-cyanopyridine⁶⁹ (Table 4).

5. Future Perspectives in CO₂ Capture and Conversion

There are about 15 pilot plants for direct air capture of CO₂ in the world today.⁷⁷ Together, they can capture up to 9 kt of CO₂ per year, but the forecast points to about 30 Mt of CO₂ captured directly from air by 2030, at a cost of US\$ 90 to US\$ 200 per ton, or even lower. Hence, the future of CO₂ capture indicates the growing importance of DAC.

The design and engineering aspects of DAC units is an important issue that deserves attention.⁷⁸ The system must operate at atmospheric pressure, blowing air through a series of adsorbent beds, to remove water and then capturing CO₂ from air. Upon saturation of the adsorbent, the CO₂ must be recovered by temperature and pressure swing to be further utilized. Thus, it is necessary to have, at least, two devices in order to operate in continuous mode (Figure 13).

Water is firstly removed on desiccant beds. Then, the water-free air is passed over the functionalized adsorbent beds to capture CO₂, exhausting to the atmosphere the air free of carbon dioxide. In order to minimize flow resistance, the beds are normally filled with ceramic monoliths or porous polymers containing the functionalized adsorbents.

Table 4. Catalyst/dehydrating agent system used in the synthesis of DMC from CO₂ and methanol

System	Pressure / bar	Temperature / °C	DMC yield / (mmol g _{cat} ⁻¹)	DMC selectivity / %	Reference
CeO ₂ /2-CP ^a	50	120	49	100	75
0.02CuCeO ₂ /2-CP ^b	50	140	84	100	69
0.02CuCeO ₂ /MTCL ^c	50	140	208	80	69

^aCeO₂ as catalyst and 2-cyanopyridine as dehydrating agent; ^bCu-doped CeO₂ as catalyst and 2-cyanopyridine as dehydrating agent; ^cCu-doped CeO₂ as catalyst and methyl trichloroacetate as dehydrating agent. DMC: dimethyl carbonate.

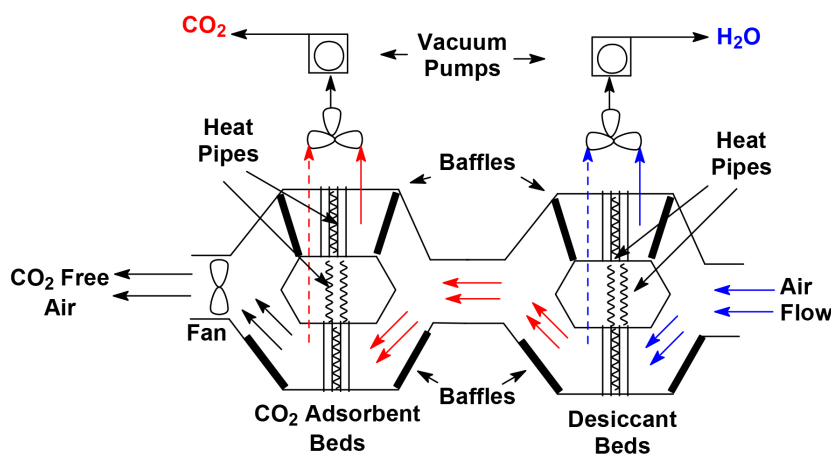


Figure 13. Schematic diagram of a CO₂ DAC device.

Thus, air may flow with minimum pressure drop between the entrance and the exhaust. It is worth mentioning that to capture 100 kg of CO₂ *per* day is necessary to blow around 140 thousand m³ of air in the system, considering the present CO₂ concentration in the air today.

Ideally, the temperatures for CO₂ desorption should be around 100 °C to avoid excessive heat exchange and decomposition of the functionalized material. Materials based on impregnation of amino compounds gradually loose functionalization through multiple temperature and pressure swings. However, these materials are easily prepared and have low costs compared with amino-grafted ones. On this scenario, the development of materials having amino groups on their structure may pave a way to the future. Therefore, studies on carbonization of nitrogen-containing biomass may fulfill this gap. We have shown that controlled carbonization of chitosan may yield functionalized adsorbents of high surface area and high efficiency for CO₂ capture, indicating their potential for DAC.

After being directly captured from air, carbon dioxide can be converted into fuels and chemical. Presently, there are few pilot and demonstration plants for this purpose in the globe. For instance, the CO₂ Raw Material from Air (CORAL)⁷⁹ is a German project that captures CO₂ from air, using functionalized adsorbents, and produces dimethyl ether via CO₂ hydrogenation. Hydrogen is obtained from water electrolysis on what is normally referred as electrofuels⁸⁰ (Figure 14). There are other initiatives on this issue, like the Pro-QR project,⁸¹ which is a partnership between Brazil and Germany. The aim is to produce aviation fuel of low environmental impact and one of the strategies is the direct capture of CO₂ from air, followed by its hydrogenation to hydrocarbons, in the aviation jet fuel range, with hydrogen obtained from water electrolysis using clean energy (solar, wind, hydro, etc).

In fact, the source of hydrogen⁸² is an important point of concern on the synthesis of methanol, DME and hydrocarbons from CO₂ directly captured from air. For the complete sustainability of the process, the hydrogen must be mainly produced from water using renewable energy. Today, electrolysis is being considered the best option to produce hydrogen from water. Notwithstanding, the high energy demand, associated with high electric power

consumption, and the moderate efficiency of the process motivates the search for other routes, not mentioning the use of wind, solar, geothermal or hydropower as a source of renewable energy. Considering the Brazil scenario, photoelectrocatalysis⁸³ and photocatalysis⁸⁴ appears as promising routes for hydrogen production from water, as the country encompasses large areas of sunlight exposure. The main issue related with photocatalytic water splitting is the use visible light. Most of the known photocatalysts are active under UV radiation, which is not abundant on the Earth surface. The use of plasmonic resonance⁸⁵ may revolutionize the technology of water splitting by employing visible light to produce H₂.

The search of promoters for the traditional Cu.ZnO methanol synthesis catalyst still deserves attention. It is of prime importance to develop catalysts that work at the thermodynamic equilibrium at lower temperatures, to maximize the methanol yield. Exotic catalysts, based on endangered elements, may not present a sustainable solution.

The direct hydrogenation of CO₂ to DME present several challenges. Besides the improvements on the metallic function, associated with hydrogenation to methanol, it is necessary to find supports with adequate acidity, to dehydrate the methanol molecule under the same reaction conditions of CO₂ hydrogenation.

The production of cyclic organic carbonates with CO₂ directly captured from air has been recently reported in the literature.^{86,87} The reaction requires use of highly active metal complex catalysts or plasma-induced conditions. Considering the high added-value of the cyclic organic carbonates, any production route using DAC would be interesting. Nevertheless, the reaction must run near atmospheric pressure, otherwise the costs of compression would surpass the benefits of DAC. Hence, development of highly active catalyst, capable of being reused several times, is of prime importance.

Processes of CO₂ direct air capture and conversion will be important to contribute with the climate agreements that project an increase of 1.5 to 2 °C in the temperature of the planet by the end of this century. Although the concept has already been proven, there are plenty of opportunities to develop new or improved technologies, especially concerning the production of fuels and high-

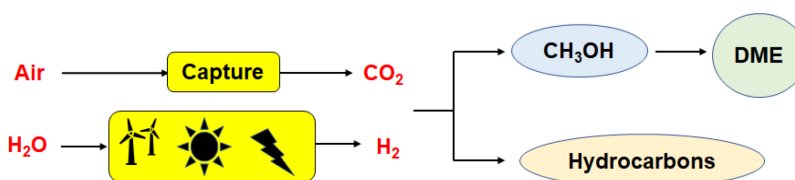


Figure 14. Schematic concept of electrofuels (PtX) from CO₂ captured from air and H₂ produced from water and renewable energy.

value chemicals. While the development of advanced materials will play an important role for the production of functionalized adsorbents and highly active and selective catalysts, engineering aspects will also share a relevant role, as DAC devices still require better solutions of heat and mass transfer, as well as integration with the conversion units, which usually work at high pressures.

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