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The teraton challenge. A review of fixation and transformation of carbon dioxide

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The increase in atmospheric carbon dioxide is linked to climate changes; hence there is an urgent need to reduce the accumulation of CO_2 in the atmosphere. The utilization of CO_2 as a raw material in the synthesis of chemicals and liquid energy carriers offers a way to mitigate the increasing CO_2 buildup. This review covers six important CO_2 transformations namely: chemical transformations, photochemical reductions, chemical and electrochemical reductions, biological conversions, reforming and inorganic transformations. Furthermore, the vast research area of carbon capture and storage is reviewed briefly. This review is intended as an introduction to CO_2, its synthetic reactions and their possible role in future CO_2 mitigation schemes that has to match the scale of man-made CO_2 in the atmosphere, which rapidly approaches 1 teraton.

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Broader context

The level of carbon dioxide in the atmosphere has risen significantly since pre-industrial times and today there is an excess of 1 teraton of carbon dioxide in the atmosphere. The contribution of this extra teraton toward global warming have resulted in a considerable effort towards mitigating carbon dioxide. Various approaches ranging from reduction of emission, a change to renewable energy sources, and methods to safely capture and store carbon dioxide have been investigated. The good news is that there is plenty of space to store captured carbon dioxide and the capacity underground and in the deep sea is vast compared to the problem at hand. The more challenging part of the problem is that the 24 gigaton annual increase in atmospheric carbon dioxide is man-made and unlikely to reduce significantly in the next decades. This naturally raises the problem of how to actively remove carbon dioxide from the atmosphere. Currently the 120 megaton scale at which we are able to industrially convert carbon dioxide is significantly lower than the annual emission. We review the problem of getting a carbon-dioxide-emission-free source of carbon dioxide and try to identify the currently available chemistry that could possibly be upscaled and thus enable handling carbon dioxide on an annual multi gigaton scale such that annual emission can be matched by annual capture and conversion.

1. Introduction

Climate change is considered to be one of the greatest environmental threats of our times.[1] The atmospheric concentration of green house gases can roughly be divided into carbon dioxide (CO_2), nitrous oxide (N_2O), methane (CH_4), fluorocarbons (CFs) and chlorofluorocarbons (CFCs). The atmospheric concentrations of these gases have increased steadily over the past century.[2] Current research shows that there is an excess of approximately 3.9% CO_2 with respect to the natural "carbon cycle". The natural carbon cycle is the carbon-flow between the atmosphere and oceans and the fixation of CO_2 by plants and microorganisms, which is balanced by emission of CO_2 from plants, animals and volcanoes. Human activities therefore produce an annual excess of 3.9% CO_2 to the carbon cycle.[3] The largest source of CO_2 emitters comes from power generation, public electricity and heat production from fossil fuel combustion.

This increase in CO_2 emission, which is not balanced by CO_2 fixation mainly due to deforestation, has resulted in an increase in atmospheric CO_2 during the last 200 years from approximately 270 ppm to 385 ppm. This increase is thought to cause atmospheric warming, due to the prevention of infrared re-emission. The atmospheric warming is associated with a global climate change and a planetary temperature increase.[3] Furthermore, as atmospheric CO_2 increases, the global mean temperature increases, and this will put more water vapor into the atmosphere. Water vapor is also a very effective greenhouse gas and this will increase the earth's temperature even further.[4] The International Panel on Climate Change (IPCC) predicts that, by the year 2100, the atmosphere may contain up to 570 ppm CO_2, causing a rise in the mean global temperature of around 1.9 °C. IPCC predicts that this will give an increase in the mean sea level of up to 1 m by 2100, increased desert formation and the extinction of species.[5]

There is an ongoing research in finding ways to reduce CO_2 emission into the atmosphere and there are, in principle, three possible strategies for reducing the CO_2 buildup in the atmosphere: reduction of the amount of CO_2 produced; usage of CO_2; and storage of CO_2.[5,6]

The first strategy can be addressed by increasing the energy efficiency or a change in the primary energy source to decrease the amount of CO_2 emitted. The replacement of a C-rich energy carrier (coal) by other less C-rich fossil fuels (oil or natural gas) is an option that with relative ease leads to a reduction in CO_2 emission. However the largest reduction in CO_2 would be gained by switching to non-fossil fuels such as hydrogen and renewable energy. The second strategy involves the use of CO_2 as a chemical feedstock in different applications. The third strategy involves the development of new technologies for capture and sequestration of CO_2.[5,6] There is an excess of 115 ppm by volume of CO_2 in the atmosphere with respect to the pre-industrial value

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CO_2 transformations	(1) Chemical	Non-hydrogenative	Carbonates, carbamates, etc.
		Hydrogenative	Hydrocarbons, MeOH, EtOH, etc.
	(2) Photochemical		CO, HCO_2H, CH_4
	(3) Electrochemical		CO, HCO_2H, MeOH
	(4) Biological		EtOH, Sugar, CH_3CO_2H
	(5) Reforming		CO + H_2
	(6) Inorganic		Carbonates: M_2CO_3

Fig. 1 CO_2 transformations covered in this review.[7]

of 270 ppm that amounts to approximately 900 Gt CO_2. In order to bring the CO_2 level back to where it was, we need to develop processes, techniques and applications capable of handling CO_2 on the scale of 1 teraton. Handling CO_2 at this scale implies significant challenges in terms of how we extract CO_2 from the atmosphere, how we transform it and how we either use it or store it safely.

1.1 Scope of this review

A lot of research has gone into the field of CO_2 transformations, where CO_2 is used as raw material in reactions. In Fig. 1 the transformations are divided into six categories and the typical product for these transformations are listed.[7] This review will cover all of the categories listed, but due to the vastness of this area some of the transformations are only described briefly. However in the reference list recent reviews and/or original literature can be found for all the categories.

Another vast research area, namely carbon capture and storage (CCS), will also be covered briefly in this review. The synthetic reactions and their possible role in future CO_2 mitigation schemes will also be evaluated.

1.2 The carbon dioxide molecule

The molecular geometry of CO_2 is linear in its ground state; therefore it is apolar even though it has two polar C=O bonds. The molecule is a bi-functional catalyst due to its two different reaction sites. The carbon atom is an electrophile, while the oxygen atoms are nucleophiles.

The physical state of CO_2 varies with temperature and pressure. CO_2 is a solid at low temperatures, and will, on warming below 5.1 bar, sublime directly into the vapor state. Above the critical point (31.1 °C, 73.9 bar), which means at higher temperature and/or pressure, CO_2 is said to be in a supercritical state, where it behaves like a gas while its density is approaching or even exceeding the density of liquid water.[2]

Infrared (IR) and nuclear magnetic resonance (NMR) techniques are used as diagnostic tools of the state of the CO_2 molecule or for its quantitative determination.

Even though CO_2 is an abundant and renewable carbon source only a few industrial processes utilize CO_2 as a raw material. The reason for this is that the carbon atom in CO_2 is in its most oxidized form and is therefore relatively unreactive. A large input of energy is required to transform CO_2 into other chemicals. There are four way of altering this:

(1) By using high energy starting materials such as hydrogen and organometallics.

(2) Choosing low energy synthetic targets.

(3) Removing a compound on the product side, and thereby forcing the equilibrium to the right.

(4) Supplying physical energy, *i.e.*, light or electricity.

Choosing the right conditions for the CO_2 transformation is crucial in order to achieve a negative Gibbs energy for the reaction.[5]

2. Chemical transformations

CO_2 has a strong affinity toward nucleophiles and electron-donation reagents; therefore CO_2 can be classified as "anhydrous carbonic acid", which rapidly reacts with basic compounds.

However CO_2 is not used extensively as a source of carbon in current laboratory and industrial practices. This can, in part, be ascribed to thermodynamic aspects. Thus the carbon atom in CO_2 is as stated above electrophilic and a chemical reaction necessitates a reductive supply of energy in the form of electrons.[8]

2.1 Industrial use of carbon dioxide

The industry uses approximately 120 Mt CO_2 per year, excluding use for enhanced oil recovery. In Fig. 2 a bar chart shows the amount CO_2 fixed annually for different chemical applications.

The industrial use amounts to only 0.5% of the total anthropogenic CO_2 emissions, which is about 24 Gt CO_2 annually.[9] The

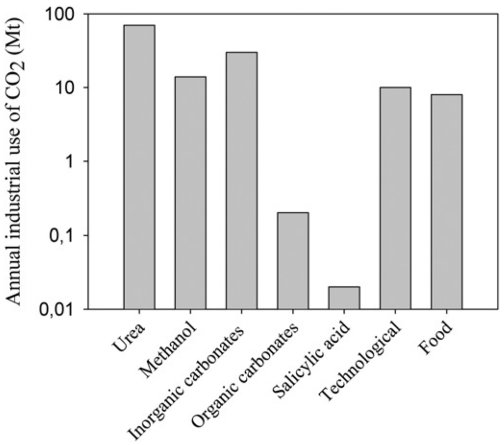
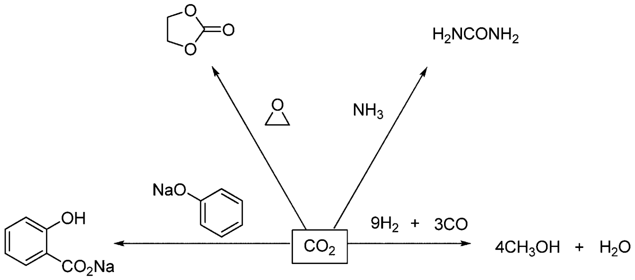


Fig. 2 The annual industrial use of CO_2 in megatons. Note the logarithmic scale on the *y*-axis. Urea accounts for more than 50% of the annual usage.



Scheme 1 Industrial syntheses with CO_2.[8]

usage can be divided into two groups: those using its physical aspects and those using its chemical aspects. The physical properties of CO_2 are used in the beverage industry, in enhanced oil recovery and in its supercritical state as a technological fluid for applications in reactions as solvents and in nano-particle or composite production. As an inert and safe gas it is also used as a protective gas (in chemical or steel industries, in food preservation, in welding *etc.*) and as a fire extinguisher. CO_2 is also used in its solid state for refrigeration especially in refrigerated railcars and trailers to substitute the use of CFCs that are harmful to the atmosphere. CO_2 can also be used chemically as a reactant and can be converted into chemicals such as urea, salicylic acid, inorganic carbonates, pigments, cyclic organic carbonates or used as an additive in the synthesis of methanol.

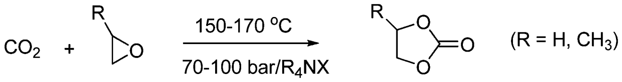
2.2 Industrial syntheses with carbon dioxide

The industrial use of CO_2 as a source of chemical carbon is very limited. CO_2 is used in carboxylation reactions and in certain transformation reactions, which are represented in Scheme 1.

2.2.1 Carboxylic acids. Phenols in the form of their potassium or sodium salt are converted into carboxylic acids by reaction with CO_2. Industrially the preparation of numerous pharmaceutical products and dyestuff intermediates, *e.g.*, *o*- and *p*-hydroxybenzoic acids, *p*-aminosalicylic acid, 2-hydroxynaphthalene-3(and -6)-carboxylic acids and 2-hydroxycarbazole-3-carboxylic acid have been made. The practical synthesis, the Kolbe–Schmitt process, is performed by heating the sodium salt under pressure in an autoclave. The acid is recovered by acidification with H_2SO_4.[8]

One of the most important acids prepared by this synthesis is salicylic acid (intermediate in the synthesis of acetylsalicylic acid (aspirin)) as shown in Scheme 2. The reaction has been used in the industrial synthesis of salicylic acid since 1874. The yield is increased from *ca.* 50% to 90%, when CO_2 is introduced under pressure (5–7 bars).[6,8]

2.2.2. Organic carbonates. CO_2 reacts with epoxides in the presence of quaternary ammonium halides to give the corresponding carbonates as shown in Scheme 3. The synthesis of five-membered cyclic carbonates (ethylene and propylene carbonate) from CO_2 has been industrialized since the 1950s.



Scheme 3 Synthesis of carbonates from CO_2 and epoxides.

Cyclic organic carbonates have a high boiling point and have therefore found many applications as solvents. Furthermore they can react with ammonia or amines to form carbamates. The carbamates can then be converted into polyurethane, a versatile material with a high commercial value.[6,10,11]

The alkene carbonates are in general excellent solvents for the production of various polymers: polyacrylonitrile, nylon, terylene and polyvinylchloride.[8]

The production of polycarbonates, which is also an industrialized process, comprises the same reactants as the synthesis of five-membered cyclic carbonates. The polymerization is often catalyzed by zinc complexes.[7]

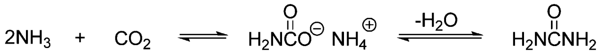
2.2.3 Urea. The industrial production of urea is about 100 million tonnes a year by using CO_2.[12] The production of urea is carried out in two steps at elevated pressure (150 to 250 bar) and temperature (150 to 200 °C). The first step is the formation of ammonium carbamate from ammonia and CO_2. The second step is the dehydration of the carbamate to urea as seen in Scheme 4.

Different processes have been designed for the production of urea. The only difference between them is the techniques used for the recovery and recycling of the unreacted ammonium carbamate.[8] Urea is used as a chemical fertilizer, urea resins, urea–melamine resins and as an animal feed additive.

2.2.4 Methanol. Commercially, methanol is produced from synthesis gas using natural gas or coal, mainly containing CO and H_2 along with a small amount of CO_2 as seen in Scheme 5. The reaction is catalyzed by copper/zinc oxide based catalysts, which have a high reactivity and selectivity.

The annual production of methanol is around 40 Mt and it is used as an intermediate for the production of a variety of chemicals including formaldehyde, methyl *tert*-butyl ether and acetic acid.[13]

The current and estimated industrial use of CO_2 is summarized in Table 1.[3,14]

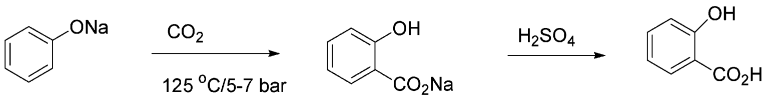


$$2NH_3 + CO_2 \rightleftharpoons H_2N\overset{O}{\overset{\|}{C}}O^{\ominus}\,NH_4^{\oplus} \xrightleftharpoons{-H_2O} H_2N\overset{O}{\overset{\|}{C}}NH_2$$

Scheme 4 Industrial production of urea from ammonia and CO_2.

$$3CO + 9H_2 + CO_2 \longrightarrow 4CH_3OH + H_2O$$

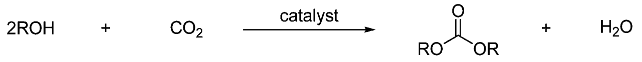
Scheme 5 Methanol production from synthesis gas along with a small amount of CO_2.



Scheme 2 Industrial synthesis of salicycic acid.

Table 1 Current and estimated annual use of CO_2 in Mt

Chemical product or application	Industrial volume/Mt y^{-1}	Industrial CO_2 use/Mt y^{-1}	Future expectations in the use of CO_2	Endothermic or exothermic reaction
Urea	100	70	10^2 Mt	Exothermic
Methanol (additive to CO)	40	14	Gt	Exothermic
Inorganic carbonates	80	30	—	Exothermic
Organic carbonates	2.6	0.2	10^2 Mt	Exothermic
Salicylic acid	0.06	0.02	10^2 kt	Exothermic
Technological	10	10		
Food	8	8		



Scheme 6 Formation of carbonates from alcohols by a dehydrative condensation with CO_2.

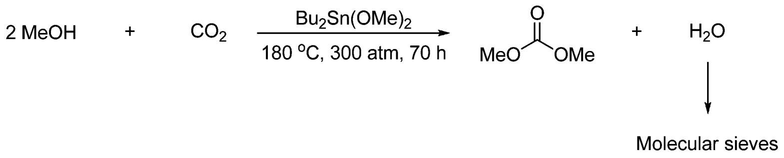
2.3 Chemical reactions with carbon dioxide

2.3.1 Organic carbonates. Organic carbonates are commercially produced from (toxic) phosgene, *e.g.*, dimethyl carbonate is produced from methanol and phosgene and bisphenol A polycarbonate is produced from phenol and phosgene to give diphenyl carbonate that is then reacted with bisphenol A to give the polymer.[8,10] Since phosgene is very toxic and environmentally harmful, alternative routes to organic carbonates are being pursued. Organic carbonates can be produced from alcohols by a dehydrative condensation with CO_2 under catalysis (often tin based) as shown in Scheme 6.

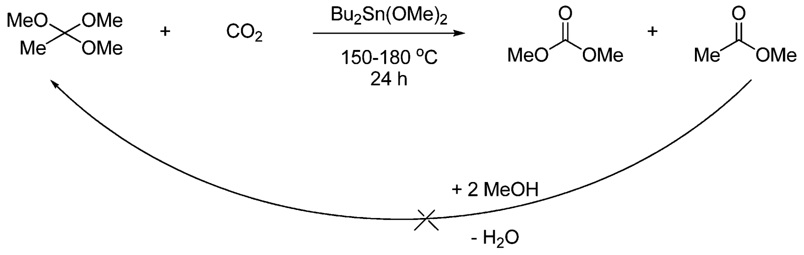
These reactions do not proceed in high yields, due to hydrolysis of the esters and decomposition of the catalyst from the byproduct water.

The organic carbonates can be divided into: (1) acyclic carbonates (dimethyl carbonate (DMC) and diethyl carbonate (DEC)), (2) polycarbonates and (3) cyclic carbonates (ethylene carbonate and propylene carbonate). The formation of carbonates require energy either brought in externally or *via* the reactants with high free energy content.[10] Important for these reactions are the development of new heterogeneous catalysts to replace the homogeneous catalyst used in this reaction for reasons of product separation, catalyst recovery and cost.[10,15]

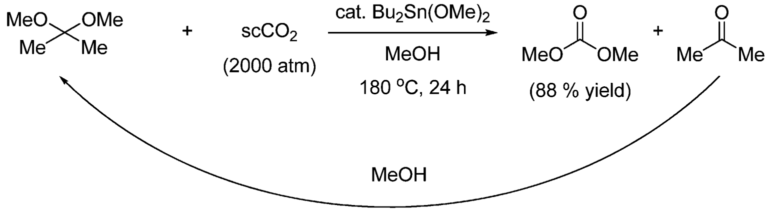
2.3.3.1 Acyclic carbonates. DMC is used for the production of polycarbonate, polyurethane and other chemicals. Some of the best results obtained for the formation of DMC from methanol and CO_2, which suffers only from thermodynamic limitations, is a 11% methanol conversion in supercritical CO_2 (9.3 MPa).[10,15] However the reaction can be improved significantly by employing a dehydrating agent, *e.g.*, molecular sieves as exemplified in Scheme 7. The reaction gives under these optimized conditions 50% methanol conversion.[16]



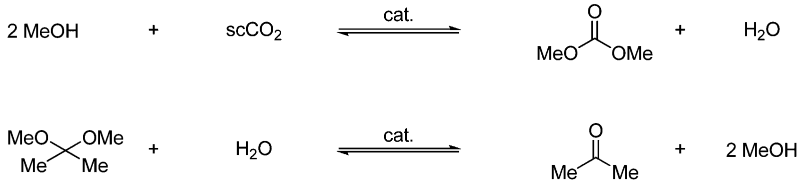
Scheme 7 Employing molecular sieves to the reaction between alcohols and CO_2 improves the yield significantly.



Scheme 8 Synthesis of DMC from trimethyl orthoacetate and CO_2.



Scheme 9 Synthesis of DMC from an acetal by reaction with supercritical CO_2 under tin catalysis.



Scheme 10 The reaction in Scheme 9 can be divided into these two reactions, which overall gives DMC.

Other dehydrating agents which could be employed are non-recyclable agents: dicyclohexyl carbodiimide (DCC), orthoesters,[17] (*e.g.*, orthoacetate, $Si(OMe)_4$) and Mitsunobu's reagent, and recyclable agents: acetals and molecular sieves.[18]

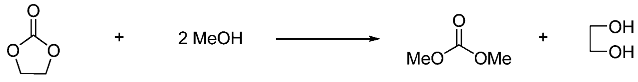
An example with the synthesis of DMC using an orthoester as starting material and dehydrating agent is illustrated in Scheme 8.[17]

Trimethyl orthoacetate which acts as both the starting material and dehydrating agent captures water to produce two molecules of methanol and one molecule of methyl acetate. Surprisingly the reaction proceeds without the addition of methanol to give DMC in 70% yield (based on the orthoester).[17] A downfall to this synthesis method is that the orthoesters are relative expensive as starting materials and are difficult to regenerate from esters and alcohols.[17]

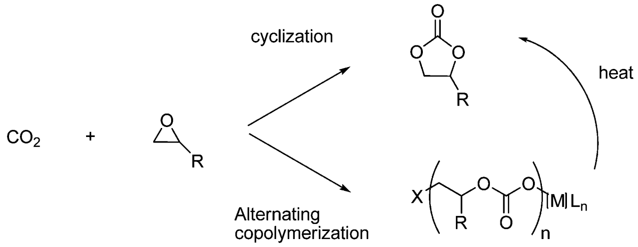
DMC can also be obtained in high yield by reaction with 2,2-dimethoxypropane and supercritical CO_2 under tin catalysis as shown in Scheme 9. The reaction gives acetone as a byproduct, which can be utilized by reaction with methanol, which regenerates the starting material.[19]

Increased pressure and concentration of methanol will increase the yield. The reaction is therefore carried out in a solvent mixture of methanol and supercritical CO_2. Another benefit of using supercritical CO_2 is the efficient product/catalyst separation, which can be done by phase separation without having to completely depressurize the reaction mixture.[18] Methanol is in fact a prerequisite for this reaction since the reaction in Scheme 9 proceeds by an alcohol reaction and a dehydration by the acetal as shown in Scheme 10.

The DMC synthesis using acetals as dehydrating agents in the presence of a weakly basic tin catalyst can be significantly accelerated by employing small amounts of acid catalyst, (*e.g.*, Ph_2NH_2OTf, $Sc(OTf)_3$, *etc.*).[18,20]



Scheme 11 Synthesis of DMC and ethylene glycol from ethylene carbonate and methanol.



Scheme 12 Reaction with oxiranes and CO_2 can lead to cyclic or polymeric carbonates.

This reaction type, however, has some downfalls compared to the direct synthesis of DMC from alcohols, since molecular sieves are recyclable and only some acetals are recyclable. Furthermore, there are ketone byproducts in the synthesis of DMC from acetals, while water is the byproduct in the DMC synthesis from alcohols.

DMC can also be produced by a transesterification of cyclic carbonates as shown in Scheme 11. The synthesis of cyclic carbonates from CO_2 and oxiranes is described later in this section.[21]

A near 100% conversion of methanol with propylene carbonate to DMC (CaO/C as catalyst) has been reported.[10,11b,15]

The reaction of DMC from cyclic carbonates is more favorable than the direct synthesis of DMC from CO_2 and methanol, since the equilibrium naturally is more to the right. However the starting material for ethylene carbonate, ethylene oxide, is highly flammable and also highly toxic, which makes the synthesis of DMC from methanol and CO_2 more favorable.[18,22]

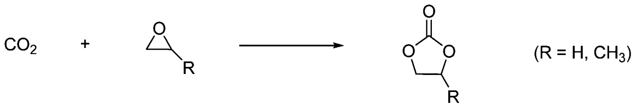
2.3.3.2 Cyclic carbonates. The reaction between oxiranes and CO_2 produces cyclic or polymeric carbonates as shown in Scheme 12.

The reaction takes place easily due to the high steric energy of the oxiranes. It should be noted that cyclic carbonates are thermodynamically more stable than the linear carbonates.[18]

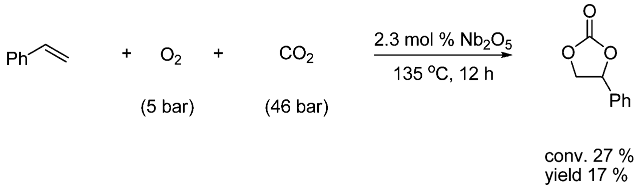
The current industrial synthesis of cyclic carbonates is typically catalyzed by halide salts such as Et_4NBr and KI. The halide salts are also suitable in view of catalyst recycling, since they are soluble in cyclic carbonates and do not precipitate upon concentration.

Ethylene carbonate (boiling point: 521 K) and propylene carbonate (boiling point: 513 K), are as previously described produced industrially from a reaction between CO_2 and ethylene oxide and propylene oxide respectively as shown in Scheme 13.

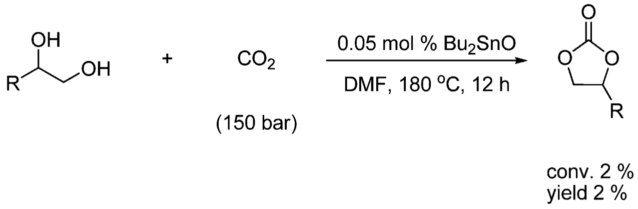
These two cyclic carbonates are used as high-boiling solvents for natural and synthetic polymers such as lignin, cellulose ester, nylon, and PVC. Some of the best results for the synthesis of ethylene- and propylene-carbonate are obtained with a heterogeneous KI-based catalyst giving 99% selectivity and a 100% epoxide conversion.[6,10,23] Excellent results for the synthesis of propylene carbonate have also been obtained by applying



Scheme 13 Synthesis of ethylene and propylene carbonate from their respective oxiranes and CO_2.



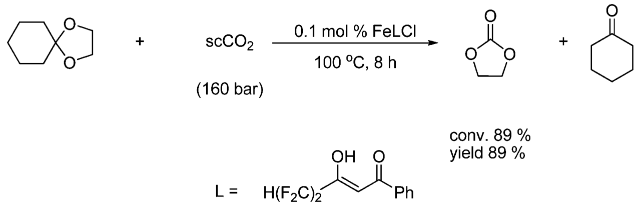
Scheme 14 Synthesis of cyclic carbonates from a Nb-catalyzed oxidative carboxylation with olefins and CO_2.



Scheme 15 Synthesis of cyclic carbonates from a reaction with diols and CO_2 under tin catalysis.

polyfluoroalkylphosphonium iodides ($(C_6F_{13}C_2H_4)_3MePI$) as catalyst to propylene oxide in supercritical CO_2. The reaction gives a high yield (93%) and high selectivity (99%). The catalyst is furthermore soluble in supercritical CO_2 while the resulting product is not, which gives a facile catalyst/product separation.[18,24]

Cyclic carbonates can also be obtained by other pathways than the reaction between oxiranes and CO_2, *e.g.*, olefins react with CO_2 in the presence of an oxidizing agent to give cyclic carbamates as shown in Scheme 14.[25]



Scheme 16 Synthesis of cyclic carbonates from acetals reaction with supercritical CO_2 under iron catalysis.

Another example is the dehydrative condensation of 1,2-diols and CO_2 under CeO_2-ZrO_2 or Bu_2SnO catalysis to give cyclic carbonates, however in a very poor yield as shown in Scheme 15.[26]

Yet another example is an iron- or copper-catalyzed reaction of a cyclic ketal with supercritical CO_2 to give ethylene carbonate in an excellent yield as shown in Scheme 16.[27]

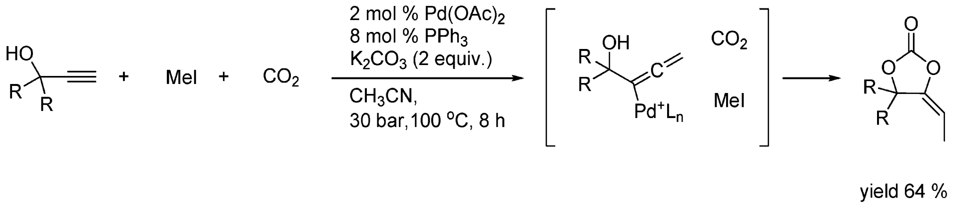
The reaction of propargyl alcohols with methyl iodide and CO_2 proceeds in the presence of a palladium catalyst to give a substituted cyclic carbonate in a good yield as shown in Scheme 17.[28]

A recent review on the formation of carbonates from CO_2 by Sakakura *et al.* describes recent progress in new reaction types, reaction conditions and catalysts.[18]

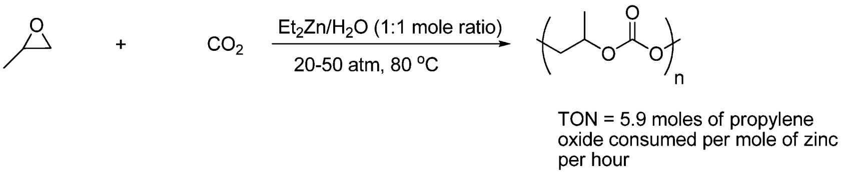
2.3.3.3 Polycarbonates. Polymeric carbonates produced from alternating copolymerization comprise the same reactants as the synthesis of five-membered cyclic carbonates; polymers are kinetic products, while cyclic carbonates are thermodynamic ones.[29]

Polycarbonates process excellent properties, which include strength, lightness, durability, high transparency, heat resistance and good electrical insulation. Hence these materials have found a wide variety of applications from soft drink bottles to building materials, automobile parts and electrical components.[30] Inoue and co-workers first discovered that a mixture of $ZnEt_2$ and H_2O catalyzed the alternating copolymerization of propylene oxide and CO_2 to give poly(propylene carbonate) as shown in Scheme 18.[31,32]

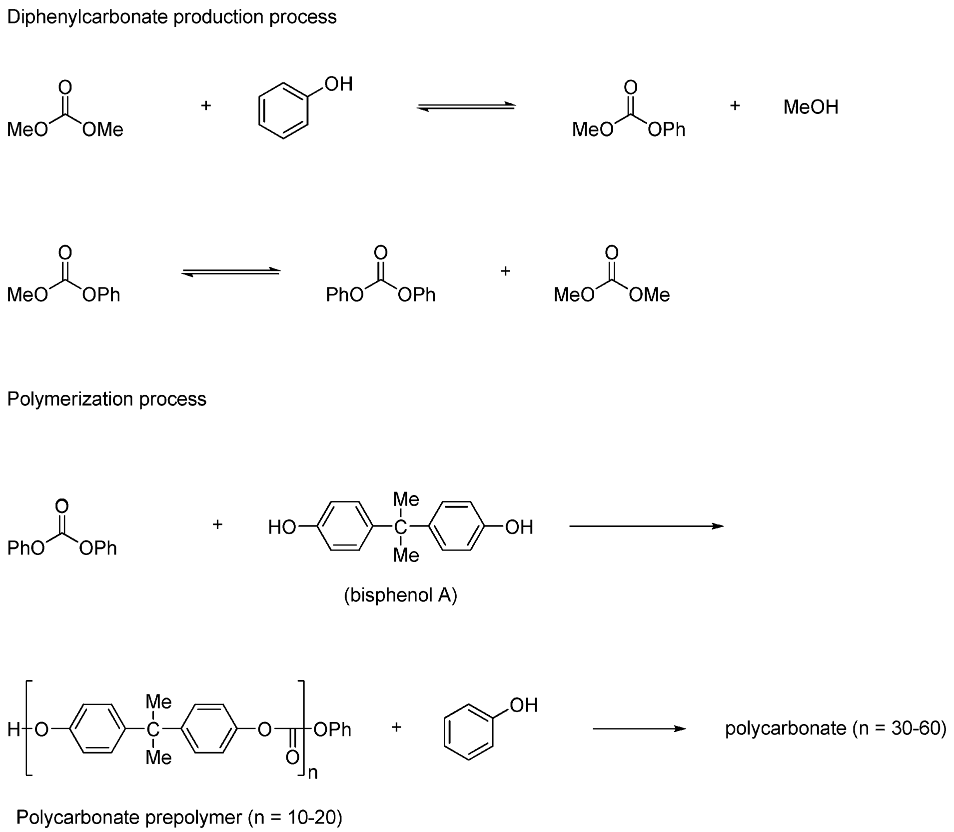
Zinc complexes were the first generation of catalysts for this reaction and are typified by a mixture of diethylzinc and an equimolar amount of a compound having two active hydrogen atoms, such as water, a primary amine, an aromatic dicarboxylic acid and an aromatic diol.[31a] In general it is found that polycarbonates are formed when di- or tri-protic sources and $ZnEt_2$ catalyze the reaction, while monoprotic sources such as alcohols and secondary amines and $ZnEt_2$ catalyze the formation of cyclic carbonates.[29,33] Other zinc complexes have been developed and the zinc iminate complexes are the most intensively studied.[34] The highly active zinc iminate catalysts give, under optimized conditions, a high reaction rate, a high molecular weight, and a narrow polydispersity. Other metal catalyst complexes have



Scheme 17 Synthesis of alkene carbonates from the reaction with propargyl alcohols.



Scheme 18 Alternative copolymerization of CO_2 with propylene oxide.

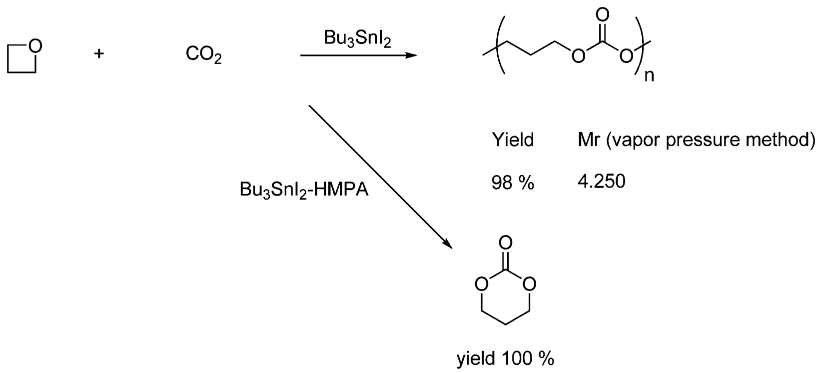


Scheme 19 Asahi Chemical Industry's production of bisphenol A polycarbonate.

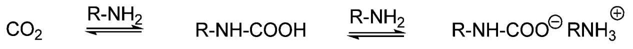
been developed for the catalysis of the aliphatic polycarbonate synthesis, *e.g.*, cobalt,[35] chromium,[36] lanthanide[37] and manganese complexes.[38]

An aromatic polycarbonate, which is based on bisphenol A is widely employed as an engineering plastic in various applications. About 2.7 million tons of this polycarbonate is produced annually and has until recently been produced from phenol, phosgene and bisphenol A. However complications with using phosgene led to the development of an alternative route where diphenyl carbonate is produced from phenol and DMC. Currently this alternative route amounts to 15% of global production capacity. The alternative route, which is carried out in four production steps, was industrialized by Asahi Kasei Chemicals.[39] The first step is the formation of ethylene carbonate form ethylene oxide and CO_2 as shown in Scheme 13. The second step is the formation of DMC and ethylene glycol from the transesterification of ethylene carbonate by methanol as shown in Scheme 11. The third and fourth step is shown in Scheme 19. In the third step diphenyl carbonate is formed by reaction between DMC and phenol under $Pb(OPh)_2$ catalysis, which gives methylphenyl carbonate, which is in equilibrium with diphenyl carbonate and DMC. The fourth step is the polymerization step where diphenyl carbonate reacts with bisphenol A to produce a clear amorphous prepolymer. The polymerization consists of multiple steps where the final polymer has an average molecular weight of 11.700.[21,40]

Current research focus on the development of a route to produce diphenyl carbonate from phenol and CO_2, circumventing the use of DMC.[10]



Scheme 20 Polycarbonate or trimethylene carbonate synthesis from oxetane and CO_2.



Scheme 21 Formation of alkylammonium alkylcarbamate from two molecules of amine and CO_2.

Oxetanes, four-membered cyclic ethers, have a considerably lower reactivity than oxiranes. Nonetheless they react in the presence of organotin iodide with CO_2 forming aliphatic poly (propyl carbonate) in excellent yield as shown in Scheme 20. By employing a different catalyst, Bu_3SnI–hexamethylenephosphoric triamide (HMPA), the oxetanes undergo a cycloaddition with CO_2 to give a six-membered ring carbonate in quantitative yield.[41]

Recent reviews on alternating copolymerization and its catalysts to produce polymeric carbonates have been comprehensively covered by Coates and Moore[29] and more recent Darensbourg.[30]

2.3.2 Organic carbamates and ureas.

Carbamates are a stable class of compounds derived from the unstable carbamic acid by substitution of amide or ester ends. Carbamic acids are believed to be the intermediate when two molecules of primary or secondary amines react with CO_2 as illustrated in Scheme 21. The first amine molecule reacts with CO_2 forming the unstable carbamic acid, which then reacts with the second amine molecule forming alkylammonium alkylcarbamate. In the absence of an appropriate electrophile or dehydrating agent the two latter molecules revert to their corresponding starting materials.[42]

Carbamates can be formed by reaction with an *in situ* generated carbamate ion and with electrophiles such as organic halides. These carbamates are synthesized in high yields in the presence of K_2CO_3 and a tetraalkylammonium salt as shown in Scheme 22.[43]

The yields for this reaction are improved by using different basic reagents, which provide stabilization to the intermediate alkylammonium alkylcarbamate ionic species.[44] This synthesis has also been achieved by using a phase-transfer catalyst (18-crown-6 ether) instead of a base.[45] Good to excellent yields have also been reported for the use of metallic carbonates (caesium carbonate) as basic reagents together with a phase transfer catalyst.[46]

Carbamates can also be formed from primary amines and alcohols in the presence of an organotin catalyst and an acetal as a dehydrating agent under high CO_2 pressure, thereby replacing the organic halide with an alcohol as shown in Scheme 23.[47]

This means that the byproduct is water instead of H–X. The yield for this reaction is limited due to thermodynamic limitations and catalyst deactivation caused by water. The key to achieve high yields is therefore to add acetals, which act as dehydrating agents.[7, 19a,42,47] The CO_2 pressure is kept high for this reaction to avoid side reactions: (a) imine formation by reaction of the amine and the formed carbonyl compound and (b) alkylation of the amine by the alcohol.[18]

Substituted urea can be formed by using a dehydrating agent. The synthesis of *N*,*N*′-dialkylurea has been achieved by using hydrophilic ionic liquids as reaction media and dehydrating agent as shown in Scheme 24.[48]

O-Allyl carbamates can also be obtained through nucleophilic addition of carbamate ion to alkenes in 66–100% yield. The preformed carbamate ion is generated from primary or secondary amines, CO_2 and base as shown in Scheme 25. The carbamate ion is added to a solution of allylic chlorides under palladium/phosphine catalysis.[5,49]

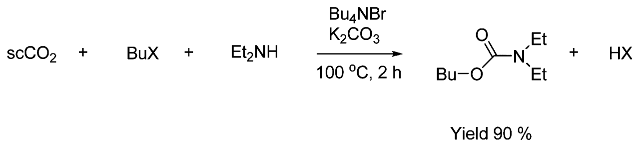
Isocyanates can be obtained from thermolysis of carbamates as shown in Scheme 26. This is an important reaction since it is a non-phosgene route to isocyanates.[7,50]

A mild and efficient procedure has been developed for the synthesis of isocyanates from carbamates employing chlorocatecholborane as illustrated in Scheme 27. Chlorocatecholborane intercepts the formed alcohol and the recombination of the formed isocyanate and alcohol is avoided.[50]

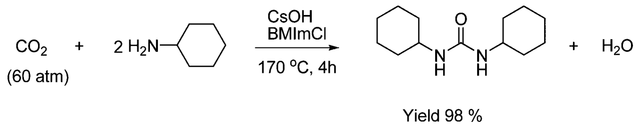
Yet another way of synthesizing isocyanates without employing phosgene is from carbamic acids, which as described above are in equilibrium with amine and CO_2. By dehydrating carbamic acids with, *e.g.*, $POCl_3$ or P_4O_{10} in the presence of tertiary amines isocyanates can be synthesized as shown in Scheme 28.[51]

Epoxides react with CO_2 and the same applies for nitrogen containing three-membered rings (aziridine) which reacts with CO_2 to form a five membered ring (oxazolidinone).[52] Typical reaction conditions are listed in Scheme 29. Various compounds are used to promote the reaction. Typical promoters are quaternary ammonium salts, chromium salen complexes or as exemplified in Scheme 29 the alkali metal salts.

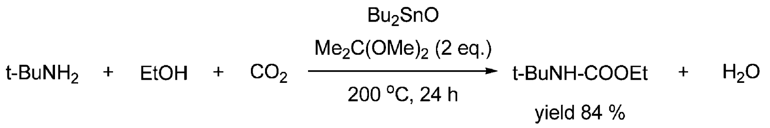
The regioselectivity in this ring-opening reaction leads to only one final product.[52c]



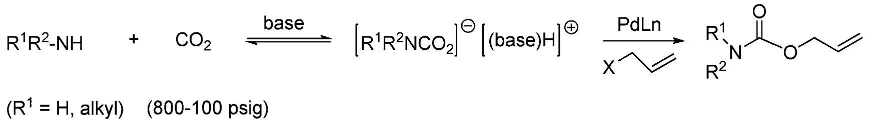
Scheme 22 Formation of carbamates from the *in situ* generated carbamate ion and an organic halide.



Scheme 24 The synthesis of substituted ureas from CO_2, primary amines, base and an ionic liquid BMImCl (1-*n*-butyl-3-methyl imidazolium chloride).



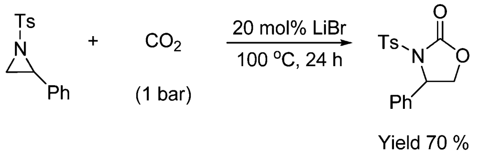
Scheme 23 Urethane synthesis with an alcohol.



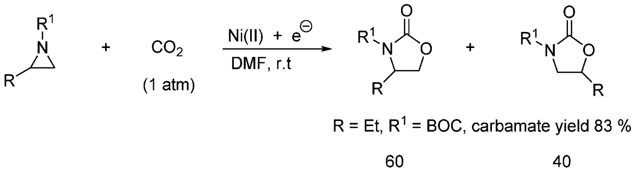
Scheme 25 Synthesis of *O*-allyl carbamates from a carbamate ion and allylic chlorides.

$$RNHCO_2R^1 \overset{\Delta}{\rightleftharpoons} R\text{-}N{=}C{=}O + R^1OH$$

Scheme 26 Thermolysis of carbamates to give isocyanates.



Scheme 29 Typical reaction procedure for formation of oxazolidinones from aziridines.



Scheme 30 Subsituted oxazolidinones obtained from a mono-substituted aziridine and CO_2 by an electrochemical procedure.

Another way to produce oxazolidinones in good yields is by an electrochemical procedure. The reaction is catalyzed by a Ni(II) complex (10 mol %) and performed in a single compartment cell fitted with a consumable magnesium anode and an inert cathode as shown in Scheme 30. The two regioisomers are obtained in ratios from 50 : 50 up to 86 : 14 mixtures depending on the substitution and reaction conditions. The major isomer corresponds to the incorporation of CO_2 at the less hindered side of the mono-substituted aziridine.[53]

2-Oxazolidinones can also be formed in good to excellent yields from substituted 1,2-aminoalcohols and CO_2 under dibutyl tin oxide catalysis with 1-methyl-2-pyrrolidinone (NMP) as solvent as shown in Scheme 31. 2-Oxazolidiones were obtained in 53–94% yields depending on the substitution and degree of substitution.[54]

It is found that the amino alcohols react with CO_2 to give a carbamic acid intermediate with the unexpected stereoselectivity of the Mitsunobu transformation.[51b,55] The stereochemical course of the Mitsunobu reaction depends on whether N in the carbamic acid intermediate is substituted with two hydrogen atoms or a carbon atom. The former gives retention of configuration, while the latter gives inversion of configuration as illustrated in Scheme 32.[56]

Unsaturated compounds such as acetylenes and olefins are able to react directly with CO_2 and amines to afford carbamates using ruthenium catalysis. An example of this is shown in Scheme 33.

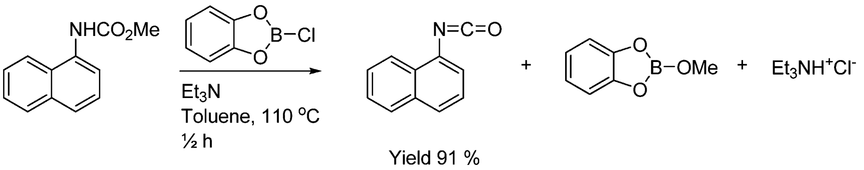
A secondary amine, CO_2 and hex-1-yne react under ruthenium catalysis to give three vinylcarbamates. However, in a low overall yield.[57]

Cyclic carbamates can also be obtained in good yield by the reaction of CO_2 with *N*-substituted terminal propargylamines in the presence of a ruthenium and tertiary phosphine catalyst as shown in Scheme 34.[58]

The reaction between aziridine and CO_2 will lead to ring-opening polymerization, when the reaction is performed under supercritical conditions as shown in Scheme 35.[59]

Amines (primary and secondary) and CO_2 reacts with epoxides to afford hydroxycarbamates and aminoalcohols, and/or an oligomer of the epoxide, depending upon the nature of the amine and epoxide, and reaction conditions as shown in Scheme 36.[60]

It can be seen from Scheme 36 that the reaction leads to isomer mixtures of the desired carbamate and an amine alcohol. This side reaction can be minimized by adding the (5,10,15,20-tetraphenylporphinato)aluminium(III) acetate, Al(TPP)(O_2CCH_3) to the mixture. The aluminium porphyrin complex is for example found to catalyse the formation of 2-hydroxypropyl diethylcarbamate from CO_2, diethylamine and 1,2-epoxypropane as shown in Scheme 37. The desired dialkylcarbamic ester is obtained at 60 °C under a pressure of 50 atm of CO_2 in 47% yield.[61]

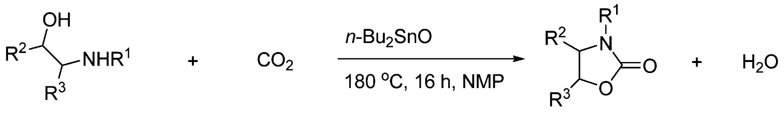


Scheme 27 Formation of isocyanates from carbamates, chlorocatecholborane and base.

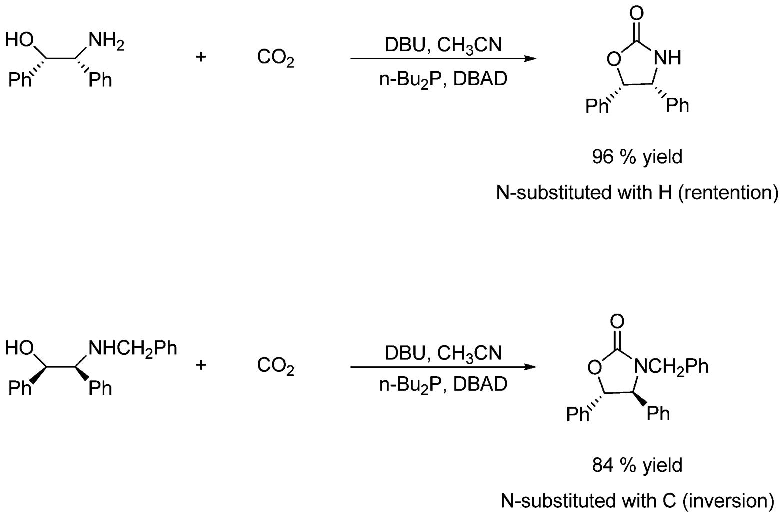
$$RNH_2 + CO_2 \rightleftharpoons RNHCO_2H \overset{Et_3N}{\rightleftharpoons} [RNHCO_2]^{\ominus}\,[Et_3NH]^{\oplus} \xrightarrow[P_4O_{10}]{POCl_3\ \text{or}} R\text{-}N{=}C{=}O$$

$$(R = C_8H_{17}\ \text{Yield 97 \%})$$

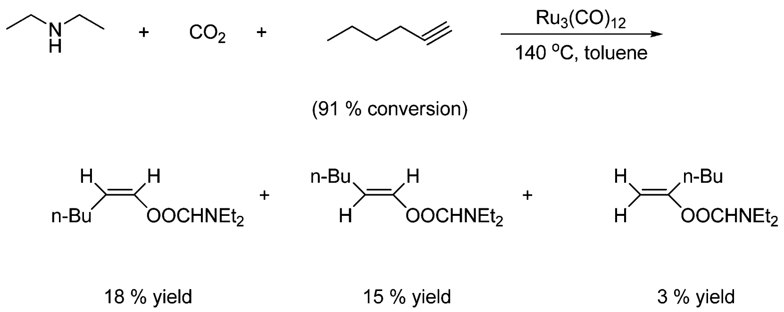
Scheme 28 Synthesis of isocyanates by dehydrating a carbamic acid salt.



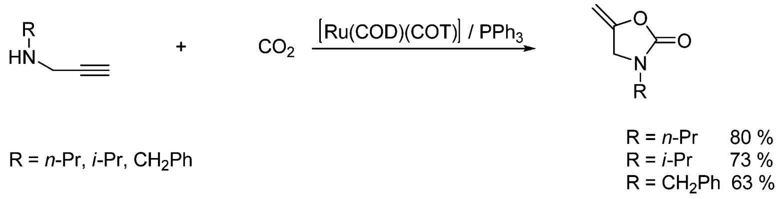
Scheme 31 Oxazolidinone can be obtained from substituted 1,2 aminoalcohols and CO_2.



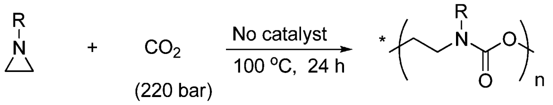
Scheme 32 The stereochemical outcome of a reaction between a primary amino alcohol and CO_2 and the outcome between a secondary amino alcohol and CO_2 is illustrated.



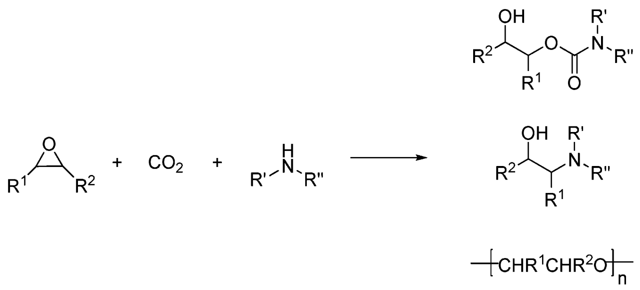
Scheme 33 Synthesis of vinylcarbamates from an amine, CO_2 and an alkyne.



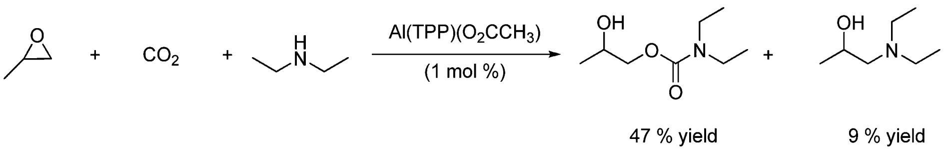
Scheme 34 Synthesis of a cyclic carbamate from CO_2 reaction with a *N*-substituted terminal propargylamine.



Scheme 35 Polyurethane is formed when aziridine reacts with supercritical CO_2.



Scheme 36 CO_2 reacts with amines (primary and secondary) and epoxides to afford hydroxycarbamates and amino alcohols and/or oligomers of the epoxides.

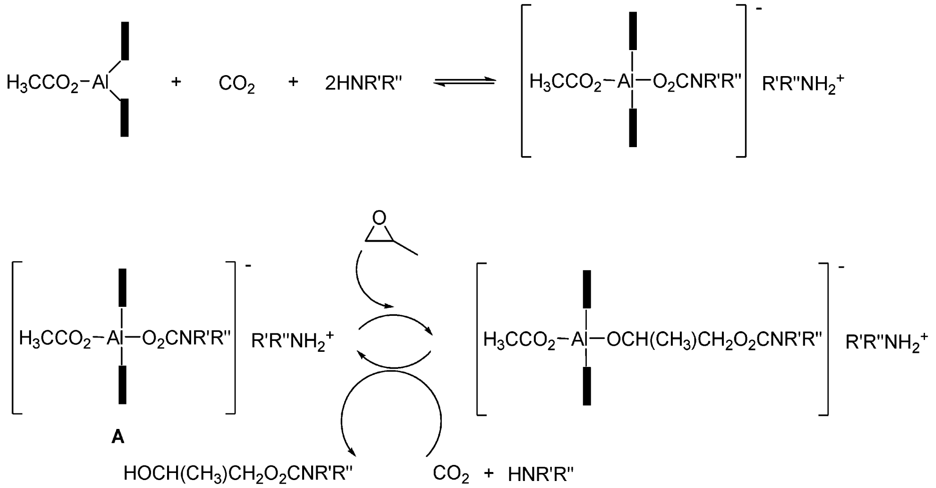


Scheme 37 Formation of dialkylcarbamic ester under aluminium porphyrin complex catalysis.

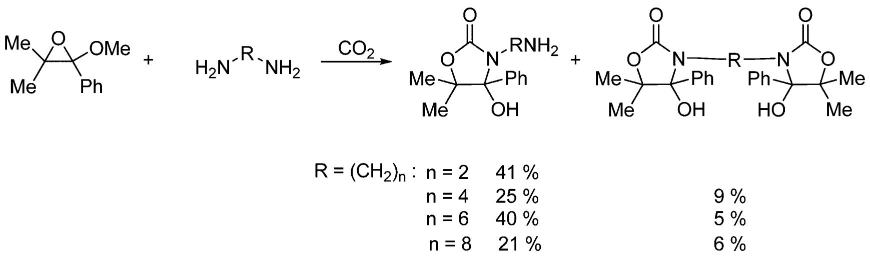
The catalytic formation of the dialkylcarbamic ester is believed to proceed by the insertion of the epoxide between the aluminium–oxygen bond of the (porphinato)aluminium carbamate (A) to form an aluminium alkoxide, followed by cleavage by diethylcarbamic acid (from CO_2 and diethylamine) to give the desired product and regenerate the active species (aluminium carbamato group) as seen in Scheme 38.

An example of the formation of a cyclic carbamate is shown in Scheme 39. A tetra substituted oxirane reacts with CO_2 and an α,ω-diamine to afford cyclic carbamate bis(2-oxazolidione) derivatives. The yields for this reaction average around low to fair.[62]

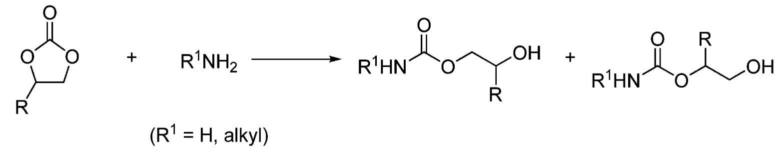
Cyclic organic carbonates (formed from epoxide and CO_2) reaction with ammonia or primary amines gives carbamates by



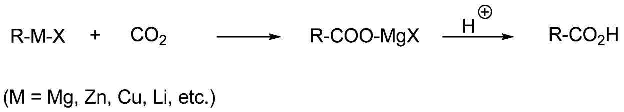
Scheme 38 Proposed mechanism for the aluminium porphyrin complex catalyzed formation of the dialkyl carbamic ester. The black rectangle symbolizes the porphyrin.[61]



Scheme 39 Formation of a cyclic carbamate from a tetra substituted epoxide, a diamine and CO_2.



Scheme 40 Cyclic carbonates react with ammonia or primary amines to form carbamates.



Scheme 41 Carboxylic acids can be synthesized from reaction with, *e.g.*, Grignard reagents and CO_2.

a non-phosgene route at room temperature as shown in Scheme 40.[63]

Carbamate synthesis is a vast area of research and continued progress is made in the development of new synthetic routes to carbamates. Recent reviews on carbamate synthesis from CO_2 are made by Chaturvedi *et al.*[42] and Sakakura *et al.*[7]

2.3.3 Synthesis of carboxylic acids, esters and lactones. Carboxylation of carbon nucleophiles under atmospheric pressure of CO_2 as an electrophile is a straightforward method to obtain carboxylic acids. They can be synthesized from carbon nucleophiles such as Grignard reagents, alkyllithiums, active methylene compounds, and metal enolates, which attack CO_2 under relatively mild conditions as shown in Scheme 41.[7,64]

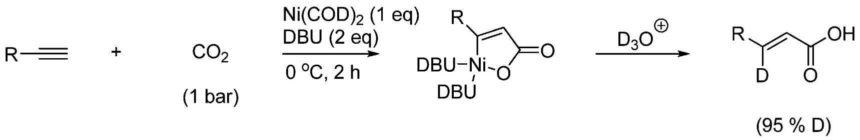
These reactions provide a convenient route to aliphatic, aromatic, olefinic and acetylenic acids.

Acrylic acids can be formed from acetylene and CO_2 using catalysis. The reaction often requires a strong base, (*e.g.*, DBU) which presumably promotes the reaction by trapping CO_2 in the form of carbamate or bicarbonate.[65] During the reaction a five-membered metallolactone intermediate is formed when the low-valent metal complex (catalyst in stoichiometric amounts), CO_2 and the unsaturated compound reacts as shown in Scheme 42.[66]

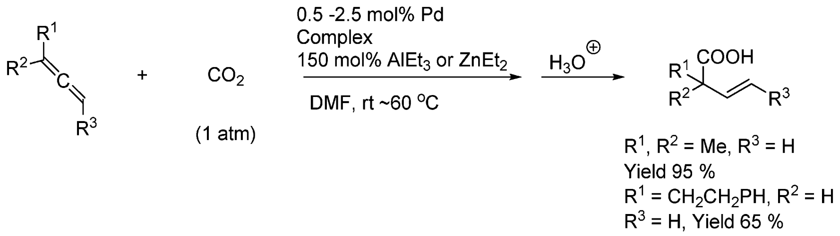
Acrylic acids can also be formed from 1,3- butadiene[67] and allenes *via* metallacycles.[68]

Another recent approach to the synthesis of acrylic acids uses a palladium hydride complex (in catalytic amounts) as the active catalyst in the presence of a reducing agent as shown in Scheme 43.[69]

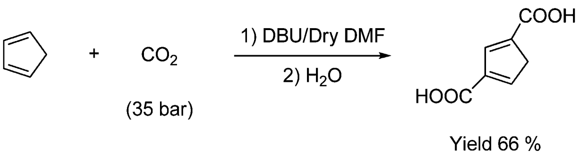
Carboxylation with CO_2 can be carried out under either basic or acidic conditions. An example of a basic carboxylation is the



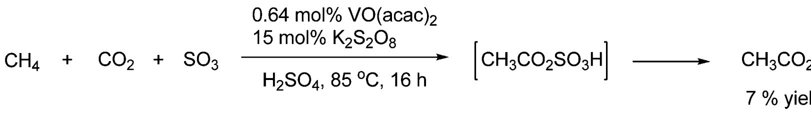
Scheme 42 An acrylic acid is formed from acetylene with a five-membered metallolactone as intermediate.



Scheme 43 Synthesis of substituted acrylic acids from allenes under palladium hydride complex catalysis.



Scheme 44 Synthesis of 1,3-dicarboxy cyclopentadiene from cyclopentadiene and CO_2 under basic conditions.

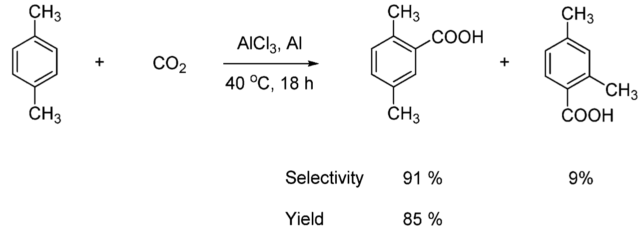


Scheme 45 Carboxylation of methane to acetic acid.

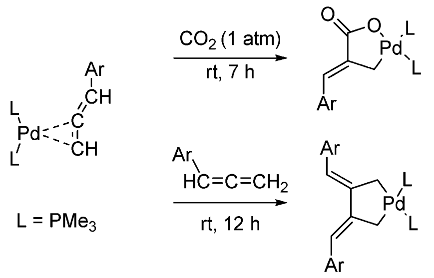
Kolbe–Schmidt reaction, which is described under industrial synthesis of hydroxybenzoic acid. Another example is the fixation of CO_2 (at up to 50 bar pressure) into cyclopentadiene under basic conditions (DBU) to produce 1,3-dicarboxy cyclopentadiene as shown in Scheme 44.[70]

An example of acidic carboxylation is the synthesis of acetic acid form methane and CO_2. The reaction is an example of a hydrocarbon transformation to carboxylic acid. The reaction is catalyzed by a vanadium[71] or palladium[72] catalyst in the presence of an oxidizing agent such as $K_2S_2O_8$ as shown in Scheme 45.

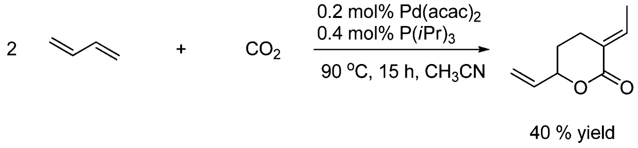
Another example of insertion of CO_2 into a C–H bond is a Friedel–Crafts reaction. Aromatic carboxylic acids are synthesized in high yields by the carboxylation of aromatics with CO_2 and $AlCl_3$ (Lewis acid) under mild conditions as shown in Scheme 46.[73]



Scheme 46 Friedel–Crafts reaction where aromatic carboxylic acids are formed from a CO_2 insertion into a C–H bond.



Scheme 47 Five-membered palladacycles are formed from the oxidative addition of CO_2 or an additional allene to a metal π-complex.



Scheme 48 1,3 butadiene reacts with CO_2 under palladium catalysis.

Combining various unsaturated compounds and CO_2 with transition metal complexes results in the formation of esters and lactones. Unsaturated compounds such as monoolefins, dienes, allenes and acetylenes react with transition metal complexes to form metal π-complexes. Both CO_2 and carbon–carbon unsaturated compounds can be activated by the same metal π-complex as exemplified in Scheme 47. An allene reacts with a palladium complex to form a metal π-complex. Oxidative addition with either CO_2 or an additional allene molecule gives a five-membered palladacycle.[74]

CO_2 is able to react with unsaturated compounds in the presence of transition metal complexes as catalysts to give six-membered unsaturated lactones. An example of this is shown in Scheme 48. 1,3-Butadiene reacts with CO_2 in the presence of a palladium catalyst.[75]

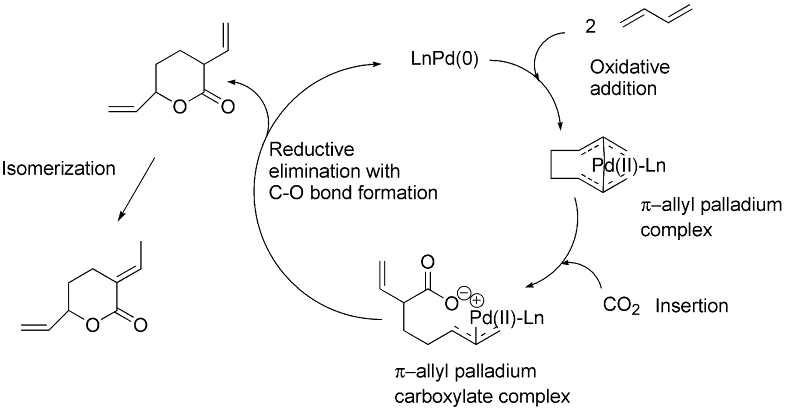
The catalytic cycle is shown in Scheme 49. The reaction proceeds by the oxidative addition of two molecules of 1,3-butadiene to a low-valent transition metal (palladium(0)) to form a π-allyl palladium complex. Next step in the cycle is the insertion of CO_2 to form a π-allyl palladium carboxylate complex. This step is followed by a reductive elimination with C–O bond formation to obtain, after isomerization, the desired lactone and regenerates the low-valent metal complex to complete the catalytic cycle.[21]

Acetylenes also react with CO_2 in the presence of a low valent transition metal complex to form lactones as shown in Scheme 50.[76]

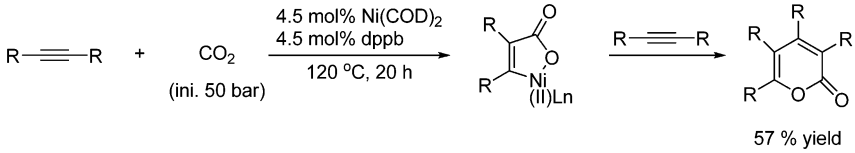
The first intermediate formed in the reaction is a five-membered metallacycle, which is formed from oxidative addition of CO_2 and one molecule of acetylene to a low-valent transition metal (nickel(0)). The next step is the insertion of another molecule of acetylene which leads to a ring expansion of the metallacycle to give a seven-membered intermediate. Reductive elimination with C–O bond formation gives the desired lactone and regenerates the transition metal complex as shown in Scheme 51.[21]

Lactones can also be formed from allenes as exemplified in Scheme 52.[77]

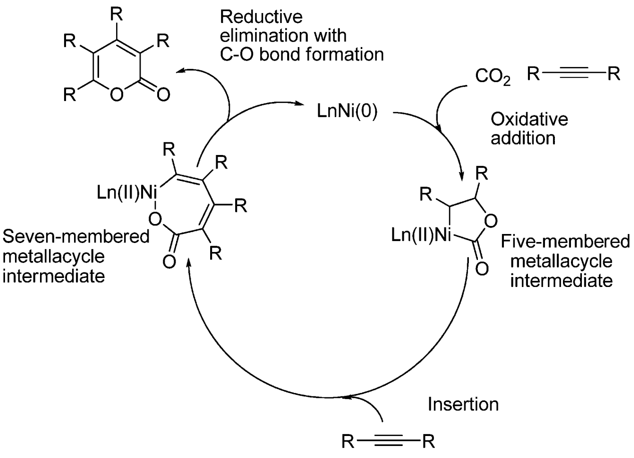
Diynes (RC≡C–$(CH_2)_m$–C≡CR) will react with CO_2 in the presence of a zero-valent nickel catalyst to give either 2-pyrones



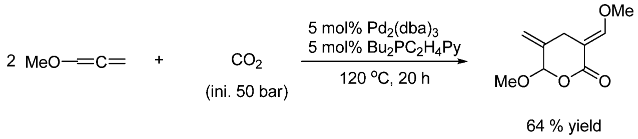
Scheme 49 Catalytic cycle for the formation of a lactone from 1,3-butadiene.



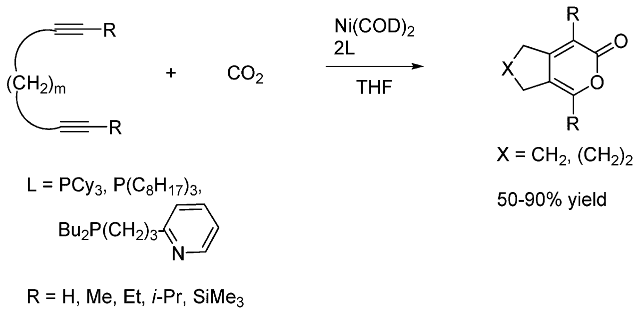
Scheme 50 Lactones can be formed from acetylenes and CO_2 with $Ni(COD)_2$ as catalyst.



Scheme 51 The catalytic cycle for the formation of a lactone from acetylene.



Scheme 52 Formation of lactones from allenes and CO_2 with a palladium catalyst.



Scheme 53 Intramolecular cycloaddition to give cyclic 2-pyrones from diynes reaction with CO_2 under Ni complex catalysis.

or poly(2-pyrones) depending on the value of *m*. When the value of *m* is 3 or 4, the reaction proceeds by an intramolecular cycloaddition to give two cyclic 2-pyrones as shown in Scheme 53.

When the value of $m \leq 2$ or $m \geq 6$ then the reaction proceeds by an alternating copolymerization of the diynes and CO_2 to give poly(2-pyrone) by an intermolecular cycloaddition, since the intramolecular cycloaddition is not feasible as shown in Scheme 54.[78]

Diynes react with CO_2 and alkyl dihalides under catalysis by a copper(I) salt in the presence of K_2CO_3 to form poly (alkyl alkynoates) as shown in Scheme 55.[79]

The alternate copolymerization affords good yields with several aromatic diynes, CO_2 and 1,4-dibromobutane.

The 2 + 2 + 2 cycloaddition between diynes and CO_2 is efficiently catalyzed by nickel complexes with bulky carbene ligands under mild conditions to afford six-membered cyclic lactones as shown in Scheme 56.[80]

When one of the terminals on the diyne bears a bulky substitute (R = *i*-Pr or TMS) then a high regioselectivity is obtained as shown in Scheme 57.[80]

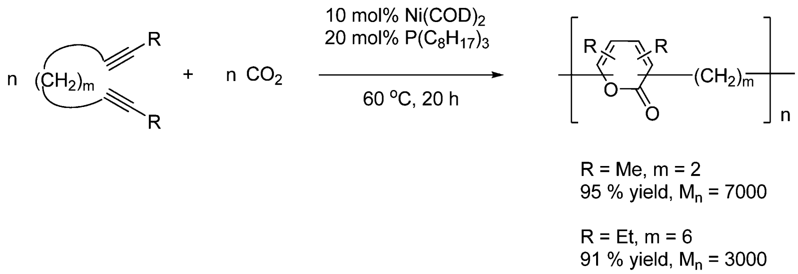
Recent reviews on the synthesis of carboxylic acids, esters and lactones from CO_2 are made by Sakakura *et al.*[7] and Omae.[21]

2.3.4 Carbon dioxide coordination with transition metal centers.

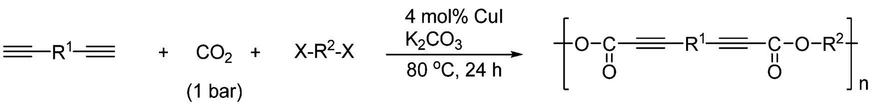
Transformations with CO_2 often require a catalyst, and the development of suitable catalysts is therefore crucial. Interaction between CO_2 and transition metals is therefore an area of high importance.

Even though CO_2 is an inert molecule, it exhibits a great variety of coordination modes in its metal complexes as shown in Table 2. The nomenclature for these structures includes a simple descriptor which indicates the bonding type. η^n signifies the number of bonds between each coordinated CO_2 and the metal atom or atoms, whereas μ_n signifies the number of metal atoms involved in bonding to each CO_2 ligand.[81]

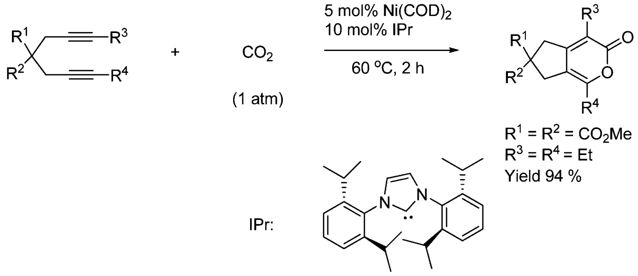
The CO_2 molecule has three potential modes of bonding to a metal atom. CO_2 can bind "end on" through an oxygen atom (η^1-O), "side-on" to a C–O bond (η^2-C,O) or *via* the central carbon atom (η^1-C). CO_2 can also be bound by two or more



Scheme 54 The reaction between diynes of a certain size and CO_2 proceeds by an alternating copolymerization.



Scheme 55 Synthesis of alkyl alkynoates from 1-alkynes, CO_2 and alkyl halides mediated by copper(I) salt.



Scheme 56 Nickel complexes with bulky carbene ligands efficiently catalyze the 2 + 2 + 2 cycloaddition.

metal centers *via* coordination of the carbon atom to one metal and either one or both oxygen atoms of the CO_2 to other metal(s). Thus, a great number of complexes with bridging CO_2 ligand can be formed as shown in Table 2.[3]

These products are potential intermediates in the catalytic transformation of CO_2, and have therefore been extensively studied.[81,102,105]

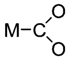
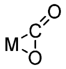
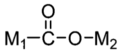
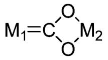
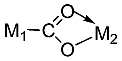
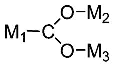
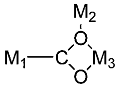
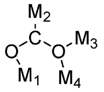
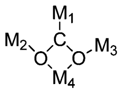
2.3.4.1 Reaction with transition metal hydrides. The reaction between CO_2 and transition metal hydrides can be considered as the first and crucial step in the homogeneous catalytic reduction or transformation of CO_2. The initial reaction between the two can proceed in either of two ways: the formation of a mono dentate formato-metal complex (1) which is in equilibrium with the bidentate formato-metal complex (2); the second is the formation of a hydroxycarbonyl-metal complex (3) as shown in Scheme 58.

Among the examples known to date the one that predominates is the formation of the formato complexes. The metallocarboxylic acid complex is quite unstable, and therefore a much less common product. Furthermore the known examples also show that not all transition metal hydrides react with CO_2 as such but rather with carbonic acid or simple derivatives thereof, *e.g.*, carbamic acid and $HOCONR_2$.[8,105] Recent reviews in this area can be found in the literature list.[105,106]

2.4 Reductive hydogenative conversion of carbon dioxide

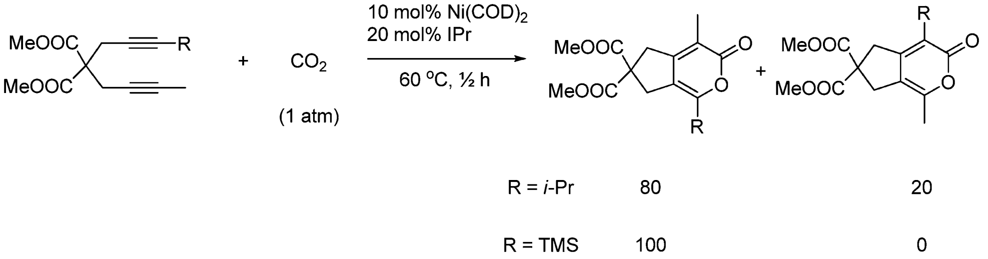
Hydrogenation of CO_2 has been widely investigated for the utilization of CO_2. The reactions are carried out with both homogeneous and heterogeneous catalysts.

Table 2 Structural types of metal-CO_2 complexes.[3]

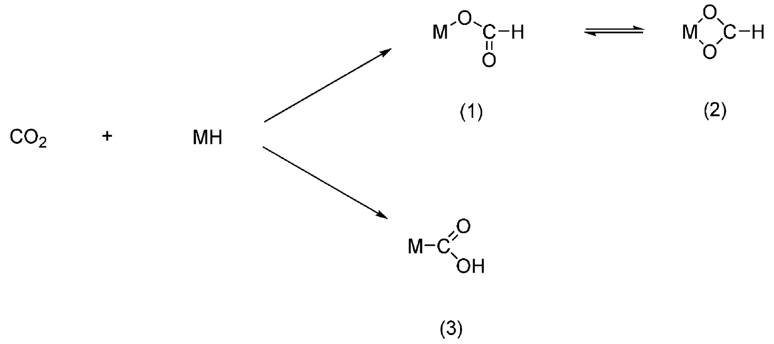
Mode of bonding	Structural types of metal-CO_2 complexes	Type of M [ref.]
η^1-O	M–O–C=O	U[82]
η^1-C		Rh,[83] Ir[84]
η^2-C,O		Ni,[85] Rh,[86] Fe,[87] Pd[88]
μ_2-η^2		Pt,[89] Ir/Zr,[90] Ir/Os,[91] Rh,[92] Ru,[93] Re/Ge[94b]
μ_2-η^3 (class I)		Re/Zr,[95] Ru/Zr, Ru/Ti, Fe/Zr, Fe/Ti[96]
μ_2-η^3 (class II)		Re/Sn,[97] Fe/Sn[98]
μ_3-η^3		Os,[95,99] Re[100]
μ_3-η^4		Co[94,101]
μ_4-η^4		Ru[102,103]
μ_4-η^5		Rh/Zn[104]

2.4.1 Formation of methanol. One of the most studied hydrogenative conversions of CO_2 is the catalytic conversion to methanol as shown in Scheme 59.[13]

The catalytic hydrogenation of CO_2 to methanol produces water as a byproduct. A third of the hydrogen is thus converted to water, which is a considerable waste compared to the commercial production of methanol *via* synthesis gas. Furthermore the thermodynamics for methanol production from H_2 and CO_2 are not as favorable as those for production of methanol from H_2 and CO. For example, at 200 °C the equilibrium yield of methanol from CO_2 is slightly less than 40% while the yield from



Scheme 57 The bulky ligands provide a high degree of regioselectivity when applied to a diyne with one large terminal substitute.



Scheme 58 CO_2 initial reaction with metal hydrides can proceed in two ways.

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

Scheme 59 Catalytic hydrogenative conversion of CO_2 to methanol.

CO is greater than 80%.[107] The general composition of the catalyst developed for this conversion is based on metals and their oxides, in particular copper and zinc oxide. The most widely used catalyst is $Cu/ZnO/Al_2O_3$.[13,108]

A crucial factor in the development of pilot scale to large scale is the availability of the raw materials namely CO_2 and H_2. Large amounts of CO_2 can be obtained from various exhaust sources such as power plants and industrial plants, *e.g.*, cement factories, aluminium production and fermentation plants. There are also large amounts of natural CO_2 sources, *e.g.*, CO_2 accompanying natural gas and geothermal energy producing wells.

Hydrogen can either be generated by still-existing fossil fuel sources (mainly natural gas) or from splitting of water.[13] The latter can be done electrochemically, thermally or photolytically. However water splitting is a very energy consuming process and it has been estimated that in water electrolyzers with a production capacity of 1000 kg of H_2 per day, the cost of electricity has been estimated to represent about 80% of the cost of hydrogen produced.[109] The electricity needed for this process can however come from any renewable energy source, *e.g.*, solar, hydro, geothermal, wind, wave, tides *etc.*

Another way to produce methanol is *via* the "Carnol-process" developed at the Brookhaven National Laboratory. In this process, hydrogen is produced by thermal decomposition of methane with carbon formed as a byproduct.[4,110] The generated hydrogen is then reacted with CO_2 recovered from point continuous sources, such as power plants to produce methanol. The Carnol process is shown in Scheme 60.

The byproduct, solid carbon, can be handled and stored more easily than gaseous CO_2. Solid carbon can be used in applications such as carbon black in the tire industry and pigments for inks and paints.[13] Methanol itself can be used as a liquid energy carrier either pure or mixed with other fuels. It is found that using methanol as a fuel produces less environmentally harmful

Methane thermal decomposition $$CH_4 \longrightarrow C + 2H_2$$

Methanol synthesis $$CO_2 + 3H_2 \longrightarrow CH_3OH + H_2O$$

Overall Carnol process $$3CH_4 + 2CO_2 \longrightarrow 2CH_3OH + 2H_2O + 3C$$

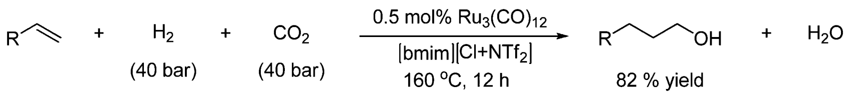
Scheme 60 The overall Carnol process consists of two steps: methane thermal decomposition and methanol synthesis.

$$CO_2(g) + 4H_2(g) \longrightarrow CH_4(g) + 2H_2O(l) \qquad \Delta H^o\ (kJ/mol) = -259.9 \qquad \Delta G^o\ (kJ/mol) = -132.4$$

$$CO_2(g) + 3H_2(g) \longrightarrow CH_3OH(l) + H_2O(l) \qquad \Delta H^o\ (kJ/mol) = -137.8 \qquad \Delta G^o\ (kJ/mol) = -10.7$$

$$CO_2(g) + 3H_2(g) + CH_3OH(l) \longrightarrow C_2H_5OH(g) + 2H_2O(l) \qquad \Delta H^o\ (kJ/mol) = -221.6 \qquad \Delta G^o\ (kJ/mol) = -88.9$$

Scheme 61 Hydrogenations of CO_2 to produce methane, methanol and ethanol.



Scheme 62 Formation of alcohols from alkenes by hydroformylation with CO_2.

gases, *e.g.*, hydrocarbons, SO_x and NO_x compared to regular gasoline. However there are some downfalls to using methanol as a fuel, it increases formaldehyde emission due to its lower heat capacity (compared to gasoline), a larger tank is needed, methanol is more corrosive than gasoline and cautionary measures have to counter this.[6,111]

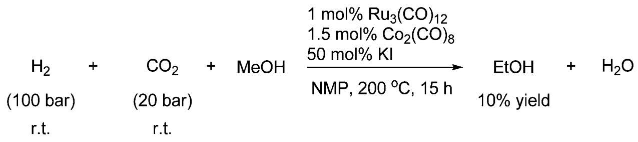
2.4.2 Hydrogenation of carbon dioxide to form hydrocarbons and alcohols. Many of the conversions of CO_2 are surprisingly enough exothermic despite the high stability of CO_2. However these reactions have a highly positive Gibbs free energy implying that the reaction is not thermodynamically favored. The hydrogenations of CO_2 have, in general, a negative Gibbs free energy and the reason for this is that water is formed. The stability of water is the reason that the overall Gibbs free energy becomes negative for many of the hydrogenation reactions. However the economics are unfavorable for the same reason. Examples of some of these hydrogenations are listed in Scheme 61.

The heterogeneous catalysis of hydrogenation of CO_2 to methanol and hydrocarbons is an area which has been widely investigated. However, only few reactions using homogeneous catalysis have been described.

In the first reaction (called the "Sabatier reaction") CO_2 is converted into methane by reaction with four moles of hydrogen. Heterogeneous catalysts of nickel, ruthenium and rhodium have proven to provide the best results for the Sabatier process.[112]

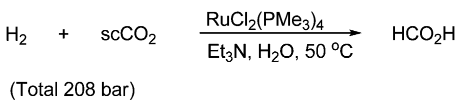
Hydrogen needed for these reactions has to be produced, which is, as mentioned above, highly energy demanding. The fact is that none of these transformations are favorable for CO_2 mitigation unless the energy needed comes from renewable energy.

Alkenes can be hydroformylated with CO_2 under medium pressure to afford alcohols and aldehydes in the presence of a ruthenium catalyst as shown in Scheme 62.[113]



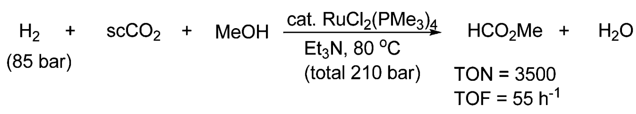
$$\underset{\substack{(100\text{ bar})\\ \text{r.t.}}}{H_2} + \underset{\substack{(20\text{ bar})\\ \text{r.t.}}}{CO_2} + MeOH \xrightarrow[\text{NMP, 200 °C, 15 h}]{\substack{1\text{ mol\% }Ru_3(CO)_{12}\\ 1.5\text{ mol\% }Co_2(CO)_8\\ 50\text{ mol\% KI}}} \underset{10\%\text{ yield}}{EtOH} + H_2O$$

Scheme 63 Methanol homologation with CO_2 in the presence of H_2.



$$\underset{(\text{Total }208\text{ bar})}{H_2 + scCO_2} \xrightarrow[Et_3N,\ H_2O,\ 50\ °C]{RuCl_2(PMe_3)_4} HCO_2H$$

Scheme 64 Formation of formic acid from H_2 and supercritical CO_2.



$$\underset{(85\text{ bar})}{H_2} + scCO_2 + MeOH \xrightarrow[\substack{Et_3N,\ 80\ °C\\ (\text{total }210\text{ bar})}]{\text{cat. }RuCl_2(PMe_3)_4} HCO_2Me + H_2O \quad \substack{TON = 3500\\ TOF = 55\ h^{-1}}$$

Scheme 65 Hydrogenation of CO_2 under supercritical conditions with methanol affords methylformate.

The reaction is believed to proceed *via* the formation of carbon monoxide through the reverse water gas shift reaction.[7] In the next reaction carbon monoxide is also believed to be the real reactant. Methanol is homologated with CO_2 in the presence of hydrogen under high pressure and temperature to afford ethanol in a low yield as shown in Scheme 63.[114]

2.4.3 Hydrogenation of supercritical carbon dioxide. Synthesis of formic acid, formic acid esters and formamides is carried out with both homogeneous and heterogeneous catalysts. The latter has several technical advantages such as stability, ease of separation, handling and reuse of catalyst. Despite these obvious advantages, the range of compounds synthesized by the heterogeneous pathway is still comparatively narrow.[115]

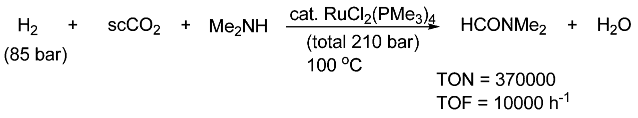
Homogeneous catalysts of, *e.g.*, ruthenium and rhodium are used in the synthesis of a large number of compounds. A reason for this is that high turnover numbers are achieved when applied in supercritical CO_2.

Hydrogenation of supercritical CO_2 has gained a growing interest since CO_2 can have a dual significance as both reactant and solvent, which does not produce waste. Furthermore it is possible to achieve very high H_2 concentrations with supercritical CO_2. Formic acid can be produced from hydrogen and supercritical CO_2 under ruthenium catalysis as shown in Scheme 64. With the ruthenium catalyst, 7200 moles of formic acid are formed per 1 mole of Ru with turnover frequencies up to 1400 h^{-1}.[106,116] The presence of triethylamine and a small amount of water is a prerequisite for the formation of formic acid by the hydrogenation of CO_2 in its supercritical phase.

Formic acid esters can be prepared by the hydrogenation of CO_2 in alcohol solvents. For example methylformate can be synthesized very efficiently by hydrogenation of supercritical CO_2 with methanol under ruthenium catalysis as shown in Scheme 65.[117] Formic acid is formed initially, which then reacts with methanol to afford methylformate.

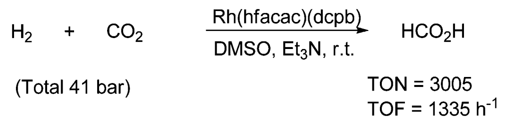
Exchanging alcohols with secondary amines affords formamide derivatives under nearly identical conditions. The hydrogenation of CO_2 under supercritical conditions in the presence of dimethyl amine results in the formation of *N*,*N*-dimethylformamide as shown in Scheme 66.[49c,118]

2.4.4 Hydrogenation of carbon dioxide to formic acid. Hydrogenations can also proceed efficiently at a lover pressures by alternating the reaction conditions. As an example formic acid can also be produced by hydrogenation of CO_2 at medium pressure in the presence of a catalyst with bulky ligands



$$\underset{(85\text{ bar})}{H_2} + scCO_2 + Me_2NH \xrightarrow[\substack{(\text{total }210\text{ bar})\\ 100\ °C}]{\text{cat. }RuCl_2(PMe_3)_4} HCONMe_2 + H_2O \quad \substack{TON = 370000\\ TOF = 10000\ h^{-1}}$$

Scheme 66 Formation of *N*,*N*-dimethylformamide by hydrogenation of supercritical CO_2 with dimethyl amine.



Scheme 67 Formation of formic acid by hydrogenation of CO_2 under rhodium catalysis.

(dcpb = $Cy_2P(CH_2)_4PCy_2$, hfacac = hexafluoroacetylacetonate) in an organic solvent as shown in Scheme 67.[119]

3 Photochemical reduction

In artificial photosynthesis, the goal is to mimic the ability of green plants and other photosynthetic organisms in their use of CO_2, which is reduced to make high energy compounds, *i.e.*, fuels or chemicals.[120] In order for the high energy compounds to be economically and environmentally attractive, the compounds must be formed from abundant, inexpensive raw materials such as water and CO_2.[121]

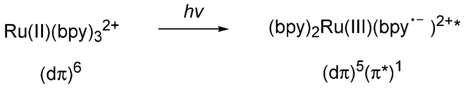
Transition-metal complexes have often been employed as catalysts and solar energy converters for the photochemical reduction of CO_2. Transition-metal complexes have found wide application in this area, since they are able to absorb a significant portion of the solar energy spectrum, have long-lived excited states, are able to promote the activation of small molecules and are robust.[122] Therefore they have been used as catalysts in the photochemical conversion of CO_2 using water as the source of electrons.

The systems studied for photochemical CO_2 reduction can be divided into several groups: $Ru(bpy)_3^{2+}$ both as a photosensitizer and a catalyst;[123] $Ru(bpy)_3^{2+}$ as a photosensitizer and another metal complex as a catalyst;[123a,124] $ReX(CO)_3(bpy)$ or a similar complex as a photosensitizer;[124a,125] $Ru(bpy)_3^{2+}$ and $Ru(bpy)_3^{2+}$-type complexes as photosensitizers in microheterogeneous systems;[126] metalloporphyrins both as photosensitizers and catalysts;[127] and organic photosensitizers and transition-metal complexes as catalysts.[122,128]

Table 3 summarizes some of the systems which have been studies for photochemical CO_2 reduction and their main products.[129]

The photochemical reduction is normally carried out at room temperature under 1 atm CO_2, which implies that the concentration of dissolved CO_2 in solution is low. The typical product for these systems is formate and carbon monoxide. DMF solutions containing $Ru(bpy)_3^{2+}$, $Ru(bpy)_2(CO)X^{n+}$ (X = CO, Cl, H, ect) and triethanolamine as a sacrificial electron donor have been used for photochemical CO_2 reduction.[123a,124c,d,132] These systems produce in a total quantum yield of up to 15% formate as the major product and CO as a minor product.[129] Some of the best systems are able to produce a total quantum yield for the reduced products of up to 40%.[122,125c] The turnover number and frequency is dependant on irradiation wavelength, light intensity, irradiation time and catalyst concentration.[122]

A photoactive system converts sunlight into electrical energy, which is used to reduce CO_2 with the help of a catalyst. The first part of a photochemical reduction is light absorption. The absorption of light is the energy input step that must trigger the photosynthetic reaction. The light is absorbed at the molecular level and the incident light energy is converted into transient stored chemical energy in the exited state. In artificial photosynthesis, ruthenium polypyridyl complexes have been used extensively to mimic plant chlorophylls, which play a major part



Scheme 68 An electron is promoted from a metal-based dπ to a low lying π* level on the polypyridyl ligand.

Table 3 Photocatalytic reduction of CO_2. (after ref. 129)

Sensitizer	Catalyst or relay	Donor	Product/s	Φ^b (mol/Einstein)	Ref.
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$	0.049[c]	123*a*
$Ru(bpy)_3^{2+}$		TEOA	$HCOO^-$	0.096[d]	123*a*
$Ru(bpy)_3^{2+}$	MV^{2+}	TEOA	$HCOO^-$	0.01	123*b*
$Ru(bpy)_3^{2+}$	Co^{2+}/bpy	TEA	CO, H_2		130
$Ru(bpy)_3^{2+}$	Co^{2+}/Me_2phen	TEA	CO, H_2	0.012 (CO), 0.065 (H_2)	131
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	TEOA	$HCOO^-$	0.14	124*c*,*d*, 132
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)_2^{2+}$	BNAH	$HCOO^-$, CO	0.03 ($HCOO^-$), 0.15 (CO)	124*c*,*d*, 132
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)(H)^+$	TEOA	$HCOO^-$	0.15	123*a*
$Ru(bpy)_3^{2+}$	$Ru(bpy)_2(CO)(X)^{n+}$, X = Cl and Co	TEOA	$HCOO^-$		123*a*
$Ru(bpy)_3^{2+}$	$CoHMD^{2+}$	H_2A	CO, H_2		133
$Ru(bpy)_3^{2+}$	$Nicyclam^{2+}$	H_2A	CO, H_2	0.001 (CO)	124*e*,*f*
$Ru(bpy)_3^{2+}$	NiPr-cyclam2+[a]	H_2A	CO, H_2	*Ca.* 0.005 (CO)	124*g*
$Ru(bpz)_3^{2+}$	Ru colloid	TEOA	CH_4, H_2	10^{-4} (CH_4)[e]	126*a*,*b*
$Ru(bpy)_3^{2+}$	$Bipyridinium^+$, Ru or Os colloid	TEOA	CH_4, H_2	10^{-4} (CH_4)[e] 10^{-3} (H_2)[e]	126*b*
$ReCl(bpy) (CO)_3$		TEOA	CO	0.14	124*a*, 134
$ReCl(bpy) (CO)_3$		TEOA	CO	0.15	125*a*,*b*
$[ReP(OEt)_3 (bpy)(CO)_3]^+$		TEOA	CO	0. 38	125*c*
p-Terphenyl	$Cocyclam^{3+}$	TEOA	CO, $HCOO^-$, H_2	0.25 (CO + $HCOO^-$)	135, 136
p-Terphenyl	$CoHMD^{2+}$	TEOA	CO, $HCOO^-$, H_2		136, 137
Phenazine	$Cocyclam^{3+}$	TEOA	$HCOO^-$	0.07[e]	138
FeTPP		TEA	CO		127*a*
CoTPP		TEA	$HCOO^-$, CO		127*b*

[a] Pr-cyclam 6-((*N*-R)pyridin-4-yl)methyl-1,4,8,11-tetraazacyclotetradecane where R = *p*-methoxybenzyl and benzyl. [b] The quantum yield of product formation is defined as the formation rate divided by the light intensity. [c] With 15% water in DMF. [d] With 15% water and excess bpy in DMF.

in the light-harvesting cycle. In the ruthenium complexes the absorption of light comes from metal-to-ligand charge transfer (MLCT) transitions. The transitions involves an electron being exited from a metal based dπ orbital to a low lying π* level on the ligand as shown in Scheme 68.[120,139]

The MLCT have several desirable features. They are quite stable and their lifetime is therefore sufficiently long to undergo chemical reactions. The absorption range of these complexes can be tuned and extended by varying the transition metal or the ligand. Thereby the complexes can absorb from the near infrared to the ultraviolet region. In order for the MLCT excited state to be useful it must be reached with high efficiency following light absorption and must have a long lifetime to undergo chemical reactions.[120,140] The energy in the exited state must undergo a chemical reaction, before it decays to the ground state, in order for it to be used chemically. Electron transfer chemistry provides a basis for utilizing the stored energy. The half-reactions in Scheme 69 involves net electron transfer and combined they give the overall reaction where CO_2 as an example is reduced to formic acid and H_2O is oxidized to O_2.

In order to avoid recombination by back electron transfer, a directional charge-transfer character must be built into the system. In plant photosynthesis, a gradient separates the photo chemically produced oxidative and reductive equivalents by electron transfer and directs them to different places of the molecular structure. In plants there are specific catalytic sites for the reduction of CO_2 and the oxidation of H_2O. In artificial photosynthesis this problem have been addressed by synthesizing molecules which consist of a light absorber (chromophore) and electron transfer donors and acceptors which are chemically attached to the chromophore at spatially separated sites. In these molecules the light induced redox splitting is directional due to the existence of an intermolecular free energy gradient. The gradient arises from differences in redox potentials between the exited state couples and the quencher (ground state) couples.[140,141]

$$2CO_2\,(g) + 2H_2O\,(l) \longrightarrow 2HCO_2H\,(aq) + O_2\,(g) \qquad E^o = -1.43\ V$$

$$CO_2 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow HCO_2H \qquad E = -0.61\ V$$

$$2H_2O \longrightarrow O_2 + 4e^{\ominus} + 4H^{\oplus} \qquad E = -0.82\ V$$

Scheme 69 The overall reaction which produces formic acid from CO_2 and H_2O is an oxidation–reduction reaction and consists of two half reactions.

$$CO_2 + e^{\ominus} \longrightarrow CO_2^{\ominus\cdot} \qquad E^o = -1.9\ V$$

$$CO_2 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow CO + H_2O \qquad E^o = -0.53\ V$$

$$CO_2 + 2H^{\oplus} + 2e^{\ominus} \longrightarrow HCO_2H \qquad E^o = -0.61\ V$$

$$CO_2 + 4H^{\oplus} + 4e^{\ominus} \longrightarrow HCHO + H_2O \qquad E^o = -0.48\ V$$

$$CO_2 + 6H^{\oplus} + 6e^{\ominus} \longrightarrow CH_3OH + H_2O \qquad E^o = -0.38\ V$$

$$CO_2 + 8H^{\oplus} + 8e^{\ominus} \longrightarrow CH_4 + 2\,H_2O \qquad E^o = -0.24\ V$$

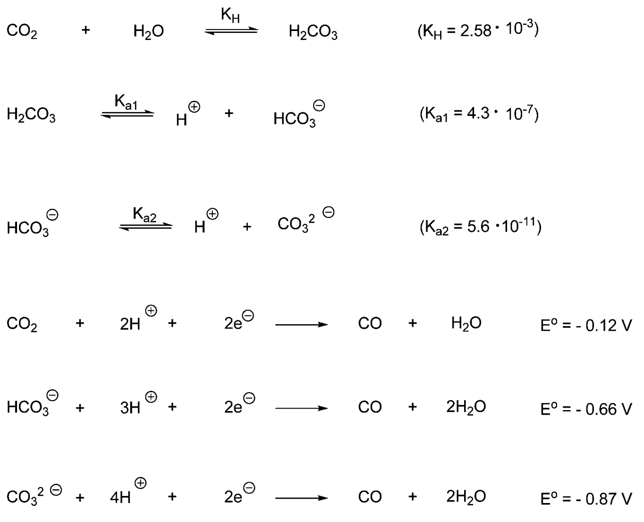
$$H_2O \longrightarrow HO^{\cdot} + H^{\oplus} + e^{\ominus} \qquad E^o = 2.38\ V$$

$$2\,H_2O \longrightarrow O_2 + 4H^{\oplus} + 4e^{\ominus} \qquad E^o = 0.82\ V$$

$$2H^{\oplus} + e^{\ominus} \longrightarrow H_2 \qquad E^o = -0.41\ V$$

Scheme 70 Potentials for the reduction of CO_2 to various products and potentials for the oxidation of H_2O to various products (potentials measured at pH 7 in aqueous solution *versus* NHE, 25 °C, 1 atmosphere gas pressure, and 1 M for the other solutes).[140,141]

The stability of H_2O and CO_2 is evidenced by their high electrochemical overpotential for direct electron transfer. One-electron transfer to H_2O and CO_2 are highly unfavorable thermodynamically because they involve the formation of high-energy intermediates such as $^{\bullet}OH$ or $CO_2^{\bullet\ominus}$. The potential for the reduction of CO_2 to $CO_2^{\bullet\ominus}$ is for example −1.9 V *versus* NHE. Furthermore there is a large kinetic 'overvoltage' for the one-electron reduction, due to structural differences between the linear CO_2 and the bent $CO_2^{\bullet\ominus}$.[129,140] Thus multi-electron reduction processes are thermodynamically favored over the single electron transfer transformations, as shown in Scheme 70.[140] Redox reagents must therefore be designed to carry out the oxidation of water and the reduction of CO_2 in synchronous multielectron steps near the thermodynamic potential of the CO_2/desired reduction product.[120] Thus one-electron products generated in photochemical transformations should be transferred into electron-sink entities or multi-electron charge relays, capable of inducing multi-electron oxidation or reduction processes. Catalysts should provide effective charge storage entities for such multi-electron redox transformations. A limitation of artificial photosynthetic devices is as evidenced in Scheme 70 that the reduction of CO_2 could lead to five different C_1-reduction products. Furthermore, the reduction of CO_2 in water is expected to be accompanied by the competitive reduction of H_2O to give H_2 evolution.[140] A further complication from performing the reduction of CO_2 in aqueous media relates to the different hydration products of CO_2 present in water. CO_2 undergoes in water hydration to form carbonic acid that undergoes stepwise dissociation to bicarbonate HCO_3^- and carbonate CO_3^{2-}. The predominant species in solution is dependent on pH. At pH below 4.5 CO_2 is the dominant component, at pH between 7.5–8.5 bicarbonate is the major form and at pH above 11.5 is only carbonate present. The thermodynamic reduction potentials for generating certain products are strongly affected by the form of CO_2 (hydrated and non-hydrated). The reduction potentials are exemplified for the formation of CO in Scheme 71.



Scheme 71 Dissociation constants for CO_2 in aqueous media and reduction potentials for CO_2, bicarbonate and carbonate to give CO.

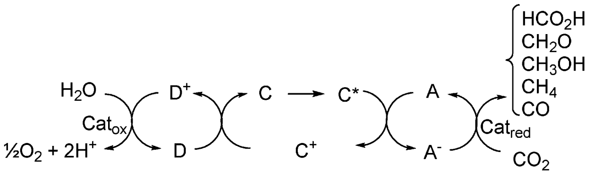


Fig. 3 Photocatalysis of water or another electron donor and CO_2-fixation in an artificial photochemical system.

It is evident from Scheme 69 that tuning the pH of the aqueous solution provides a means to thermodynamically control CO_2 reduction and eliminate H_2 evolution.[140]

Thus the photochemical process could yield a mixture of products. By employing heterogeneous or homogeneous catalysts it is possible to induce selectivity into the system and control a desired route that utilizes the electron transfer products. The catalysts should furthermore activate the substrate towards the redox transformation and act as a multielectron redox relay.[140]

The basic requirements of the artificial photosynthetic system are summarized in Fig. 3.

The system should comprise a light absorber (chromophore), which upon photoexcitation results in an electron transfer and formation of the redox products A^- and D^+. Subsequent catalytic reduction of CO_2 and concomitant catalytic oxidation of H_2O or another electron donor, (*e.g.*, triethanolamine and triethylamine) by A^- and D^+ respectively recycles the system components and light energy is converted into chemical energy, provided that the process has a favorable free-energy change with $\Delta G^\circ < 0$. The photochemical system should be placed in a membrane, which facilitates the physical separation of the formed products.[121,140]

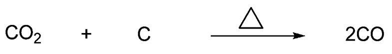
Since renewable energy is used for the CO_2 transformation, this technology leads to CO_2 mitigation. However while some progress has been made on each aspect of artificial photosynthesis, integration of various components in a working system has not yet been achieved. There are some unresolved issues with selectivity of the reactions and in particular limited efficiency, which has to be solved before it is possible to assess the potential of photoreduction for CO_2 mitigation.[6,121]

4 Electrochemical and chemical reduction of carbon dioxide

4.1 Chemical reduction

As mentioned earlier, the catalytic hydrogenation of CO_2 to methanol produce water as a byproduct. This means that one third of the energy-costly hydrogen is used to produce water. One way to avoid this is by reducing CO_2 to CO to minimize water formation. Methanol can then be produced by adding the right amount of hydrogen to CO and thereby make synthesis gas, which in turn can be converted to methanol with the right catalyst.

This can be done chemically by the reverse Boudouard reaction *via* the thermal reaction of CO_2 with carbon or coal itself, as seen in Scheme 72.[13]



Scheme 72 Chemical reduction of CO_2 with carbon or coal to produce CO.

The reaction is endothermic and is run at temperatures above 800 °C. This reaction has been investigated for the conversion of solar heat into liquid fuels. This reaction allows solar energy to be stored and transported in the form of a liquid energy carrier such as methanol. The reverse Boudouard reaction is not limited to coal; in general, all carbonaceous materials can be gasified into CO. An example of this is gasification of waste material.[6]

4.2 Electrochemical reduction

For the reduction of CO_2 to liquid fuels or fuel precursors such as CO/H_2 (synthesis gas) proton-coupled electron steps are, as mentioned earlier and exemplified in Scheme 67, generally more favorable than single electron reductions, as thermodynamically more stable compounds are produced.[141] The multielectron reductions of CO_2 become more favorable, in a thermodynamic sense, the more reduced the product. However the difficulty of transfer of multiple electrons to the site of the reduction is a limiting factor in the feasibility of such processes.[142]

Electrochemical reduction using an unreactive metal or carbon electrode gives a CO_2 radical anion, which may undergo dimerization to oxalate or disproportionation to CO and carbonate. By contrast, active metals, through active sites on their surface, can direct CO_2 reduction to hydrogenated products at a much lower applied voltage because of the high efficiency of the heterogeneous catalysis. In these systems the metal serves a dual role, both delivering electrons and stabilizing the reduced fragments.[143] The electrochemical reduction has been studied with various metal cathodes in aqueous media, and studied in some organic solvents.[144] The most common reduction products are formic acid, carbon monoxide and oxalic acid, although some examples of successful 6-electron and 8-electron conversions to methanol and methane, respectively, have been described.[141,144*b*,145] When the reaction is performed in water or methanol, hydrogen will also be formed in competition with CO_2 reduction. It can, however, be advantageous to generate CO and H_2 concurrently at the cathode in a H_2/CO ratio close to 2 : 1, and thereby producing synthesis gas. The synthesis gas can then by further reaction be transformed into methanol. This reaction is however still in the research phase, and has some efficiency problems which must be overcome.[146] The reaction has an advantage over commercial production of synthesis gas from natural gas or coal in that no purification step is necessary and no impurities such as sulfur are present that can deactivate the catalyst used for methanol production.[13]

The nature of the electrode metal for CO_2 reduction in aqueous electrolytes is able to strongly effect the product composition. Metallic electrodes such as Hg, Cd, Pb, Tl, In and Sn can reduce CO_2 with a high current efficiency. However these metals are poor catalysts in the sense that the primary product is formate, (*i.e.*, there is no breaking of the carbon–oxygen bond). Pb and Hg have been shown to give oxalate in nonaqueous media.[144*a*,147] Metals like Pt, Ni, Fe, Al, Ga and Ti will reduce CO_2 to form CO, however due to the low turnover of CO the principle product for these electrodes is hydrogen.[148] Electrode materials such as Au, Ag, Zn and Cu will produce CO with a high current efficiency. However Cu is able to convert CO into more-reduced species such as methane, ethane, aldehydes and alcohols in significant amounts.[145,149] Cu electrodes are able to reduce CO_2 into methane in bicarbonate solutions with current efficiencies as high as 65%, although the overpotential is very large (1.5 V).[122,150] The overvoltage or overpotential can be considered to be the difference between the applied electrode potential and the equilibrium potential.[141,151] The product composition for the electrochemical reduction of CO_2 can also be affected by the electrolyte medium. Zinc electrodes in 0.1 M $KHCO_3$ at potentials of −1.5 to −1.7 V (*vs.* Ag/AgCl) will give a mixture of CO and formic acid, while in 0.05 M K_2SO_4, the predominant product is CO, in up to 80% Faradaic efficiency, with small yields of formic acid. This electrolyte dependency can be explained by the higher rate of dissolution of the Zn electrode in the K_2SO_4 solution (pH 4.2) than in the $KHCO_3$ medium (pH 6.8). The dissolved Zn^{2+} ions promote the formation of CO.[4,152]

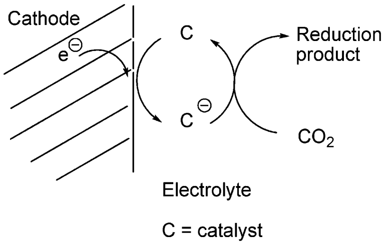


Fig. 4 Schematic representation of the catalyzed electrochemical reduction of CO_2.

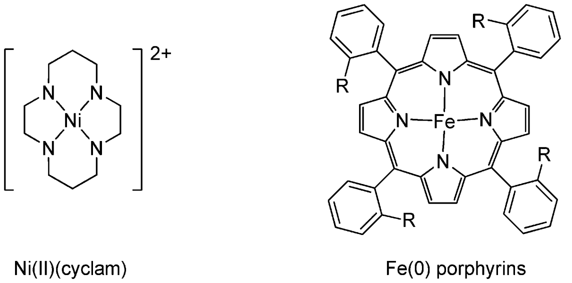
The electrochemical reduction to hydrocarbons will give rise to bond breaking and bond formation and hence will pose some kinetic challenges. One possibility is to identify a single catalyst which can direct the complete sequence of steps for reducing CO_2 to firstly CO, then to CH_2O and further to hydrocarbons or alcohols. All steps take place with low kinetic barriers. A second option is to create catalyst panels where each panel catalyzes the specific step in the overall transformation of CO_2 to a hydrocarbon or alcohol. An electrocatalyst is able to participate in the electron transfer reaction and increase the reaction rate and hence the current at a potential as close as possible to the equilibrium potential. The electron transfer and chemical kinetics must be fast for an efficient electrocatalyst. These factors can be optimized by chemical variations of the electrocatalyst metal centre *via* appropriate ligand design. The catalyzed electrochemical reduction of CO_2 is illustrated in Fig. 4.[141,151]

Direct electrochemical reduction of CO_2 on most electrode surfaces requires large overvoltages which consequently lowers the conversion efficiency. Electrocatalysts can be employed to lower the overpotential, improve selectivity and increase the reaction kinetics for the CO_2 reduction.[141,151]

Homogeneous electrocatalysts for the reduction of CO_2 can be divided into three major categories that depend on the ligand type: (1) metal catalysts with macrocyclic ligands; (2) metal catalysts with bipyridine ligands; and (3) metal catalysts with phosphine ligands.[141]

4.2.1 Metal complexes with macrocyclic ligands.

Ni(II) cyclam complexes are able to catalyze the reduction of CO_2 to CO. The complexes are stable, highly selective and are able to reach Faradaic efficiencies of up to 96% at −0.86 V *vs.* SCE under aqueous conditions.[153] Fe(0) porphyrins are able to reduce CO_2 to CO in the presence of Brønsted acids such as 1-propanol,



Ni(II)(cyclam) Fe(0) porphyrins

Fig. 5 The metal complexes with macrocyclic ligands used in the mentioned examples.

2-pyrrolidine and CF_3CH_2OH. The catalyzed reaction can reach turnover numbers as high as 350 h^{-1} at a catalyst decay rate of 1% per catalytic cycle, although at a large negative potential of approximately -1.5 V *vs.* SCE and with a mercury electrode.[154] The two metal complexes are shown in Fig. 5.

4.2.2 Metal complexes with bipyridine ligands. Re(bpy)$(CO)_3Cl$ complexes are able to catalyze selectively the reduction of CO_2 to CO. The selective reaction is performed at a potential of -1.49 V *vs.* SCE using a 9 : 1 DMF–H_2O solution. The reaction shows a solvent dependency, since increased amounts of water will decrease the selectivity for CO. Under an argon atmosphere the reduction product will be solely H_2. The electrocatalyst gives high current efficiencies (98%) and excellent selectivity for CO over H_2 formation; however the limiting factor for this reduction is the low turnover frequency at 21.4 h^{-1}.[155] Rhodium complexes, *cis*-$[Rh(bpy)_2X_2]^+$ (X is Cl or OTf), reduce CO_2 to predominantly formate at -1.55 V *vs.* SCE. CO is not formed in any of the experiments; however H_2 is formed presumably by the degradation of the supporting electrolyte. The electrocatalyst gives poor current efficiencies for formate (64%) and H_2 (12%).[156] It is unusual for homogeneous catalysts to form reduction products that require more than two electrons. However by using $[Ru(tpy)(bpy)(CO)]^{2+}$ complexes (tpy = 2,2′:6′,2″-terpyridine) as electrocatalysts CO_2 can be reduced to a mixture of glycolate ($HOCH_2COO^-$), glyoxylate ($OCHCOO^-$), formic acid, formaldehyde and methanol in a 8 : 2 EtOH–H_2O solution at -20 °C. Although turnover numbers are not given for these highly reduced species, their formation shows that a single-site catalyst can give rise to a multielectron reduction of CO_2.[157]

4.2.3 Transition metal phosphine complexes. Examples of the third category include $[Pd(triphosphine)(CH_3CN)]^{2+}$ complexes which catalyse the electrochemical reduction of CO_2 to CO. These catalysts have shown catalytic rates in the range of 10 to 300 M^{-1} s^{-1} and with excellent (over 90%) current efficiencies for the formation of CO. Overpotentials were in the range of 100–300 mV, however the limiting factors for this catalyst type are the low (10–100) turnover numbers and the decomposition to Pd(I) dimers and hydrides which eventually cause termination of catalytic activity. The tridentate phosphine catalyst is shown in Fig. 6.[158]

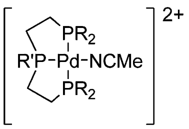


Fig. 6 The tridentate phosphine catalyst.

The relatively mild conditions and low overpotentials required for some of the homogeneous catalysts make them attractive for future studies; however a number of efficiency problems must be overcome before this technology is useful for fuel production.[122]

In this review electrochemical reductions employing semiconductors, alloy electrodes, gas diffusion electrodes[4] and bioelectrochemical reductions have been omitted.[159]

4.3 Photocatalysis

The difference between electrochemical reduction and photocatalysis is the source of electrons. Electrons from electrochemical process are supplied by an applied current; electrons from photocatalysis are supplied by a semiconductor exposed to light.[160] Semiconductors[161] are used to reduce CO_2 to give products like CO, HCOOH, HCHO, CH_4 and CH_3OH.[3,160,162] Unlike metals which have continuum of electronic states, semiconductors exhibit a void energy region, or band gap, that extends from the top of the filled valence band (VB) to the bottom of the vacant conduction band (CB) when exposed to light as illustrated in Fig. 7.[160]

The photocatalysis over semiconductors is initiated by the absorption of a photon with equal or greater energy than the band gap of the semiconductor. The excitation of an electron from the VB to the CB gives an electron vacancy or a positive charge called a hole (h^+) in the VB and the electron–hole (e^-/h^+) pair is produced. The generation of the electron–hole pair and its reverse process are represented in Scheme 73.[160,163]

The separated electron–hole pair can follow one of four pathways. Migration of electrons and holes to the semiconductor surface is followed by a transfer of electrons to acceptors and the holes can combine with electrons from donor species. The electron-transfer process is more efficient if the species are absorbed on the surface.[164] The last two pathways are recombination producing thermal energy either in the volume of the

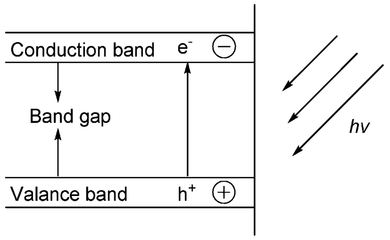


Fig. 7 Illustration of the band-gap formation in semiconductors arising from light.[160,163]

$$\text{Photocatalyst} \xrightarrow{hv} e^- + h^+$$

$$e^- + h^+ \longrightarrow \text{heat}$$

Scheme 73 Generation of electron–hole pairs by light absorption and the recombination of the pair. (*hv* is the photon energy, e^- represents a conduction band electron, and h^+ a hole in the valance band).

Table 4 Summary of some of the CO2 photocatalysts studied in the literature.[160]

Photocatalyst	Reductant	Primary product(s)	Ref.
TiO_2/zeolite	Water	CH_3OH	168, 173
TiO_2	H_2	CO	175*b*
TiO_2 (P-25)	Isopropyl alcohol	CH_4, HCOOH	169
TiO_2 nanocrystals in SiO_2	Lithium nitrate/ 2-propanol	Formate, CO, NH_3, urea	173*k*
Rh/TiO_2	H_2	CO, CH_4	177
Pd/RuO_2/TiO_2, Pd/TiO_2	NaOH, aqueous Na_2SO_3	Formate	173*c*
MgO	H_2	CO	178
ZnO on activated carbon	—	CO, H_2	174

semiconductor particle or on the surface. The lifetime of an excited electron–hole pair is a few nanoseconds,[165] but this is adequate for promoting redox reactions in the solution or gas phase in contact with the semiconductor.

When the photoreduction of CO_2 is performed with water as the reductant the amount of organic products are very low. This may be ascribed to the solubility of CO_2 in water, which is low at neutral pH, and the CO_2 photoreduction process competing with H_2 and H_2O_2 formation, which consumes H^+ and e^-. However, it is primarily because H_2O is a much poorer electron donor compared to organic solvents. Therefore improving the efficiency by employing sacrificial electron donors such as triethylamine,[166] triethanolamine,[167] dimethylformamide[166b] and isopropyl alcohol[169] have been extensively studied. Photocatalysis of CO_2 can also be achieved in the gas phase using sacrificial electron donors such as H_2S,[170] H_2[165,171] and CH_4.[172] Sulfide and sulfite ions are often available as waste products from the petrochemical industry and from fossil-burning fuel stations. The oxidation of these waste products is environmentally beneficial and the development of efficient photocatalytic reduction of CO_2 using sulfides or sulfites is therefore highly beneficial for CO_2 mitigation and removal of waste compounds.[4]

A number of semiconductor materials such as TiO_2,[159,168,173] ZnO,[174] ZrO_2,[175] CdS,[166b168] Fe_2O_3,[176] WO_3[161,176] and their various combinations have been employed as photocatalysts. Some of the studied catalysts and their products are summarized in Table 4.

However, it is generally accepted that TiO_2 and its related materials are the most reliable materials for photocatalytic reactions, due to its low cost, high catalytic activity and high stability under irradiation with light.[163,179] Furthermore, large-band gap semiconductors such as TiO_2 are more suitable as photocatalysts for CO_2 reduction, because they provide sufficient negative and positive redox potentials in conductance and valance bands, respectively. The large band-gap requires a high energy input and TiO_2 (anatase) is only active in the ultraviolet region of the solar spectrum.[160] Photocatalytic CO_2 reduction using TiO_2 as the catalyst has been performed in liquid[168,169,173,180] and gas phase[173e,o,181] systems. The efficiency of the photocatalytic system is reduced by the recombination of the photoexcited electron–hole pair. Studies have shown that doping the semiconductor with a metal improves the photocatalytic efficiency, since the metal acts as an electron trap. The metals suppress the recombination of the electron–hole pair and increase the lifetime of the separated electrons and holes.[160,179] Methane production is observed for the photocatalytic reduction of CO_2 when using a Cu/TiO_2 suspension in water.[182] Photoirradiation to CO_2 saturated water with 3 wt% CuO-doped TiO_2 shows the best results for methanol production. The quantum efficiency of the catalyst reaches 0.19, whereas unmodified TiO_2 shows only 0.06.[179,180d] The metal loading must be optimized and uniformly dispersed over the semiconductor surface. An excess metal loading will result in a decrease in the photocatalytic activity, since the semiconductor surface cannot be illuminated as photons cannot be absorbed due to reflection.[160]

High photocatalytic efficiency and selectivity for the formation of methanol can be achieved by employing zeolite or silicate containing highly dispersed Ti-oxide species. The zeolite or silicate framework offers unique nanoscaled pores, unusual internal surface topologies, and ion-exchange capacities.[173o,181a,b,c]

Photocatalysis is affected by the increase of CO_2 pressure since a larger amount of CO_2 is dissolved in the water or organic medium, thus improving the CO_2 reduction selectivity towards liquid products.[160,173o]

Most of the photocatalytic CO_2 reduction reactions require the presence of sacrificial electron donors such as iso-propanol, tertiary amines or DMF in order to achieve substantial yields. These compounds are usually more valuable than the CO_2 reduction products. In the absence of such sacrificial electron donors the yields are very low. Therefore it can be concluded that photocatalytic CO_2 reduction is not a useful CO_2 mitigation technology at the present stage and further research is needed.[4]

Photoinduced CO_2 fixation systems containing enzymes are omitted, however reviews can be found in the reference list.[183]

5 Biological transformations of CO_2

Photosynthetic organisms may be quite different, but all of them use basically the same strategy in which light is initially absorbed by antenna proteins containing many chromophores, followed by energy transfer to a specialized reaction center protein, in which the captured energy is converted into chemical energy by means of electron-transfer reactions.[184]

Fossil fuels, by which modern day society depends upon, are formed from anaerobic decomposition of then-living plants and microorganisms. The fossil fuels: coal, oil and natural gas were formed during the carboniferous period—roughly 360 to 290 million years ago. Oil and gas were formed from the organic remains of prehistoric zooplankton and algae, which have settled down on the sea floor in large quantities under anaerobic conditions. As the sediment pile becomes deeper the organisms within it are subjected to heat and pressures which lead to formation of oil and then gas. Coal, by contrast, is typically formed in non-marine settings from the remains of land vegetation in lowland and swampy environments. Due to the anaerobic conditions the accumulated plant debris is prevented from breaking down. The plant debris initially forms a material known as peat. Then by action of the heat and pressures of geological forces, peat is eventually hardened into coal in a process called coalification.[185]

Biological carbon sequestration using technologies such as controlled photosynthetic reactions helps to alleviate greenhouse gas problems in a sustainable way. An example of this is the use of

$$6CO_2\,(aq) \quad + \quad 6H_2O\,(l) \quad \xrightarrow[\Delta]{h\nu} \quad C_6H_{12}O_6\,(aq) \quad + \quad 6O_2\,(g)$$

Scheme 74 The photosynthetic reaction gives glucose and oxygen.[5]

a photo-bioreactor system, where natural photosynthesis takes place in a controlled environment, *i.e.*, the light flux is delivered in the right wavelength, since the uniform distribution of light will affect the CO_2 uptake rates. A constant climate is kept to promote the photosynthetic process, where light, heat and CO_2 is converted into useful products such as carbohydrates, hydrogen and oxygen as shown in Scheme 74.[186] The type of biological strains used in the bioreactor depends on the product outcome.

It is estimated that glucose is formed at a rate of 1 g per hour per square meter of leaf surface, which means that approximately 200 Gt of glucose is produced annually by the photosynthetic process.[63]

The development of closed system bioreactors have been an ongoing process for the last 50 years, despite this commercial viability has yet to be achieved.[5]

5.1 Algae

In most plants, photosynthesis is an inefficient reaction with slow kinetics. This is especially the case for larger plant species which have to use significant amounts of energy to build their structure, uptake and transport water, and reproduce. With simpler and smaller plants, the efficiency of the photosynthesis reaction is moderately higher as they do not need to invest as much energy to build large structures. At the extreme end of this scale are single-cell algae. They are the smallest and simplest forms of plants and they lack traditional plant structures relying instead on water as their supporting structure, which allows the cells to use all their energy for reproduction. Microalgae have the ability to fix CO_2 using solar energy with an efficiency 10 times greater than that of terrestrial plants.[187] There have therefore been considerable efforts to apply the microalgae culture for both CO_2 fixation and the production of valuable materials. Research has looked into finding and isolating suitable algal strains. Furthermore, photobioreactors have with higher fixation rates and possible scale-up have been investigated. It has been proposed to combine the wastewater treatment with fixation of CO_2 from exhaust gases. Algal cultures may be combined with wastewater, which is rich in nutrients such as nitrate and phosphate, with exhaust gases from, *e.g.*, power stations and steel mills for fixation of CO_2.[4] The development of suitable algal strains with not only a high tolerance for increasing CO_2 concentrations but also towards temperature and toxic compounds (NO_x and SO_x) is therefore ongoing.[188]

Photobioreactor systems are of high importance since the CO_2 fixation rate is very low, which implies that a large area is required to perform the CO_2 sequestration. The most widely used photobioreactor for commercial production of microalgae is an open pond called a raceway pond. It is found that an area of 1.5 km^2 is required for the fixation of CO_2 emitted from a 150 MW thermal power plant by using a raceway pond.[188] Open ponds have the advantage of using free light from the sun. However, these systems are easily contaminated by other organisms, which make it difficult to maintain a monoculture in open systems.[189] Therefore research have gone into designing closed systems, which give rise to an improved environmental control over important parameters such as temperature, pH and partial pressure of CO_2. Closed systems gives furthermore an increased biomass concentration which makes harvesting easier and allows for an easier upholding of a monoculture.[189] The productivities of various photobioreactors have been compared in Table 5.

Only three commercial closed photobioreactors have been constructed and are under operation. One of the systems consists of running compact glass tubes of a total length of 500 000 meters and a total reactor volume of 700 m^3. The systems occupies 10 000 m^2 and fixate 260–300 tons of CO_2, which results in the annual production of 130–150 tons of dry biomass.[188]

Recent research shows that certain specialized algae can convert 50 to 80% of their energy into lipids. The process begins with flue gases being passed over clear tube bioreactors that are filled with water and suspended algae. The bioreactors are oriented to receive maximum exposure to the sun. As the algae mix with the flue gas, they fixate CO_2. The surplus of algae is continually collected and removed from the bioreactor in order to maintain a relatively constant concentration of algae to water in the bioreactor. The harvested algae are passed through a two-stage dewatering process. The recovered water is returned to the reactors, leaving a dewatered high lipid containing algae cake. The productivity for the pilot plant is 100 g dry mass m^{-2} per day. After passing through the photobioreactor, the flue gas is vented to the atmosphere. Results from the pilot plant shows that CO_2 in the flue gas slip stream was reduced by 82.3% ±12.5% on sunny days and 50.1% ±6.5% on cloudy days. The dewatered algae cake can be collected and converted into biofuels using commercial available processes.[198]

5.2 Nonphotosynthetic pathways

Nonphotosynthetic pathways for CO_2 fixation are those performed by the bacteria methanogens. In these anaerobic microorganisms, the Calvin cycle for CO_2 fixation does not work, and

Table 5 Productivity of biomass grown outdoors in different photobioreactors (from Ref. 188)

Photobioreactor	Microalgae stains	Culture volume/L (light path/cm)	Highest productivity/g $m^{-2}day^{-1}$	Ref.
Raceway pond (open)	*Chlorella* sp.	200 (20.0)	13.2	190
Raceway pond (open)	*Chlorophyta* sp.	200 (20.0)	8.2	190
Helical tubular	*Chlorella* sp.	30 (2.5)	28.1	191
Vertical flat-plate (closed)	*Synechocytis aquatilis*	24 (1.5)	31.0	192
Vertical flat-plate (continuous)	*Nannochloropsis* sp.	1000 (10.0)	12.0	193
Tubular (in vertical arrangements)	*Chlorella* sp.	700 000 (5.0)	35.7	194
Tubular (horizontal)	*Haematococcus pluvialis*	25 000 (41.0)	13.0	195
Tubular (inclined)	*Chlorella pyrenoidosa*	50 (1.2)	130.0	196
Annular (closed)	*Nannochloropsis* sp.	140 (3.5)	52.5	197

acetyl-coenzyme A (CoA) is the central intermediate in carbon metabolism.[199] The methanogens grow in freshwater and marine sediments, peats, swamps and wetlands, rice paddies, landfills, sewage sludge, manure piles and the gut of animals. The bacteria grow optimally in temperatures between 20 and 95 °C. They are able to use CO and H_2 or CO_2 and H_2 as their only source of carbon and energy. They convert CO or CO_2 together with H_2 into methane, and more than half of the methane released into the atmosphere is due to the actions of the methanogens.[4]

It has been proposed to use the methanogenic bacteria for fixation of CO_2 from waste gases from blast furnaces. The bacteria will then transform the waste gases into methane, which may be used as fuel for steam boilers. Experiments show that by using H_2 as the reducing agent and mixtures of CO and CO_2 as carbon source, methane is formed by thermophilic methanogens in a column bioreactor. When the gas recirculation rate is 18 L h^{-1}, the daily rates of H_2 consumption and CH_4 production are 1380 and 300 mmol L^{-1}.[200]

By employing a mixture of three bacteria cultures it is possible produce methane in a completely biocatalytic conversion from a mixture of CO, CO_2 and H_2. The photosynthetic bacterium *Rhodospirillum rubrum* transforms CO and H_2O into CO_2 and H_2 *via* the water–gas shift reaction resulting in a 100% conversion. Simultaneously, a mixture of two methanogens, *Metanobacterium formicium* and *Methanosarcina barkeri* converts CO_2 into methane in 83% of the theoretically required by the reaction shown in Scheme 75.[4]

Conventional gas-phase catalytic methods for methanation of CO_2 require temperatures in the range of 300 to 700 °C and pressures in the range of 3 to 20 atm. The catalysts used are furthermore sensitive to catalyst poisoning, *e.g.*, by sulfur compounds from exhaust gases. In contrast to this is the biological conversion with the triculture system able to operate at 37 °C, and is not affected by the presence of sulfur compounds or variations in the composition of the feedstock gases.[201]

A possible way to obtain methane from biogas, which consists of a mixture of methane, CO_2, H_2S, H_2 and N_2 and at the same time completely removing H_2S from the off-gases, is by employing the chemoautotrophic methanogen *Methanobacterium thermoautotrophicum* as a biocatalyst. This bacterium has a specific requirement for H_2S, and is therefore able to remove it from exhaust gases. Under optimized conditions the biocatalyst gave a purified sulfur-free biogas containing about 96% methane.[202]

Certain bacteria cultures are able to transform methane into methanol, which may be used as a liquid energy carrier. Methanol is produced by using whole-cell cultures of *Methylosinus trichosporium* on a 1 : 1 mixture of methane and oxygen, which gives methanol by oxidation of methane, with a yield of 30% based on the methane utilized.[203]

Large-scale methane production by methanogens using CO_2 and H_2 is at present not a feasible solution for CO_2 mitigation, since H_2 is currently formed by steam reforming (see chapter 6) of natural gas, which is an energy demanding process.

$$CO_2 + 4H_2 \longrightarrow CH_4 + H_2O$$

Scheme 75 Biocatalytic conversion of CO_2 into CH_4 by two methanogens.

6 Reforming with carbon dioxide and methane

Synthesis gas can be formed by reacting CO_2 with methane. This process is called "dry reforming", since it does not involve steam, as shown in Scheme 76.

The reaction is strongly endothermic and is carried out at temperatures around 800–1000 °C using a catalyst based on nickel (Ni/MgO, $Ni/MgAl_2O_4$, *etc.*).[13,204] With 3 mol % Ni/uscMgO (ultrafine single-crystal magnesium oxide) as catalyst system, methane conversion at 800 °C was 96%.[205] The composition of the formed synthesis gas makes it ideal as feed gas for iron ore reduction and Fischer–Tropsch synthesis of long–chain alkanes. The composition is, however not suitable for commercial production of methanol in which a H_2/CO ratio 2 : 1 is needed. Additional H_2 can be tuned *via* the water–gas shift reaction as shown in Scheme 77.[6]

The right composition of synthesis gas can be produced from methane directly by combining CO_2 (dry reforming) and H_2O (steam reforming) in a process called bireforming as illustrated in Scheme 78. Thereby large amounts of CO_2 is consumed, while the water–gas shift reaction is avoided, which reduces the process cost. The reactions are performed in a temperature range between 800 and 1000 °C.[6,13]

The catalysts for bireforming can be those used for the separate steam and dry reforming, combining the two streams afterwards. However a process which combines the dry and steam reforming in a single step has been reported.[13]

In practical use, natural gas is the major source of methane. Besides methane, natural gas consists of higher hydrocarbon is various concentrations, which also can undergo bireforming to give synthesis gas as shown in Scheme 79.

It is advantageous to use natural gas from geothermal sources, since it often contains substantial amounts of CO_2.[13]

In order to produce synthesis gas without either consuming or producing much heat, some plants combine the exothermic partial oxidation with the endothermic CO_2 reforming to give synthesis gas with a H_2/CO ratio of 1 : 1 in a thermal neutral reaction. The exothermic oxidation reaction generates the heat needed for the process but produces water as a byproduct as shown in Scheme 80.[4,13]

By employing a Ni–CaO catalyst the simultaneous catalytic partial oxidation and dry reforming can be achieved with more than 95% conversion and with more than 90% H_2 selectivity.[4,206]

In the present commercial production of methanol from synthesis gas with traces of CO_2 Cu/ZnO based catalysts are used. Hydrogen from other sources has to be added to this mixture in order to produce methanol as shown in Scheme 81.[13]

$$CO_2 + CH_4 \rightleftharpoons 2CO + 2H_2$$

Scheme 76 Dry reforming: CO_2 reacts with methane to produce synthesis gas.

$$CO + H_2O \longrightarrow CO_2 + H_2$$

Scheme 77 Water–gas shift reaction forms CO_2 and H_2. The latter can be added to the gas mixture from dry reforming, thereby getting the right composition of synthesis gas.

$$\text{Steam reforming} \qquad 2CH_4 + 2H_2O \longrightarrow 2CO + 6H_2$$

$$\text{Dry reforming} \qquad CH_4 + CO_2 \longrightarrow 2CO + 2H_2$$

$$\text{Bireforming} \qquad 3CH_4 + 2H_2O + CO_2 \longrightarrow 4CO + 8H_2 \longrightarrow 4CH_3OH$$

Scheme 78 Bireforming involves a 3 : 2 : 1 ratio of $CH_4/H_2O/CO_2$.

$$3C_nH_{(2n+2)} + (3n-1)\,H_2O + CO_2 \longrightarrow (3n+1)\,CO + (6n+2)\,H_2$$

Scheme 79 Bireforming performed with natural gas.

$$2CH_4 + O_2 + CO_2 \longrightarrow 3CO + 3H_2 + H_2O$$

Scheme 80 Combining partial oxidation with dry reforming gives a thermal neutral reaction.

$$CO + 2H_2 \rightleftharpoons CH_3OH$$

Scheme 81 Commercial synthesis of methanol from carbon monoxide and hydrogen in a ratio 1 : 2.

$$2CO \rightleftharpoons C + CO_2$$

$$CH_4 \rightleftharpoons C + 2H_2$$

Scheme 82 Formation of carbon from the Boudouard reaction and by cracking of methane.

$$C + H_2O \rightleftharpoons CO + H_2$$

Scheme 83 Carbon may be volatilized during steam reforming to produce CO and H_2.

The main problem which has hindered industrial applications of dry reforming is the formation of coke, which is thermodynamically favored except at very high temperatures, above 900 °C. Formation of coke quickly deactivates conventional reforming catalysts if used without the presence of steam. Carbon deposition may occur by the exothermic Boudouard reaction and by the endothermic cracking of methane as shown in Scheme 82.[4,207]

Coking is also a problem with steam reforming, however it is less severe since the carbon formed can be volatilized by the reaction shown in Scheme 83.[4]

The main contributor to carbon deposition during dry reforming is the Boudouard reaction; however its equilibrium is shifted to the left by increasing the temperature. Hence by performing dry reforming at high temperatures carbon deposition is minimized.[208]

There is no effective commercial catalyst to date exists which operates without carbon formation. In the past decade, efforts have focused on the development of catalysts which show high activity and stability for methane dry reforming with CO_2 to syngas.[209,210] Nickel-based catalysts[209,211] and noble metal-supported catalysts (Rh, Ru, Pd, Pt, Ir)[210,211,212] were found to have promising catalytic performance in terms of conversion and selectivity. The catalysts based on noble metals are reported to be less sensitive to coking compared to the nickel-based catalysts for dry reforming.[210] However, considering the high cost and limited availability of noble metals, it is more practical to develop improved Ni-supported catalysts which exhibit stable operation for a long period of time.

The formation of synthesis gas by dry reforming of methane could provide a substantial use for CO_2 from industrial and natural sources. This capture provides a renewable, inexhaustible carbon source and could also provide a means for the continued use of derived carbon fuels in an environmental friendly and carbon neutral way. New methods of combined partial oxidation and dry reforming considerably improve the energy economy for the production of synthesis gas.

7 Inorganic transformation of carbon dioxide

CO_2 can be captured from the atmosphere using basic absorbents such as calcium hydroxide ($Ca(OH)_2$) or potassium hydroxide (KOH), which react with CO_2 to form calcium carbonate ($CaCO_3$) and potassium carbonate (K_2CO_3) respectively.[208] The CO_2 absorption is an exothermic reaction, which liberates heat, and is readily achieved by mixing CO_2 with an adequate base. The reverse step, the desorption, is however an endothermic process which requires energy to regenerate the base and recover CO_2. Both calcium and sodium carbonate requires a large input of energy to recover the base, and is therefore not well suited for the capture and release of CO_2. There is an ongoing effort to find

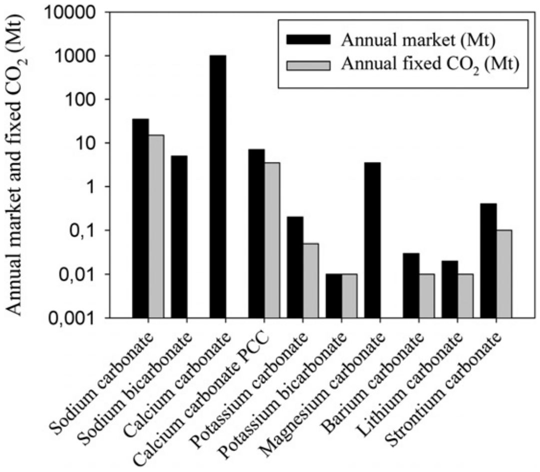


Fig. 8 The annual market volume and fixed CO_2 in megatons. Note the logarithmic scale on the *y*-axis. For the minerals where part of the annual market stems from mining the materials in their mineral form, the annual fixation of CO_2 is smaller.

suitable absorbents to remove CO_2 from the atmosphere for its recycling with minimal input of energy. One of the promising absorbents is KOH, where it is shown that the electrolysis of K_2CO_3 in water could efficiently produce not only CO_2 but also H_2 with relatively modest input of energy.[13,213]

Limestone (major components are calcium carbonate and magnesium calcium carbonate) is used industrially to produce synthetic precipitated calcium carbonate (PCC) for which the production was more than 7 Mt in 2003 worldwide. The limestone is calcinated to form lime (CaO), which is treated with water to form $Ca(OH)_2$. The PCC is formed by carbonating $Ca(OH)_2$ using an industrial (in few cases natural) CO_2 source. About 75% of the PCC production is used in the paper industry.[10,214]

The annual market and fixed CO_2 for various inorganic carbonates is illustrated in Fig. 8.

$SrCO_3$ is produced at 0.3–0.4 Mt y^{-1} primarily from Celestine (strontium sulfate) mineral by carbonation using coal or soda ash, which implies CO_2 fixation of around 0.1 Mt y^{-1}.[10,215] $SrCO_3$ is used in glass (monitor screens), batteries, photochemicals and catalysts.

Besides $CaCO_3$, CO_2 is also used to prepare $NaHCO_3$ and Na_2CO_3. CO_2 is also used to prepare carbonates of La^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+} and Ho^{3+}. The carbonates are formed by reaction with an aqueous solution of the corresponding oxide M_2O_3 and supercritical CO_2. The reaction occurs to 300–320 K and at pressures around 70–250 bar, yielding above 95% of the desired product.[6]

The market volumes for inorganic carbonates have been summarized in Table 6.[10]

Different lithium derivatives have been investigated for the purpose of the development of a suitable adsorbent for the separation, capture and release of CO_2 from flue gases. Lithium zirconate (Li_2ZrO_3) has been investigated as a high temperature absorbent. Li_2ZrO_3 reacts with CO_2 to form lithium carbonate as shown in Scheme 84. The reaction is reversible in a temperature range of 450–590 °C.[221]

Lithium silicate (Li_4SiO_4) also reacts with CO_2 as shown in Scheme 85. It is found to have a larger CO_2 adsorption capacity than that of lithium zirconate. Furthermore Li_4SiO_4 is found to have desirable features like rapid absorption at a wide range of temperatures and concentrations of CO_2 and to be stable under the different conditions. Li_4SiO_4 adsorbs CO_2 below 720 °C and releases CO_2 above 720 °C.[222]

Table 6 Market volumes for inorganic carbonates (Mt y^{-1})

Product	Year	Market/Mt y^{-1}	CO_2 fixed/Mt y^{-1}	Ref.
Na-carbonate	2003	35, ~25% is mined	~15	216
Na-bicarbonate	2003	5	—	10
Ca-carbonate	2005	Several 1000	Mainly mined	217
Ca-carbonate PCC	2003	>7	>3.5	214
K-carbonate	2005	0.1–0.2	0.03–0.05	10
K-bicarbonate	2005	<0.01	<0.01	10
Mg-carbonate	2005	3.5	Mainly mined	218
Ba-carbonate	2005	0.02–0.03	~0.01	219
Li-carbonate	2003	0.01–0.02	~0.01	220
Sr-carbonate	2003	0.3–0.4	~0.1	215

$$Li_2ZrO_3\,(s) + CO_2\,(g) \rightleftharpoons Li_2CO_3\,(s) + ZrO_2\,(s)$$

Scheme 84 Lithium zirconate reacts with CO_2 to form lithium carbonate.

$$Li_2SiO_4\,(s) + CO_2\,(g) \rightleftharpoons Li_2CO_3\,(s) + Li_2SiO_3\,(s)$$

Scheme 85 Lithium silicate adsorbs CO_2 below 720 °C to give lithium carbonate.

8 Carbon dioxide capture and storage (CCS)

One of the countermeasures for global warming is CO_2 capture from massive emission sources such as thermal power plants and coal fired power plants. The purpose of the capture is to produce a concentrated stream of CO_2 at a high pressure that can be transported readily to a storage site.[2] This process is known as carbon dioxide capture and storage (CCS). CCS technologies attract a lot of attention because they would reduce our CO_2 emissions to the atmosphere while continuing to use fossil fuels. Fossil-fueled power plants are responsible for roughly 40% of the total CO_2 emission, coal-fired plants being the main contributor.[5] The capture of CO_2 from flue gases of coal-, oil- or gas-fired power plants is a mature technology which is commercially available. Three processes are available for the capture of CO_2 from large point sources: post-combustion capture, pre-combustion capture and oxygen-fired combustion. In post-combustion systems CO_2 is separated from the flue gases produced by the combustion of the primary fuel in air. These systems primarily uses a liquid solvent to capture the small fraction of CO_2 (typically 10–15% by volume) present in the flue gas stream in which the main constituent is nitrogen (from air). This process is usually employed for pulverized coal power plants or a natural gas combined cycle power plant. In pre-combustion systems the primary fuel is treated in a reactor with steam and air or oxygen to produce synthesis gas (CO and H_2). Additional hydrogen, together with CO_2, is produced by reacting CO with steam in a second reactor. The production of synthesis gas comprises the steam reforming, partial oxidation and water gas shift reaction as shown in Scheme 86.

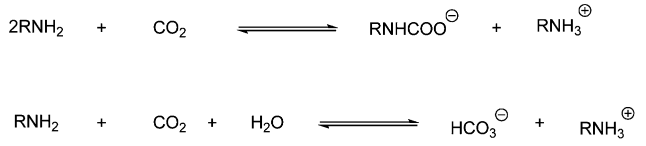
The capture of CO_2 from the resulting CO_2 and hydrogen mixture can then applied at high CO_2 concentrations and take place at pressures which are at least 50 times higher than in the post-combustion process. The capture is usually done by physical absorption, where the CO_2 and hydrogen mixture can be separated into two streams by reduction of pressure. Oxygen-fired combustion proceeds by an approach where air separation

$$C_xH_y + X\,H_2O \rightleftharpoons x\,CO + (x + y/2)\,H_2$$

$$C_xH_y + x/2\,O_2 \rightleftharpoons x\,CO + y/2\,H_2$$

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

Scheme 86 Steam reforming, partial oxidation and the water gas shift reaction takes place in the pre-combustion system process.



Scheme 87 In the CO_2–alkanolamine reaction, it is possible for two different paths of carbamate and bicarbonate formation to occur.

precedes combustion. The hydrocarbon fuel is then combusted in a mixture of O_2 and CO_2 rather than air to produce an exhaust of CO_2 and water vapor. Because oxygen is used instead of air, the nitrogen part and its combustion products are ideally eliminated from the exhaust gas stream. The net flue gas, after cooling to condense the water vapor, contains ideally 80–98% CO_2 depending on the fuel used and the particular type of oxygen-fired combustion process so only simple CO_2 purification is required prior to transportation and storage.[2,223] A challenge of oxygen-fired combustion is improving the necessary technology for air separation needed to produce oxygen. Negative pressure and air leaks in the system are common problems for this technology, which makes it difficult to remove nitrogen from the system. The most common method is to separate oxygen from air by cryogenic separation, which is highly energy demanding, thus reducing overall plant efficiency.[223]

The technologies for capture from the three processes are based on either absorption into a liquid solution, adsorption onto suitable solids, cryogenic separation and permeation into membranes.[224] Amine solution based CO_2 absorption/desorption systems using the liquids mono-ethanolamine (MEA), diethanolamine (DEA) and methyl-diethanolamine (MDEA) are some of the most widely employed capture technologies. MEA, the least expensive of the alkanolamines, is the traditional absorbent for CO_2 removal from flue gas stream as its reaction is fast even at low CO_2 pressure.[225] The aqueous amine based CO_2 absorption can proceed by to different paths, where carbamate and bicarbonate formation are possible to occur as shown in Scheme 87.[226]

When carbamate formation is the dominant reaction, two moles of amine react with one mole of CO_2, whereas a one-to-one ratio is required to form bicarbonate. This indicates that the bicarbonate formation has a capacity for CO_2 absorption twice as high as for the formation of carbamate.[226,227]

The relative amounts of formed carbamate and bicarbonate which result from carbamate instability can largely be attributed to structural types of amines.[226,228] It is shown that the increase of structural bulkiness of the substituents bound to the nitrogen atom makes the general carbamate stability decrease and makes the CO_2 loading capacity increase. The decrease in carbamate stability favors carbamate reversion to bicarbonate and free amine, leading to loadings approaching one mole of CO_2 per mole amine.[227]

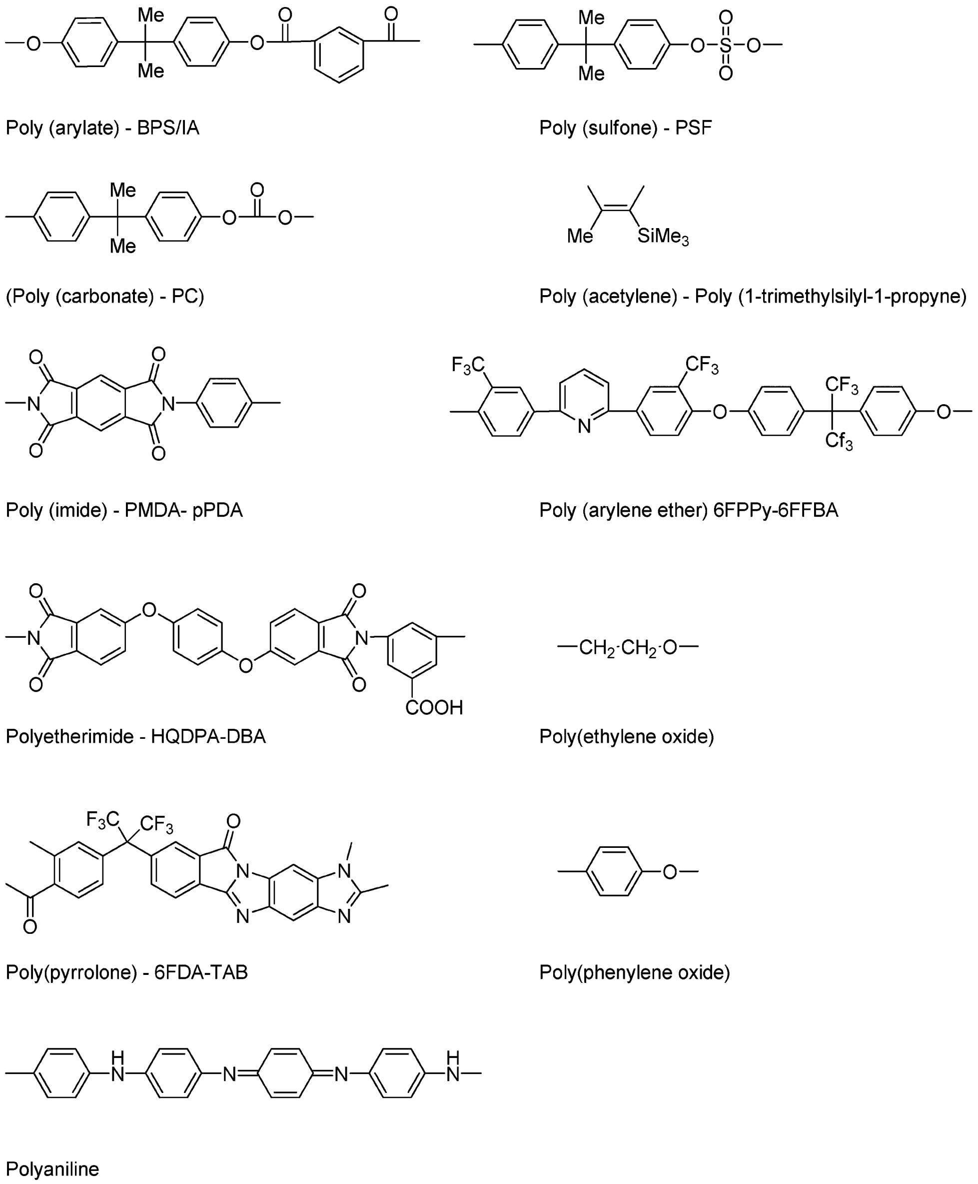
MEA, being a primary amine, reacts with CO_2 to give a high percentage of MEA carbamate. The CO_2 rich MEA solution is then sent to a stripper where it is reheated to release almost pure CO_2. The CO_2 recovery rate is 98% for MEA. The MEA solution is then recycled to the absorber.[5,229] However there are some major drawbacks for this technology including high energy requirements for the regeneration step (regenerated at 110 °C[230]) and limited loadings of the amine, due to corrosion problems and amine degradation. MEA has some specific disadvantages since it has a relative low absorption capacity caused by the formation of carbamates as the main reaction product. There is therefore an ongoing research into replacing MEA with other sterically hindered alkanolamines for the purpose of increasing CO_2 loading capacity.[225]

The adsorption process onto suitable porous solids such as zeolites and activated carbon is based on the same principle as the amine liquids.[5] Polymeric membranes have more recently been introduced for CO_2 separation. The flue gas passes through the polymeric membrane by a solution-diffusion mechanism. Some of the most widely employed polymers are illustrated in Fig. 9.[231] Polymers used in the construction of gas separation membranes include polyacetylenes,[232] polyanilines,[233] poly(arylene ethers)s,[234] polyarylates,[235] polycarbonates,[236] polyetherimides,[237] poly(ethylene oxide),[238] polyimides,[239] poly(phenylene oxide)s,[240] poly(pyrrolone)s[241] and polysulfones.[236*a*,*b*,242] Membrane materials with a high selectivity for CO_2 over oxygen or nitrogen have been developed, however at the present stage a sufficiently high selectivity with a large flux has yet to be achieved for membranes. Membranes are more expensive than, *e.g.*, MEA, but less space demanding.[5,13,243]

There is however a number of issues associated with the capture of CO_2 from flue gases, which limits the applications for which polymeric membranes can be used. The high temperature of flue gases will rapidly destroy the membrane; therefore the gases need to be cooled below 100 °C prior to membrane separation. The polymeric membranes need to be chemically resistant, due to the harsh chemicals within the flue gases, or these chemicals need to be removed prior to the separation process. Furthermore, the low concentration of CO_2 in the flue gases is a problem, since large quantities of gases need to be processed.[5] Recent research has been directed towards the development of inorganic membranes, due to the demand in new application fields such as fuel cells, membrane-reactors and other high-temperature separations.[5] In the cryogenic separation method, compressed and liquefied CO_2 gas is expanded adiabatically to separate a certain element gas depending on its different evaporation point. This method is more costly than other separation methods and is not suitable for separating CO_2 from gases with a low CO_2 concentration. This method is applied to obtain CO_2 in a high purity.[244]

The capture of CO_2 contributes 75 percent to the overall CCS cost and CCS increases the electricity production cost by 10 to 40 percent. Hence there is a need for further development in CO_2 separation and capture to reduce the overall energy cost before CCS technologies successfully can enter the energy market.[2]

The captured CO_2 is then transported either as a liquid, gas or in its supercritical state to the storage site. The transportation is done *via* pipelines and/or shipping. 50 million tones of CO_2 is annually transported in pipelines that extend over more than 2500 km in the western USA, carrying CO_2 from natural and anthropogenic sources to enhanced oil recovery projects. Upon designing CO_2 pipelines, factors like the properties of CO_2, corrosion rates, and the gas mixture are important considerations toward establishing the material specifications. The water content in the CO_2 gas is crucial since corrosive carbonic acid is formed. In order to inhibit hydrate formation and prevent excessive corrosion rates the water content is reduced to



Poly (arylate) - BPS/IA
Poly (sulfone) - PSF
(Poly (carbonate) - PC)
Poly (acetylene) - Poly (1-trimethylsilyl-1-propyne)
Poly (imide) - PMDA- pPDA
Poly (arylene ether) 6FPPy-6FFBA
Polyetherimide - HQDPA-DBA
Poly(ethylene oxide)
Poly(pyrrolone) - 6FDA-TAB
Poly(phenylene oxide)
Polyaniline

Fig. 9 Some of the most commonly used polymers for membranes.[231]

ppm-levels by employing either molecular sieves, glycol (MEG/TEG) or alumina desiccants.[2,223] Ships can be used for long distance transport of CO_2 across oceans. Ships have the advantage of introducing flexibility in the CO_2 value chain, allowing collection of concentrated CO_2 from various sources at volumes below the critical size for pipeline transportation. Ships are not suitable for large-scale transport of CO_2, because at these pressures, the ship must be constructed as a pressure vessel, which is very costly. Ship-based transport requires liquefaction plants, intermediate storage facilities, ships, loading and unloading systems at each site, which makes ship-based transport a costly solution. Currently ships carrying up to 900–1200 tons of CO_2 are in operation.[2,223]

8.1 Sequestration

Following the capture and transport process CO_2 needs to be stored. CO_2 can be disposed of in natural sites such as deep geological cavities, saline aquifers, spent oil or gas fields, coal mines or on the ocean floor, or may be chemically fixed into solid substances, *e.g.*, inorganic carbonates.[245] Large scale geological storage has already demonstrated feasibility, while other technologies like ocean and carbonate CO_2 storage is still in the research phase.[245] Geological storage involves injecting CO_2 at depths greater than about 1 km into porous sedimentary formations using technologies derived from the oil and gas industry.[246] CO_2 can be stored in its supercritical state at depths below 800–1000 m, which provide the potential for efficient utilization of the space, due to the liquid-like density of supercritical CO_2. Ocean storage involves injecting CO_2 into the deep ocean below the depth of 3500 m taking advantage of the very slow natural interchange between the deep ocean layers and its surface layer. Below 3000 m stored CO_2 would form a lake of liquid CO_2 or CO_2 hydrate.[2] However each of the mentioned storage options has its limitations and uncertainties that will require further research before there is a guarantee of no significant losses of confined CO_2.[245]

The CCS technology is already implemented in Norway and Algeria where the technology is employed for the separation of liquefied natural gas into CO_2 and methane. The captured CO_2 is stored underground in the scale of one million tons per year. In Canada the technology is used to separate and capture CO_2 from gasified coal. The captured CO_2 is utilized for the enhanced oil recovery on the scale of one million tons per year.[244] Carbon dioxide injection into geological formations for enhanced oil recovery (EOR) is a mature technology. In 2000, 84 commercial or research-level CO_2-EOR projects were operational worldwide. In most CO_2-EOR projects, much of the CO_2 injected into the oil reservoir is only temporarily stored. This is due to the technique used to maximize oil recovery. This technique results in CO_2 being released, with a small but significant amount of the injected CO_2 remaining dissolved in the immobile oil.[247] This point can be illustrated by the fact that 48 Mt y^{-1} CO_2 (from natural and anthropogenic (25%) sources) are used annually in USA for EOR and it is estimated that 9 Mt y^{-1} CO_2 is sequestered.[248] However, in the Canadian field, a different technique has been employed for the EOR, which will allow for permanent CO_2 storage. Over the anticipated 25-year life of the project, it is expected that the injection of some 18 million tons of CO_2 will produce around 130 million barrels of enhanced oil. This has been calculated to be equivalent to approximately 14 million tons of CO_2 being sequestered.[247]

Another way to reduce the amount of CO_2 in the atmosphere is to enhance the natural sequestration of CO_2. Options which could increase the amount of fixed CO_2 could be an enhancement of the natural sinking process, such as forestation, ocean fertilization and mineral carbonation.[5] Forestation, reforestation of arid lands and greening of deserts will increase the amount of fixed CO_2. At the beginning of the forestation the amount of fixed CO_2 is higher than the amount which is released by decomposition of organic matter. At a later stage when the forestation is fully developed, the net CO_2 capture becomes zero, due to a balance between what is captured and what is released. The potential for CO_2 sequestration in terrestrial systems is estimated to be 5–10 Gt of carbon annually.[229] A second option is ocean fertilization where fertilizer is added to areas with limited nutrients to increase the production of phytoplankton. It is estimated that the current phytoplankton production has an annually uptake of 50–100 Gt of carbon, which is considerably higher than that of terrestrial vegetation.[229] Part of the carbon is released back into the atmosphere by the respiration process, and the remaining part descends deeper into the ocean in the form of organic matter, either by the death of the phytoplankton or by grazing.[5] There are some considerable drawbacks to this sequestration method, since ocean fertilization may interfere with the marine ecosystem, which could give rise to unforeseen consequences and possible fatal impact for the ecosystem. Furthermore, an increase in the decomposition of sinking organic matters could give raise to an increased production of stronger greenhouse gases, such as methane and nitrogen monoxide. As pointed out there some unresolved areas connected to ocean fertilization and the method is therefore still in the research phase.[5]

$$(Mg,Ca)_xSi_yO_{x+2y} + xCO_2 \longrightarrow x(Mg,Ca)CO_3 + ySiO_2$$

Scheme 88 Formation of calcium or magnesium carbonate from natural weathering of silicate rocks.

Large amounts of CO_2 is fixed by a process called mineral carbonation, which is natural or artificial fixation of CO_2 into rocks. Mineral carbonation results in the storage of CO_2 in solid form as a stable and environmentally benign mineral carbonate. Mineral carbonates are thermodynamically very stable, and the storage of CO_2 into rocks is therefore a safe and long-term solution. The natural weathering of rocks such as silicates, containing calcium or magnesium happens over geologic time scales. The silicate rocks are turned into carbonates by reaction with CO_2 as shown in Scheme 88.[5,249]

Artificial mineral carbonation seeks to accelerate the fixation of CO_2 into rocks. Two methods have been studied the first is to perform a direct carbonation, which binds CO_2 from its gaseous form with minerals in the solid state at suitable temperature and pressure levels. The second is an aqueous process which extracts magnesium and calcium ions from minerals into solution, followed by precipitation of either the carbonate or an intermediate product which is carbonated in a separate step. The advantage of the direct carbonation approach is its inherent simplicity. However, the direct gas-solid reactions are to slow for practical applications for the most abundant silicate rocks and are only feasible at reasonable pressures for rare, refined materials like the oxides and hydroxides of calcium and magnesium. The increased CO_2 pressure will furthermore give rise to increased energy consumption.[5,249,250,251,252]

The solution of minerals in water and subsequent carbonation is believed to proceed by the equations in Scheme 89.[253]

In Scheme 89 magnesium carbonate is formed when CO_2 is dissolved in water to give carbonic acid (H_2CO_3), which dissociates to H^+ and HCO_3^-. Then, H^+ ions hydrolyze the mineral, liberating Mg^{2+} cations and forming silicic acid or free silica and water. Finally the free Mg^{2+} cations react with the bicarbonate ions to form the solid carbonate.

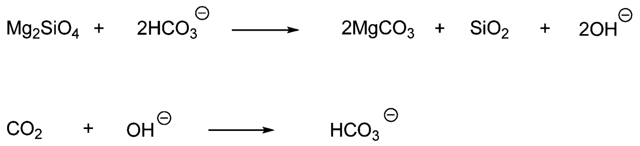
Dissolution catalysts can be added to the aqueous solution such as strong and week acids,[249,254] bases[255] and chelating agents

$$CO_2 + H_2O \longrightarrow H_2CO_3 \longrightarrow H^{\oplus} + HCO_3^{\ominus}$$

$$Mg_2SiO_4 + 4H^{\oplus} \longrightarrow 2Mg^{2\oplus} + H_4SiO_4 \text{ Or } SiO_2 + 2H_2O$$

$$Mg^{2\oplus} + HCO_3^{\ominus} \longrightarrow MgCO_3 + H^{\oplus}$$

Scheme 89 The solution of a mineral (olivine) in order to react with bicarbonate ions to give solid carbonate.



$$Mg_2SiO_4 + 2HCO_3^{\ominus} \longrightarrow 2MgCO_3 + SiO_2 + 2OH^{\ominus}$$

$$CO_2 + OH^{\ominus} \longrightarrow HCO_3^{\ominus}$$

Scheme 90 Mineral carbonation performed in a $NaHCO_3$/NaCl solution.

to extract SiO_2 or MgO groups from the mineral.[254] All three approaches have been investigated and it is found that catalyst recovery is a significant issue, which needs to be addressed.[9] Hydrochloric acid dissolution of silicates is performed in a number of steps in order to precipitate magnesium hydroxide, which can then react with gaseous CO_2 and thereby form the carbonate species. The steps alternate between being exothermic (from which heat recovery is not always possible) to being endothermic. It is found that the overall reaction has a negative CO_2 balance and is therefore at present not viable.[9] The use of a strong acid can furthermore give environmental problems and there are also problems associated with corrosion of the reaction facilities.[5,249,250,251,252]

Recent studies show that by employing a $NaHCO_3$ (0.64 M)/NaCl (1 M) solution the reaction rate compared to distilled water can be dramatically increased.[256] It is believed that the bicarbonate ion hydrolyzes the silicate as shown in Scheme 90, forming the carbonate, hydroxide (OH^-) ions, and free silica (SiO_2). The OH^- ion is believed to react immediately with the additional CO_2 being injected into the solution to reform the bicarbonate maintaining a relatively constant solution chemistry.[253]

Four different minerals (olivine (Mg_2SiO_4), lizardite ($Mg_2Si_2O_5(OH)_4$), antigorite ((Mg, Fe(II))$_3Si_2O_5(OH)_4$) and wollastonite ($CaSiO_3$)) were tested under these reaction conditions. Their reactivity, measured as the extent of the carbonation reaction after one hour under specified reaction conditions, is found. All the minerals have been subjected to a pretreatment, which is mineral specific. The activated minerals have been subjected to an ultra-fine grinding and in some cases thermal activation. The results of these experiments are shown in Table 7.[256]

The Table shows that the more energy used to activate the mineral the higher the conversion rate. However, the heat treatment and the grinding make the economics of the process unattractive.[256] Further improvements are needed to make this process viable.

The capacity for CO_2 fixation by employing artificial carbonation is vast; Mineral carbonates have been estimated to have a carbon storage capacity in the range of 100 000 to 1 000 000 carbon equivalents.[257] However, as mentioned throughout this section, there are some considerable drawbacks to this technology and mineral carbonation is therefore still in the research phase and considerable research is still needed prior to commercialization.[245,251]

Table 7 Aqueous mineral carbonation of four different minerals.[256]

Mineral	Conversion after 1 h (%)	Reaction conditions
Olivine	61	185 °C, 15 MPa
Olivine (activated)	81	185 °C, 15 MPa
Lizardite	9	155 °C, 11.5 MPa
Lizardite (activated)	40	155 °C, 11.5 MPa
Antigorite	62	155 °C, 11.5 MPa
Antigorite (activated)	92	155 °C, 11.5 MPa
Wollastonite	43	100 °C, 4 MPa
Wollastonite (activated)	82	100 °C, 4 MPa

Table 8 Estimated storage capities for various sequestration options.[257,258]

Sequestration option	Worldwide capacity (order of magnitude in Gt-carbon)
Mineral carbonates	10 000s–1 000 000s GtC
Ocean	1000s GtC
Deep saline formations	100s–1000s GtC
Depleted oil and gas reservoirs	100s GtC
Coal seams	10s–100s GtC
Terrestrial	10s GtC
Enhanced oil recovery	10s GtC
Utilization (chemical conversion)	<0.1 GtC per year

Estimated storage capacities for various sequestration methods are summarized in Table 8.

Current estimates predict that the remaining fossil fuel resources exceed 5000 GtC,[259] which implies that the world energy consumption will be based on fossil fuels for many years to come. There is, therefore, an urgent need to find sinks which can sequester some if not all of the emitted CO_2. Mineral sequestration has, as shown in Table 8, the capacity to bind all the CO_2 that could ever be generated and thereby limit the environmental impact that growing CO_2 concentrations in the atmosphere may have. However, this option is currently too energy-intensive, and therefore still in the research phase.[257] Saline aquifers imply huge storage capacities. However, because of uncertainties in storage lifetimes, seismic instability, and potential migration of CO_2, long-term integrity must be established for each site, which makes this technology costly.[257]

The 900 Gt CO_2 (245 GtC) which is currently in excess in the atmosphere can ideally be sequestrated by many of the options mentioned in Table 8. However, most sequestration methods require a concentrated stream of CO_2.

EOR is a proven technology and therefore probably the easiest route to large scale sequestration. Injecting CO_2 into reservoirs in which it displaces and mobilizes oil or gas will also give additional revenues that partly will offset sequestration costs. However, oil and gas sites have limited capacity and this technology is only able to temporally mitigate the growing CO_2 concentrations.[257]

Capacity constraints leave many sequestration methods, such as biomass sequestration and CO_2 utilization, insignificant for mitigation the growing CO_2 concentration.[257]

Table 8 shows that there are sequestering options which ideally could store all of the emitted CO_2 and future CO_2 emissions, but these options are still and in the foreseeable future in the research phase.

9 Summary and outlook

Warming of the planet due to man-made increases in the atmospheric CO_2 concentration is now an indisputable fact. There have been observations of an increase in the global average air and ocean temperature, observed widespread melting of snow and ice and an increase in the global average sea level. These changes will in time give rise to irrevocable changes in both local and global climate. The main contributor to these climate changes is the release of CO_2 into the atmosphere from the combustion of fossil fuels. This leads to an increased level of CO_2 in the atmosphere, which traps heat and prevents it from being radiated back to space. This effect is named the greenhouse effect. The consequence of the increase in average global temperature is, among others, increasing desert formation and a rise in sea level from melting of the glaciers, the Antarctic ice caps and expansion of sea water. Options for reducing the current annual emissions from fossil fuel consumption, which is about 24 Gt CO_2 are a reduction of the amount of CO_2 produced, usage of the emitted CO_2 and capture and storage of the emitted CO_2. Utilization of CO_2 in industrial applications is not expected to mitigate the increased CO_2 concentration with current available technologies. At present the typical lifetime of the CO_2 currently used in chemical applications is only days to months. The stored carbon is then degraded to CO_2 again and emitted into the atmosphere. With such short lifetimes it is difficult to contribute significantly to the mitigation of the CO_2 problem by the industrial utilization of CO_2. However there are some promising processes which in time potentially could utilize some of the emitted CO_2. A possible large scale use of CO_2 could potentially be in the polymer (polycarbonates and polyurethanes) synthesis area. In particular plastics and laminates used in the construction industry, where the lifetime of the materials can be decades.[4] Another promising area is the production of liquid carbonaceous transportation fuels. Methanol can be formed from CO_2 and H_2 under catalysis and subsequently catalytically dehydrated to a hydrocarbon fuel such as gasoline. The production of synthetic liquid fuels is attractive due to their high energy density and ease of use in an already well-established infrastructure (cars, petrol stations, ships, cargo transport, mass transit systems, planes, *etc.*). The energy requirement for the production depends of the method used for capture of CO_2 from large scale emitters and the method used for production of H_2. However, the production of liquid carbon-based fuels from CO_2 only reduces CO_2 emissions if the energy used for the conversion is not based on fossil energy. The hydrogen needed for the reductive conversion of CO_2 could be produced from water hydrolysis, using hydropower, nuclear energy, solar energy or wind energy. As long as some power generation using fossil fuels remains, CO_2 for this conversion will be available.[9] Alternatively, it might be possible to develop a recycling system, where CO_2 is being captured from the atmosphere by biological or chemical means. This cycle would rely on the availability of cheap and abundant non-fossil energy and the same applies for the H_2 economy.[9] Even though the lifetime of methanol may only be days, this proposed closed cycle would ideally be CO_2 emission neutral.

Another area is the utilization of the physical aspects of CO_2, which is done in enhanced oil recovery. As fossil fuel resources become scarce it is projected that enhanced oil recovery and enhanced coal bed methane recovery using supercritical CO_2 will provide additional revenues for the oil and gas industry. This in turn will increase the demand for CO_2, which could be provided from large stationary CO_2 emitters. The storage time for the injected CO_2 is expected to be 10 000 years or more.[9]

However, in the near future improvements in the energy efficiency, a significant growth in renewable energies and further developments in emission free methods for separating and capturing CO_2 from flue gases will help to stabilize the concentration of CO_2 in the atmosphere.

10. Conclusions

This review has covered a number of CO_2 transformations, which are all still in the research phase, but are potential technologies for mitigating the still-increasing atmospheric CO_2 concentration. The utilization of CO_2 as a raw material could well be a technology contributing to the reduction of the atmospheric CO_2 loading in conjunction with the CCS technology. An example of this could be development of ways to recycle CO_2 *via* its chemical reduction with hydrogen to produce a liquid energy carrier such as methanol. The recycling would preferably be done from the atmosphere to deal with small and dispersed emitters, which contribute to more than half of the CO_2 emission induced by humans. Recycling of CO_2 from anthropogenic sources provides a renewable, inexhaustible carbon source and could allow the continued use of derived carbon fuels in an environmentally friendly, carbon neutral way. In principle when the recycling of CO_2 becomes a feasible technology we would no longer rely on the diminishing and nonrenewable fossil fuels for our energy needs. However there are still many years of research ahead before the utilization of CO_2 as a raw material becomes a CO_2 mitigating technology, therefore efforts must be directed towards fast and low energy pathways for extraction and the utilization of CO_2.

11. Abbreviations

A	acceptor
acac	acetylacetonato
Ac	acetyl
Ar	aryl
bmim	1-butyl-3-methylimidazolium
BMImCl	1-*n*-butyl-3-methyl imidazolium chloride
BNAH	1-benzyl-1,4-dihydronicotinamide
BOC	*tert*-butyloxycarbonyl
bpy	2,2′-bipyridine
Bu	butyl
C	carbon
CB	conduction band
CCS	carbon dioxide storage and capture
CF	fluorocarbon
CFC	chlorofluorocarbons
CoA	acetyl-coenzyme A
COD	1,5-cyclooctadiene
COT	cyclooctatetraene
cyclam	1,4,8,11-tetraazacyclotetradecane
D	donor
DBAD	ditbutylazodicarboxylate
DBU	1,8-diazabicyclo[5.4.0]undec-7-ene
DCC	dicyclohexyl carbodiimide
dcpb	1,4-bis(dicyclohexylphosphino)butane
DEA	diethanolamine

DEC	diethyl carbonate
DMC	dimethyl carbonate
DMF	dimethylformamide
dppb	1,4-bis(diphenylphosphino)butane
EOR	enhanced oil recovery
Et	ethyl
hfacac	hexafluoroacetylacetonate
Gt	gigatons
H_2A	ascorbic acid
HMPA	hexamethylenephosphoric triamide
IPCC	Intergovernmental Panel on Climate Change
IPr	1,3-bis-(2,6-diisopropylphenyl)-imidazole-2-ylidene
i-Pr	*iso*-propyl
IR	infrared radiation
L	ligand
M	metal
MDEA	methyldiethanolamine
Me	methyl
MEA	monoethanolamine
MEG	monoethylene glycol
Me_2phen	2,9-dimethyl-1,10-phenanthroline
MLCT	metal ligand charge transfer
M_n	number average molecular weight
Mt	megatons
MV2+	methylviologen
n	integer
NHE	normal hydrogen electrode
NMP	1-methyl-2-pyrolidione
NMR	nuclear magnetic resonance
OTf	trifluoromethanesulfonato
PCC	precipitated calcium carbonate
PCy_3	tricyclohexylphosphine
Ph	phenyl
Py	pyridine
PVC	polyvinyl chloride
rt	room temperature
sc	supercritical
SCE	standard calomel electrode
TEA	triethylamine
TEG	triethylene glycol
TEOA	triethanolamine
Tf	trifluoromethanesulfonyl
TMS	trimethylsilyl
TOF	turnover frequency
TON	turnover number
TPP	5,10,15,20-tetraphenylporphinato
tpy	2,2′:6′,2″-terpyridine
Ts	*p*-tolunenesulfonyl
usc	ultrafine single-crystal
VB	valence band
X	halogen

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