



CO₂ utilization: Developments in conversion processes

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ABSTRACT

Carbon dioxide capture, utilization and storage (CCUS) –including conversion to valuable chemicals—is a challenging contemporary issue having multi-facets. The prospect to utilize carbon dioxide (CO₂) as a feedstock for synthetic applications in chemical and fuel industries –through carboxylation and reduction reactions—is the subject of this review. Current statute of the heterogeneously catalyzed hydrogenation, as well as the photocatalytic and electrocatalytic activations of conversion of CO₂ to value-added chemicals is overviewed. Envisaging CO₂ as a viable alternative to natural gas and oil as carbon resource for the chemical supply chain, three stages of development; namely, (i) existing mature technologies (such as urea production), (ii) emerging technologies (such as formic acid or other single carbon (C1) chemicals manufacture) and (iii) innovative explorations (such as electrocatalytic ethylene production) have been identified and highlighted. A unique aspect of this review is the exploitations of reactions of CO₂ –which stems from existing petrochemical plants—with the commodity petrochemicals (such as, methanol, ethylene and ethylene oxide) produced at the same or nearby complex in order to obtain value-added products while contributing also to CO₂ fixation simultaneously. Exemplifying worldwide ethylene oxide facilities, it is recognized that they produce about 3 million tons of CO₂ annually. Such a CO₂ resource, which is already separated in pure form as a requirement of the process, should best be converted to a value-added chemical there avoiding current practice of discharging to the atmosphere.

The potential utilization of CO₂, captured at power plants, should also be taken into consideration for sustainability. This CO₂ source, which is potentially a raw material for the chemical industry, will be available at sufficient quality and at gigantic quantity upon realization of on-going tangible capture projects. Products resulting from carboxylation reactions are obvious conversions. In addition, provided that enough supply of energy from non-fossil resources, such as solar [1], is ensured, CO₂ reduction reactions can produce several valuable commodity chemicals including multi-carbon compounds, such as ethylene and acrylic acid, in addition to C1 chemicals and polymers. Presently, there are only few developing technologies which can find industrial applications. Therefore, there is a need for concerted research in order to assess the viability of these promising exploratory technologies rationally.

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1. Introduction

CO₂ emissions into atmosphere is a global concern and a recent theoretical model provides a quantitative approach for its connection with global warming and climate change [2]. Combustion stoichiometry gives that burning 1 ton of carbon in fossil fuels results more than 3.5 tons of CO₂; whose accumulation in the atmosphere is now approaching 1 tera ton [3]. According to a model developed by IEA [4], in order to limit the temperature increase within 2 °C by 2050, the CO₂ levels should not exceed 15 giga tons annually. In this quest, increasing both the energy

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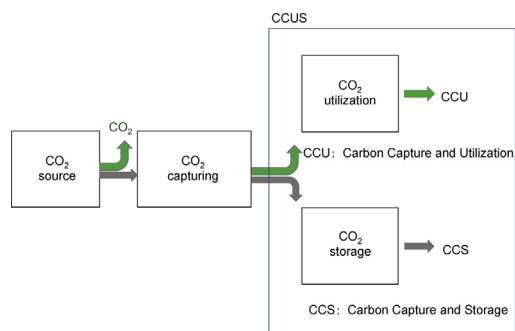


Fig. 1. The schematic representation of concept of carbon capture, utilization and storage (CCUS) (adapted from Ref. [27]).

efficiency and the use of renewable sources is going to have the most profound effects. However, the share of carbon dioxide capture is estimated to be about 14% which means that mammoth amount of relatively pure CO₂ will be available [4].

Hence, the past concept of CCS is no longer adequate and it has already been amended to CCUS involving significant carbon dioxide utilization as illustrated in Fig. 1. Utilization itself should

be divided into two parts. First, CO₂ alone without any conversion has certain uses, such as, enhanced oil recovery by CO₂ flooding [5] or physical solvent applications—especially in the supercritical state [6]. Indeed, injection of CO₂ into an oil reservoir increases the production due to high mutual dissolving capability of supercritical CO₂ and hydrophobicity of oil. Also, the increase in pressure lowers the viscosity of the CO₂–oil mixture. Consequently, CO₂ flooding can raise the production by about 15%. The oil containing dissolved CO₂ is then brought to the surface and the gases are flashed and CO₂ is separated for reinjection. In the second class of utilization, CO₂ moiety is converted to chemicals [7] and fuels [8] via carboxylation or reduction avenues. Indeed, using CO₂ as a viable feedstock for the chemical industry has been the foresight of visionary scientists and the pioneering studies towards converting CO₂ to C1 building block chemicals have already made significant achievements [9–13]. Table 1 shows some of the chemicals produced from CO₂, but this list is only the tip of the iceberg. Already, around 130 Mt (mega or millions tons) CO₂ are used annually to manufacture urea, salicylic acid, cyclic carbonates, and polycarbonates. Among them, urea process consumes most of the CO₂ industrially [7]. Urea is produced at around 185–190 °C and at pressure range of 180–200 atm by reacting

Table 1

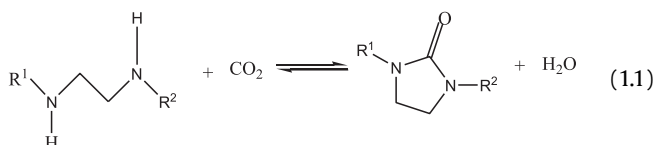
Some of the chemicals which can be produced from CO₂.

Chemical	Molecular formula	Annual production [7]	Annually utilised CO ₂ as feedstock [7]
Urea (commodity)		150 million tons	112 million tons
Methanol	CH ₃ OH	100 million tons	2 million tons
Salicylic acid		70 thousand tons	30 thousand tons
Formaldehyde		9.7 million tons	
Formic acid		700 thousand tons	
Cyclic carbonates		80 thousand tons	40 thousand tons
Ethylene carbonate			
Di-methyl carbonate		10 million tons	
Copolymers			
Polymer building blocks			
Fine chemicals (for instance, biotin)			

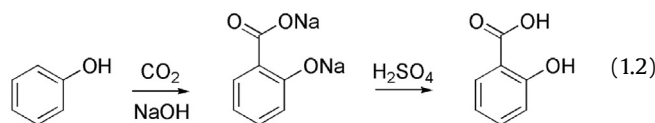
Table 2
Approximate chemical energy of some C1-chemicals and hydrogen relative to carbon dioxide.

C1-molecule	Property			Heat of formation
	Relative energy level (Gibbs free energy)	Carbon bond strength	Characteristic	
Carbon dioxide	Very low (–394 kJ/mol)	Very high	Double bonds with oxygen are very strong. Very stable.	–394 kJ/mol
Formic acid	Low (–361 kJ/mol)			–427 kJ/mol
Carbon monoxide	Intermediate (–137)			–110 kJ/mol
Formaldehyde	Intermediate (–102 kJ/mol)		Weaker carbon bonds with hydrogen	–109 kJ/mol
Methanol	Medium (–166 kJ/mol)		No stable double bond of carbon	–239 kJ/mol
Methane	High (–51 kJ/mol)	Lowest	Only carbon-hydrogen bonds. Reacts more easily with other molecules.	–74 kJ/mol
Hydrogen	Very high (0 kJ/mol)	–	No carbon-hydrogen bonds. Reacts easily with other molecules	

CO₂ with ammonia. There are two equilibrium reactions in the process, with incomplete conversion of the reactants. In the first step, ammonium carbamate (H₂N–COONH₄) is formed by contacting liquid ammonia with gaseous CO₂ at high temperature and pressure where complete CO₂ moiety is attached to ammonia. This reaction is fast and exothermic. Then, ammonium carbamate decomposes into urea and water. This second reaction is slow and endothermic so that it is the rate determining step. Unconverted CO₂ and ammonia, together with carbamate which is not decomposed, must be recovered and re-used [14]. This is not an easy task. Another complexity arises by the formation of biuret (NH₂CONHCONH₂) which is a dimer. It is believed that it adversely affects the growth of some plants so that its concentration in the fertilizer must be kept low. The overall reaction of CO₂ and ammonia to form urea is exothermic. Therefore, the heat produced by the first reaction is used for driving the second [14]. Similarly, ethylene diamines react with CO₂ to give 2-imidazolidinones which are cyclic ureas:



Kolbe-Schmitt reaction, which is given by Eq. (1.2), uses also CO₂ as a feedstock. Here, CO₂ reacts with the phenolate anion through electrophilic substitution to give salicylic acid. Subsequently, salicylic acid can be used to manufacture large number of valuable fine chemicals, such as, acetylsalicylic acid (that is, synthetic aspirin), salicylic amide, phenyl salicylates amongst others [15]:



Recently, Liquid Light company [16] was able to produce mono-ethylene glycol (MEG), which finds irreplaceable applications in industrial polyester manufacture, through electrochemically produced oxalic acid intermediate. Even though, the production of certain chemicals/polymers can contribute to the fixation problem, the main purpose of both commodity and fine chemicals productions, as exemplified above, are to add value rather than to fix CO₂ since the magnitude of their participations in this process is going to be very limited. Indeed, this route of chemicals production will be vital beyond oil and gas in future [11,17]. This review will concentrate on the evolving CO₂ conversion processes, especially those relevant to petrochemical

industries. The coverage of utilization of CO₂ for the manufacture of inorganic materials [18] is kept at minimum. Further, CO₂ conversion to fuels [8] will be addressed but it will not be elaborated. Finally, the utilization of CO₂ in the biotechnological processes as a feedstock or for producing biomass (such as, microalgae) is beyond the scope of this review and authoritative discussions could be found elsewhere [19].

2. Basic reaction kinetics and energetics aspects of CO₂ conversion

Final-products resulting from combustion of hydrocarbon fuels are water and carbon dioxide which is thermodynamically very stable (see Table 2). Song et al. gives the free energy of formation (that is, Gibbs energy) of CO₂ and other related molecules. Indeed, only inorganic and organic carbonates, which contain the CO₃ moiety, are more stable than CO₂. This stability is commonly misinterpreted as if CO₂ is “unreactive” implying that any chemical conversion of it will necessarily require high energy input. Consequently, it is often presumed that the use of CO₂ for chemicals manufacture is not appropriate. This opinion is undoubtedly true with respect to oxidants such as O₂. On the other hand, there are several reactions of CO₂ for which there is no need for any external energy because the co-reactant can supply enough energy to enable the conversion to take place at ordinary temperatures. Reactions of CO₂ with hydroxides, amines or olefins fall to this category. Further, CO₂ is a carboxylation reagent via heterogeneous catalysis under moderate conditions [17]. Therefore, CO₂ is a convenient carbon and oxygen source and by reacting it with so-called “active hydrogen” containing organic compounds, valuable chemicals, such as ethylene/propylene carbonate, can be manufactured commercially [20]. Styring et al. classifies CO₂ conversion reactions as (i) CO₂ reduction, (ii) CO₂ insertion, (iii) condensation and (iv) CO₂ addition [21]. However, it is more logical and convenient to classify the CO₂ conversion reactions into two main categories, according to their energetics:

- Reactions which do not require substantial amount of external energy. Here, the reaction takes place by attaching the whole CO₂ moiety to the other reactant. Such reactions are often named as carboxylation reactions which will be adopted by us also. Therefore, this category includes –amongst others–the production of carboxylates and lactones (RCOOR), carbamates (R₁R₂NCOOR₃), ureas (RRNCONRR), isocyanates (RNCO), and carbonates (ROC(O)OR).
- Reactions which produces reduced forms of CO₂. These reduction reactions require naturally considerable amount of external energy. They include products such as; HCOO[–] (formates), [C(O)O]₂^{2–} (oxalates), H₂CO (formaldehyde), CO, CH₃OH, CH₄ and C₂H₄.

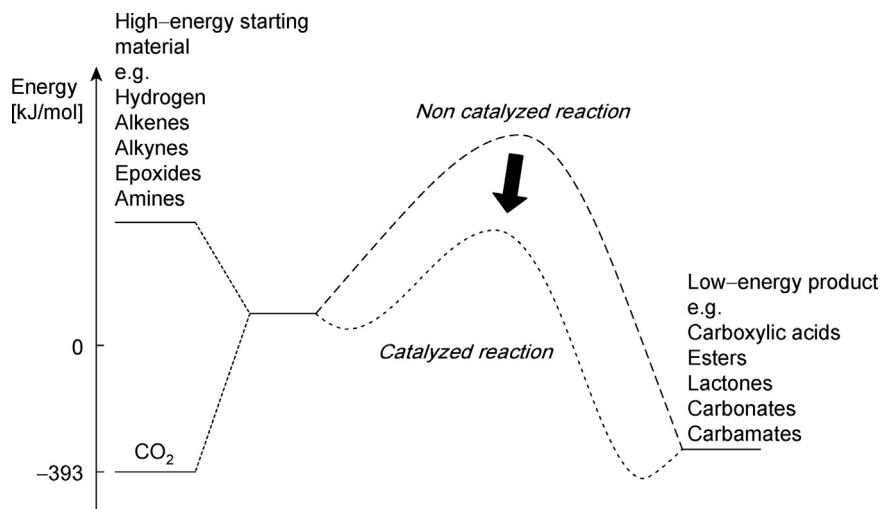


Fig. 2. Energy levels of carbon dioxide, high energy reactants and low energy products.

The external energy, required by the second group of reactions, can be supplied as; (i) heat, (ii) electrons and (iii) irradiation/photons. Then, the processes are respectively called as thermal, electrochemical and photochemical. This input of considerable amount of external energy is needed to break the strong bonds as shown in Table 2. Each C1 molecule in this sequence has a higher chemical energy than the one above. A simple way of supplying this chemical energy is to blend carbon dioxide with high energy chemicals. Although this step is a prerequisite, it is not at all adequate to reach to the desired energy levels. Thus, some form of catalysis, as well as high pressure and temperature, is necessary for lowering the energy barrier as illustrated schematically in Fig. 2.

As given in Table 2, the reduction of CO₂ into other C1 chemicals produces molecules with higher C/O and lower C/H ratios and requires significant amount energy input. Co-reactant may supply some of such energy and the rest can be provided in one of the following forms: heat, electrons or irradiation alone or in combination. However, if the chemical conversion is considered as a route of CO₂ fixation, then the required energy input must come from non-fossil sources as schematized in Fig. 3.

As a final note, the appropriateness of the utilization of CO₂ as carbon source to produce fuels (high H/C ratio) or intermediates (oxygenates) requires a life cycle analysis (LCA) study which is beyond the scope of this review.

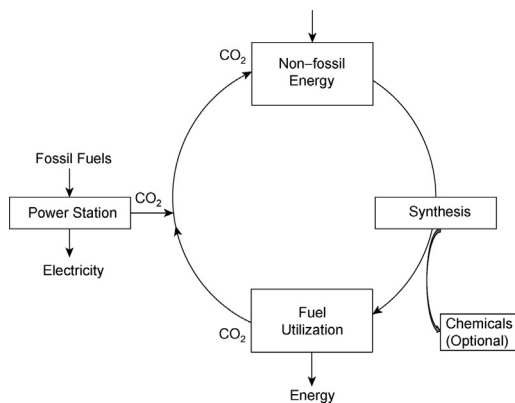


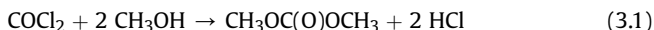
Fig. 3. Schematic representation of CO₂ conversion cycle by using non-fossil energy.

3. C1-building block chemicals

The utilization of CO₂ as a C1-chemicals building block has already been explored extensively. Indeed, several routes are currently available [11–13,15] and many more can be envisaged. In principle, these processes use catalytic hydrogenation for CO₂ reduction. However, because hydrogen is mostly obtained from fossil fuels by steam reforming, a decrease in the CO₂ emission could be achieved only by using hydrogen from non-fossil resources, such as electrolysis of water by solar energy [1].

Methanol from CO₂ may be considered as a potential entry point to the non-fossil C1 chemistry. Here, methanol can be selectively oxidized to formaldehyde and this chemical provides an entry into polymer industry (that is, thermosetting plastics, such as, polyoxymethylene (POM) also known as polyacetal) [22]. Conversion of CO₂ to formic acid is also economically feasible. In a nutshell, CO₂ is a convenient C1 chemicals building block and provides several opportunities through the carbonyl, carboxylic acid, carbonate and carbamate functional groups [23,24].

CO₂ can also react with alcohols directly to produce carbonates [25]. This reaction is carried out under base-catalyzed conditions at high pressures and dialkylcarbonates are produced. By this route a versatile product, namely DMC (dimethyl carbonate) can be produced without using the conventional -undesired-phosgene route as given by:



CO₂ can react directly with epoxides to produce organic carbonates and polycarbonates, once again replacing the phosgene route. Indeed, CO₂ is often considered as a convenient polymer building block due to not only its low cost but also its high contribution to the final product mass -which can be as much as 50 wt percent.

When capitalising on CO₂ as a C1-building block in industry, its low energy level is certainly a major barrier as shown in Table 2 [26]. Therefore, high-energy co-reactants, such as hydrogen, unsaturated compounds, or strained cyclic molecules must be used [27,28]. Consequently, the overall energy balance and the primary source of energy employed to generate the starting materials should be carefully evaluated to assess the net effect of envisaged CO₂ utilization. A typical example is the

hydrogenation of CO₂ to formic acid, where this aspect has been considered in detail elsewhere [29–31].

4. Catalysis relevant to CO₂ conversion

As seen in Fig. 2, effective catalysts are required to lower the energy barrier for converting CO₂ to C1-building block chemicals [32]. The catalyst is usually a metal complex of CO₂, discovered in mid-70's, which led to large number of investigations of the coordination chemistry of CO₂ with an ultimate aim of discovering new catalysts for CO₂ conversions. In this respect, homogeneous catalysis is important and its potential for CO₂ conversion is discussed in several authoritative reviews [30,31,33]. Value-added chemicals including the production of organic carbonates [25], urethanes [34,35], carbamates [35], lactones [35], pyrenes [35], formic acid and its derivatives [29] could be synthesized by using not only heterogeneous catalysts [36] but also homogeneous catalysts [31].

4.1. Conventional heterogeneous catalysis

Fig. 4 shows the outline of CO₂ conversion processes schematically. It is seen that catalysis (in the form of conventional, electrocatalytic and photocatalytic [37]) is the essential element and therefore will be discussed here to a certain extent.

In practice, although homogeneous catalysis is also used, heterogeneous catalysis is the preferred choice of chemical reaction engineers. The advantages of heterogeneous catalysis include, amongst others, easy separation of fluid from solid catalyst, convenient handling in a fixed-, fluidised- or moving-bed reactors, regeneration of catalyst and –above all– established reactor design principles. The production of dimethyl carbonate, cyclic carbonates, and synthesis gas (CO, H₂) as well as methanol synthesis from CO₂ hydrogenation are now carried out commercially by using heterogeneous catalytic reactors [38]. If we analyse the mechanisms of heterogeneous catalysis in detail, it is clear that the function of the catalyst is to provide a highly reactive intermediate by interaction with the second reactant such as hydrogen [39]. Then this intermediate reacts readily with CO₂ through one of the nucleophilic attack, insertion or cycloaddition pathways. Dual-functional catalysts that allow a concerted action on the reactant and the CO₂ molecule at two different sites are often used. Fig. 5 illustrates the envisaged mechanism for a bifunctional catalyst consisting of a metal (e.g., Pt) for hydrogenation and a support (e.g., alumina) which enables structural changes. Here, CO₂ first adsorbs on oxygen defects of Al₂O₃ thin film to form carbonate-like species, and then reacts with hydrogen to form CO [40].

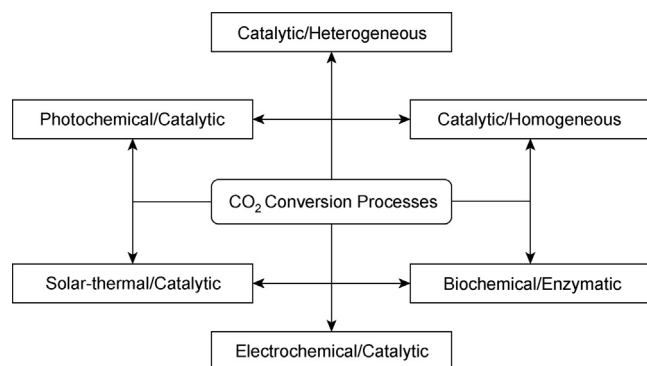


Fig. 4. Outline of chemical conversion processes of carbon dioxide excluding inorganics.

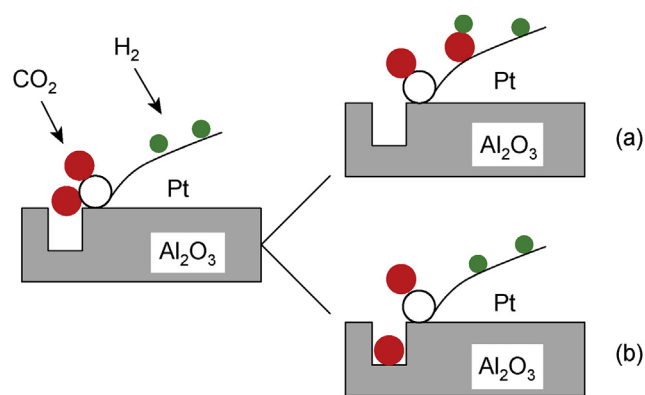


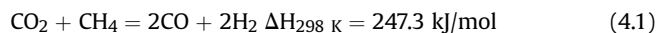
Fig. 5. Mechanism of bifunctional catalysis of Pt/Al₂O₃ for CO₂ hydrogenation/reduction involving CO [42].

Studies on direct reactions of CO₂ with diols, amino alcohols and diamines to form cyclic carbonates, cyclic carbamates and cyclic ureas by using heterogeneous catalysts are available in the literature [41].

Some selected examples of well-known CO₂ conversion reactions, which use heterogeneous catalysis, will now be examined in more detail and they include (i) CO₂ reforming of CH₄, (ii) hydrogenation of CO₂ to methanol (iii) dimethyl carbonate from CO₂ and methanol and (iv) cyclic carbonate from CO₂ and epoxide.

4.1.1. CO₂ reforming of methane

Just like CO₂, methane (CH₄) is also not expensive. Hence, production of value-added chemicals by combining these two cheap molecules has always been attractive. Reforming with CO₂ –rather than with steam– to produce synthesis gas (i.e., CO + H₂) is also known as “dry reforming” and the gas produced can subsequently be utilised in well-established Fischer–Tropsch process to produce different ranges of valuable liquid hydrocarbons [43]. As expected, the CO₂ reforming of methane is an endothermic reaction:



Catalyst is bifunctional and while CH₄ adsorbs on a noble metal (such as, Pt), CO₂ adsorbs on support (such as, ZrO₂). The simplified mechanism of the reaction is shown schematically in Fig. 6 The key aspect is that CH₄ and CO₂ adsorb on different active sites and that the carbonate (formed by strong CO₂ chemisorption at the support/noble metal interface) is reduced to formate by CH_x species formed by methane dissociation on the noble metal. However, a different reaction mechanism involving the direct reaction of CO₂ with surface carbonaceous species formed by CH₄ dissociation may also be proposed. This second mechanism is thought to be dominating for certain catalysts such as Rh/Al₂O₃.

The problem in the dry reforming is the formation of filamentous-type coke on the catalyst via CH₄ decomposition or, most likely, CO disproportionation. Among the catalysts, supported nickel was the most studied, but interesting results have been also obtained with supported noble metals (Rh, Ru, and Pt). The role of the support is very important to limit deactivation. MgO, Al₂O₃, or Ca aluminates are often used. Recent trends include the use of alkaline-earth or rare-earth oxides (as support for Ni) to prevent coke formation, and the use of ZrO₂ (or doped ZrO₂) as support for Pt or Ni [7]. One of the motivation for the

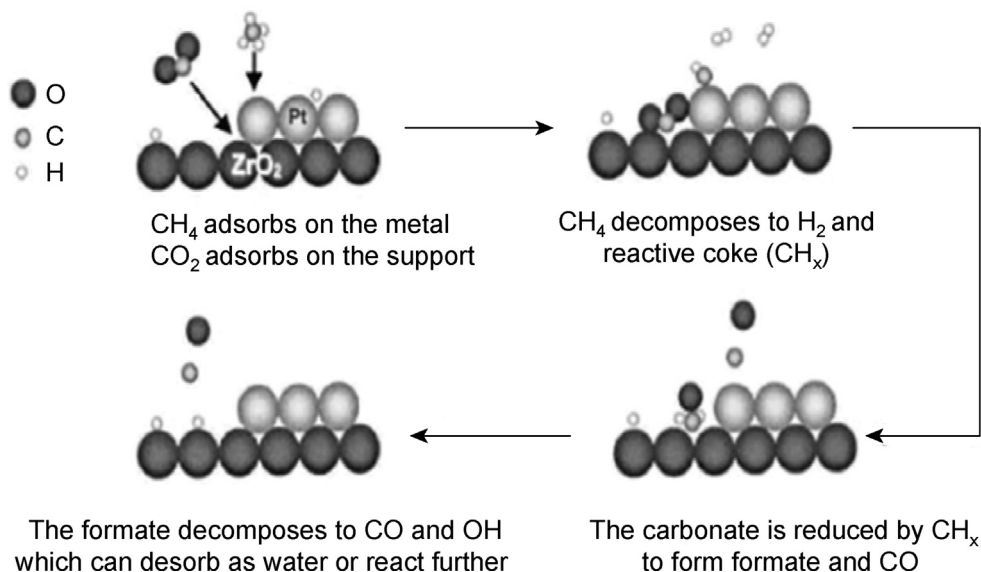


Fig. 6. Simplified mechanism of reaction between methane and CO_2 [36].

lower coking rate on zirconia is that stable carbonates are formed, due to the acid character of the support.

Noble metals such as Rh, Ru, Pd, Pt and Ir are studied thoroughly [44–49]. Among them, Rh and Ru show both high activity and stability for methane dry reforming. While the catalytic activities of Rh and Ru are similar, they are higher than those of Ir, Pt and Pd. The nature of the support has also some effects on the activity of noble metals. This behavior is -of course-characteristics of any bifunctional catalysis as illustrated in Fig. 5. For instance, Rezaei et al. investigated a number of noble metal catalysts supported on alumina-stabilized magnesia for synthesis gas production and found that the catalyst activity followed the order of $\text{Rh} \geq \text{Ru} > \text{Ir} > \text{Pt} > \text{Pd}$ [44]. Nielsen et al. found that for MgO supported catalyst, the activity followed the order of Ru, $\text{Rh} > \text{Ir} > \text{Ni}, \text{Pd}, \text{Pt}$ [45]. The effect of support on activity followed the order of $\text{Rh}/\text{Al}_2\text{O}_3 > \text{Rh}/\text{TiO}_2 > \text{Rh}/\text{SiO}_2 > \text{Rh}/\text{MgO}$ [46]. Even though, these noble metal-based catalysts have shown both high activity and stability, Ni-based catalysts have continued to receive considerable attention due to cost considerations [45,47,48,50]. However, deactivation due to coking and sintering is common for Ni-based catalysts. Presumably, the catalytic coke formation is due to dissolution of carbon in Ni followed by solid diffusion [51]. In order to keep the deactivation at minimum, Liu et al. studied Ni/MCM-41 catalysts which were prepared by different methods. Their work showed clearly that the metal loading of the catalyst and its preparation method had significant effects on the accompanying deactivation [52]. Liu et al. studied Ni/SiC monolithic foam catalyst and reported that both activity and stability were excellent [53]. Catalyst preparation 4.1 shows the significant effect of catalyst preparation for the CO_2 methanation – that is, Sabatier reaction which is however not covered in this review [40]. Development of Ni-based catalysts will continue to be an active research area and the optimisation of the activity and the stability will be a key issue [54,55]. For instance, Ma et al. found that when most pores of Ni/ ZrO_2 had a diameter of smaller than 15 nm, the catalyst showed high thermal stability and low deactivation due to low sintering and crystalline growth [55].

4.1.2. Hydrogenation of CO_2 to methanol

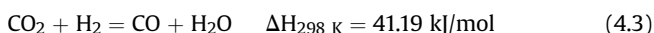
Methanol is already a commodity chemical but its production could increase even further if olefins can be produced

commercially by “methanol-to-olefins” (MTO) route [56]. The potential use of CO_2 , as an alternative feed in place of CO in the methanol production has therefore received considerable attention [57,58]. Although, CO_2 hydrogenation yields to desire methanol formation, it is accompanied by a side reaction. That is, the reverse water-gas-shift reaction also take place simultaneously as shown below [59]:

Methanol formation



Reverse water-gas-shift reaction



Here, the methanol formation is an exothermic reaction and the molecular weight of carbon containing molecule decreases. Hence, the thermodynamics foresees a decreased temperature and an increased pressure for selectivity. However, since CO_2 is not very reactive, considerably high reaction temperatures (typically, above 513 K) is necessary for acceptable CO_2 conversion. The accompanying reverse water-gas shift reaction is undesirable as it consumes hydrogen resulting decreased yield for methanol. Meanwhile, the large amount of water produced by both reactions has certain inhibitory effect on the catalyst [60,61], leading to its deactivation eventually. Other hydrogenated products, such as higher alcohols and hydrocarbons, are also produced in this process. Therefore, catalyst selectivity has critical importance. Currently, a catalyst which is totally satisfactory from an industrialist point of view is not yet available. In fact, satisfactory mechanistic understanding of CO_2 hydrogenation is not yet developed although it has been shown that methanol is produced by direct hydrogenation of CO_2 rather than through CO. CO_2 hydrogenation reaction is often carried out by using a ternary Cu–Zn–Al oxide catalyst at 5.0–10.0 MPa and 473–523 K which was originally developed for CO hydrogenation. However, this catalyst is not sufficiently active for hydrogenating pure CO_2 [62–65]. Nevertheless, most of the catalyst employed in CO_2 hydrogenation continues to be a certain modified form of methanol catalyst for CO hydrogenation. In

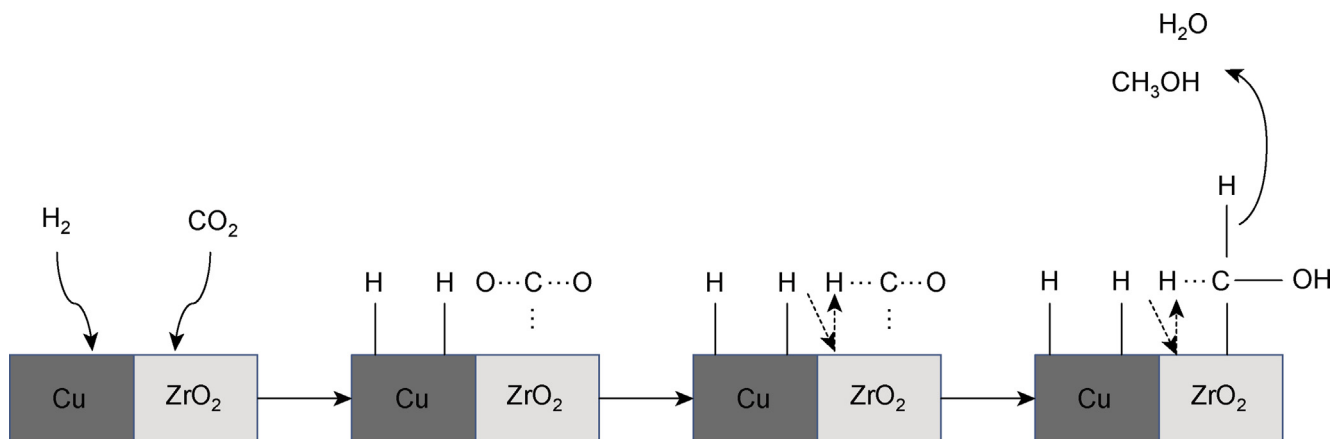


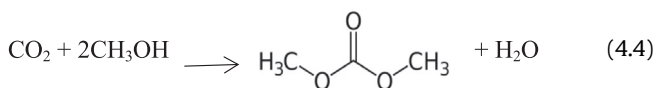
Fig. 7. Reaction pathway for the formation of methanol by CO₂ hydrogenation with Cu/ZrO₂ bifunctional catalyst [40].

order to improve the catalyst performance, the current research concentrates on multiple parameters, such as chemical composition, supports, additives, different preparation methods/conditions and morphology. The majority of the catalysts for methanol formation using CO₂ contains Cu and Zn as the main components together with different modifiers, such as Zr, Ga, Si, Al, B, Cr, Ce, V, Ti, etc. [66–69]. Fig. 7 shows the proposed reaction mechanism for a bifunctional catalyst consisting of Cu and ZrO₂.

The search for a catalyst contemplating conversion, selectivity and deactivation problems is still continuing and some researchers have tried to use transition metal carbides. Different carbides were then tested and the results indicated that Mo₂C and Fe₃C showed high CO₂ conversion and good methanol selectivity, while TaC and SiC were almost inactive [70]. Therefore, there is a significant room for further catalyst development studies incorporating also reaction engineering aspects. For instance, rather than using one conventional single catalyst bed system, two-stage bed system performance was found to be superior [71]. The incorporation of methanol itself –through MTO process- and its products such as formaldehyde through urea-formaldehyde type resins in polymeric materials promises sufficiently long CO₂ fixation periods and large quantities.

4.1.3. Dimethyl carbonate from CO₂ and methanol

Dimethyl carbonate (DMC) is a linear carbonate and it is used in industry widely as shown in Table 3. It is produced according to following reaction [20,61–63].



Keller et al. reported catalysts, reaction mechanisms and industrial processes for producing DMC [72]. Lee et al. studied the performance of supported copper catalyst and found that the

Table 3

Comparison of activities of CO₂ methanation on Ni catalysts: Effect of preparation method (RHA: Rice Husk Ash) [40].

Catalyst	Preparation ^a	Dispersion (%)	T/K	TOF (10 ³ s ⁻¹)
4.3 wt% Ni/SiO ₂ -RHA	IE	40.7	773	17.2
4.1 wt% Ni/SiO ₂ -GEL	IE	35.7	773	11.8
3.5 wt% Ni/SiO ₂ -RHA	DP	47.6	773	16.2
3.0 wt% Ni/SiO ₂	I	39.0	550	5.0

^a IE: ion exchange; DP: deposition-precipitation; I: impregnation.

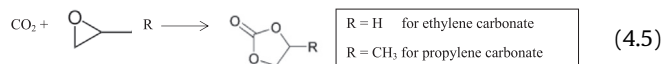
reaction temperature and pressure had strong influence on the DMC yield [73]. Kizlink et al. found that Sn(IV) and Ti(IV) alkoxides was effective using metal acetates as support [74–76].

Ballivet-Tkatchenko et al. [77] compared the catalytic behavior of new SnO₂-based catalysts with that of ZrO₂. He found that Silica-supported SnO₂ and ZrO₂ exhibited reaction rates which are an order of magnitude higher than those of the unsupported oxides. Tin-based catalysts also promote methanol dehydration which makes them less selective than their zirconium analogues.

In the recent past, the industrial use of DMC has considerably grown, due to its chemical properties and its non-toxicity, an outstanding example being represented by the non-phosgene production of aromatic polycarbonates. Other promising fields of large-scale DMC applications include –amongst others-usage as a solvent and as oxygenate in transportation fuels [78].


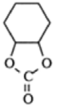

4.1.4. Cyclic carbonate from CO₂ and epoxide

Cyclic carbonate is produced by cycloaddition of CO₂ to an epoxide. This process is an effective route for CO₂ conversion and has a market exceeding 20 millions tons/year:



These cyclic carbonates are used as aprotic polar solvents, electrolytes in secondary batteries, precursors for polycarbonates and other polymeric materials, and intermediates in the production of fine chemicals like dialkyl carbonates, glycols, carbamates, pyrimidines, etc. (see Table 4). The catalysts development as well as the reaction mechanisms had been reported over alkali metal halides [79–83], organic bases [33,83,84], metal oxides [85–88], zeolites [89,90] and metal complexes [54,84,90–97]. Although the process is now reached to industrial scales, the activity, stability and recovery of the catalysts are far from being satisfactory. Certain ionic liquids which can dissolve CO₂ favourably [98–100] can also be used [101]. In ionic liquid applications, the activity for propylene carbonate synthesis followed the order of imidazolium > pyridinium for cation and of BF₄⁻ > Cl⁻ > PF₆⁻ for the anion. Although ionic liquid media showed a high performance for the reaction of carbon dioxide and epoxide, the heterogeneous catalyst system still remains the

Table 4
Linear and cyclic carbonates and their market and use (total market 20 Mt year⁻¹).

Carbonates				Uses
Linear (CH ₃ O) ₂ CO	(CH ₂ CH=CH ₂ O) CO	(EtO) ₂ CO	(PhO) ₂ CO	Solvents, reagents (for alkylation or acylation reactions), additive for gasoline
DMC (dimethyl carbonate)	DAC (diallyl carbonate)	DEC (diethyl carbonate)	DPC (diphenyl carbonate)	
Cyclic				Monomers for polymers, synthesis of hydroxyesters and hydroxyamines, component of special materials
EC (ethylene carbonate)	PC (propylene carbonate)	CC (cyclohexane carbonate)	SC (styrene carbonate)	

preferred choice due to ease of separation by using a fixed-bed reactor.

4.2. Electro- and photochemical conversion of CO₂

In the long term, some form of electro- and/or photochemical reduction of CO₂ will be an intelligent way of utilising CO₂ [102]. These processes have interesting analogies to the synthesis route of nature as in photosynthesis. However, the performance provided by present systems, such as the heterogeneous catalysts (mainly based on TiO₂ as photosensitizer) or the homogeneous catalysts (mainly based on rhenium- and ruthenium-bipyridyl complexes), has to be improved before feasible efficiencies can be attained.

Possible scenarios for the utilization of solar energy or electricity generated by renewable sources to convert CO₂ and water are given in Ref. [103] and listed below:

- Electrocatalytic
- Photovoltaic-electrocatalytic (combination of photovoltaic cell with an electrochemical cell)
- Photoelectrocatalytic (anode + photo cathode)
- Photoelectrocatalytic (photo anode + cathode)
- Photocatalytic (photo anode + photo cathode)
- Photocatalytic reaction using semiconductor particles

Among the photocatalytic, photoelectrocatalytic, and photovoltaic systems, the photovoltaic system is the most established and efficient technology to convert the solar energy into electric energy [104]. Electric current and potential can then be adjusted by stacking photovoltaic cells, and thus any desired electric potential can be applied for optimal electrocatalytic CO₂ reduction. Detailed studies showed that TiO₂, which has been studied intensively for water splitting and decomposition of organic compounds, is a representative photo anode. Because these approaches involve converting solar energy to chemical energy via electrical energy, electrochemistry is an important enabling technology. To make use of the most of those technologies in combination with solar light utilization, finding an appropriate electrode (cathode) for the electrocatalytic CO₂ reduction is important so that valuable products can be produced at minimum overpotentials (or at minimum energy loss).

4.2.1. Electrochemical activation of carbon dioxide

Electrochemical reduction or activation of CO₂ –all in all– is a known technique [105]. A number of valuable products, such as oxalic acid [106], CO, formic acid, methane, methanol, ethane, ethylene, ethanol, and other hydrocarbons and oxygenates can be produced by this technique [107–109]. Jhong et al. examined

current status of electrochemical conversion of CO₂ as well as remaining challenges and future opportunities [110]. They stated that electrochemical production is cheaper than their traditional manufactures only for CO and formic acid (see Fig. 8).

Fig. 9 shows the cost analysis of carbon monoxide as function of current density schematically. It is seen that below a current density of 250 mA/cm², the cost to produce CO is a strong function of it. Otherwise the cost is nearly constant.

Fig. 10 shows a typical laboratory set-up of an electrochemical cell. Using such a set-up and a copper electrode, CO₂ has been reduced to large number chemicals, significant ones being hydrogen, methane, formate, CO and ethylene [111]. In the context of petrochemical industries, the most valuable product among them is ethylene and therefore there are concerted studies on ethylene selectivity. For instance, Li et al. were able to achieve significant ethylene selectivity by using monodisperse Cu nanoparticles assembled on a pyridinic-N rich graphene support [112].

The reduction of protons to hydrogen competes as a side-reaction in protic solvents (that is, those having O–H or N–H

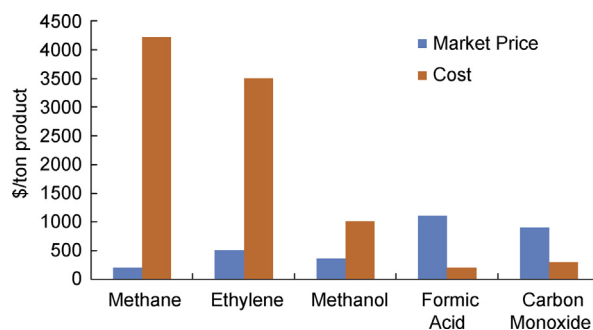


Fig. 8. Schematic representation of cost of electrochemically produced chemicals.

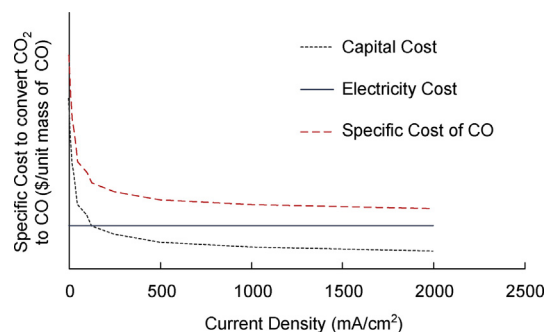


Fig. 9. Scheme representation of capital and energy costs for producing CO as function of current density.

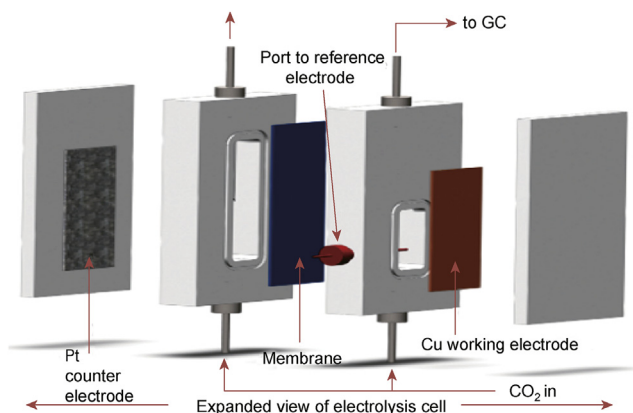
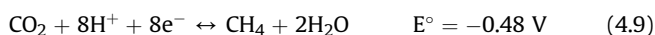
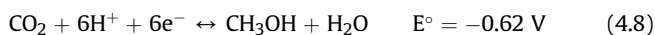
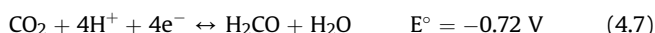


Fig. 10. Schematic of a typical electrochemical cell and the experimental set-up [93].

bonds) [109]. There are extensive studies with noble-metal cathodes at laboratory scale which demonstrate the reduction of CO_2 . However, large over-potentials are necessary to achieve sufficient transfer of electrons [107,109]. On the other hand, by the addition of metal complexes as homogeneous catalysts, reduction of over-potential can be realised. In addition, they help to direct the reduction to a certain product selectively [113]. A representative example for such a homogeneous catalyst is the dicationic ruthenium complex $[\text{Ru}(\text{bpy})_2(\text{CO})_2]^{2+}$ [114]. Also, pyridinium salts have been tried as homogeneous catalyst in order to achieve selectivity for methanol [115,116]. Generally, an additional sacrificial molecule (e.g., an alcohol, amine, or sulphite) is used as electron donor [117]. CO_2 reduction into major products such as formic acid, formaldehyde, methanol and methane are listed below:



For producing high-energy chemicals by electrochemical CO_2 reduction, the electricity must come from non-fossil fuels. For instance, if solar energy can be employed to generate electricity,

then there is a potential for developing a sustainable technology. In this perspective, Kortlever et al. [118] highlight several heterogeneous and molecular electrocatalysts for the reduction of CO_2 and discuss the reaction pathways through which they form various products. Among those, copper is a unique catalyst as it yields hydrocarbon products, mostly methane, ethylene, and ethanol, with acceptable efficiencies. Alternatively, the utilization of light for CO_2 conversion appears to be attractive [119].

4.2.2. Photocatalytic activation of carbon dioxide

Photocatalysts use light energy to enhance a chemical reaction. First, they absorb photons. Then, they bond to the reactants and transfer the absorbed energy to them. Splitting water photocatalytically is an imitation of natural photosynthesis. Initial studies employed titanium oxide as catalyst and UV as the light. Currently, there is a quest for photocatalysts which can work in the visible range of the spectrum.

The photocatalytic reduction of CO_2 to valuable products, such as CO, methanol, ethanol, methane, and higher hydrocarbons continues to be the primary scientific hurdle. Current statute is overviewed by Ameta et al. [120]. Their work summarizes efforts in photosplitting water as an energy source and photoreduction of CO_2 for producing synthetic fuels. To avoid the use of a sacrificial electron donor, the photoreduction should be coupled to water splitting [119]. CO_2 reduction to hydrocarbons by using photons may—in principle—solve two problems simultaneously: CO_2 fixation and fuel production. Uner and Oymak [121,122] reported a comparative study of photocatalytic reduction of CO_2 with water and H_2 over sol-gel coated TiO_2 films promoted with Pt and proposed a dual site mechanism schematically as shown in Fig. 11.

Different types of photocatalysts, such as SiC and ZnSe [123], have been investigated for these reactions. Titanium dioxide-based catalysts consist mainly the photocatalytically activated modification of anatase—which is one of the three mineral forms of titanium dioxide. Anatase is formed preferentially during precipitation or sol-gel processes [124]. The major products by these systems are hydrocarbons, mainly methane besides methanol. Since the anatase band gap corresponds to 3.2 eV, TiO_2 is very effective with near UV-light. The light conductor of the photoreactor can be coated with Cu/Fe-doped TiO_2 [125]. By this way, a total energy efficiency of 0.04% was achieved for the products methane and ethylene. Another photoactive semiconductor is indium tantalite (InTaO_4) [126]. The product spectrum resembles that of titanium dioxide, but methanol

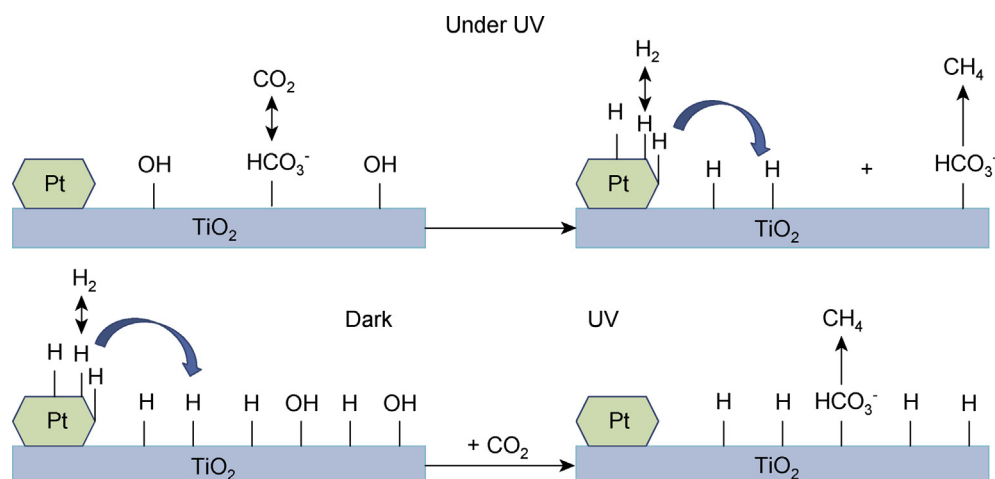


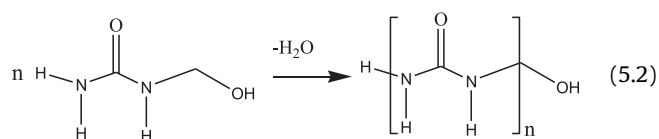
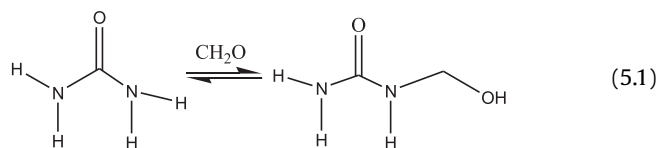
Fig. 11. Simplified mechanism of photocatalytic reduction of CO_2 [122].

predominates. Complexes of dipyridine ligands with platinum metals, mostly rhenium (ReI) or ruthenium (RuII) are another class of photocatalysts [127]. In this case, CO is the main product formed and hydrogen often occurs as by-product. These catalysts are heterotrimetallic complexes with tripodal, bipyridine-carrying units, which simultaneously contain ReI and RuII as metal ions [128]. Even though, significant progress has been made in this area, achievements are not yet satisfactory for commercial applications [129,130]. Currently, the low energy efficiency continues to be restrictive. Therefore, technical realization is not in the horizon.

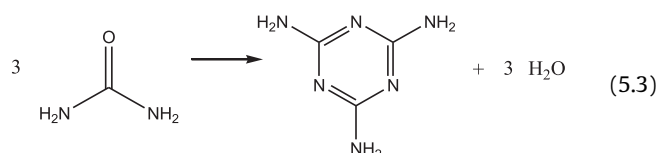
In a nutshell, the photocatalytic reduction is a convenient way to utilize carbon dioxide, since it imitates the synthesis performance of nature in photosynthesis. However, current heterogeneous and homogeneous catalysts still need to be improved before they can reach technically viable efficiencies [121,131].

5. Polymers from carbon dioxide

A promising CO₂ conversion/fixation potential is the incorporation of CO₂ into polymers whose annual production exceeds 200 million tons worldwide [132]. Preferred polymer types are those where the use of CO₂ as C1 source is sufficient to construct the macromolecule. In this respect, urea–formaldehyde resins (UF resins) and melamine–formaldehyde resins (MF-resins) have high CO₂ fixation potentials. As noted before, urea and formaldehyde are both produced from CO₂ and the following two-step reaction yields thermosetting UF resin:



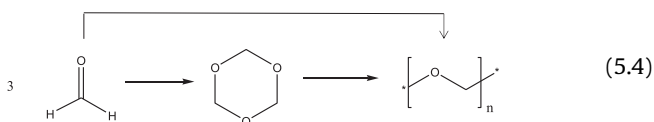
Melamine is produced from urea according to:



Similarly, thermosetting MF resins are obtained first reacting melamine and formic acid to obtain hexamethylolmelamine followed by polymerization. The carbon framework of both UF and MF resins can be structured totally from CO₂ (formaldehyde via methanol; urea directly from CO₂). Their annual production is in the range of several million tons, and the carbon can be provided entirely from the captured CO₂. Application areas include, amongst others, wood additives and electrical insulators.

Polyalkylene carbonates, which are produced by reacting CO₂ with epoxides or transesterification of diols with dimethyl carbonate, offer potential uses as substitutes for polyethers in polyurethane production [133,134]. They can take part in applications such as manufacture of thermoplastic polyurethanes (TPU), foams, elastomers, varnishes, impact-resistant modifiers,

adhesives, or sealants. Polyoxymethylene (POM) is another polycondensation polymer that might be produced from CO₂ via the intermediate formic acid and 1,3,5-trioxane:



As an engineering thermoplastic, POM could challenge polyolefins and might partially replace polypropylene and polyethylene. However, POM is more expensive than polyethylene or polypropylene but better mechanical properties may compensate the price for certain applications. Beside olefins, CO₂ can be coupled to other unsaturated compounds, such as butadiene or acetylenes and several catalysts have already been available for such applications. In the context of petrochemicals, such unsaturated compounds are produced at liquid-based steam crackers and they are not often processed beneficially.

Another important subsequent product of methanol is methyl-methacrylate (MMA) which can be polymerized at large quantities [135]. (In 2000, MMA production was around 0.8 million tons [136]). CO₂ could then be fixed for long-term use in polymethyl-methacrylate (PMMA). Different polycarbonates constitute another group of carbon dioxide-based polymers. Among them, aliphatic polycarbonates can be directly produced by reacting epoxides with CO₂. In addition, aromatic polycarbonates based on bisphenol A (BPA) can be produced by reacting an epoxide with carbon dioxide to produce an intermediate which is then polymerized. Manufacture of CO₂-based polymers, containing up to 50% carbon dioxide, can be produced. A report which examines the status of production of CO₂-based polymers, specifically poly(propylene carbonate), poly(propylene carbonate) polyol and BPA polycarbonate is available [137].

6. Fine chemicals

The direct carboxylation of hydrocarbons by insertion of CO₂ moiety into the CH bond of alkanes, aromatics, or olefins is one of the –so called– “dream reactions”. The synthesis of acetylsalicylic acid (CH₃COOC₆H₄COOH) from CO₂ and phenols is an example of such a carboxylation reaction and requires stoichiometric use of a metalation reagent. Extending this principle to other reactants can open up a fruitful avenue for producing several other fine chemicals. Amongst others, feasible reactions are that of methane and CO₂ to acetic acid [138], of benzene and CO₂ to benzoic acid using AlCl₃/Al catalyst [139], and of ethylene and CO₂ to acrylic acid [140,141]. Another interesting study is the carboxylation of aromatics by CO₂ under “Si/Al based frustrated Lewis Pairs” [142]. Here, The reaction mechanism was proposed, involving the activation of CO₂ mainly contributed by AlCl₃ in cooperation with organosilane, forming an intermediate consisting of CO₂, AlCl₃, and R₄Si, as well as the subsequent electrophilic attack to aromatics, thus to promote the carboxylation reaction. In another study, Behr considered CO₂ as building block for fine chemical synthesis by homogeneous catalysis via the formation of C–C bonds between CO₂ and hydrocarbons [143]. He reported that CO₂ reacts with alkenes, dienes and alkynes to produce several carboxylic acids, dicarboxylic acid esters, lactones and pyrenes due to both direct and catalytic reactions.

Although some of these reactions are thermodynamically possible under similar conditions as those of formic acid and fundamental organo-metallic research provides valuable insights, there are no satisfactory solutions yet. In general, the

synthesis of fine chemicals is typically directed towards the attachment of certain functional groups [144]. Hence, the utilization of CO₂ should inherently match the requirements of these structures. Various products seem particularly attractive in this area, such as carbonic acids, esters, lactones, and heterocyclic. Such functional groups are found in a wide range of products and some of them may have large scale applications (e.g., solvents, plasticizers, detergents, antioxidants, sun-protection agents, deforming agents). In particular, plasticizers based on monomeric or oligomeric carbonate or oxalate esters could be produced from captured CO₂ [143].

An interesting utilization of CO₂ was recently reported by Motietti et al. [145] who produced carbon nano tube (CNT) by reacting carbon dioxide with magnesium (Mg) in a closed cell for 3 h at 1000 °C. This technique produces magnesium oxide (MgO) and carbon and MgO can be removed by treating the reaction products with aqueous hydrochloric acid (HCl). CNT's which are normally produced –amongst others [146] by catalytic pyrolysis of hydrocarbons. CNT's [51] have unique properties and several potential applications such as superconductors have already been reported [147].

It should be understood that while the production of fine chemicals enables a high value creation, its contribution to carbon dioxide utilization should be considered –at best-very limited.

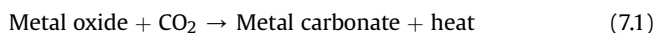
7. Production of inorganics

The mineralization of CO₂ or carbonation could be considered as a means of storage in geologic formations [148–150]. Roughly speaking, 1.6–3.7 tons of rock is needed to fix one ton of CO₂.

As a product, calcite (CaCO₃) is obtained from CO₂ and calcium hydroxide and it is synthesized in well-defined purity grades and grain sizes [151,152]. Calcite finds applications as a filling material in the building and pharmaceutical industries. Hydrotalcite is produced from magnesium oxide, CO₂, and sodium aluminate, whereby a fraction of the CO₂ remains in the product [153]. It is used widespread as a neutralizing agent for stomach acid. Hydrotalcite is also a catalyst for a number of reactions, such as aldol reactions and transesterification of polyesters. Last but not least, CO₂ is often used as a precipitating agent for separation of metal oxides [154,155].

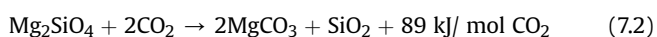
From a thermodynamic point of view, inorganic carbonates are in a lower energy state than CO₂; hence the carbonation reaction is exothermic and can theoretically yield energy. However, the kinetics of natural mineral carbonation is slow; hence all currently implemented processes require energy intensive preparation of the solid reactants to achieve affordable conversion rates and/or additives that must be regenerated and recycled using external energy sources.

When CO₂ reacts with metal oxides, the corresponding carbonate is formed and heat is released according to the following chemical reaction:

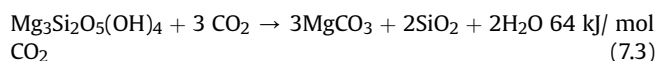


The amount of heat released is significant and it depends on the specific metal, such as calcium. Natural silicates take part in the following exothermic carbonation reactions [156]:

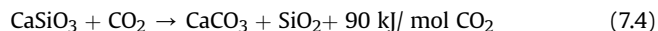
Olivine:



Serpentine:



Wollastonite:



Since all the reactions are exothermic, the formation of carbonates is thermodynamically favoured at low temperatures. On the other hand, at high temperatures (that is, above 900 °C for calcium carbonate) and at a CO₂ partial pressure of one atm, the reverse reaction, which is known as calcination, is favoured.

8. Past, present and future prospects

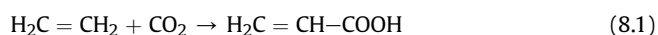
CO₂ is now a recognized carbon feedstock for the chemical supply chain and it is becoming an alternative of oil and gas in that respect. Three stages of development, which can be classified as (i) mature, (ii) currently developing and (iii) future applications, can be identified (see Table 5).

For the presently existing mature technologies, the CO₂ is an unlimited resource and several value-added chemicals, such as urea, can be produced profitably. On the other hand, only a small number of emerging technologies are on the threshold to industrial realization implying that fundamental research is needed in order to assess exploratory technologies rationally. One of the most concerted supports of CO₂ utilization comes from German Ministry of Research as summarised in Table 6. The areas covered together with examples are given in Table 6 [157]. The overall goal of these projects is to reduce CO₂ emissions and also to conserve limited fossil fuel reserves.

Among the projects in Table 6, three of them, namely, dream productions, ACER and utilization of CO₂ as a carbon building block (mostly using renewable energy), are directly relevant to this review and therefore they will be elaborated. Dream productions in Table 6 are carried out by Bayer where they use the CO₂ to produce a key building block, namely polyol (or, CO₂-based poly ether poly carbonate) which is used in polyurethane production by mixing with isocyanate. Normally, the polyols are 100% oil based so that by using a CO₂-based one some portion of oil is surely saved.

The project coded ACER (Acrylates ex renewables) aims to use CO₂ to manufacture sodium acrylate. Sodium acrylate, which is made from acrylic acid, is a base material for high-performance polymers. These polymers are used –amongst others– in baby diapers and have a production of more than 2 million tons annually.

Acrylic acid is currently produced in a two-stage reaction from propylene. Propylene is a by-product of steam cracking process and there is always shortage of it as it finds numerous applications as a monomer and/or as co-reactant in important processes such as acrylonitrile (ACN) manufacture. ACER project aims to produce acrylic acid from CO₂, ethylene and a base according to following reaction:



Several catalytic pathways, some of them including nickel lactones, are known for syntheses of acrylic acid and its derivatives from ethylene and CO₂ [133,158,159]. Ethylene is more available than propylene. Further, it can be obtained from bio-ethanol if a totally renewable process is envisaged. The third

Table 5
Development stages CO₂ conversion technologies.

	Mature	Emerging	Applied R & D
Level of industrial scale	Full industrial production	Demonstration plant	Laboratory bench- pilot plant scale
Chemical	Urea (110 million ton/year) Methanol (2.5 million ton/year) Cyclic carbonate (0.05 million t/year) Salicylic acid (0.03 million ton/year)	CO ₂ based polymers Dry reforming CO ₂ hydrogenation to formic acid Fuels, including DME	Isocyanates Organic carbonates Lactone synthesis Carboxylic acid etc.

project “Utilization of CO₂ as a Carbon Building Block Mainly Using Renewable Energy” foresees reaction of CO₂ with hydrogen which will be produced through water electrolysis. The electrolysis system is specially designed to react to power fluctuations within fractions of a second. CO₂ will then react with hydrogen using a heterogeneous catalyst to deliver a partially reduced reactive intermediate. It is envisaged to produce high performance plastic polycarbonate from this intermediate which could also be used to manufacture DVDs, LEDs, flexible solar models and optical part of spectacles. There are also intentions to produce isocyanates which mean that both monomers of polyurethanes can then be manufactured by using CO₂ as one of the feedstocks.

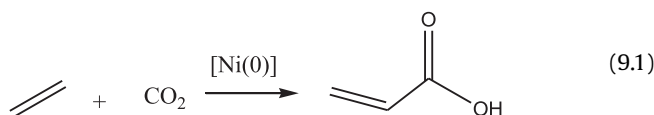
9. Examples of utilization of CO₂ in petrochemical plants

Good quality CO₂ is produced and currently discharged to atmosphere in majority of integrated petrochemical sites. For instance, ethylene oxide facilities alone discharge more than 3 millions tons CO₂ annually [160] (Both, 1.5 millions and 6.2 millions tons annual production is reported for this CO₂ source indicating also lack of information). Urea production is a clear example of CO₂ conversion where produced ammonia is reacted with CO₂ from the same facility. Several other processes can be identified, such as polycarbonate productions in ethylene and/or propylene oxide plants which are recently implemented [161]. Two cheap chemicals, namely methane and CO₂, can be turned to acetic acid [138]. Production of benzoic acid from CO₂ and benzene is an alternative feasible route and could well be implemented. In this section, manufacture of selected number of

value-added products will be reviewed briefly. The choice is somehow arbitrary since there are gigantic numbers of possibilities which can be envisaged by employing products of a large integrated complex.

9.1. Acrylic acid

Nowadays, acrylic acid is produced from propylene by oxidation with oxygen over molybdenum/bismuth catalysts, leading to acrolein as intermediate compound [162]. Subsequently, it is oxidized over molybdenum/vanadium catalysts to acrylic acid. However, this pathway has certain shortcomings. First, the steam crackers' feedstocks shift towards the associated gas –that is, the gas co-produced with crude oil–rather than to the light naphtha, made the availability of propylene difficult if not scarce [162]. Second, propylene is also in demand not only as polypropylene feed stock but also as co-reactant for other routes, such as acrylonitrile (ACN) production. Therefore, an alternative acrylic acid route will be most welcome in industry. Further current process is limited to propylene as a reactant and thus to acrylic acid only. Then, additional modifications of the carboxylic group need to be performed separately in order to obtain derivatives. Thus, novel routes to acrylic acid replacing C3 resources with cheap and easily available C2 building blocks as raw materials are desirable [152]. Besides the oxycarbonylation of ethylene with CO and water, the nickel-catalyzed direct carboxylation of ethylene with CO₂ (Eq. (9.1)) represents also one promising approach for an industrial application [153]. Ni(0)-catalyzed synthesis of acrylic acid from ethylene and CO₂ is shown below:



Postulations about the catalytic employment of nickel-lactone intermediates toward acrylic acid [154,155] attracted attention leading to an exponential increase in the number of investigations. Over three decades after their discovery, catalytic processes have been successfully established to synthesize acrylate derivatives from ethylene and CO₂ [163]. This reaction is particularly suited to core petrochemical complexes which have certainly ethylene factories. Generally, ethylene plants have an ethylene oxide factory too where CO₂ by-product stream (consisting of 93 wt % CO₂, 7 wt % water, 100 ppm ethylene and 100 ppm methane) is continuously discharged to air. The recent research on C–C bond formation with olefins led to modern strategies through cleavage auxiliaries. Different approaches were examined as the choice of cleavage agent and the corresponding ligand is crucial for the reaction control and suppression of undesired pathways. Methylation of the lactone species led to a first successful liberation of methyl acrylate in stoichiometric amounts. Upon addition of Lewis acids or strong sodium

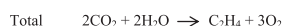
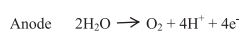
Table 6
German research program on “Technologies for Sustainability and Climate Protection – Chemical Processes and Use of CO₂”.

Emphasis area	Examples
CO ₂ utilization	<ul style="list-style-type: none"> • Dream productions • ACER
Chemical energy storage	<ul style="list-style-type: none"> • Integrated CO₂ capture, Conversion and cycling iC₄/CO₂ as a building block for Efficient Sustainable Energy Storage Technology • Storage of Electrical Energy from Renewable Resources in the Natural Gas Grid-Water
Energy-efficient processes and avoidance of CO ₂ emissions	<ul style="list-style-type: none"> • Electrolysis and gas Component Synthesis • Organophilic Nanofiltration for Energy-Efficient Processes • Innovative Equipment and System Design for Increased Production Process Efficiency • Utilization of Low-Calorific Industrial Heat by Means of Sorption Heat pump using Ionic Liquids and Thermochemical Accumulators • New Catalysts and Technologies for Solar Chemical Hydrogen Production • Utilization of CO₂ as a Carbon Building Block Mainly Using Renewable Energy

bases, catalytic routes have been established [164]. From the point view of atom- and process-economical chemistry, the most concise and promising route for acrylic acid derivatives synthesis would be direct carboxylation of olefins or alkynes with carbon dioxide. Indeed, discussions and updates of the latest advances on synthesis of acrylic acid derivatives from unsaturated hydrocarbons and carbon dioxide could be found in the literature [165].

9.2. Electrochemical Ethylene

Ethylene is the workhorse of any integrated petrochemical company. It is produced by steam cracking of either ethane, extracted from the associated gas, or the light straight run naphtha (LSRN), obtained by fractional distillation of crude oil [162]. Then the process is known as either gas- or liquid-based steam cracking. The current trend is to shift towards gas based crackers and one newly developing feedstock option being shale gas. Even though gas-based crackers –which can crack also LPG (C3 and C4) have a high yield of ethylene, there is always a need for additional ethylene sources. In this respect, electrochemical reduction of CO₂ appears to be attractive. For instance, Ogura [166] has developed the electrochemical process that CO₂ is selectively converted to ethylene at cathode with accompanying the evolution of oxygen gas at anode in aqueous solution. The energy source for this process is the electric power supplied by a solar panel. The overall reaction is represented by reaction (9.2)



(9.2)

This reaction is thermodynamically uphill, and solar energy is stored in the chemical bonds of ethylene. Zhai et al. [167] performed the electrolysis at a three-phase interface in a 2 M KCl solution with a porous copper working electrode against a glass frit, where CO₂ gas was continuously poured from the glass frit side to the electrolyte side of the electrode during the electrolysis. It is interesting that nitrogen oxide contained in the initial gas as an impurity has no effect on the selective formation of ethylene in such an electrolysis manner [167]. Wang et al. have described that a three-phase interface is essential to the formation of hydrocarbons in the photolysis from CO₂, water and sunlight on cobalt nanostructures [168]. Goncalves et al. have accomplished the electrochemical reduction of CO₂ with a copper foil electrode in an aqueous solution containing CuSO₄ with slow agitation during the electrolysis, and reported the products including methane and ethylene [169]. Afterward, they employed a Cu mesh electrode with electrodeposits of copper as the cathode, and found that ethylene is selectively generated in the detriment of methane [170]. In the electroreduction of CO₂, Yano et al. have selectively obtained ethylene by applying a periodic anodic polarization in a potential pulse mode [171]. They attributed the improved selectivity to the catalytic activity of a copper oxide generated during the anodic scan. Indeed, nanostructured surfaces have been shown to greatly enhance the activity and selectivity of many different catalysts. For instance, nanostructured Cu surface gives high selectivity for ethylene formation for electrocatalytic CO₂ reduction. Ogura et al. suggested that the most desirable process is an artificial photosynthesis in which CO₂ is converted to valuable chemicals with a solar cell as the energy source at room temperature [172]. To attain such a process, they have developed the catalytic

electrolysis process in which CO₂ is converted selectively to ethylene at room temperature. The conversion reaction takes place at the three phase (gas/liquid/solid) interface on a Cu (I) halide-confined Cu-mesh electrode. The major gases generated in the electro-reduction of CO₂ were C₂H₄, CO and H₂. They found that the current efficiencies increased when the applied amount of electric charge in a 4 M KBr solution was increased before finally leveling off. The reduction of CO₂ was performed with a CuBr-confined Cu-mesh electrode at a constant current of 250 mA. The pH of the catholyte was lowered by adding a H₂SO₄ solution at intervals to the anolyte and by applying such a pH control, 90% conversion could be achieved. The selective conversion of CO₂ to C₂H₄ is believed to be due to the immobilized CuX which operates as a heterogeneous catalyst by offering adsorption sites for reduction intermediates such as CO and methylene radicals. It is suggested that part of CuX is reduced to Cu (CuX + e⁻ → Cu + X⁻) simultaneously with the reduction of CO₂, but new copper(I) halide is always formed on the Cu-mesh electrode by the reduction of Cu²⁺ ions (Cu²⁺ + X⁻ + e⁻ → CuX) which are afforded through the cation-exchange membrane from the anode compartment. Therefore, the electrochemical conversion of CO₂ proceeds through the catalytic reactions involving CuX. The process appears to be industrially appealing and the handling of gas mixture consisting of mostly CO₂, CO, H₂ and C₂H₄ can present little problem for an integrated ethylene plant.

9.3. Electrochemical mono-ethylene glycol

Mono-ethylene glycol (MEG) is an important petrochemical and it is currently produced by hydration of ethylene oxide which is produced by direct oxidation of ethylene using Ag₂O catalyst. The yield to ethylene oxide is low (typically, 85%) where some of the ethylene (typically, 15%) is converted also to undesired CO₂ and water [162]. Because of the low conversion (about 12.5%) of the ethylene per pass, the reactor exit gas is recycled. After the ethylene oxide is scrubbed from mixed gas, the cycle gas is sent through the CO₂ removal section where CO₂ produced is captured and often released to the atmosphere. Therefore, co-production of ethylene oxide and CO₂, as well as presence of ethylene, is tempting as a potential feedstock for other conversion processes. Indeed, ethylene carbonate, polycarbonates, polyols and others are currently produced. Recently, Liquid Light [16] constructed a commercial mono-ethylene glycol plant through oxalic acid intermediate. Their core technology is centered on electrocatalysis to convert CO₂ to multi-carbon chemicals. A Stanford Research Institute (SRI) report on “Process technology to convert CO₂ to major chemicals” gives details of this process. The process is shown schematically in Fig. 12.

Currently, the only commercial product of this technology is mono-ethylene glycol. However other multi-carbon chemicals could be produced including propylene, isopropanol, acrylic acid, methyl-methacrylate and acetic acid. Table 7 gives the world demand for some of these chemicals which can be produced using this technology. The total market of these chemicals exceeds USD300 billion per year.

Among the chemicals listed in Table 7, mono-ethylene glycol is the only commercially important product. It can be reacted with terephthalic anhydride to produce a condensation polymer, polyethylene terephthalate (PET), and this polyester is mainly used for bottling and packaging. The conventional method of mono-ethylene glycol production involves catalytic oxidation of ethylene followed by hydration of ethylene oxide. Large amounts of clean CO₂ (about 2–3 million tons/year) is also produced which is captured partially and discarded before recycling. Since

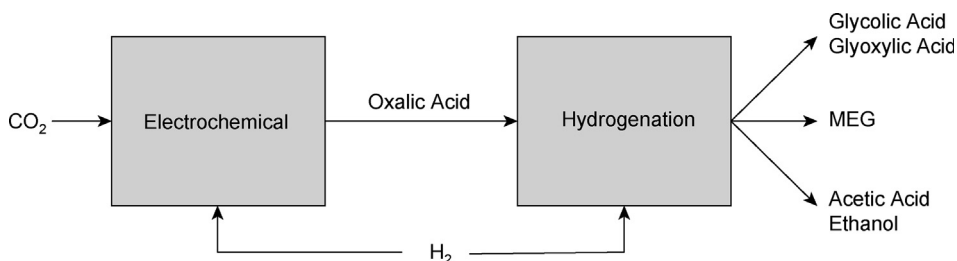
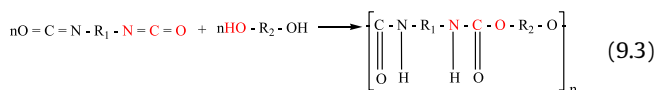


Fig. 12. Liquid Light process for producing MEG and other multi-carbon chemicals from CO₂ [16].

there is a clean source of CO₂, and the product is the same, it makes sense to couple CO₂ conversion by using catalytic electrochemistry to produce additional mono-ethylene glycol.

9.4. Monomers of polyurethanes

Polyurethanes are produced by reacting alcohols with two or more reactive hydroxyl (–OH) groups per molecule (diols, triols, polyols) with isocyanates which have more than one reactive isocyanate group (–NCO) per molecule (diisocyanates, polyisocyanates). For example a diisocyanate reacts with a diol according to following exothermic condensation reaction:



The reaction product is known as the 'urethane linkage' and it is the essential part of the polyurethane molecule. Currently there are considerable interests to manufacture both polyols and isocyanates from CO₂ [173].

9.4.1. Polyols

The polyols consumption was about 6 Mt/year in 2003 and the conventional polyols which are used in polyurethanes manufacture are either hydroxyl-terminated polyethers or hydroxyl-terminated polyesters. These polyols have been designed to have the appropriate reactivity with the isocyanate that will be used and to produce polyurethanes with specific properties.

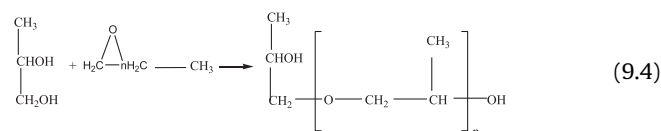
The properties of chosen polyol, especially the number of hydroxyl groups per polyol molecule and the size and flexibility of its molecular structure, ultimately determines the degree of cross-linking between molecules which has an important effect on the mechanical properties of the polymer.

Table 7

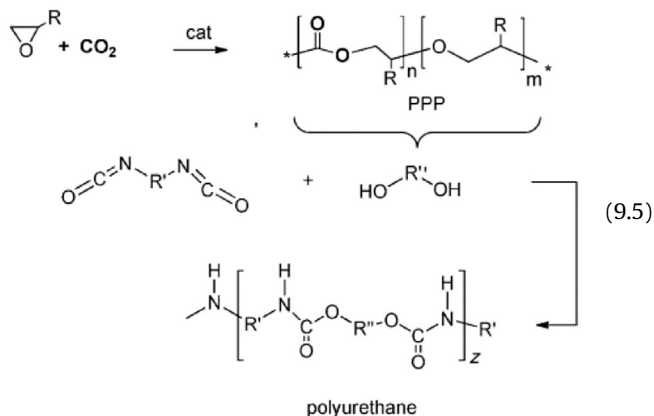
Chemicals which can be produced by catalytic electrochemistry from CO₂ and their market sizes.

Product	Market size, kt/year
Mono-ethylene glycol	22,800
Acrylic acid	4700
Acetic acid	14,200
Methyl methacrylate	3700
Glyoxylic acid	135
Oxalic acid	265
Glycolic acid	98
Formic acid	700

An example of a polyol with two hydroxyl groups (i.e., a long chain diol) is one made from propylene oxide (epoxypropane), by interaction with propane-1,2-diol, (which itself is formed from propylene oxide, by hydrolysis):



Another example of a polyol which contains three hydroxyl groups is produced from propane-1,2,3-triol (glycerol) and propylene oxide. Triglycerol based polyols which have roots to renewable sources can also be utilised. However, manufacturing polyols using CO₂ as a feedstock appears to be attractive. Indeed, Bayer Material Science and Bayer Technology Services, in collaboration with the RWTH University of Applied Science in Aachen (Germany) and RWE Power are currently developing a process for polyether carbonates polyols (PPP) from CO₂. The project, named "Dream Production", has been tested at pilot plant scale where PPP is produced on a kilogram scale [94]. The PPP results from the copolymerization of CO₂ with a starter molecule (mono-, di- and poly-ols; alkoxylated oligomers of glycols) and an alkylene oxide with terminal OH functionalities. Then PPP reacts with isocyanates to give urethane groups as shown below:



9.4.2. Isocyanate or equivalent

There are many aromatic and aliphatic polyisocyanates. However, only two of them are industrially important. About 95% of all the polyurethanes are derived from them. These are:

- Toluene diisocyanate or methylbenzene diisocyanate (TDI)
- Methylene diphenyl diisocyanate or diphenylmethane diisocyanate (MDI)

In turn, the amines, known commercially as Toluene Diamines or TDA, are heated with carbonyl chloride (phosgene) to produce the diisocyanates and this process can be carried out in the liquid phase with chlorobenzene as a solvent at about 350 K. Because of hazardous phosgene, there is a concerted effort to develop phosgene-free processes and Kathalewar et al. studied recently non-isocyanate polyurethanes [174]. The cyclic carbonate–primary amine addition reaction which results in hydroxyurethanes is a unique reaction and has been extensively studied over the last few years. This chemistry is now attracting research interest due to its potential application in the preparation of “green”, non-porous, moisture-insensitive, isocyanate free polyurethanes.

The mechanism involved in the formation of Non-Isocyanate Polyurethanes (NIPU) from five-membered cyclic carbonates and the reaction kinetics for their synthesis has been reviewed recently [167]. These studies showed that the higher homologues of the cyclic carbonate family, the six-membered cyclic carbonates, are similar to, but more reactive than, the five-membered cyclic carbonates and can also serve as a source for production of isocyanate free polyurethanes [175].

10. Conclusions

CO₂ is potentially a suitable resource of carbon which can partially replace oil and gas in many synthetic applications. Benefits can also extend to safety considerations since it is not toxic. It can replace certain toxic building blocks such as CO and phosgene in several commercially important processes, such as methanol or polyurethane manufactures. In addition, it can be used as a viable technological fluid with distinct advantages over other possible solutions in applications such as enhanced oil recovery and supercritical solvent. In near future, the use in carboxylation processes (synthesis of carbonates, carbamates and carboxylates, including cyclic compounds in both monomeric and polymeric forms) appears to be the most likely synthetic applications. In these cases, CO₂ serves as both carbon and oxygen sources. Replacing CO for making acrylic acid and use as a mild oxidant are other interesting applications. Reduction by catalytic and electrocatalytic hydrogenation necessitates energy from non-fossil fuels and solar and renewable energy resources should then be incorporated. The photocatalytic reduction of CO₂ in water under solar light irradiation, which is known as artificial photosynthesis, is a potential option that would increase carbon recycling.

All such uses reduce CO₂ emissions and currently, some 120 Mt CO₂/year are used in several applications: for a correct estimate of the amount of CO₂ not emitted into the atmosphere, LCA methodology must be applied. Presently, a rough estimate of the amount of CO₂ that may be avoided in the short-medium term is 300 Mt CO₂ annually, should all options of CO₂ utilization be implemented. A key point is the cost of CO₂ that does not have a natural origin, but should be recovered from industrial or power plants. The existing separation techniques, such as absorption by chemical solvents are quite expensive [176], while large amounts of very pure CO₂ are vented in industrial facilities

such as ethylene oxide plants. However, should the capture of CO₂ be implemented on a large scale, large amounts of CO₂ need to be handled. Therefore development of alternative processes which does not yield CO₂ is especially important. For instance, instead of current ethylene oxide process which produces CO₂, a new CO₂-free process can be developed [134]. Here, by appropriate choice of the catalyst (methyltrioxorhenium), oxidant (H₂O₂) and reaction medium (methanol/water), a homogeneous liquid phase catalytic system could be developed that eliminates CO₂ formation while producing ethylene oxide at > 90% selectivity at near-ambient temperatures [177]. Recently, Mobley et al. reported a revolutionary technology whereby oxygen is abstracted from CO₂ using reduced mixed-metal oxide catalysts, followed by the reaction of abstracted oxygen with ethylene. In this way, two desirable products, namely CO and ethylene oxide, are co-produced using CO₂ [170].

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