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Review

Methods of Capture and Transformation of Carbon Dioxide (CO_2) with Macrocycles

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Abstract: Rapid industrialization and the indiscriminate use of fossil fuels have generated an impact that is affecting the climate worldwide. Among the substances that are causing climate change are several gases such as carbon dioxide (CO_2), methane (CH_4), nitrous oxide (N_2O) and sulphur hexafluoride (SF_6), among others. Particularly, carbon dioxide is one of the substances that has attracted the most attention from researchers, as it is responsible for more than three quarters of greenhouse gases. Because of this, many efforts have been directed towards the capture of CO_2, its separation, adsorption and transformation into products that are less harmful to the environment or that even have added value in the industry. For this purpose, the use of different types of macrocycles has been explored mainly in the last 5 years. This review seeks to present the advances that have occurred in recent years in the capture and transformation of CO_2 by different methods, to finally focus on the capture and transformation through macrocycle systems such as azacompounds, heterometallic macrocycles, calixpyrrols, modified cyclodextrins and metallic porphyrins, among others.

Keywords: CO_2; greenhouse gases; macrocycles; cyclodextrins; porphyrins; calyxarenes

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1. Introduction

The generation of greenhouse gases has been increasing over the years, and it is even indicated that in the last decade, the net anthropogenic emissions of greenhouse gases were the highest in the history humanity [1]. The development of industrial activities, and the different ways of producing energy from oil, coal and natural gas, among others, have resulted in the increase in CO_2 and CH_4, which are the main gases that cause adverse effects on the global climate [2–4].The effects generated include the melting of glaciers, rising sea levels, ocean storms and various environmental problems, which affect normal life and have become a threat worldwide [5]. There are three ways to deal with this problem: the first is to prevent its generation, the second is to extract CO_2 from the atmosphere and store it, and the third is to use it [2,6]. In the first case, the Paris Agreement, signed by 196 countries in 2015, shows that measures have been taken worldwide to reduce greenhouse gases and to limit the increase in global temperature to below 2 °C, keeping it at 1.5 °C. However, net zero emissions were projected to be achieved only by the end of the

century [5]. Meanwhile, according to NASA, 2023 was the warmest year in human history, with an increase of 1.2 °C above the average, taken as a reference between the years 1951 and 1980. In the second case, the spatial and temporal limitations to the capture and storage of CO_2 have not been fully resolved [7]. For this purpose, several CO_2 capture methods have been applied at an industrial level based on non-electrochemical principles, such as capture with ammonia, at low temperatures, the membrane method and the adsorption method, among others. However, some of these methods present high energy consumption, energy losses during the process and problems in generating the adsorbents, which is why their use is currently being reconsidered [5]. It has even been suggested that CO_2 can be mineralized with alkaline solid waste [8]. In addition to the above, there is already talk of the scarcity of fossil fuels, so humanity urgently requires environmentally friendly and efficient solutions that are within our reach. This seems to be provided by the third case, since the methods of transforming greenhouse gases (mainly CO_2 and CH_4) into value-added substances or even liquid fuels become a good option for using them, supplying energy needs and reducing their effect on climate change [1]. Considering the type of injected gas, the conversion methods can be by decomposition of pure CO_2, by reduction with water and by hydrogenation of CO_2 and dry reforming of methane [2]. Among the products that can be obtained and that are desirable for the industry are CH_3OH, CO, CH_3COOH, HCOOH, C_2H_4, CH_3CH_2OH, CH_3CHO [9], liquid fuels [1], polyurethane [10] and synthesis gas [1], among others. In this context, several articles can be found in the literature in which efforts are focused on finding materials that can capture and transform carbon dioxide [11–16].

Continuing with our research on the usefulness of macrocyclic systems such as Calixarenes [17–19] or Cyclodextrins [20,21] in the capture of various types of molecules, this paper therefore aims to review the methods of capturing and transforming CO_2: conventional methods and also those that include the use of macrocycles. Finally, a proposal is described for managing the combustion reaction conditions, which could produce substances that are more reactive than CO_2 and which can be more easily transformed into other substances with added value, without considerably reducing the energy production of the process.

2. Methodology

This work is the result of a systematic review of the literature, which began by defining the research question: What are currently the methods of capturing and transforming the most important greenhouse gas, CO_2, and how are macrocycle systems used for this purpose? Once the research question and the objective of the review were defined, the information was searched in databases such as Science Direct, Web of Science, Scopus, PubMed, Springer and MDPI, among others. The search strategy was based on the use of Boolean operators combined with terms such as capture and transformation of carbon dioxide, capture or complexation of CO_2, macrocycles and carbon dioxide, and non-adsorbent CO_2 capture methods, among others. Additionally, in this last case, the specific name of the macrocycle was also searched, for example, cyclodextrin and carbon dioxide. Subsequently, the articles found were selected according to the inclusion and exclusion criteria. The inclusion criteria taken into account were that articles have recent publication dates (preferably less than 5 years old), that they were of good methodological quality, and that there was no evidence of bias on the part of researchers; additionally, that they would help to meet the stated objective and allowed the research question to be answered. In this way, data were extracted from those that met the eligibility criteria, and the main results of the included studies were synthesized, interpreted and analyzed. The study concludes by presenting the findings found in these works and presenting the conclusions of the review. Finally, a

suggestion is given for managing the combustion reaction conditions that could serve to improve CO_2 transformation methods.

3. Description of the CO_2 Molecule, Advantages and Challenges for Its Capture and Transformation

As indicated above, the greenhouse gases that most influence global warming are CO_2 and CH_4. However, seen from a more optimistic perspective, they also have enormous potential since the former is a renewable and environmentally friendly source of C [22] and the latter of H. In this way, their capture and use cannot only serve to alleviate the greenhouse effect problem, but also to provide value-added products used by industry, and even to produce other forms of liquid fuels that alleviate the global energy problem that is already looming. To analyse the above, this section aims to show those challenges that have to be overcome when trying to use CO_2 as a raw material for the production of the aforementioned products.

As shown in Figure 1, the CO_2 molecule is a triatomic linear molecule. The bonds between carbon (C) and oxygen (O) are the result of sharing eight electrons, four contributed by oxygens and the other four by carbon. The two double bonds formed have a distance (1.16 Å) shorter than that of a typical double bond (1.22 Å) and are very close to a triple bond (1.10 Å), with a bond energy of 803 kJ/mol. The C hybridization is *sp*, and they form two π and two σ bonds with oxygen. This molecule exhibits horizontal symmetry, a centre of symmetry and an asymmetric circular plane. Thus, it is possible to conclude that the high stability of CO_2 is the combination of several factors, low polarity, high symmetry and high binding energy. Therefore, in any process that aims to convert CO_2 under less extreme conditions, it is necessary to consider reducing the activation energy, using suitable catalysts, so that the process can be carried out at feasible temperatures. For the above, there is the advantage that CO_2 also has empty orbitals at low energy levels and that these have high electron affinity, so that substances rich in electrons can activate the molecule [2,23].

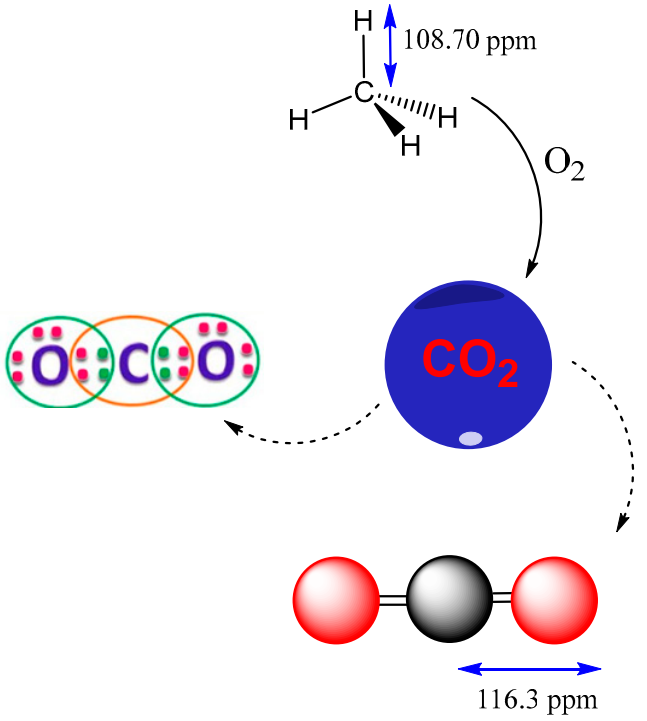


Figure 1. Forms of representations of the CO_2 molecule.

It is then possible to consider that the process must be carried out in two stages, the first involving the origin of the energy and the initiation method, and the second consisting of the preparation of the catalyst and its use [2]. In the first case, the methods that have been explored to break the high-energy CO bonds and reduce the CO_2 activation barrier include electrochemical (electricity), photochemical (light) and photoelectrochemical. In the second case, mono and multicomponent, homogeneous and heterogeneous, thermal and non-thermal processes of catalysis have been used, which directly affect the distribution of the products obtained [2].

4. General Methods for Capturing and Transforming CO_2

Below, the main common methods of capturing and transforming CO_2 without the use of macrocycles are shown (Figure 2), followed by a brief description of each.

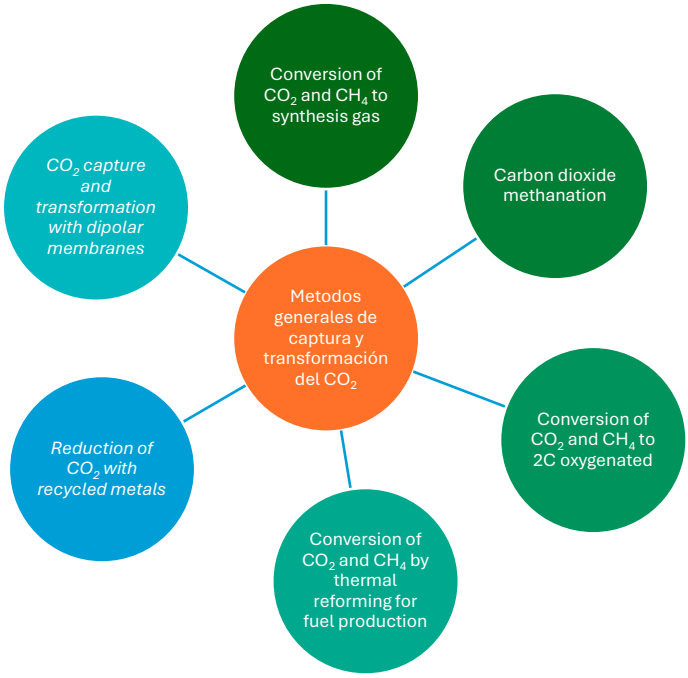


Figure 2. Main methods of capturing and transforming carbon dioxide.

4.1. Conversion of Carbon Dioxide and Methane to Synthesis Gas

One of the methods that have been recently proposed is carried out with heterogeneous Ni-Al catalysts, encapsulating Ce species at their interface, with the aim of achieving the capture and transformation of CO_2 and CH_4 within the same container [24]. Ni is a metal with very good catalytic properties, comparable to those of the noble metals, in dry methane reforming, with the advantage that it is cost effective and can therefore be used in widespread industrial applications. The problem is that it is prone to sintering and carbon deposition at high temperatures, which leads to a significant reduction in its surface area as a catalyst and ultimately to its deactivation. To avoid this, efforts are being made to improve its surface properties and modulate its crystalline structure, for example, by doping it with metallic Ce particles. Nickel at the heterogeneous interface passes through different forms, such as oxides and C-Ni compounds, while Ce induces the precipitation of nickel grains on the support, allowing the CO_2-CH_4 reforming process in a multi-stage reaction where the thermodynamic barrier is broken and multicarbon coupling is favoured. In this work, the $Ce_xNi_y/\gamma Al_2O_3$ based catalyst is subjected to a modification process resulting in a large amount of Ce^{3+} that turns into Ce^{4+} and vice versa on the surface, which promotes internal electronic interaction processes and favours the reaction of interest

(the CO_2 conversion rate achieved is 81.69%). In addition, it gives the catalyst a high oxygen storage capacity (provides oxygen vacancies) and improves methane adsorption for the multi-step reaction, controls surface properties (Ce forms soluble complexes with CO, which improves the removal rate of C deposited on the metal active sites, reduces poisoning, thus extending catalyst life, and increases the surface area between the catalyst and the reactants) and inhibits side reactions. Additionally, during the preparation of the catalyst, an alkaline environment is created which favours the adsorption and location of CO_2 on the active sites.

The reactions that occur on the catalyst do so at 800 °C with a Ni/Ce molar ratio of 0.2 and are as shown below:

$$NiO + 2CO_2 \rightleftharpoons CO + NiCx + 2O_2 \quad (1)$$

$$O_2 + CH_4 + NIC_x \rightleftharpoons 2CO + Ni + 2H_2 \quad (2)$$

$$O_2 + 2Ni \rightleftharpoons 2NiO \quad (3)$$

Among the equipment and techniques that can be used for the characterization of the catalyst, before and after the reaction, are an X-ray diffractometer, a Raman imaging microscope (to evaluate the type and quantity of carbon deposited) and an automatic surface porosity analyser where a N_2 adsorption and desorption test is applied to measure the surface areas, porosity and size distribution and pore volume. The microstructure of the catalyst is measured by SEM microscopy; the type and content of the elements that make up the catalyst is measured by elemental analysis; and finally, a thermogravimetric analysis is performed to evaluate the weight change in the operating temperature range (30 °C to 800 °C) [24].

4.2. Carbon Dioxide Methanation

Another method that could alleviate the pressure caused by the effect of CO_2 and the energy deficit is its transformation into methane, since the latter has a good energy storage capacity due to its high calorific value (energy contained in a fuel per unit of mass). The objective of the method described here is not to emit methane into the atmosphere because, as indicated before, this is another important greenhouse gas, but to be able to capture it and use it at the place of its production, achieving economic benefits and improvements in its production since costs associated with compression and transportation are saved. Methane is a very important gas for industry, transportation and as an energy source [25]. In addition, with existing infrastructure, it can be easily liquefied for safe storage in large quantities.

The key to this process is to find materials that fulfil both functions, that is, that are able to adsorb, desorb and convert CO_2 into usable substances in situ. Some studies have even achieved methane selectivity close to 100%, with the yield being limited mainly by the amount of adsorbed CO_2 [7]. The mechanism of methanation is not well known, and several variables can play a role, such as the type of catalyst (key variable), additives, carrier, temperature and grain size. However, this can be reduced to the exothermic reaction shown below:

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \quad (4)$$

The previous reaction is favoured at low temperatures, but the problem is that the conversion rate is reduced. It is important to clarify that a secondary reaction can also occur that is favoured at higher temperatures since it is endothermic, as shown below:

$$CO_2 + H_2 \rightarrow CO + H_2O \quad (5)$$

CO_2 methanation can be carried out by thermal catalytic, photocatalytic, electrocatalytic or bioconversion techniques. Among the catalysts currently used for thermal catalysis are Ni/ZrO_2, Ni/γ-Al_2O_3 and Ni/CeO_2 with different doses of Ni. Metal oxides (low cost and readily available), metal-organic frameworks (MOF), zeolites and porous carbon supported on metal/metal oxide are used as catalyst carriers. These showed their best performance in the conversion of CO_2 at approximately 300 °C, with conversion rates higher than 90%, while at low temperatures, the catalyst was deactivated.

Photocatalytic methanation uses H_2O, H_2 and solar energy to reduce CO_2 to CH_4 in the presence of a catalyst at room temperature and atmospheric pressure. The advantages of the process are several, since it does not require secondary energy input, alleviates energy shortages by converting CO_2 into high value-added fuels and chemicals with the help of natural resources, and removes gaseous and liquid pollutants, which relieves pressure and limits ecological damage. Factors affecting the process efficiency include light intensity, wavelength, and the ability to adjust the semiconductor band gap to improve conversion efficiency. Metal-organic frameworks (MOFs), covalent organic frameworks (COFs), and noble metal-based catalysts such as copper, TiO_2, C_3N_4, or metal sulphide can be used as catalysts.

On the other hand, bioconversion uses biological strains as catalysts for the conversion of CO_2 to methane, which can operate under aerobic or anaerobic conditions. However, this technique, despite being environmentally friendly, requiring low costs and low operating costs, has two problems that need to be overcome: the first is the low conversion rate compared to thermocatalytic and electrocatalytic techniques, and the second is that it does not have a good continuous CO_2 conversion capacity, making it difficult to meet the conversion demand. To overcome this, it has been thought of modifying eutotrophic photosynthetic microorganisms to achieve better results.

Finally, electrocatalysis convertgs CO_2 into high value-added fuels by reduction (CO_2RR) with the help of catalysts and electricity. The operating conditions are mild and can be controlled relatively easily. In addition, the conversion rate in high. The problem is that it has low selectivity and produces overpotential. Among the advantages of this process are that it is clean and efficient, and it also helps to solve two problems at once, the energy and the environmental. The most commonly used catalysts are metallic catalysts, metallo-organic skeletons and carbon-based catalysts.

4.3. Conversion of Carbon Dioxide and Methane to 2C Oxygenated Compounds Under Medium Conditions

The conversion of CO_2 and CH_4 to compounds such as CH_3COOH and CH_3CH_2OH, among other 2C substances, is also possible [2]. These transformation methods not only reduce pollution and are 100% environmentally friendly, but also promote the production of value-added substances. For example, the acetic acid produced can be used in various industries for the manufacture of chemicals such as alkyl acetate, vinyl acetate, acetic anhydride, cellulose acetate, chloroacetic acid, plastics, dyes, insecticides and rubber, among others. In the pharmaceutical industry, it can be used for the production of vitamins, antibiotics and hormones, and in the food industry for the production of food additives [26]. On the other hand, ethanol has been used as a fuel mixed with gasoline [27], to produce acetaldehyde [28], as a solvent and for alcoholic beverages, among others.

In order to produce any compound from CO_2 and CH_4, it is necessary to break several thermodynamic barriers, since the C=O and C–H bonds are very stable not only because of the type of bond, but also because of the molecular structures of which they are part. Various catalysts and different processes have been used in this path to be able to use them. For example, thermal and non-thermal catalysis can be performed. In the first case, the catalysts used are zeolites with metal exchange capacity and transition metal oxides. In

addition, this technique has advanced technology to identify the active sites of the catalyst, but the process normally requires high temperature and pressure conditions which cause the deactivation of the catalyst by coke deposition, so the conversion and selectivity are low. Meanwhile, catalysis at mild temperature and pressure conditions (close to ambient) can be carried out by using a hybrid plasma catalytic system, where the catalyst is generally designed from known thermal catalysts, or the process can be carried out even without a catalyst. Plasma is generated by applying an external electric field that produces a variety of active species (high chemical reactivity) including ions, electrons and free radicals; however, the mechanism of action is still unclear, and results are generally obtained by trial and error. Among the challenges of this technique are increasing the selectivity for the production of oxygenated products 2Cto a value higher than 15%, since synthesis gas, hydrocarbons and various types of oxygen are also produced. The highest conversion rates achieved with this last technique, without using a catalyst, are 64.3% for CH_4 and 43.1% for CO_2, at 60 °C and atmospheric pressure, the product mainly obtained being CH_3COOH. With Ag/Al_2O_3 or Pd/Al_2O_3 catalysts at 3%, the conversion rate is 50.9% for CH_4 and 28.1% for CO_2, with CH_3CH_2OH being the product mainly obtained.

4.4. Conversion of CO_2 and CH_4 by Thermal Reforming for Fuel Production

The conversion of carbon dioxide and methane to fuel can be achieved through the Fisher–Tropsch process. There are several methods to carry out this process; among the most prominent are co-electrolysis with high-temperature solid oxide cells to obtain synthesis gas ($CO + H_2$), which is then converted to liquid fuel through the Fisher–Tropsch process with an efficiency of 54.8%. Another method consists of capturing CO_2 with Ca at high temperature. Using this method, CO_2 is displaced from water through a reverse reaction, and then it is converted into synthesis gas, which in turn can be converted into liquid fuel. The problem with these methods is that they require a lot of energy and also produce emissions. An alternative method for producing liquid fuels is through chemical loop combustion (CLC) with oxygen carriers, which allows the gradual use of energy, reducing its losses compared to the previous process. However, this technique also produces some impurities which can also deactivate the catalysts, and the C to H ratio may not meet the required proportion, so a further improvement proposed to the method is to adjust the syngas ratio by a cyclic methane reforming process with CO, which maximizes the use of carbon sources and reduces greenhouse gas emissions; this last process is called Carbon Circulation Reforming (CCR). The complete process, called the CLC-CCR process, has a conversion efficiency of 53.10%, while that of the CCR process is 50.69%. Furthermore, it is also more economical since it reduces costs by 9.21%, generates 21.51% less CO_2 emissions and consumes 7.74% less energy [1].

A complete CCR system consists of multiple subunits, including a reforming unit, a combustion unit, a steam conversion unit, a Fischer–Tropsch synthesis unit, and rectification unit. In this process, CO_2 and CH_4 are fed in a 1:1 ratio, and the mixture is compressed to 0.5 MPa and preheated to 500 °C, then passed to the reforming reactor, where the pressure is maintained but the temperature is increased to 980 °C, obtaining the synthesis gas (Equation (6)).

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \quad \Delta H = 247.31\ kJ{\cdot}mol^{-1} \tag{6}$$

The syngas is then cooled in a heat exchanger to 130 °C, afterwards with air to 25 °C and subsequently transformed into liquid fuel by the Fisher–Tropsch process, which contributes to alleviating fuel shortages [29].

$$CO + 2H_2 \rightleftharpoons (\text{-}CH_2\text{-}) + 2H_2O \quad \Delta H = -165\ kJ{\cdot}mol^{-1} \tag{7}$$

4.5. Reduction of CO_2 Through Synergy with the Purification of Valuable Metals

To recover lithium from used batteries, which is very valuable for its properties but also known for its scarcity, as well as to recover Al and transition metals, which are valued in industry, such as Ni and Co, which are used as cathodes in batteries, these recycled metals are reacted in a CO_2 atmosphere to produce Li_2CO_3 and nickel and cobalt oxides. This process has low emissions, consumes CO_2 and at the same time helps to solve the problems of resource scarcity (the composition of a 20 g spent cathode is 5.93% Li, 26.07% Ni, 9.79% Co, 14.55% Mn, 10.71% Al and 1.82% C). The materials do not require prior classification, only to be disassembled because their reactivity is what distinguishes them. The process is carried out in a reductive roasting process at 650 °C for 1 h, where Al at the cathode is the reducing agent. The roasted product is then leached with carbonated water, allowing the recovery of 91.4% of Li (the product thus obtained contains less than 0.1% Al and transition metals). Metals such as Al and Ni are subsequently leached with basic and acid solutions, with recovery rates of 98% and 99%, respectively, as well as other metals such as Co and Mn. This method has additional advantages to those mentioned above. Among them, it is simple, cost-effective and can be easily adapted. Several possible reactions have been proposed that can take place at the cathode in the presence of a CO_2 atmosphere; some of them are as follows [30]:

$$Al + \frac{3}{2}CO_2 \rightarrow \frac{1}{2}Al_2O_3 + \frac{3}{2}CO \quad (8)$$

$$LiNi_{0.5}Co_{0.2}Mn_{0.3}O_2 + \frac{2}{15}CO \rightarrow \frac{1}{2}Li_2O + \frac{2}{15}CO_2 + \frac{1}{2}NiO + \frac{1}{15}Co_3O_4 + \frac{3}{10}MnO_2 \quad (9)$$

$$Co_3O_4 + CO \rightarrow 3CoO + CO_2 \quad (10)$$

$$MnO_2 + CO \rightarrow MnO + CO_2 \quad (11)$$

$$Li_2O + CO_2 \rightarrow Li_2CO_3 \quad (12)$$

4.6. CO_2 Capture and Transformation Methods with Dipolar Membranes

Carbon capture, utilization and storage (CCUS) by electrochemical methods is very effective in reducing greenhouse gases while producing high value-added products. This technique is environmentally friendly and has flexible operating processes. To carry out these processes, electrochemical devices, called bipolar membranes (BPMs), are normally used, facilitating the CO_2 reduction process. CO_2 capture is performed through acid–base pH oscillations. First, CO_2 is captured in an alkaline environment in BPMs, and then it is converted to carbonate/bicarbonate that can be stored. As more CO_2 is captured, the pH decreases, and its desorption can be carried out under these acidic conditions. Then, electrocatalysis is carried out with transition metals (Zn, Cu and Ni) within a simple electrode. The water dissociation mechanism is key in the capture process, and this, in turn, is essential to optimize the operating conditions, capture and transformation of CO_2. The process is isothermal and does not require external temperature and pressure conditions, thus reducing energy demand and process cost. The bipolar membrane is a type of ion exchange membrane that has an anion exchange layer, a cation layer and a final catalytic layer with metal, i.e., $Al(OH)_3$. When the BPM is charged, the water molecules are dissociated by means of electrolysis, and OH- and H^+ are generated; then, a potential difference is created that leads the H^+ to the cathode through the cation exchange layer, while the OH- is conducted to the anode through the anion exchange layer. The H^+ thus produced has a high reducing power, so it reduces CO_2 through a complex process of multiple charge transfer reactions involving between two and 18 electrons. Among the products are CH_4, HCOOH, CH_3OH, C_2H_4, C_2H_5OH, C_2H_6, CH_3COOH, CH_3COOH,

CH_3CHO, C_2H_5CHO and C_3HOH. Electrochemical processes offer several advantages: one being that they are not limited to capture only at CO_2 generation sites, but can also be applied to the capture and transformation of carbonate from oceans, air and gaseous and liquid waste. On the other hand, electrochemical processes have a modular nature that can offer multiple types of battery cells, which translates into low material costs for interconnection, diffusion layers and catalytic layers. Finally, BPMs have good efficiency and can be carried out in small areas and scaled up as needed. However, they also have some disadvantages, for example, commercial ones form blisters, delaminate easily and have high resistance due to thick layers, although they can be made thinner, which improves conductivity and selectivity and reduces delamination [5].

5. Macrocyclic Systems Used for CO_2 Fixation and Transformation

As is well known, macrocyclic compounds have gained much interest in recent decades for their applications in various areas, mainly due to their ability to generate host–guest interactions with different types of ions and molecules. In the specialized literature, there are various macrocyclic systems that can be used for carbon dioxide fixation and also for its transformation. In this context, the most commonly used macrocyclic systems are discussed below (Figure 3).

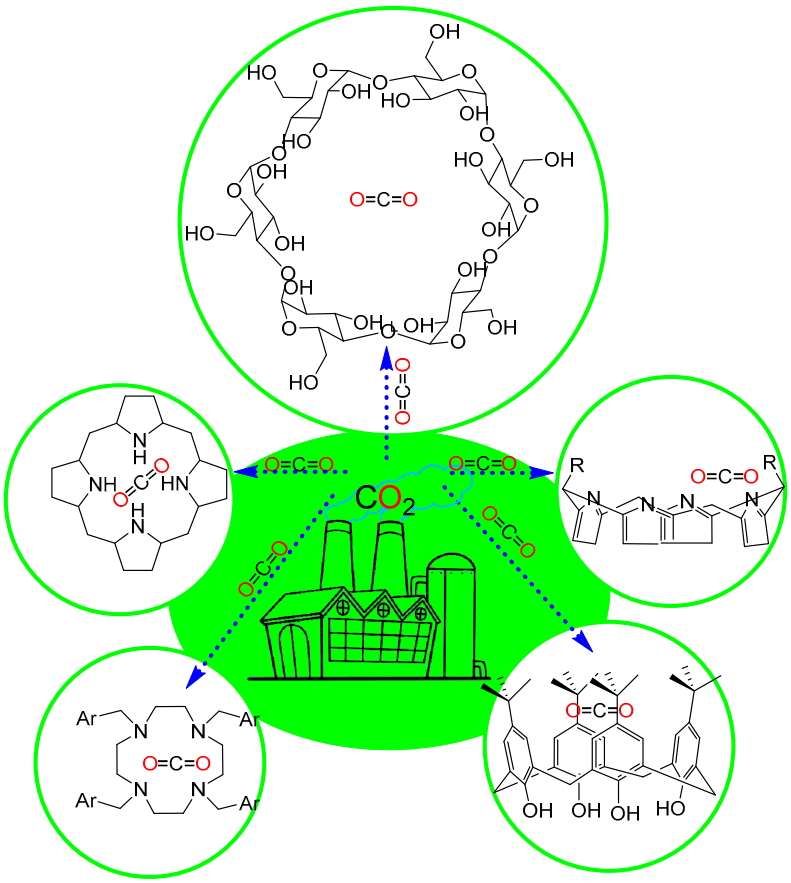


Figure 3. Some macrocyclic systems used in carbon dioxide fixation.

5.1. Cyclodextrins

Cyclodextrins (CDs), first isolated in 1891 by Villiers [31], are cyclic oligomers composed of glucopyranose units interconnected by 1,4 glycosidic bonds. Among the most frequently found CDs are alfa-, beta- and gamma-cyclodextrins (Figure 4), consisting of six, seven and eight glucose units, respectively [32].

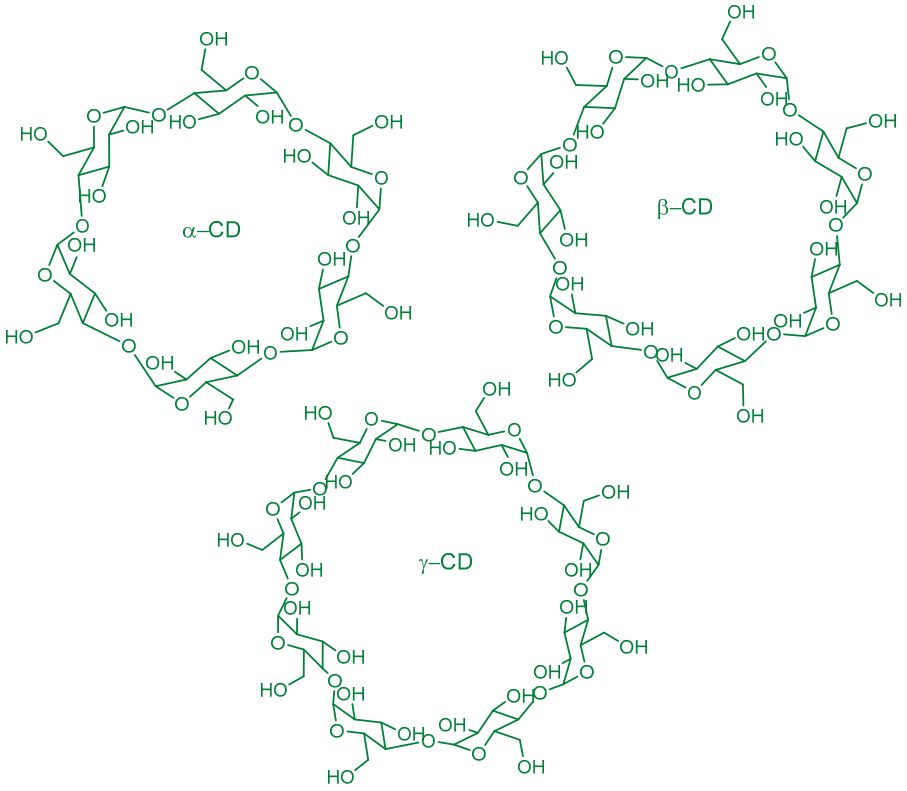


Figure 4. Alpha-, beta- and gamma-cyclodextrins.

Due to their structural characteristics, they have an amphiphilic character that allows interactions with different molecules of interest: the hydrophobic cavity allows the formation of supramolecular structures of the host–guest type through non-covalent interactions, and the hydrophilic outer surface allows interaction with polar compounds, allowing their dissolution in aqueous systems. Their solubility in water results from the ability of the free hydroxyl groups to interact with the aqueous medium [33].

In addition to this unique "microenvironment", CDs exhibit high reactivity as a consequence of the hydroxyl groups being protonated or tosylated, and easily participate in substitution or elimination reactions, which facilitates the occurrence of copolymerization reactions directly with monomers selected to form lattice structures, or the insertion of organic or inorganic materials [34]. It should also be noted that this characteristic also allows its functionalization, and more than 11,000 CD derivatives have already been reported in the literature [35,36].

In recent years, several CD derivatives have been developed in order to extend the physicochemical properties and complexation capacities. The vast majority of modified CDs result from natural β-CD. By introducing functional groups at the level of the hydroxyl groups of CDs, it is possible to change their complexation capacity, as well as considerably increase their solubility [36]. All the factors mentioned above underlie the ability of CDs to interact with a large number of compounds, namely antibiotics, surfactants, organic pollutants, dyes and metal ions, among others [37], making their application in different areas quite comprehensive [38]. For example, in the pharmaceutical industry, CDs have been used in medicines, either for complexation or as auxiliary additives, solubilizers, diluents or as tablet ingredients, to improve the physical and chemical properties or to increase the bioavailability of poorly soluble medicines. In the chemical industry, CDs and their derivatives are used as catalysts to improve the selectivity of reactions, as well as for the separation and purification of products on an industrial scale. In the food, cosmetics, and hygiene product industries, CDs have been widely used for the stabilization of flavours

and fragrances or for the removal of unwanted flavours, microbiological contaminations, and other unwanted compounds [35]. In summary, CDs have shown great promise as potential hosts with specific properties and functions.

The supramolecular chemistry principles, such as the formation of host–guest complexes, have also been applied to improve carbon dioxide (CO_2) retention capabilities. In fact, relevant results have already been obtained on the encapsulation and complexation of CO_2 by using these macrocycles as a host. As examples, we can mention that β-cyclodextrin (β-CD) forms cyclodextrin-based nanosponges capable of capturing CO_2 gas [39], and other modified CDs at their hydroxyl groups (e.g., the primary face of β-CD was functionalized with an amino group showing excellent CO_2/N_2 adsorption) [40].

Other authors [41–43] have focused on obtaining new amide-type macrocycles, revealing that they are highly efficient materials for CO_2 capture. More recently, Patamia et al. [44] adopted a new strategy that uses dimethylcarbamoyl chloride to carry out a simple and rapid functionalization of some CDs (-α, β-, and γ-CD) and to obtain new amide-type derivative macrocycles and test them for CO_2 capture. This strategy is advantageous because it avoids the long synthesis and separation processes used to date to prepare this type of material. Among the different macrocycles produced, the functionalized α-CD has been proven to be the most efficient.

Ho et al. [45] have conducted a comprehensive review of the studies on gas encapsulation using CD powders. In this review paper, the description of the amorphization of CD powders by spray drying, the properties of amorphous CD powders in comparison to their crystalline counterparts, gas encapsulation using amorphous CD powders, and the applications of gas-CD powders in food and agriculture production are reported. It is shown that α-, β- and γ-CD powders, whose structures are completely amorphous, can be used to develop an innovative approach for molecular encapsulation of gases (e.g., CO_2), which is a simple and fast process. Although further research on the production of gaseous powders is imperative (e.g., possible modification of the chemical and molecular structure of CD molecules in order to increase the encapsulation capacity and to expand the ability of CD powders to encapsulate many other types of functional gases), all of these findings are highly relevant.

In another recent study presented by Jessen et al. [46], CDs have also been studied as potential CO_2 capture agents. From the analysis of their results, it was found that the crystal structure of α-cyclodextrin with CO_2 has a 1:1 stoichiometry and that a number of simple and modified cyclodextrins bind CO_2 in water with a kg of 0.18–1.2 bar^{-1} (7–35 M^{-1}) with α-cyclodextrin modified by O-methyl having the highest affinity for CO_2. It should be noted that, according to the authors, that affinity between CO_2 and CDs can be improved with a smaller cavity and a more lipophilic derivative of cyclodextrin.

In summary, the articles consulted on the use of cyclodextrins in carbon dioxide adsorption experiments revealed that functionalized cyclodextrins have an adsorption capacity similar to that of BEA zeolite, a material currently used in industry for gas adsorption. Furthermore, these adsorption properties could also be exploited to improve the adsorption capacity of drugs, a field in which cyclodextrins are widely used. Carbamoyl-functionalized cyclodextrins were synthesized to improve the ability of CDs to absorb CO_2. α-, β- and γ-CD were functionalized with an amide group to increase CO_2 retention of the macrocycle. Among the different macrocycles produced, the α-CD functionalized material has proven to be the most efficient. Carbon dioxide adsorption experiments showed that functionalized α-CD has an adsorption capacity similar to BEA zeolite. Gas encapsulation using amorphous CD powders should focus on increasing the encapsulation capacity of CD powders so that gas powders can achieve the same degree of utility as those coming from pressurized cylinders or tanks.

Modifying the chemical and molecular structure of CD molecules will likely increase encapsulation capacity and expand the ability of CD powders to encapsulate many other types of functional gases.

5.2. Porphyrins

Porphyrins (Figure 5) are a family of host macrocycles with four pyrrole units connected by methine bridges. The central cavity plays a crucial role in the process of complex formation with various cations. Porphyrins are widely used for catalysis in various processes and in medicinal chemistry and chemical sensors, among other applications. Additionally, porphyrins can be functionalized in various positions, which allows changing their chemical reactivity, expanding their applications in various fields and enhancing their activity as catalysts. The planar structure of porphyrins and their ability to coordinate metal cations in their central cavity, electron-rich from pyrrolidine nitrogens, allows the formation of metal complexes with great applicability. In this context, metalloporphyrins have been used as catalysts for various organic reactions such as intramolecular cyclopropanations, carbene carbonylation and intramolecular Buchner reactions, among others [47–51].

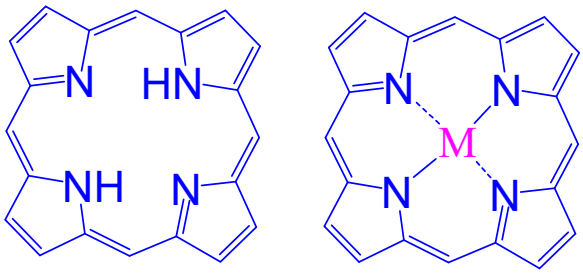


Figure 5. Structure of porphyrins and metalloporphyrins.

There are several articles in the literature on the use of porphyrins in the fixation and transformation of carbon dioxide. An interesting example was reported by Zhang et al. [51]. In that article, the authors developed a gas–solid interface for the reduction of atmospheric carbon dioxide, using a Cu-porphyrin-based catalyst. The catalyst, which includes other components such as titanium oxide, showed an increase in photothermal catalytic efficiency in the transformation of CO_2. The use of this metalloprophyrin-modified catalyst suggests a simple method of capturing and transforming carbon dioxide. Wang et al. [52] discussed the obtention of two zinc(II) porphyrin-modified organic polymers which were synthesized via the free-radical copolymerization of flexible 1,4-butanediol diacrylate (BDDA) with these metalloporphyrins. The organic polymers thus obtained presented two active sites (Zn^{2+} and I^-), showing a high efficiency in carbon dioxide fixation. Moreover, it was noted that one of the modified polymers obtained presented a great catalytic capacity for the cycloaddition of carbon dioxide with different epoxides towards the formation of cyclic carbonates. Finally, the authors highlighted the great stability of these materials in their use and the relatively low activation energy required for the fixation and transformation of carbon dioxide.

Another example of using metalloporphyrins as polymer modifiers for CO_2 fixation and transformation was reported by Youm et al. [53]. In this work, the authors reported the synthesis of three porphyrin-based azo-porous organic polymers which have the ability to capture and convert carbon dioxide in a single step. The last stage of conversion is performed with styrene oxide and phenyl glycidyl ether in the presence of tetra-n-butylammonium bromide as a co-catalyst. Using metal-organic frameworks, Tayebi et al. [54] examined the catalytic cycloaddition of CO_2 with epoxides to produce cyclic carbonates. The authors reported the use of porphyric MOFs as catalytic platforms for

efficient fixation and conversion of carbon dioxide. The reaction with epoxy compounds occurs under solvent-free conditions at room temperature, and the formed cyclic carbonates are obtained in good yields.

Bai et al. [55] also investigated the immobilization of Zn-metalloporphyrin on carbon nanotubes using a simple one-pot method. The obtained composite material exhibited high stability and a great ability to fix and transform carbon dioxide into cyclic carbonate derivatives. Another research work with metalloporphyrins has been reported by Nagaraja et al. [56]. These authors reported obtaining a Mg-centred porphyrin-based metal-organic framework, which exhibited good carbon dioxide fixation. Another relevant aspect of that research was the ability of these derivatives to catalyse the cycloaddition reaction between CO_2 and epoxides under visible light irradiation. In the process, the catalytic activity was attributed to the Mg-porphyrin unit, which decreases the activation barrier in the cycloaddition process.

In this context, porphyrins offer a wide range of possibilities in the fixation and transformation of carbon dioxide because porphyrins are highly sensitive to light, it is possible to manufacture a series of metal-organic structures, PMOFs, for fixation of CO_2 and its transformation into cyclic carbonates driven by sunlight. This technique is especially important since the reaction conditions are solvent-free, and the process is carried out at atmospheric pressure and at room temperature, so it does not need additional energy other than that provided by the sun's rays. This radiation generates electrons in the semiconductor that are capable of activating CO_2 in such a way that it can participate in an epoxide cycloaddition reaction to give rise to cyclic carbonates with maximum reaction times of 7 h, achieving a yield greater than 99%. The different metal-organic structures (PMOFs) constructed are based on a three-layered columnar porphyrin with double impenetrated network configurations known as Co-PMOFs, which contain pores that allow absorption of CO_2 and catalytically active centres for its transformation. Therefore, the use of porphyrins is an important way to achieve the capture and transformation of CO_2 and the reduction of its emissions (Figure 6).

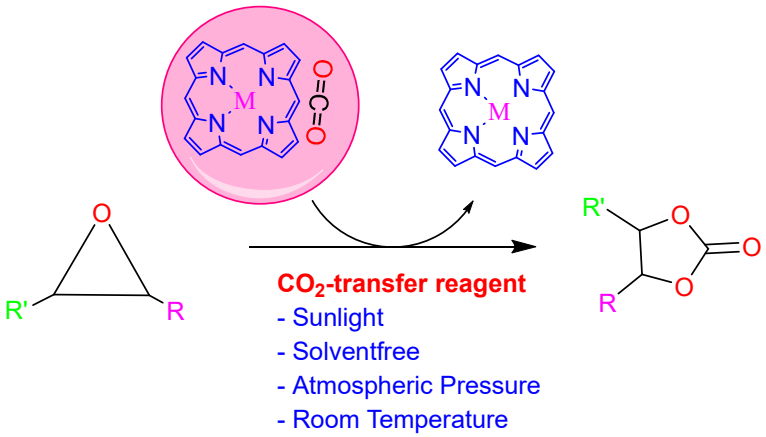


Figure 6. Participation of metallo-porphyrins in CO_2 transformation.

5.3. Calyxarenes

Calixarenes are a family of macrocyclic substances with many applications in various areas of knowledge. These polyhydroxylated platforms are characterized by having a cavity that allows them to interact with ions and neutral molecules [57–59]. As shown in Figure 7, the family of calixarenes, resorcinarenes or pyrogalloarenes can act as receptors depending on their structural properties [19,60,61]. Due to their multiple functionalization possibilities, these macrocyclic systems can be modulated in terms of interactions and

cavity extension. In this section, we discuss the use of these macrocyclic systems in the interaction and transformation of carbon dioxide.

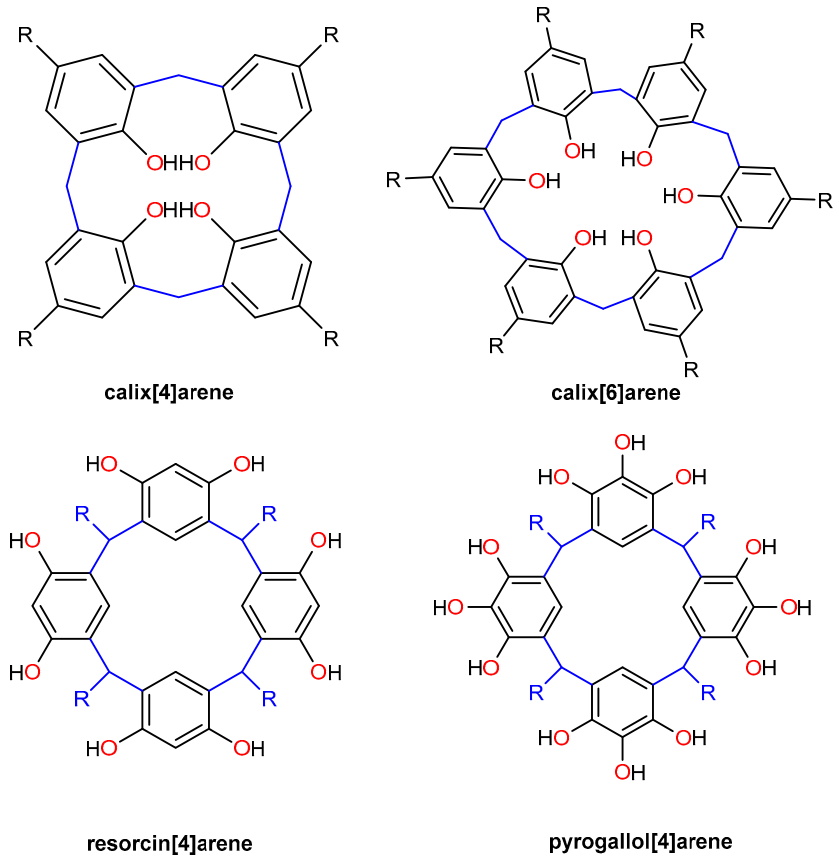


Figure 7. Structure of calixarenes, resorcinarenes and pyrogallolarenes.

A first example of the use of these platforms in the fixation and transformation of CO_2 is found in the work of Fisher et al. [62]. In this article, the authors show the reaction between tert-butylcalix[4]arene and crown ethers to form a complex macrocyclic system, characterized by presenting an Na_6O_6 skeleton consisting of two fused open heterocubanes. Two Na^+ ions are encapsulated in the cavities of the calix[4]arene units. An interesting aspect presented by some of these systems is related to their capacity to absorb carbon dioxide in THF, and they are active reagents for transferring CO_2 to 2-fluoropropiophenone. The authors highlighted the importance of the subtle influence of the structure of the alkali metal complexes on the CO_2 reactivity in these type of complexes. Hou et al. characterized and examined the use of tert-butylcalix[6]arene in the construction of polynuclear metal clusters, specifically in titanium-oxo clusters (TOCs). These authors highlight that this type of cluster exhibits a high carbon dioxide fixation capacity and a superior catalytic activity due to the presence of more metal catalytic sites. Finally, the article highlights the importance of the use of tert-butylcalix[6]arene in the flexibility, stability and high nuclearity of TOCs [63].

Recently, resorcinarenes have also been characterized for their use in carbon dioxide fixation and transformation. In this context, Wang et al. [64] report the obtention of a porous organic cage (POC) based on calix[4]resorcinarenes. An interesting aspect of these materials is that they can crystallize in different types of solvents, generating solvatomorphic materials. These crystallized materials showed a great ability for carbon dioxide sorption, as well as separation abilities. This research suggests the possibility of adjusting gas sorption and separation properties of POC materials by controlling their solvatomorphs. Another example is the research of Guo et al. [65]. This research reports the obtention of a

[Co12] coordination cage based on calix[4]resorcinarenes, assembled with two bowl-shaped calix[4]*resorcinarenes*, 10 angular 1,3-benzenedicarboxylates, and 12 Co(II) cations. This coordination cage based on polynuclear metal clusters exhibits a high capacity for CO_2 conversion with epoxides in efficient cycloaddition processes due to the Lewis acid sites.

According to the above, complexes based on calix[4]arenes or calix[4]resorcinarene have a significant impact on carbon dioxide utilization. We can also highlight the catalytic effect of these complexes in carbon dioxide cycloaddition reactions with epoxides, in particular, the reaction of CO_2 with 2-(Chloromethyl)oxirane where conversions of less than 50% are obtained when using n-Bu4NBr as catalyst. However, if this reaction is carried out with a Tetra(2-(4H-pyrazol-3-yl)pyridine)calix[4]resorcinarene-based [Co_{12}] coordination cage, as cocatalyst, 98% conversion is obtained. Therefore, the high catalytic activity of the complexes based on polyhydroxylated platforms is confirmed. Figure 8 shows some examples of the participation of calixarenes in the capture and transformation of carbon dioxide.

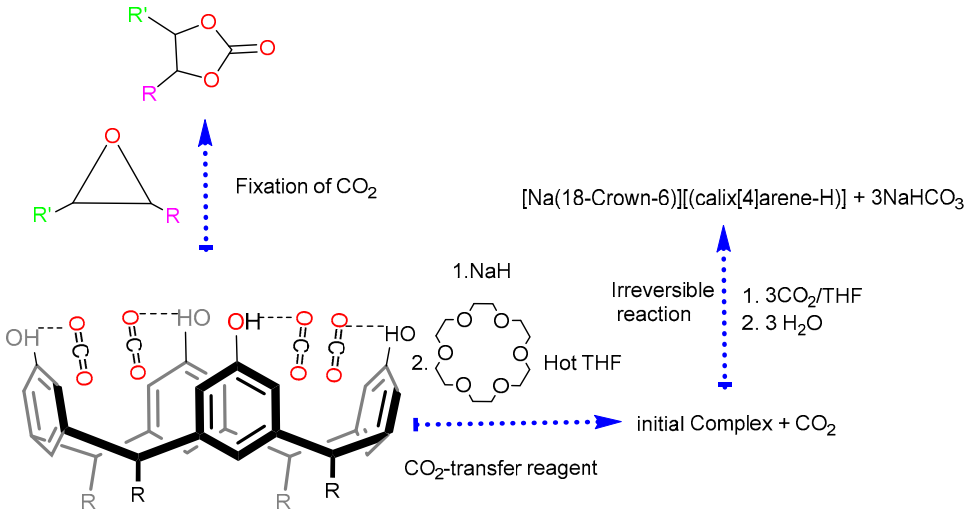


Figure 8. Participation of calixarene-type systems in CO_2 transformation.

5.4. Other Macrocyclic Systems

In recent decades, other types of macrocyclic systems have been evaluated for carbon dioxide fixation and transformation. An early work to cite is the one published by He [66], in which the use of calix[4]pyrrole for carbon dioxide fixation is presented. Specifically, with the meso-bis(benzimidazolium)calix[4]pyrrole derivative, carbon dioxide can be fixed on the upper rim of the macrocycle cavity and form carbonate esters. The process occurs under room temperature and neutral pH conditions. Also, Stackhouse and Ma examined the use of azamacrocycles in the incorporation of MOFs, and evaluated the use of carbon dioxide fixation in these frameworks [67]. The authors highlight the high absorption capacity of these azamacrocyclic-based metal-organic frameworks at one atmosphere of pressure and at room temperature conditions; additionally, they suggest a high selectivity for the CO_2 molecule.

Table 1 below shows a summary of the most relevant aspects of the interaction of macrocycles with carbon dioxide.

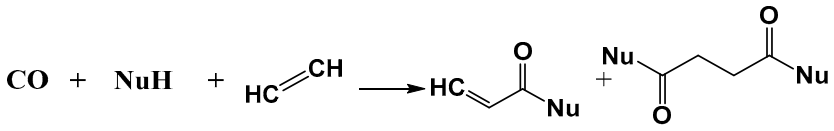
Table 1. Main macrocycles used in the interaction with carbon dioxide.

Macrocycle	Interaction/Transformation with CO_2	Ref.
Cyclodextrins (CDs)	They have been used as hosts for CO_2 encapsulation and complexation: ♣ In the modified CDs at their hydroxyl groups, the primary face of β-CD was functionalized with an amino group, showing excellent CO_2 adsorption. ♣ β-cyclodextrin (β-CD), which forms nanosponges capable of capturing CO_2 gas. ♣ CDs have also been studied as potential CO_2 capture agents. From the analysis of their results, it was found that the crystal structure of α-cyclodextrin with CO_2 has a 1:1 stoichiometry and that several simple and modified cyclodextrins bind CO_2 in water. That affinity between CO_2 and CDs can be improved with a smaller cavity and a more lipophilic derivative of cyclodextrin.	[39] [40] [46]
Porphyrins	The use of porphyrins in the transformation of carbon dioxide has been researched: ♣ Development of a gas–solid interface for the reduction of atmospheric carbon dioxide, using a Cu-porphyrin-based catalyst. ♣ The obtention of two zinc(II) *porphyrin*-modified organic polymers which were synthesized via the free-radical copolymerization of flexible 1,4-butanediol diacrylate (BDDA) with these metalloporphyrins, showing a high efficiency in carbon dioxide fixation. ♣ Using metalloporphyrins as polymer modifiers for CO_2 fixation and transformation, with the synthesis of three *porphyrin*-based azo-porous organic polymers that have the ability to capture and convert carbon dioxide in a single step.	[51] [52] [54]
Calyxarenes	The use of these macrocyclic systems in the interaction and transformation of carbon dioxide is becoming increasingly relevant: ♣ The reaction between tert-butylcalix[4]arene and crown ethers to form a complex macrocyclic system, characterized by presenting an Na_6O_6 skeleton. An interesting aspect presented by some of these systems is related to their capacity to absorb carbon dioxide in THF. ♣ The obtention of a porous organic cage (POC) based on calix[4]resorcinarenes. An interesting aspect of these materials is that they can crystallize in different types of solvents, generating solvatomorphic materials. These crystallized materials showed a great ability for carbon dioxide sorption, as well as separation abilities. ♣ The obtention of a [Co12] coordination cage based on calix[4]resorcinarenes, assembled with two bowl-shaped calix[4]*resorcinarenes*. This coordination cage based on polynuclear metal clusters exhibits a high capacity for CO_2 conversion with epoxides in efficient cycloaddition processes.	[62] [64] [65]

6. New Approach to Reducing CO_2 in the Atmosphere by the Management of Fossil Fuel Reaction Conditions

Complete combustion of gasoline occurs with excess oxygen and generates CO_2 and H_2O, while incomplete combustion occurs when there is little oxygen and produces CO, C and water. The first reaction produces more energy, so it is used, among other things, for the transportation of people and goods in general, while incomplete combustion produces 55.7% of the previous reaction [68]. The main source of carbon monoxide comes not only from gasoline, but also from gas stoves, heating systems, garbage incineration, coal-fired power plants, boilers and biomass combustion, among others. Carbon dioxide is not a toxic gas in normal concentrations, while carbon monoxide is a toxic gas to people and animals. In the blood, it displaces the oxygen carried by haemoglobin, so the oxygen cannot reach the cells, and people die from asphyxiation, presenting initial symptoms such as headache, nausea, vomiting, dizziness and weakness, and then alterations in the level of consciousness, behavioural alterations, convulsions, dyspnoea and respiratory failure, among others. However, not everything is negative with CO, as has been demonstrated

throughout this work, since carbon monoxide, unlike CO_2, is a very reactive molecule capable of reacting vigorously with acetylene in carbonylation reactions, with easily accessible nucleophiles and Ni-based catalysts, such as $Ni(CO)_4$, nickel halides or acetates, among others (Equation (13)), to produce acrylic acid, methyl acrylate, and dimethyl succinate, which are substances used in the textile industry and in industrial polymers among others, whose global demand is around 10 millions tons per year [69].



(13)

It also reacts with oxygen to produce CO_2 with CuO_x/MnO_2 catalysts, with a conversion rate of 96% at 150 °C [70]:

$$2CO + O_2 \rightarrow 2CO_2 \quad (14)$$

with chlorine to produce phosgene, in the presence of activated carbon catalysts, which is used in industry to produce polyurethanes, polycarbonates, pharmaceuticals and agrochemicals [71].

$$CO\ (g) + Cl_2\ (g) \rightarrow COCl_2\ (g) \quad (15)$$

This reaction is strongly exothermic ($\Delta H = -107.6\ kJ \cdot mol^{-1}$) with nitrous oxides [72].

$$NO_2\ (g) + CO\ (g) \rightarrow NO\ (g) + CO_2\ (g) \quad (16)$$

With hydrogen, the product is a mixture called synthesis gas because it is used for the production of synthetic natural gas and is obtained through a methanation process [73]. Synthesis gas also allows obtaining liquid hydrocarbons through the Fischer–Tropsch process [74] (Figure 9). Additionally, methanol can be obtained, which in turn is an intermediate in the production of acetic acid, ethanol, formaldehyde, kerosene [75] and aldehydes and ketones [76], among others.

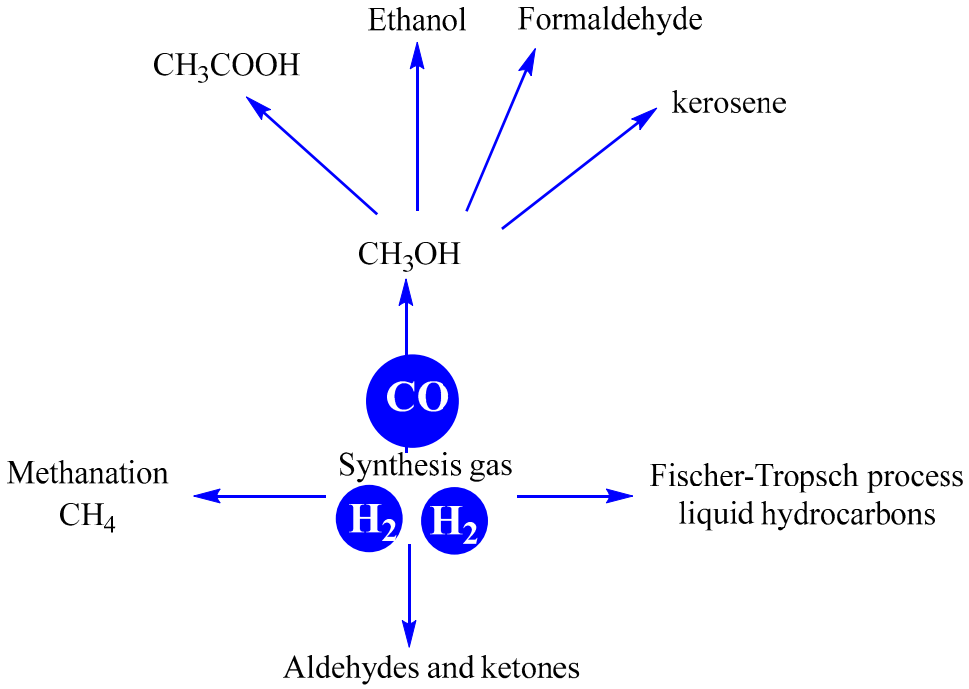


Figure 9. Synthesis gas and Fisher–Tropsch process.

Due to the aforementioned, the proposal that is intended to be made in this work is to study the possibility of modifying the combustion reaction conditions inside motor vehicles in such a way that they favour the production of CO and not CO_2. This process would have to be achieved by paying special attention to the prevention of carbon monoxide leaks because, as indicated before, this is a toxic gas. The advantage is that its handling is well known, so it can be assumed that it is easy to control [77]. The CO production reaction also generates a significant amount of energy, equivalent to 55.7% of complete combustion [68], and if at the engine outlet this energy is mixed with H_2 within a reactor coupled for injection and provided with a cobalt catalyst, the Fischer–Tropsch reaction is expected to occur for the production of synthetic hydrocarbons. This last reaction is exothermic [78] such that the energy produced from incomplete combustion, added to the previous one, serves to start and maintain the motor vehicle in motion. To carry out this work, oxygen consumption inside the engine would have to be regulated to limit it to what is necessary for the production of CO. The presence of limited quantities of O_2 would also help to reduce energy consumption because it would avoid the overheating of gases for the production of CO, and the immediate reaction of the latter, at the same production site, would avoid transport costs and facilitate obtaining value-added products. This would allow the addition, to the process occurring in the engine, of a widely known reaction such as the Fischer–Tropsch reaction, which allows the use of other fuels such as H_2 and, in turn, allows the production of synthetic fuels that can be refined again for use or for the production of other valuable products in the industry. This would reduce CO_2 generation and, at the same time, help solve the fuel shortage expected in the near future (Figure 9).

7. Conclusions

Due to the increase in greenhouse gas emissions that are producing devastating consequences such as climate change, different research works have been generated that have opened routes for the capture and transformation of CO_2, as presented in this article. In the first part, conventional methods are described, and finally, the role of macrocycle systems is highlighted. These have a long career and a positive impact in environmental applications through their molecular interactions. In addition, many researchers have chosen to use macrocycles since they are more environmentally friendly. The macrocycles of interest in these studies usually exhibit a high capacity to fix gaseous substances. The literature on general methods and on the use of cyclodextrins, porphyrins, and calixarenes is presented. Additionally, strategies to incorporate macrocycles in obtaining materials for carbon dioxide fixation and transformation are shown.

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