1

Carbon Dioxide Reduction and Uses as a Chemical Feedstock

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1.1
Introduction

The utilization of carbon dioxide (CO_2) as a source of carbon in synthetic chemistry has been a practice exploited at the industrial level since the second half of the 19th century for the synthesis of urea [1a] and salicylic acid [1b,c]. CO_2 has also long been used for making inorganic carbonates and pigments. A renewed interest in the industrial utilization of CO_2 as a source of carbon arose after the 1973 oil crisis. The topic has been comprehensively reviewed by several authors [2]. A critical assessment of CO_2 utilization is also available [3].

CO_2 is ubiquitous – it can be either extracted pure from natural wells or recovered from various industrial sources. For instance, quite pure CO_2 is recovered from urea synthesis. Several other industries, such as those using fermentation or similar methods, also provide a convenient source of pure CO_2 (above 99%) at low recovery cost, but their seasonality prevents full exploitation so that several million tons per year (Mt year^{-1}) of pure CO_2 are vented. Today, there is a growing interest in recovering CO_2 from power station flue gases that contain around 14% of CO_2, but the separation techniques are quite expensive [4] and are seldom applied on a large scale [5].

In recent years, CO_2 has also found growing application as a technological fluid in several industrial sectors, such as a cleaning fluid, in refrigeration, air conditioning and fire extinguishing equipment, as a solvent for reactions, as a solvent for nano-particle production, and in separation techniques and water treatment, as well as in the food and agro-chemical industries (packaging, additive to beverages, fumigant) [6, 7]. In all such technological applications, CO_2 is not converted and can be recovered at the end of the application or vented to the atmosphere. Most of the CO_2 used for such applications is currently extracted from natural wells, yet it is highly desirable to substitute the extracted CO_2 with that which is recovered from power stations or industrial processes. This would be in line with the need to reduce its emission into the atmosphere – a worrying accumulation since the beginning of the industrial era [8]. How

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much CO_2 is used in the chemical industry or other applications? Close to 110 Mt_{CO_2}/y are either converted into chemicals [9] such as urea (70 Mt_{CO_2} $year^{-1}$), inorganic carbonates and pigments (around 30 Mt_{CO_2} $year^{-1}$) or used as additives to CO in the synthesis of methanol (6 Mt_{CO_2} $year^{-1}$). Other chemicals such as salicylic acid (20 kt_{CO_2} $year^{-1}$) and propylene carbonate (a few kilotons per year) comprise a minor share of the market. In addition, 18 Mt_{CO_2} $year^{-1}$ are used [7] as technological fluids, and in the food and agro-chemical industries (see above). Among industrial uses, the synthesis of urea and salicylic acid are purely thermal processes, the latter being influenced by the nature of the Group 1 cation of the original phenolate reacted with CO_2. Conversely, both the carboxylation of epoxides and, more importantly, the synthesis of methanol are driven by catalysts, mainly metal systems. The development of new catalytic conversions of CO_2 requires the knowledge of the properties of metal systems.

Whether or not the utilization of CO_2 can effectively contribute to reducing its emission/accumulation into the atmosphere and, thus, if it should be considered as a technology for the control of global warming is under assessment [2e]. As effective reduction of CO_2 emission into the atmosphere requires the elimination of a few gigatons per year ($1\ Gt = 10^9\ t$), technologies for disposal in natural fields appear better suited [10]. Nevertheless, such technologies are now seldom applied and are limited, in the best of cases, to megaton-scale geological disposal; others (e.g. ocean disposal) have yet to be demonstrated. At the moment, the best approach to reducing CO_2 emission into the atmosphere would be to make a selection of a number of technologies, each able to reduce the emission by a fraction of gigaton per year. According to this perspective, the utilization of over 130 Mt $year^{-1}$ of CO_2 could well represent a technology that could significantly contribute to the reduction of atmospheric loading by recycling carbon and reducing the emission at its source. Such sustainable production technologies would reduce waste and make a better use of energy and carbon.

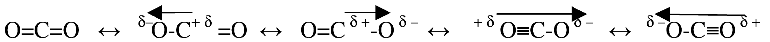
The evaluation of how much CO_2 is avoided when it is used in chemical or technological processes is not a simple task. The avoided fraction is not represented only by the amount of fixed CO_2 – one must consider the whole reaction cycle based on the emission [11]. Life cycle assessment (LCA) is the only methodology that can give an answer to such a question [12].

In the following sections, the CO_2 molecule will be considered. Its interaction with metal centers and the conversion paths that already find utilization or may find industrial exploitation in the near future are discussed, with emphasis on the most useful processes.

1.2
Properties of the CO_2 Molecule

1.2.1
Molecular Geometry

In its ground state, CO_2, a $16e^-$ molecule, is linear and belongs to the $D_{\infty h}$ point group. This makes the molecule nonpolar, although it contains two polar C–O bonds; the vectors associated with charge separation in the C–O bonds are equal in intensity and opposite in direction (Scheme 1.1).



Scheme 1.1 Polarity of the CO_2 molecule in its ground state.

Nevertheless, CO_2 maintains all the characteristics of a species containing polar bonds, with two sites that behave quite differently. The carbon atom is electrophilic, while the oxygen atoms are nucleophilic. Consequently, CO_2 often requires bifunctional catalysis [13] for its activation or conversion. It is noteworthy that the electrophilicity of carbon is higher than the nucleophilicity of each of the oxygen atoms, so CO_2 prevalently behaves as an electrophile.

The Walsh diagram [14] (Fig. 1.1) shows the energy of the molecular orbitals in the ground and excited states. Any distortion of the molecule from linearity causes the variation of the molecular energy and C–O bond length, due to the repulsive interactions generated among electrons. Figure 1.1 also shows that the energy of the molecular orbitals varies according to the plane in which the bending of the molecule occurs. In a similar way, any excitation of the molecule or interaction with electron donors that causes the population of the lowest unoccupied molecular orbital (LUMO) will also cause a distortion of CO_2 from linearity. Consequently, electronically excited CO_2, the radical anion $CO_2^{\bullet-}$ or the adduct of CO_2 with an electron-rich species, such as B-CO_2, will have a bent geometry with the O–C–O angle close to 133°, a value that minimizes the electron repulsion and the molecular energy. This is clearly shown by solid-state structural determinations – in all forms in which the carbon atom of CO_2 is bonded to a third atom, the O–C–O angle is close to 133°.

1.2.2
Spectroscopic Properties

1.2.2.1 **Vibrational**

Table 1.1 shows infrared (IR) and Raman data [15] of gaseous and solid CO_2. Due to its nonpolar character, in the ground state the symmetric stretching of the C=O bond is not IR active. In the Raman spectrum this vibration is found at 1285–1388 cm^{-1}. The IR properties of the molecule are used for many purposes, including the quantification of the amount of CO_2 in the atmosphere (by

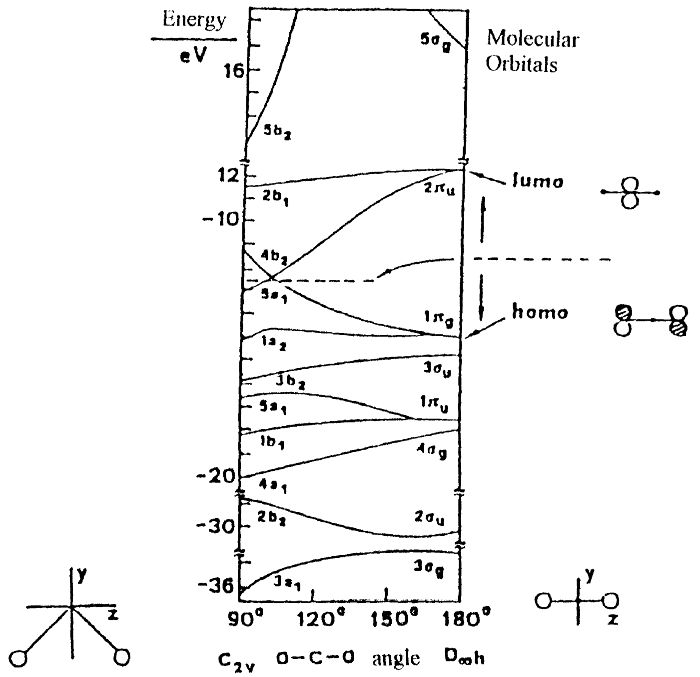


Fig. 1.1 Walsh diagram for CO_2: the energy of the MOs changes with the molecular geometry.

Table 1.1 IR and Raman data for CO_2

	$Sym_{C=O}$	Bending	$Asym_{C=O}$
Gaseous	1285–1388 (Raman)	667	2349
Aqueous solution			2342
Solid		660, 653	2344

nondispersive IR), and as a diagnostic tool for identifying CO_2 and its mode of bonding in metal systems.

1.2.2.2 UV-Vis

The UV-Vis spectrum [16] of gaseous CO_2 presents absorption bands of various intensities in the range 1700–3000 Å. The UV-Vis spectrum has not been used as extensively as the IR.

1.2.2.3 ^{13}C-Nuclear Magnetic Resonance (NMR)

CO_2 dissolved in a nonpolar solvent such as benzene or toluene shows a resonance at 126 ppm. In aqueous solutions the resonance is close to 125 ppm [17] and can be used for the quantification of free CO_2. The ^{13}C-NMR resonance is often used as a diagnostic tool for identifying the CO_2 moiety in a compound.

1.2.3 Energy Data and Reaction Kinetics Relevant to CO_2 Conversion

CO_2 is, with water, the thermodynamic end-product of the combustion of materials containing carbon and hydrogen. In fact, CO_2 is the most thermodynamically stable of all carbon-containing binary neutral species (Table 1.2). Carbonates, both organic and inorganic, that contain the "CO_3" moiety are even more stable than CO_2. The stability of CO_2 has generated the common belief that it is "nonreactive" and that any transformation of it will require an energy input that will render the use of CO_2 for the synthesis of chemicals inconvenient. The "inertness" of CO_2 is important with respect to oxidants such as O_2; indeed, CO_2 behaves as a great combustion regulator or suppressor. Conversely, there are a number of reactions in which there is no need for an external energy supply, because the coreagent brings enough energy for the reaction with CO_2 to occur at room temperature or lower (e.g. the reaction of CO_2 with hydroxide, amines or olefins). It is important to distinguish the thermodynamic from the kinetic aspects of reactions involving CO_2. In fact, quite exergonic reactions, such as

Table 1.2 Energy of formation of some chemicals relevant to CO_2 chemistry [18]

Compound	ΔH_f^0 (kJ mol^{-1})	ΔG_f^0 (kJ mol^{-1})	S_f^0 (cal K^{-1})
CO (g)	−110.53	−137.2	197.7
CO_2 (g)	−393.51	−394.4	213.8
CO_2 (l)		−386	
CO_2 (aq)	−413.26		
CO_3^{2-} (aq)	−675.23		
CaO (s)	−634.92		
HCO_3^- (aq)	−689.93	−603.3	38.1
H_2O (l)	−285.83		
H_2O (g)	−241.83		
$CaCO_3$ (s) (calcite)	−1207.6	−1129.1	91.7
$CaCO_3$ (s) (aragonite)	−1207.8	−1128.2	88
$COCl_2$ (g)	−219.1	−204.9	283
CS_2 (l)	89	64.6	151.3
CS_2 (g)	116.6	67.1	237.8
HCN (l)	108.9	125.0	112.8
HCN (g)	135.1	124.7	201.8
CH_2O (g)	−108.6	−102.5	218.8
HCOOH (l)	−424.7	−361.4	129
HCOOH (g)	−378.6		129
CH_4 (g)	−74.4	−50.3	186.3
CH_3Cl (g)	−81.9		
H_2NCONH_2 (s)	−333.6		
CH_3OH (l)	−239.1	−166.6	126.8
CH_3OH (g)	−201.5	−162.6	239.8

the formation of inorganic carbonates from CO_2 and oxides (see Table 1.2), are characterized by a high kinetic barrier that makes them proceed slowly. For example, the natural weathering of silicates [19] that converts silicates into carbonates (Eq. 1) and free silica is a very slow process that requires activation to occur in solution:

$$M_2SiO_4 + 2\,CO_2 \;\rightarrow\; 2\,MCO_3 + SiO_2 \qquad (1)$$

In general, the reactions of CO_2 can be classified into two categories, according to their energetics:

- Reactions that do not require an external energy input, such as those that incorporate into a chemical the whole CO_2 moiety, or, more generally, those in which the carbon atom maintains the formal +4 oxidation state. Such reactions produce carboxylates and lactones (RCOOR′), carbamates (RR′NCOOR″), ureas (RR′NCONRR′), isocyanates (RNCO), and carbonates [ROC(O)OR′].
- Reactions that generate reduced forms of CO_2, such as: $HCOO^-$ (formates), $[C(O)O]_2^{2-}$ (oxalates), H_2CO (formaldehyde), CO, CH_3OH and CH_4.

The latter require energy that is provided as heat (thermal processes), electrons (electrochemical processes) or irradiation (photochemical processes). The convenience of developing a process based on CO_2 does not depend on its endo- or exergonicity. As a matter of fact, several processes are today on-stream that are strongly endothermic, consume significant amounts of energy and produce large quantities of waste. Therefore, the convenience of developing a process based on CO_2 for substituting an existing one must be evaluated by comparing the two processes by applying the LCA methodology – the use of CO_2 will be convenient if it minimizes the material and energy consumption and the CO_2 emission.

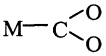
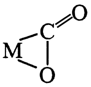
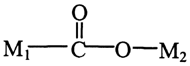
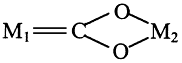
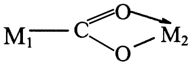
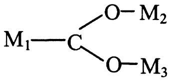
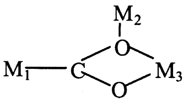
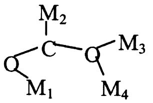
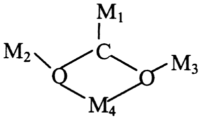
Any one of the above reactions will require a catalyst, which often is a metal system. After the discovery of the first transition metal complex of CO_2 [20], emphasis has been on the study of the coordination chemistry of CO_2 with the aim of discovering new catalysts for CO_2 chemical utilization.

1.3
CO_2 Coordination to Metal Centers and Reactivity of Coordinated CO_2

1.3.1
Modes of Coordination

The modes of coordination of CO_2 to a metal center(s) are classified in Table 1.3. While the η^2-C,O [20] and η^1-C [22a,b] coordination modes have been known for a long time, the η^1-O mode was only recently demonstrated [23]. Moving from the η^1 to the μ_4-η^5 mode [40], the C–O bond order decreases and the length of the bond increases. Nevertheless, it is not straightforward to say that coordination increases the “reactivity” of the CO_2 molecule. Whether the co-

Table 1.3 Modes of bonding of CO_2 to metal centers

Mode of bonding	Structural features of the adduct	M [reference]	ν_{asym}	ν_{sym}	C–O bond length (Å)
η^1-C		Ir [22a], Rh [22b]	1610	1210	1.20(2), 1.25(2)
η^1-O	M-O=C=O	U [23]	2188		1.122(4), 1.277(4)
η^2-C,O		Ni [24], Rh [25], Fe [26], Pd [27]	1740	1140–1094	1.17, 1.22
μ_2-η^2		Pt [28], Ir/Zr [29], Ir/Os [30], Rh [31], Ru [32]	1495	1290–1190	1.229(12), 1.306(12)
μ_2-η^3, class I		Re/Zr [33], Ru/Zr [34], Ru/Ti, Fe/Zr, Fe/Ti [34]	1348 1348	1288 1290	1.285(5), 1.281(5)
μ_2-η^3, class II		Re/Sn [35], Fe/Sn [36]	1395 1450	1188 1152	1.269(11), 2.257(7), 1.252(3), 2.394(2)
μ_3-η^3		Os [37], Re [38]			1.276(5), 1.322(5), 1.28, 1.25
μ_3-η^4		Co [39]			1.20(2), 1.24(2)
μ_4-η^4		Ru [21]			1.283(15), 1.245(16)
μ_4-η^5		Rh/Zn [40]			1.29(14), 1.322(14)

ordinated CO_2 is an activated form of CO_2 is a question that requires a detailed investigation [25b, 41]. The reduction of the C–O bond order and energy upon coordination to metal centers represents *per se* an activation of CO_2, but such an activated form may not be ready for further conversion, due to the high energy of the bonds formed with metal centers: the metal complexes may sometimes behave as "stable forms of activated CO_2".

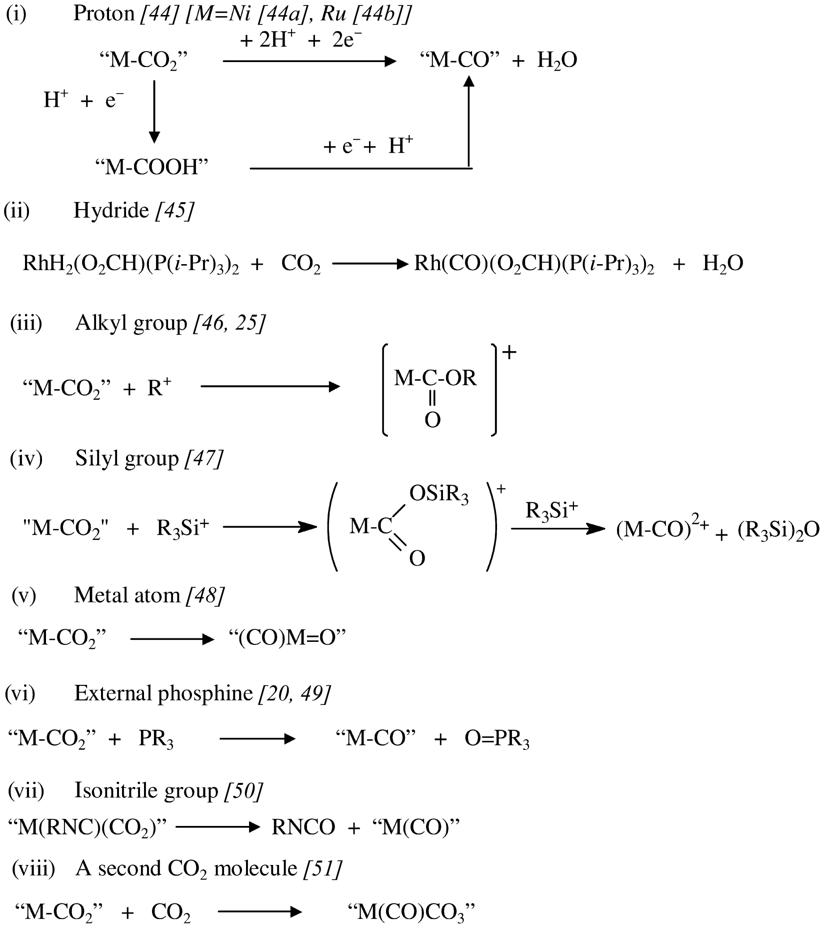
A consequent question is whether or not the coordination of CO_2 to a metal center is a prerequisite for its conversion into other chemicals. In fact, it depends on the kind of reaction CO_2 has to undergo. The data reported in Section 1.3.3 seem to suggest that the coordination to a metal center is necessary only if the reduction of CO_2 to CO is considered. In coupling reactions (C–C or C–E bond formation), CO_2 may react directly with nucleophiles produced in the reaction medium by the metal catalyst (e.g. activated olefins); pre-coordination to metal centers may not be necessary.

1.3.2
Interaction of CO_2 with Metal Atoms at Low Temperature: Stability of the Adducts

The interaction of the CO_2 molecule with main group and transition metal atoms has been studied using matrix isolation Fourier transform IR spectroscopy [42], which recently has been coupled with density functional theory (DFT) [43]. The latter has played a key role in determining the mode of coordination of the cumulene in the complex, predicting the equilibrium properties of the identified species and describing the bonding. Different behavior has been demonstrated for late transition metal atoms [Fe, Co, Ni, Ag and Cu form 1:1 $M(CO_2)$ complexes] compared to early transition elements (Ti, V and Cr insert spontaneously into one of the C=O bonds yielding oxo-carbonyl species) [43]. Isotopic experiments with $^{13}CO_2$ and $C^{18}O_2$ have permitted the spectroscopic identification of the bonding modes in organometallic species. Interestingly, the coordination of CO_2 to a metal atom is influenced by the gas matrix. For example, it has been shown that the cumulene binds in side-on fashion to nickel to afford a 1:1 complex with a binding energy equal to 75 kJ mol^{-1} in a pure CO_2 matrix, while in argon diluted matrices, no reaction occurs. Conversely, if N_2 is added to the rare gas matrix, the coordination of CO_2 occurs to preformed "NiN_2" with a binding energy equal to 133.8 kJ mol^{-1} [43]. The combination of experimental studies with DFT calculations has been fruitful for explaining the behavior of such systems and the role of N_2. Additionally, using DFT it has been shown that Ti inserts with no "energy barrier" into one of the CO bonds of CO_2, to afford a OTiCO species, which is more stable than any of the possible $Ti(CO_2)$ complexes [43].

1.3.3
Reactivity of CO_2 Coordinated to Transition Metal Systems

While several examples demonstrate that coordinated CO_2 undergoes electrophilic attack by protons or other similar reagents at the ^{2}-bonded oxygen, there is little evidence [15, 25 b, 41] that coordination promotes the formation of a C–C bond, e.g. between CO_2 and an olefin. In the latter case, it is more likely that CO_2 interacts with a M(olefin)-adduct. Alternatively, a three-molecular mechanism involving the metal center, the olefin and CO_2 may operate (see Section 1.4.1.1). Scheme 1.2 gives an overview of the documented reactions of coordinated CO_2.



Scheme 1.2 Reactions of coordinated CO_2.

1.4
CO_2 Conversion

The utilization of CO_2 for the synthesis of compounds (e.g. carboxylates) containing the entire CO_2 moiety is an example of a process that follows the "sustainable chemistry" principles [2d,e]. In fact, with respect to processes on-stream, it reduces the production of waste at source, uses less starting materials, recycles carbon, diversifies the raw materials, and may make less use of solvents if CO_2 is used as solvent ($scCO_2$) and reagent. Because of the more direct synthetic procedure, there may also be an associated reduction of energy consumption. Such benefits are rigorously assessed by making use of the LCA methodology, applied to the CO_2-based process and to the process that is being substituted [12]. Conversely, if CO_2 is reduced to other C1 molecules, an energy input may be necessary. The real benefit in this case can be evaluated by comparing the CO_2 reduction to synthesis gas (syngas) production, which represents the current route to any reduced form of carbon-based products.

1.4.1
Carbonoxylation Reactions

The incorporation of CO_2 into an organic substrate to afford C-COOH, C-COOC, E-COO-C (E = N, O) or C-OC(O)O-C moieties is of great importance from the industrial point of view as it would allow the implementation of direct methodologies in place of those on-stream that do not respond to the energy- or atom-economy principles. The formation of a terminal "carboxylic moiety" C-CO_2 is today achieved through quite lengthy and waste-producing procedures. Thus, the oxidation of an organic moiety (i.e. CH_3 or benzene skeleton) or the hydration of CN groups are typically used, via multistep procedures, with production of waste and loss of carbon [52]. Alternatively, Grignard reagents can be reacted with CO_2 with loss of 1 mol Mg per mole of carboxylate produced. Even more complex routes are used for the synthesis of cyclic compounds containing a "CO_2" moiety. The catalytic carboxylation of olefins, or other organic substrates, would be of great value in this case and would represent a step forward towards sustainable processes. Among the carboxylation reactions, the synthesis of carboxylic acids or lactones, the carbamation of amines and the synthesis of carbonates are particularly important due to the large market for the products (of the order of several megatons per year). Special attention will be dedicated to such compounds in the following sections.

1.4.1.1 **C–C Bond Formation**

The carboxylation of an organic substrate such as a saturated hydrocarbon (Eq. 2) or benzene (Eq. 3) can be considered as a formal insertion of CO_2 into the C–H bond. The enthalpy of such a reaction is in general favorable, although dependent on the reagents. In fact, the carboxylation of methane or benzene is characterized by a negative change of enthalpy. Nevertheless, it must be emphasized that the dependence on entropy is quite different in the two cases, so the free energy change may be quite different:

$$\begin{aligned} &\mathrm{CH_4(g) + CO_2(g) \rightarrow CH_3COOH(l)} \\ &\Delta H = -16.6\,\mathrm{kJ\,mol^{-1}} \\ &\Delta G_{298} = +71.17\,\mathrm{kJ\,mol^{-1}} \end{aligned} \tag{2}$$

$$\begin{aligned} &\mathrm{C_6H_6(l) + CO_2(g) \rightarrow C_6H_5COOH(s)} \\ &\Delta H = -40.7\,\mathrm{kJ\,mol^{-1}} \end{aligned} \tag{3}$$

The key step in such reactions is the heterolytic C–H bond splitting that produces a carbanion that easily reacts with CO_2 to afford a carboxylate (Eq. 4):

$$\text{R-H} \longrightarrow \text{R}^- + \text{H}^+ \xrightarrow{CO_2} \text{RCOO}^- + \text{H}^+ \longrightarrow \text{RCOOH} \tag{4}$$

The differences and similarities of natural and artificial processes will be summarized and analyzed in the next sections.

1.4.1.1.1 Natural Processes

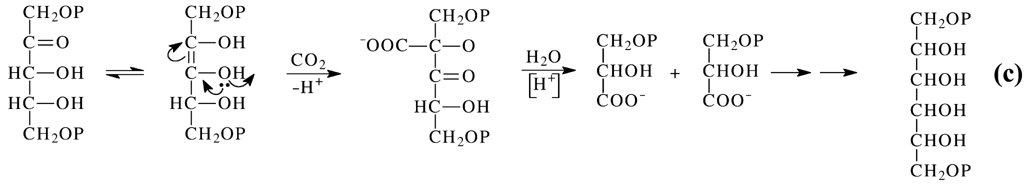
C-carboxylation reactions in nature use either CO_2 or its hydrated form, HCO_3^- (Scheme 1.3), depending on whether the enzyme active site is hydrophobic or not. Often a metal cation is required as cofactor. The most used metal ions are Mg^{2+}, Mn^{2+}, Co^{2+} and Fe^{2+}, with some evidence for the involvement of +3 cations such as Co^{3+}, Al^{3+} and Fe^{3+} (Table 1.4). The size of the cations, and their coordination number and charge density may play a key role in the stabilization of enzymes and in driving their catalytic activity. Cations with ionic radii in the range 85–110 pm [53] with a coordination number of 6 (octahedral geometry) are frequently encountered as cofactors in phosphoenolpyruvate carboxylases and other enzymes. The most abundant carboxylation enzyme in nature is ribulose 1,5-bis(phosphate)-carboxylase-oxidase (RuBisCO) [54], which is found in all eukaryotes and the majority of prokaryotes.

Table 1.4 Enzymes, substrates and metal cations implied in natural carboxylation reactions

Enzymes	Substrates	Metal cations	Products	Occurrence
RuBisCO	ribulose	Mg^{2+}	glucose	C3-plants (also higher)
Phosphoenolpyruvate carboxylase (PEPC)	pyruvic acid	Mg^{2+}, Mn^{2+}	oxaloacetate	C4-plants (mais, sugar cane, sorghum, etc.)
Phosphoenolpyruvate (PEP) carboxykinase	pyruvic acid	Mg^{2+}, Mn^{2+}	oxaloacetate	
Acetyl-CoA carboxylase	acetyl-CoA	Mg^{2+}, Mn^{2+}	malonyl-CoA	
Proprionyl-CoA carboxylase	proprionyl-CoA	Mg^{2+}, Mn^{2+}	methyl-malonyl-CoA	
Pyruvate carboxylase	pyruvate	Mg^{2+}, Mn^{2+}	oxaloacetate	
Vitamine-K-dependent carboxylases	first 10 glutamic acid residues in the N-terminal region of the precursor of prothrombin	Mn^{2+}	γ-carboxy-glutamic acid	

$$\text{R-C-H} + HCO_3^- = \text{R-C-COO}^- + H_2O \qquad \textbf{(a)}$$

$$\text{R-C-H} + CO_2 \longrightarrow \text{R-C-COO}^- + H^+ \qquad \textbf{(b)}$$



Scheme 1.3 C-carboxylation reactions (P = phosphate).

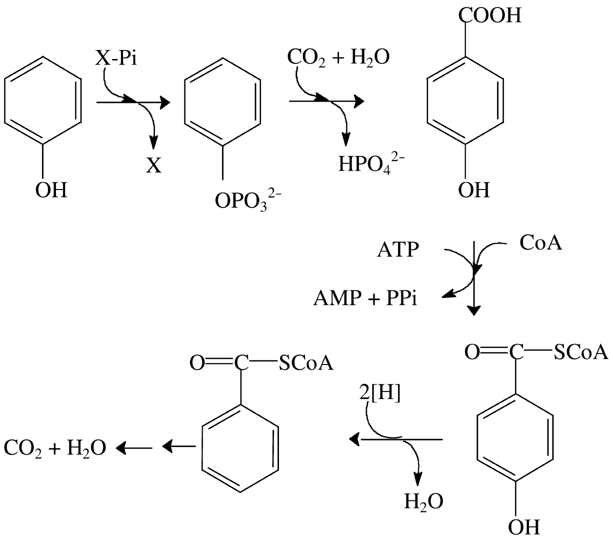
RuBisCO is constituted of a large and a small subunit, and performs both the carboxylation at C2 of ribulose and its oxidation at the same site with 50% selectivity [55]. The mechanism of action is quite complex – it has been shown that for both carboxylase and oxidase functions RuBisCO has an active site constituted by a lysine residue and a catalytic site, both placed in the large subunit. Once the two C3 moieties are formed (Scheme 1.3 c) the carboxylic functionalities are reduced and the two C3 moieties coupled to afford glucose. Formally the process consists of a CO_2 reduction to a "HCOH" moiety, inserted into a C–C bond of a C5 sugar to afford a C6 compound. This process uses some tens of gigatons per year of carbon of CO_2 in the natural carbon cycle.

The exploitation of biotechnologies for the utilization of CO_2 as source of carbon is an interesting approach to developing new, environmentally friendly synthetic technologies based on CO_2. In principle, both carboxylation and reduction reactions can be carried out, under mild conditions and using water as reaction medium, that would greatly improve the environmental quality of new processes with respect to those actually on stream [56, 58].

1.4.1.1.2 **Artificial Processes**

Despite the great industrial value of the formation of a C–C bond using CO_2, the only industrial application is represented by the synthesis of 2(or 4)-hydroxybenzoic acid, known for more than a century (Kolbe Schmitt reaction [1 b]). This reaction has been reconsidered [57] using other substrates such as 1- and 2-naphthol or hydroxypyridines.

A biotechnological synthesis has also been demonstrated to be possible [58]. *Thauera aromatica* bacteria can use phenol as the only source of carbon under anaerobic conditions; phenol is eventually converted into CO_2 and water. The first step of the degradation path is the carboxylation of phenolphosphate to 4-hydroxybenzoic acid which is then dehydroxylated to benzoic acid [59] (Scheme 1.4). The carboxylation of phenol is carried out by a phenolcarboxylase enzyme, a new type of lyase [60]. The isolation of the enzyme from the cytoplasmic portion of the cell allows its use *in vitro*. In order to extend the lifetime of the enzyme, its supported form on low melting agar can be used [61]. Cut-off membranes (that allow the passage of macromolecules of a given size) [58] can be



Scheme 1.4 Carboxylation of phenolphosphate to 4-hydroxybenzoic acid.

also used, with an easy separation of products from the mother liquid phase containing the enzyme and nutrients. Interestingly, the enzyme can also work in $scCO_2$ [62].

The direct carboxylation of hydrocarbons has been achieved only in the case of molecules containing active hydrogens using phenolate anion (PhO^-) as CO_2-transfer agent [63]. More recently, the 2-carboxylated form of imidazolium salts (Eq. 7) have been used for CO_2 transfer to molecules containing active hydrogens [64]. The resulting R^1R^2ImX can be recycled.

$$R^1R^2\text{Im-2-CO}_2 + \text{substrate-H} + MX \rightarrow R^1R^2\text{ImX} + \text{substrate-COOM} \tag{7}$$

$$R^1R^2\text{Im-2-CO}_2 = \text{1,3-dialkylimidazolium-2-carboxylate}$$

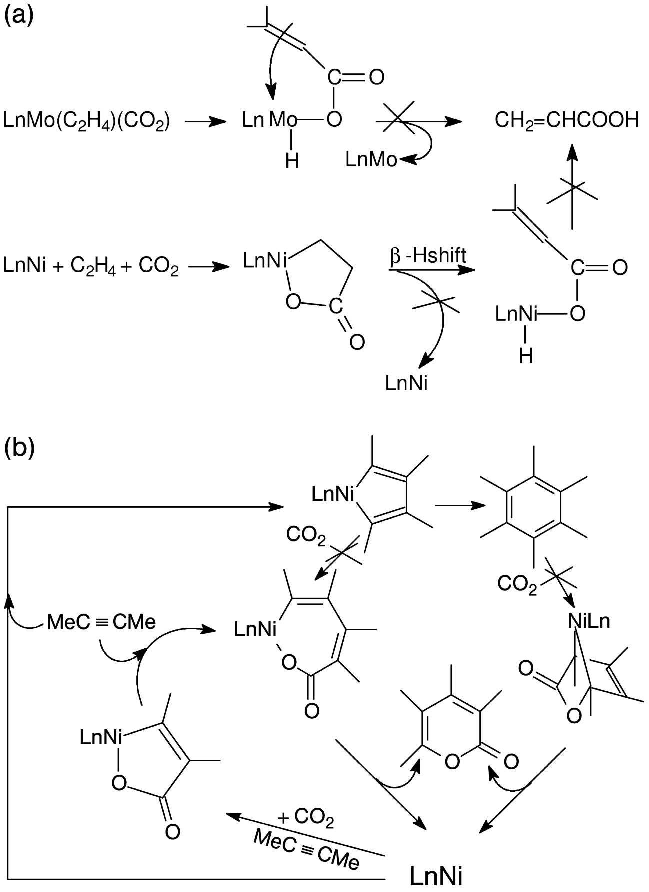
$$\text{Substrate} = PhC(O)CH_3,\ CH_3OH$$

$$MX = NaBF_4,\ NaBPh_4,\ KPF_6$$

All the reactions presented above have as a common drawback, which is the use of 1 mol Group 1 metal cation per mole of carboxylated product, resulting, thus, in a process formally similar to the carboxylation of a Grignard reagent. For practical applications, metal cations would be better substituted with protons, but that is not an easy process.

The direct carboxylation of methane to acetic acid, a process of great industrial interest, has been achieved in low yield using a two step process with Rh and Pd catalysts [65].

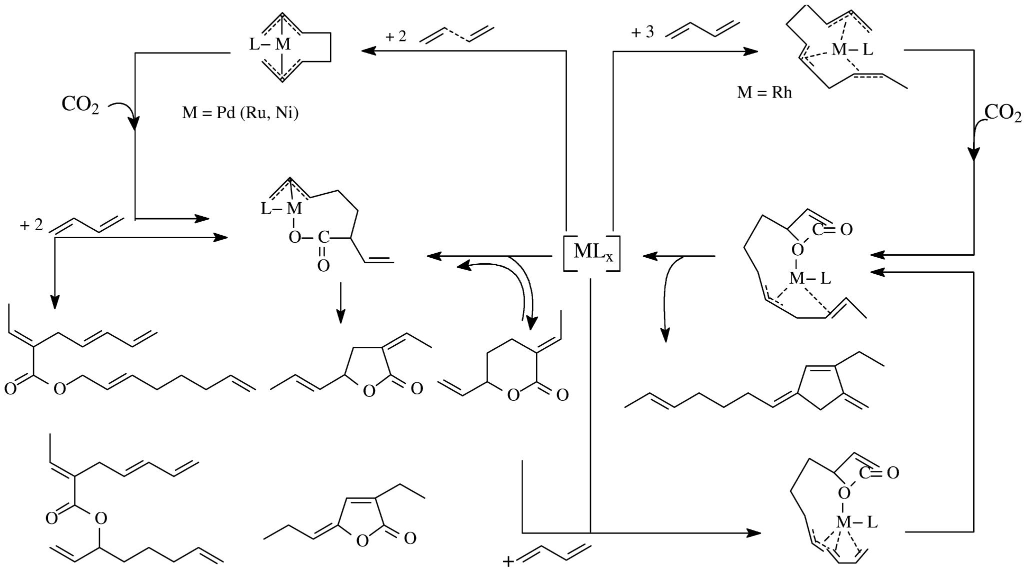
The carboxylation of alkenes has been attempted using several transition-metal systems, such as Ni(0) [66], Ti [67], Fe(0) [68], Mo(0) [69] and Rh [70] as cata-



Scheme 1.5 (a) Modes of carboxylation of an olefin: the carboxylate is released upon protonation. (b) Conversion of terminal and internal alkynes into pyrones.

lysts (Scheme 1.5 a). In all cases, a stoichiometric amount of metal atoms was used to afford stable carboxylates such as metallacycle or hydrido-acrylate, the product of formal insertion of CO_2 into the C–H bond of ethylene. These reactions have been very recently revisited using DFT calculations that have shown the existing barriers in a catalytic cycle with high turnover numbers (TONs) [71, 72]. In particular, tailored coligands may assist the elimination of acrylic acid [71]. Such information can be very useful for designing active catalysts for the synthesis of carboxylates and, in particular, acrylic acids derivatives that have a large use in the polymer industry.

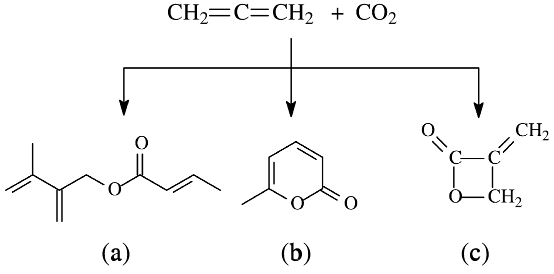
The carboxylation of alkynes (Scheme 1.5 b) and dienes has been successful, with both cumulated and conjugated systems being used (Schemes 1.6 and 1.7). In all cases high TONs have been obtained. The carboxylation of butadiene



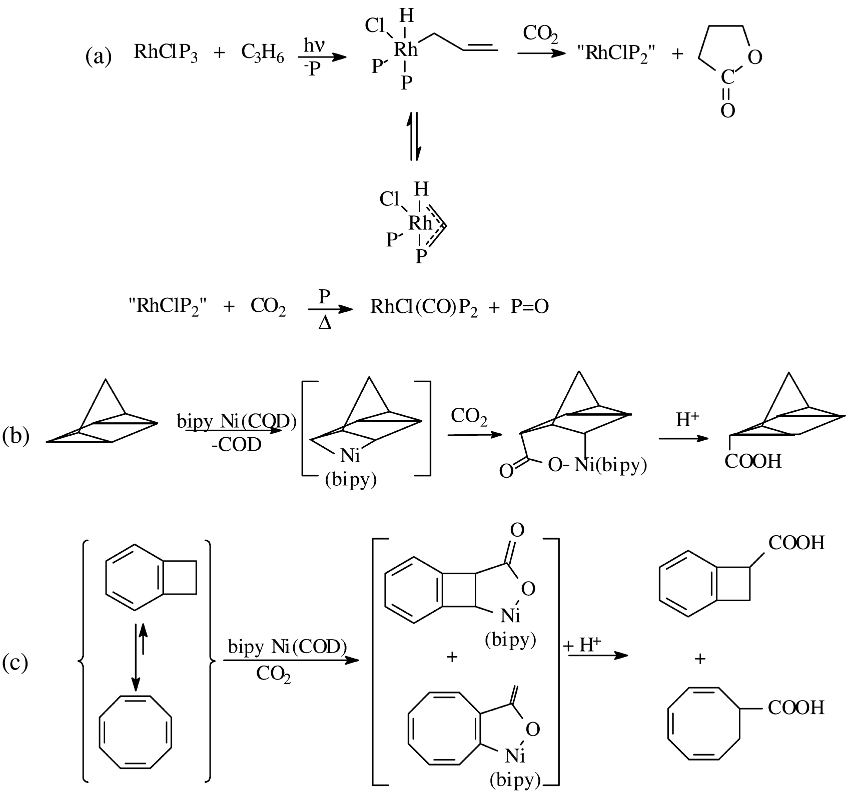
Scheme 1.6 Conversion of butadiene into lactones and linear esters using various metal catalysts.

to six-membered lactones has been performed with high selectivity and yield by using Pd systems with $(i\text{-}C_3H_7)P(CH_2)_nCN$ (n=2–5) phosphane ligands in various solvents, including pyridine [73]. The reaction also proceeds under electrochemical catalysis [73 b], and it has a good selectivity in $scCO_2$ using $Pd(dba)_3$ [73 c] as catalyst.

Allene has been converted into pyrones or linear esters [74] by using Ni or Rh catalysts (Scheme 1.7 a and b). Interestingly, allene and CO_2 undergo a formal "2+2" addition [75] to afford a four-membered lactone (Scheme 1.7 c). Both the four- and six-membered lactones have industrial application, such as for antibiotics or fragrances, respectively.



Scheme 1.7 Conversion of allene into linear esters or pyrones.



Scheme 1.8 Carboxylation of strained rings.

Strained rings can be carboxylated by using transition metal catalysts [76]. The reactivity depends on the size of the ring, the metal used and the reaction conditions (Scheme 1.8). In the cases in Scheme 1.8 (b and c), 1 mol metal is consumed per mole of carboxylated product formed, which is a serious drawback to exploitation of the process.

1.4.1.2 **N–C Bond Formation**

The formation of the N–CO_2 bond is relevant to industrial processes as it would allow the synthesis of carbamic acid derivatives avoiding the use of phosgene (Scheme 1.9).

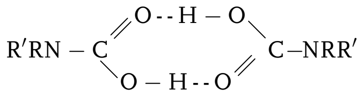
The synthesis of a labile carbamic acid has been achieved only very recently [77] using either benzylamine or $PhP(OCH_2CH_2)_2NH$. Both carbamic acids have been isolated as solid dimers and characterized in the solid state by X-ray diffraction. A common feature is the existence of the dimeric moiety represented below with an O–HO$\cdots$O distance of 122 pm, very similar to that found in di-

(a) $RR'NH + CO_2 = \frac{1}{2}[RR'N\text{-}COOH]_2$
$[R,R' = PhCH_2\text{-} \text{ or } PhP(OCH_2CH_2\text{-})_2]$

(b) $RR'NH + CO_2 + R''X + B = RR'N\text{-}COOR'' + BHX$

Scheme 1.9 Synthesis of carbamic acid (a) and carbamates (b) from amines and CO_2.

meric carboxylic acids. The monomer RR′N-COOH does not exist free, and decomposes back to the free amine and CO_2. Evidence for the formation of carbamic acid in solution has also been provided for amines like ω-(1-naphthyl)alkylamines [78].

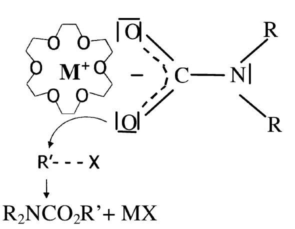


The reaction of amines with CO_2 in the presence of an alkylating agent and a base (Scheme 1.9b) is important industrially as it produces organic carbamates that find large application in the chemical [79], pharmaceutical [80] and agrochemical industries [81]. The many attempts to use transition metals as catalysts in the 1970s [82] led to the discovery that the metal-carbamato complexes LnM-OC(O)-NRR′ reacted with the alkylating agent RX to undergo an electrophilic attack by the alkyl group at the nitrogen rather than at the oxygen atom, with a net alkylation of the amine (Scheme 1.10a).

More recently, carbamic esters have been synthesized successfully under very mild conditions by using either Group 1 metal or ammonium carbamates in the presence of a crown-ether [83] (Scheme 1.10b). The latter interacts with the

(a) $LnMx + 2RR'NH = LnM\text{-}NRR' + RR'NH_2X$
$LnM\text{-}NRR' + CO_2 = LnM\text{-}OC(O)\text{-}NRR'$
$LnM\text{-}OC(O)\text{-}NRR' + R''X = LnMX + RR'NR'' + CO_2$

(b) .



(c) $RR'NH + (R''O)_2CO = RR'N\text{-}COOR'' + R''OH$

(d) $RR'NH + (R''O)_2CO = RR'R''N + R''OH + CO_2$

Scheme 1.10 Carboxy-alkylation of amines to carbamic esters.

metal or ammonium cation, increases the nucleophilicity of the oxygen and promotes the O-attack of the alkyl cation. Strong bases such as diazabicycloundecene (DBU) [84] have also been used. As the crown-ether can be easily recovered and recycled, the process is an easy, selective and high-yield route to carbamates at room temperature by directly using amines, CO_2 and alkylating agents. An alternative method for the carbamation of amines is the direct carboxy-alkylation by using carbonates (Scheme 1.10c). This reaction is of great industrial interest. It can be promoted by metal systems or other catalysts [85] with the major drawback being the alkylation of the amine, a process that occurs at higher temperature than the carboxy-alkylation (Scheme 1.10d). Either homogeneous [86] or heterogeneous [87] catalysts have been developed that work at low temperature and are very selective towards the carboxy-alkylation of amines. This route to organic carbamic esters is quite interesting as it may represent a phosgene-alkyl halides-free route if carbonates can be prepared from CO_2 and alcohols or by any other phosgene-free route.

A biomimetic catalyst has been developed for the carbamation of aromatic diamines [86h] under mild conditions.

1.4.1.3 **O–C Bond Formation**

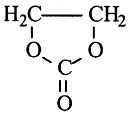
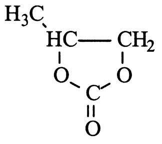
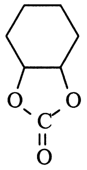
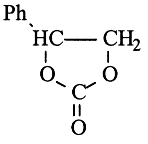
The O–C bond formation is relevant to the synthesis of organic carbonates characterized by the O-C(O)O moiety. Both linear and cyclic carbonates are of industrial interest (Table 1.5). The semicarbonate species RO-C(O)OH is labile, as is the analogous RR′N-C(O)OH. $CH_3O\text{-}C(O)OH$ has only recently been generated in solution and characterized by IR [88a] and NMR spectroscopy [88b].

1.4.1.3.1 **Cyclic Carbonates**

The most common route to cyclic carbonates is the reaction of epoxides with CO_2, which is promoted by a variety of homogeneous, heterogeneous and supported catalysts; either cyclic carbonates or polymers are obtained [89]. Main group metal halides [90a] and metal complexes [90b], ammonium salts [91] and supported bases [92], phosphines [93], transition metal systems [88, 94], metal oxides [95], and ionic liquids [96] have been shown to afford monomeric carbonates. Al porphyrin complexes [97] and Zn salts [89, 94, 98] copolymerize olefins and CO_2.

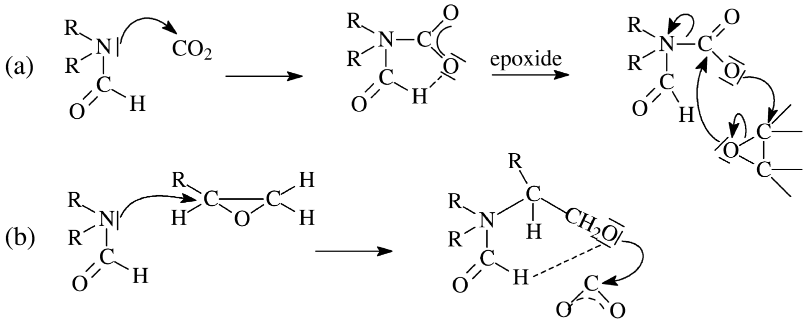
The carboxylation of epoxides is strongly dependent on the reaction conditions such as temperature and solvent. The use of ionic liquids as reaction medium seems to accelerate the reaction with respect to any other organic solvent, most probably because ionic liquids promote the formation of and/or stabilize polar or ionic intermediates. Heterogeneous catalysts such as oxides [95] or supported ammonium salts [92] or metal complexes [94] work well under these conditions. The solvent can play a key role in such reactions. Amides such as dimethylformamides or dialkylacetamides can themselves promote the carboxylation of epoxides, albeit with a low TON [100]. Most likely this is due to the abil-

Table 1.5 Linear and cyclic carbonates and their market and use (total market 18 Mt $year^{-1}$)

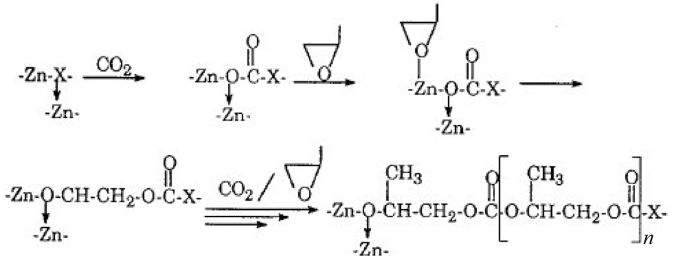
Carbonates					Uses
Linear	$(CH_3O)_2CO$	$(CH_2CH{=}CH_2O)CO$	$(EtO)_2CO$	$(PhO)_2CO$	solvents, reagents (for alkylation or acylation reactions), additive for gasoline
	DMC dimethyl carbonate	DAC diallyl carbonate	DEC diethyl carbonate	DPC diphenyl carbonate	
Cyclic	 EC	 PC	 CC	 SC	monomers for polymers, synthesis of hydroxyesters and hydroxyamines, component of special materials
	EC ethylene carbonate	PC propylene carbonate	CC cyclohexene carbonate	SC styrene carbonate	

ity of such species to activate either CO_2 or the epoxide (Scheme 1.11). $scCO_2$ also favors [99] the formation of the cyclic carbonate and copolymers.

Metal oxides have also been used for the synthesis of optically active carbonates [101] from pure enantiomers of the parent epoxide with total retention of configuration. The synthesis of optically active carbonates from a racemic mixture has been achieved with 22% *ee* in the best of cases, using Nb(IV) complexes with optically active N, O or P donor atom ligands. An NMR study [101] has demonstrated that such low percentage *ee* is caused by the de-anchoring of the ligand from the metal center, with loss of induction of asymmetry.



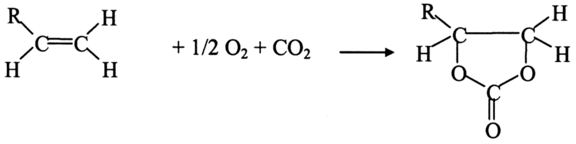
Scheme 1.11 Activation of CO_2 or the epoxide by an amide.



Scheme 1.12 Mechanism of copolymerization of propene and CO_2 with Zn complexes.

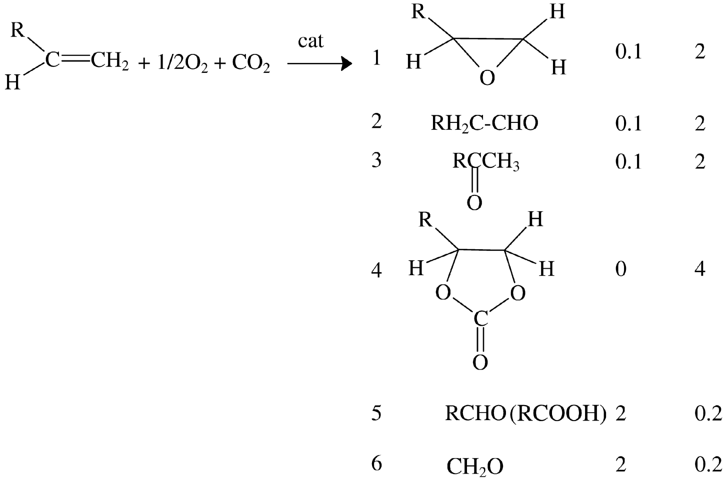
As noted above, when Al-porphyrin complexes [97] or Zn compounds [98] are used as catalysts for the carboxylation of epoxides, the formation of polymers is observed. Al catalysts are now used in a plant in China. The mechanism of the polymerization reaction has been studied and the most credited mechanism when Zn compounds are used is shown in Scheme 1.12. The molecular mass of the polymers varies with the catalyst. Primarily propene oxide and styrene oxide have been used so far, with some interesting applications of cyclohexene oxide. It is wished to enlarge the use of substrates in order to discover new properties of the polymers.

The limiting factor in the commercial development of the carboxylation of epoxides for the synthesis of monomeric or polymeric carbonates is the unavailability of large amounts of the parent epoxide. Such compounds are today prepared by using several techniques, some of which generate pollution [102]. The best route to epoxides is based on the use of H_2O_2 [103] that has as the main drawback the limited amount and the cost of H_2O_2. Finding a route to cyclic carbonates that is decoupled from H_2O_2 is of fundamental importance for developing the large volume industrial production of cyclic carbonates.



(8)

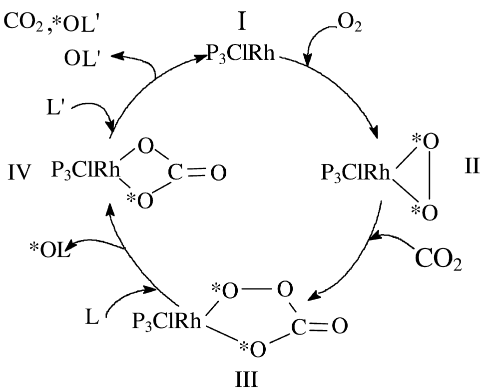
A reaction of great interest in this direction is the "oxidative carboxylation" of olefins that converts cheap products, such as olefins, and a waste, such as CO_2, into valuable compounds (Eq. 8). Such a reaction has been performed using different catalysts on substrates such as propene and styrene. Little information is available on an early process that uses a complex catalytic mixture [104], although in later studies the reaction mechanism has been elucidated for both homogeneous [105] and heterogeneous [106] catalysts. Two reactions are observed (Scheme 1.13): "two-oxygen" addition across the double bond that causes the splitting of the olefin to afford two aldehydes (compounds 5 and 6 in Scheme 1.13) and "one-oxygen" transfer to the olefin that produces the epoxide,



Scheme 1.13 Oxidative carboxylation of olefins with homogeneous and heterogeneous catalysts.

that is either converted into the carbonate or isomerized to a terminal aldehyde (compound 2 in Scheme 1.13) or a ketone (compound 3 in Scheme 1.13).

Using $RhCl(PEt_2Ph)_3$ as catalyst a maximum TON of 2–4 towards the carbonate was observed [105 a–d]. A more detailed study [105 e] showed that the reaction proceeds via formation of a peroxocarbonate that is the real oxidant and converts into the relevant Rh carbonate (Scheme 1.14). Such a pathway does not explain the observed TON, as the carbonate should not be an active catalyst. Using $^{18}O_2$, $^{13}C^{18}O_2$ or $^{13}C^{16}O_2$ it has been possible to demonstrate by accurate IR study and calculation of vibrational frequencies for the peroxocarbonate com-



Scheme 1.14 Catalytic cycle for the formation of carbonate via oxidative carboxylation of olefins.

plex [107] that the formation of the peroxocarbonate occurs via insertion of CO_2 into the O–O bond of the dioxygen–Rh complex. The formation of an asymmetrically labeled *O–O peroxo bond allowed the subsequent oxygen transfer reaction [107] to an oxophile (like an olefin) to be followed. The resulting carbonate can be converted into a Rh(I) complex via deoxygenation of the carbonate [105 e] by a free phosphine (either added or released by the complex). The resulting Rh(I) complex can restart the process. The progressive release of phosphine causes the conversion of the original Rh(I) catalyst into a species bearing a phosphine oxide ligand that is not able to promote the epoxidation of the olefin anymore. If external phosphine is added, the yield of carbonate is not improved as the free phosphine is preferentially oxidized with respect to the olefin. Using unsaturated Rh(I) complexes of the formula "RhCl(L-L)" (L-L = bidentate phosphines or N-ligands) does not improve the yield as the catalyst is deactivated via an intermolecular ligand exchange as depicted in Eq. (9). The resulting "$RhCl(L\text{-}L)_2$" or "$RhCl(olefin)_n$" species are not able to promote the epoxidation of the olefin.

$$2''\mathrm{RhCl(L\text{-}L)}'' + n(\mathrm{olefin}) \rightarrow \mathrm{RhCl(L\text{-}L)_2} + \mathrm{RhCl(olefin)}_n \tag{9}$$

Therefore, such Rh catalysts are not useful for practical applications. Using Co, Cr or Mn analogs, the yield in carbonate is always low with no real improvement of the TON.

The use of Group 1 or 2 metal oxides [106] or of transition metal oxides gives catalysts with a longer life. It must be emphasized that in the oxidative carboxylation, the catalyst must perform two roles: the oxidation of the olefin using O_2 and the carboxylation of the epoxide. This makes the selection of the catalyst more difficult. For instance, Table 1.6 shows that metal oxides that behave as oxidants are not good carboxylation catalysts (see, e.g. Ag_2O). Table 1.6 also shows that, in a nonoptimized system, the main reaction is olefinic double-bond cleavage, suggestive of a radical reaction promoted by the metal oxide. A detailed study has identified the role of P_{CO_2} and P_{O_2}, temperature, solvent, and cocatalyst in the double-bond cleavage reaction, enabling the reaction to be performed so that it is not the main process anymore and the carbonate can be synthesized with more than 50% selectivity [106 c].

1.4.1.3.2 **Linear Carbonates**

The most interesting route to linear carbonates is the direct carboxylation of alcohols (Eq. 10):

$$2\,\mathrm{ROH} + \mathrm{CO_2} \rightarrow \mathrm{(RO)_2CO} + \mathrm{H_2O} \tag{10}$$

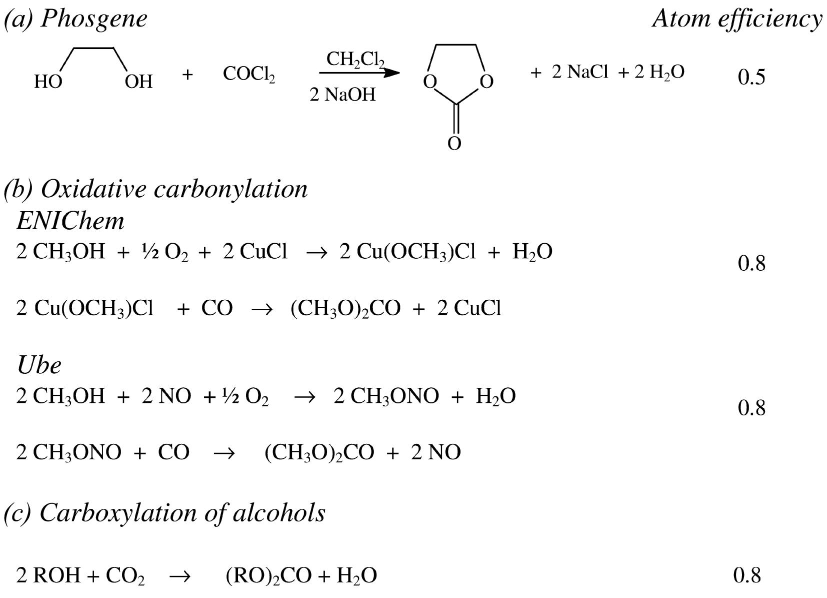
This reaction has an atom efficiency higher than the phosgene route, and is much safer and cleaner than the ENIChem and UBE processes that feature a comparable use of atoms (Scheme 1.15). The existing limitation to the exploitation of the reaction is the low yield at equilibrium that ranges between 1 and

Table 1.6 Products of the "oxidative carboxylation" of styrene using several oxides[a)]

Catalyst	Styrene conversion	Selectivity towards			
		Styrene carbonate (%)	Styrene oxide (%)	Benzal-dehyde (%)	Benzoic acid (%)
Molecular sieves 5 Å[b)]	16	3.1	11.8	67.5	3.1
SiO_2 anhydrous[b)]	23	9.1	15.2	45.6	19.1
SiO_2 hydrated[b)]	22	1.1	17.3	50.9	24.1
Ag_2O[b)]	28	–	16.4	50.8	24.5
MgO[b)]	14	6.8	13.6	58.8	8.9
Fe_2O_3[b)]	28	10.3	1.8	46.4	33.9
MoO_3[b)]	27	6.3	5.9	54.8	25.2
Ta_2O_5[b)]	27	2.9	**17**	48.5	24.4
La_2O_3[b)]	26	2.7	12.7	43	32.3
Nb_2O_5[b)]	27	**16.6**	4.4	46.3	24.1
V_2O_5[b)]	34	7.3	5	55.3	27
ZnO	12.5	1.3	14.2	41.1	36

a) Each entry is the average of three tests. The average deviation is ±5%. The operating conditions were the same in all tests. Catalyst: 7×10^{-4} mol; styrene: 1.75×10^{-2} mol; *N,N*-dimethylformamide as solvent: 10 mL; temperature: 393 K; reaction time: 5 h.

b) $P_{O_2}=5$ atm; $P_{CO_2}=45$ atm.



(a) Phosgene — Atom efficiency

$HOCH_2CH_2OH + COCl_2 \xrightarrow[2\,NaOH]{CH_2Cl_2}$ (ethylene carbonate) $+ 2\,NaCl + 2\,H_2O$ — 0.5

(b) Oxidative carbonylation

ENIChem

$$2\,CH_3OH + \tfrac{1}{2}\,O_2 + 2\,CuCl \rightarrow 2\,Cu(OCH_3)Cl + H_2O$$

$$2\,Cu(OCH_3)Cl + CO \rightarrow (CH_3O)_2CO + 2\,CuCl$$

0.8

Ube

$$2\,CH_3OH + 2\,NO + \tfrac{1}{2}\,O_2 \rightarrow 2\,CH_3ONO + H_2O$$

$$2\,CH_3ONO + CO \rightarrow (CH_3O)_2CO + 2\,NO$$

0.8

(c) Carboxylation of alcohols

$$2\,ROH + CO_2 \rightarrow (RO)_2CO + H_2O$$

0.8

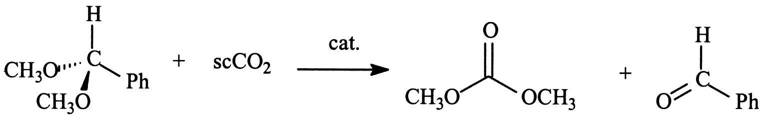
Scheme 1.15 Routes to linear carbonates and their atom efficiency.

Table 1.7 Thermodynamic properties for the direct carboxylation of alcohols

Carbonate	ΔH (kJ mol^{-1})
$(MeO)_2CO$	–4.00
$(EtO)_2CO$	–3.80
(allyl-O)$_2$CO	–3.91
$[CH_3(CH_2)_nO]_2CO$ ($n > 2$)	–4.17
$(PhO)_2CO$	+12.06

Calculated according to Ref. [108].

2% of converted alcohol, using both homogeneous and heterogeneous catalysts. Table 1.7 gives the thermodynamic properties of some carbonates (aliphatic and aromatic). The values of ΔH show that the process is not very favored for aliphatic alcohols and is disfavored with phenol and other aromatic alcohols. Nonetheless, the low equilibrium concentration may not be a drawback for process development as the reagents can be recycled. Attempts have been made to use chemical water traps in order to displace the equilibrium to the right. Molecular sieves cannot be used at the reaction temperature as the formed surface OH groups are acidic enough to protonate the carbonate and reverse the reaction. Organic water traps are better suited: aldols (Eq. 11) [109, 111], ketals (Eq. 12) [110] and dicyclohexylcarbodiimide (DCC) [111] have been used as such.



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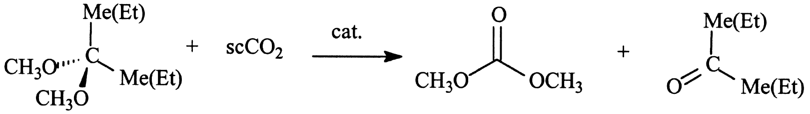
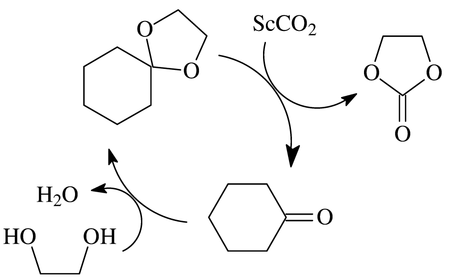
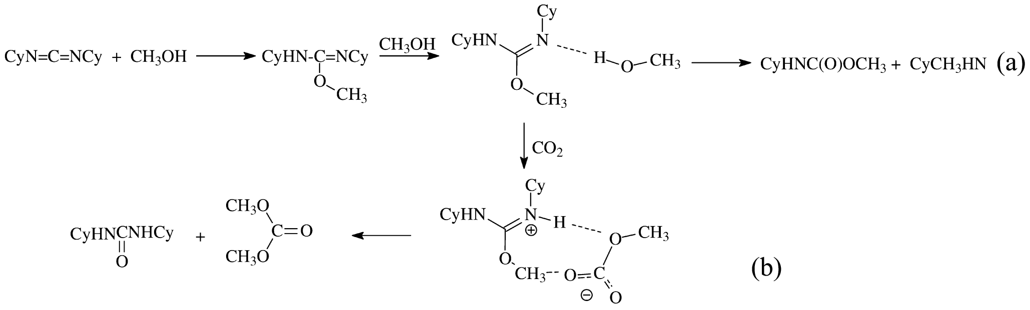


(12)

In particular, the dimethyl cyclohexanone ketal also has been reacted with ethyleneglycol to afford a cyclic carbonate and cyclohexanone [112], plus methanol (Scheme 1.16). The use of DCC as water trap deserves comment. A detailed study has shown that it is a promoter of the carboxylation in addition to being a simple water removal agent. Combining experimental studies and DFT calculations, the reaction mechanism has been completely elucidated, as shown in Scheme 1.17 [113]. Several carbonates have been produced with very high yields (90–96%) and selectivity (close to 100%). The latter is highly influenced by the temperature as above 335 K the favored reaction is the formation of carbamate (Scheme 1.17 A). With DCC, using methanol and phenol it has been possible to produce the mixed methyl-phenyl-carbonate, (MeO)(PhO)CO [113].



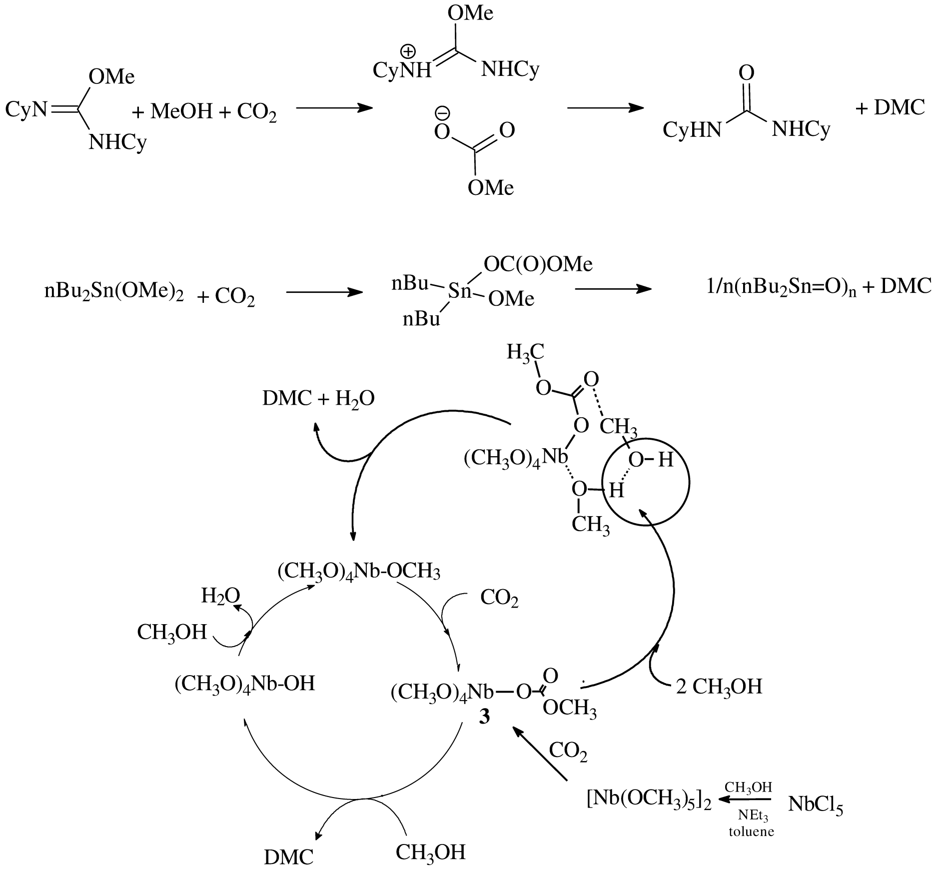
Scheme 1.16 Use of cyclohexanone-ketal in a two-step process for carbonate formation, avoiding the formation of water in the reaction medium containing the carbonate.



Scheme 1.17 Reaction mechanism of carboxylation of alcohols promoted by DCC.

The carboxylation of alcohols is an interesting reaction for the synthesis of carbonates that requires a better understanding in order to avoid catalyst deactivation by water. The reaction mechanism has been investigated for the Sn, Nb and DCC systems. Scheme 1.18 shows two different possible intra- and intermolecular mechanisms. The intramolecular mechanism that operates with Sn and DCC is based on a "double base-activation" of CH_3OH and produces an E=O double bond (E = C) that reduces the activity of the catalyst or generates an inert polymer (E = Sn). The intermolecular mechanism, that seems to be operative with Nb systems, can follow two routes that differ with respect to the intermediacy of one or two alcohol molecules. In the latter case, the reaction follows a "base plus acid activation" of methanol, and the catalysts perform much better and do not lose activity over several cycles [114]. The water formed in the reaction must be eliminated in order to push the equilibrium to right and avoid the destruction of the catalysts.

Heterogeneous catalysts also have been used [114c] that do not show better performances than homogeneous ones.



Scheme 1.18 Intra- (a and b) and inter-molecular (c) mechanism of formation of linear carbonates.

1.4.1.4 Use of Urea as an Active-CO_2 Form

Urea (H_2NCONH_2) is produced on a large scale (95 Mt year^{-1}) [9] from ammonia and CO_2 (Eq. 13):

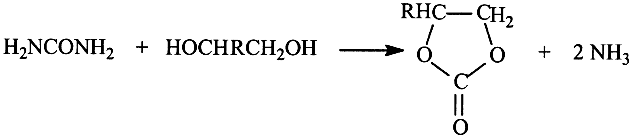
$$2\,NH_3 + CO_2 \rightarrow H_2NCONH_2 + H_2O \tag{13}$$

It can be used as an active form of CO_2 in reactions with alcohols to afford first the relevant urethane (Eq. 14) and then the carbonate (Eq. 15) [115]:

$$H_2NCONH_{2+}ROH \rightarrow H_2NCOOR + NH_3 \tag{14}$$

$$H_2NCOOR + ROH \rightarrow ROC(O)OR + NH_3 \tag{15}$$

Such reactions are usually carried out in two steps and the intermediate urethane can be quantitatively isolated if necessary [116]. Urea has also been used for the synthesis of cyclic carbonates by reaction with diols ($R=CH_3$ [117]):



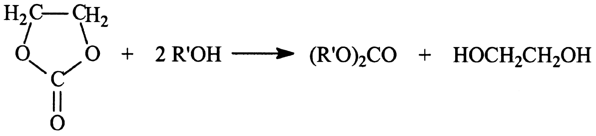
(16)

In these reactions, the released ammonia can be easily recovered and re-converted into urea by reaction with CO_2. Such a procedure can be useful for the synthesis of a number of carbonates. It must be emphasized that the separation cost of the carbonate depends on the length of the carbon chain of the alcohol and decreases with increasing the number of carbon atoms. Such technology is not yet applicable for the synthesis of dimethylcarbonate from methanol, but is more suitable for the preparation of carbonates of higher alcohols.

1.4.1.5 **Transesterification Reactions**

Any carbonate can be transformed into another one by transesterification:

$$(RO)_2CO + 2\,R'OH \rightarrow (R'O)_2CO + 2\,ROH \tag{17}$$



(18)

This process is already used for the industrial synthesis of diphenylcarbonate from DMC or ethylene carbonate, using $Ti(OPh)_4$ as catalyst [118]. Other catalysts have been developed [119] that produce a similar or better yield. In general, the reaction is very selective. This means that if a single process of those mentioned above is developed for industrial exploitation, then by transesterification other carbonates can be produced. The drawback to such a process is the coproduced alcohol that must be recycled or find utilization with a market comparable to that of carbonates (tens of megatons per year). The production system must be accurately designed so as to avoid the generation of undue amounts of byproducts. For example, one could imagine coupling two processes – the direct conversion of an olefin into the relevant cyclic carbonate and the conversion of the latter into a linear carbonate with formation of ethylene glycol. The latter could be reacted with urea to afford back ethylene carbonate and ammonia, recycled to produce urea.

1.4.2
Reduction Reactions

1.4.2.1 Energetics of the Reactions

As reported in Table 1.2, the conversion of CO_2 into other C_1 (or C_n) molecules, characterized by a lower O/C ratio or a higher H/C ratio, requires an energy input. Such energy can be provided in various forms: heat, electrons, radiation or chemicals. The convenience of the use of CO_2 as carbon source in the synthesis of products such as fuels (high H/C ratio) or intermediates (oxygenates) requires a detailed LCA study. While CO_2 lies in a deep potential well and its conversions require an external energy input, most of the routes that produce CO or syngas ($H_2/CO = 2$ mixture) from more reduced carbon [coal, liquid natural gas (LNG), HC (liquid hydrocarbons) today are quite low in energy efficiency and the reactions used are strongly endothermic. In the following sections natural and artificial processes for CO_2 reduction will be considered and compared, when possible.

1.4.2.1.1 Natural Processes

Apart from the formal reduction of CO_2 to "H_2CO" that occurs upon RuBisCO catalysis, the reduction of CO_2 to other C1 molecules with the carbon in a lower oxidation state takes place in a number of microorganisms such as algae and bacteria. The processes of CO_2 reduction most often encountered are listed in Table 1.8, with the name of the enzyme that catalyzes the reduction and the metal present as prosthetic group.

Much interest has been placed on understanding the enzymatic reaction pathways so that they can be reproduced *in vitro*. In particular, CO dehydrogenase has been studied in detail and the cycle of production of acetic acid from CO_2 [126] is quite well understood (Scheme 1.19). The active site contains a S_4Fe_4-Ni cluster. The role of the different metal centers in the process has been a matter of discussion. Through spectroscopic studies on the enzyme, using Fe-labeled species, the Fe atom (Scheme 1.19a [127]) was suggested to be involved in the

Table 1.8 Processes of reduction of CO_2 in microorganisms, the enzyme implied and the metal present as prosthetic group

Reduction process	Name of enzyme	Metal	Reference
$CO_2 + H^+ + 2e^- \rightarrow HCOO^-$	formate dehydrogenase	W, Mo	120
$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	carbon monoxide dehydrogenase	Ni, Fe	121
$HCO_2H + 2H^+ + 2e^- \rightarrow H_2CO + H_2O$	formaldehyde dehydrogenase		122
$H_2CO + 2H^+ + 2e^- \rightarrow CH_3OH$	methanol dehydrogenase		123
$CO_2 + CH_4 \rightarrow CH_3COOH$	methanogen	Ni, Fe, Co	124
$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	tetrahydrofolate	none	125

CODH-mediated synthesis of the acetyl moiety

(a)

$(CH_3)Ni\text{-}Fe(CO) \rightarrow Ni\text{-}Fe\text{-}C(O)CH_3$

$Ni\text{-}Fe\text{-}C(O)CH_3 \rightarrow H_3C(O)C\text{-}Ni\text{-}Fe$

(b)

$(CO)Ni\text{-}Fe) \rightarrow (CO)(CH_3)Ni\text{-}Fe$

$(CH_3)(CO)Ni\text{-}Fe \rightarrow H_3C(O)C\text{-}Ni\text{-}Fe$

$\text{Corrin-}CH_3 + (CO)Ni\text{-}Fe \rightarrow \text{Corrin} + CH_3(CO)\ Ni\text{-}Fe$
$CH_3C(O)\text{-}Ni\text{-}Fe + CoAS^- \rightarrow Ni\text{-}Fe + CoAS\text{-}C(O)CH_3$
$CoA\text{-}S\text{-}C(O)CH_3 \rightarrow CoASH + HOC(O)CH_3$

Scheme 1.19 Building up the acetyl moiety.

CO_2 reduction to CO and CH_3 uptake from Ni for building the acetyl moiety. Alternatively, using biomimetic synthetic systems it was shown that Ni (Scheme 1.19b) [128b] could behave as the unique active center where both the CO_2 reduction and the methyl uptake, with consequent formation of the acetyl moiety, occurred. The involvement of Fe in this part of the process has now been discarded [129] and it has been agreed that Ni is the site in the S_4Fe_4-Ni enzyme where both the CO_2 to CO reduction and the coupling of CO with CH_3 to afford the acetyl moiety take place. Considering that the methyl moiety is made from CO_2 converted under tetrahydrofolate catalysis, this route to acetic acid would be of great industrial interest, if the correct energy source can be found.

1.4.2.1.2 **Artificial Processes**

Formic Acid and its Derivatives The hydrogenation of CO_2 to formic acid and its derivatives such as formamides has been investigated by several research groups. Active catalysts have been discovered that may hydrogenate CO_2 in organic solvents or water or else directly in $scCO_2$ and ionic liquids [130f]. Among the formic acid derivatives, formamides can be produced in high yield using homogeneous catalysts [130f]. Conversely, methods for the production of methyl formate have not been developed yet. Interestingly, the hydrogenation can occur in water and bicarbonate or carbonate can be hydrogenated to formate salts at very high rates, with TOF per hour values as high as 9600 at 80 °C and 1364 at room temperature. The hydrogenation of aqueous bicarbonate is sensitive to CO_2 pressures that most likely influence the HCO_3^- concentration. Whether CO_2 itself is hydrogenated instead of HCO_3^- is not clear and requires further mechanistic studies. These reductions show limited selectivity, as products other than formate, i.e. C1 molecules such as CO or CH_4, and C2 species (glycols and others) are also formed. Among the metal complexes used as catalysts, Ru and Rh systems in aqueous and organic solvents have received great attention. In general, the production of formic acid is promoted by a base added to the reaction medium. Its role is to convert formic acid into an ammonium formate that (i) has favorable thermodynamics and (ii) converts formic acid into a weaker acid (the ammonium cation has a K_a 4–5 orders of magnitude lower than the acid) reducing the probability of a back addition to the metal center. Ligands bearing amine functional groups as pendant arms were found to improve the catalytic activity of metal complexes in the absence of an external base, but the catalytic activity was found to be much lower than with added amines.

Ru(II)-trimethylphosphine complexes, being very active [130 a, b], have been extensively investigated also from the kinetic point of view. The rate of formation of formic acid is first order in both H_2 and CO_2, which explains the influence of pressure and why scCO_2 as a solvent has a high positive influence [130 b] on the reaction rate. Catalysts active in water have been extensively studied [130 c]. It is highly probable that a cationic mechanism is operating and the active cationic species is generated with the assistance of added base or alcohol that promotes the loss of halide. This point has not been demonstrated yet, but only inferred on the basis of the fact that the effectiveness of various alcohols in promoting the hydrogenation matches their ability to promote the formation of cationic Ru complexes [130 b]. Among Rh(I) catalysts, Rh(H)(diphosphine) compounds are the most active [130 c]. Several other metal complexes have shown at least some activity, but the best, $NiCl_2$(dcpe), still has yields and rates well below those of Ru and Rh. Because the catalysts have been tested under very different conditions, it is difficult to make a ranking of them on the basis of TOF per hour values. If one assumes that the rates are first order in both H_2 and CO_2 pressures, and that they roughly double by increasing the temperature by 10 °C, then the most active catalyst precursors for formic acid production are $RhCl(TPPTS)_3$ [130 d], Rh(hfacac)(dcpb) and $RuCl(OAc)(PMe_3)_4$ [130 e]. That water may have a role is demonstrated by the fact that the aqueous-phase catalysts are the most active, which, based only on mass transfer rates, one would have not predicted. Methods have been discovered to prepare dialkylformamides [130 f, g] and even phenylformamide [130 h] from CO_2 and aniline with the assistance of DBU.

Production of CO and Syngas The production of syngas is of great importance in the energy and chemical industry. In fact, syngas can be used for the synthesis of methanol or long-chain hydrocarbons, such as gasoline, and other oxygenates. Therefore a great effort has been made to find catalysts and technologies that make use of CO_2 for producing CO or syngas, by using either methane (thermal routes) or water (photochemical conversion, Section 1.4.2.3) as the hydrogen source.

The interaction of CO_2 with a catalyst (metal or metal oxide) surface is relevant to its activation and conversion. Such chemistry has been investigated by several authors [131], who have studied the adsorption and reaction of CO_2 on clean Rh, Pd, Pt, Ni, Fe, Cu, Re, Al, Mg and Ag metal surfaces using spectroscopic methods. The formation of CO_2^- is a key step: depending on the metal, it can either dissociate to CO and O or convert into adsorbed CO_3^{2-} and CO. Adsorbed CO_2 dissociates on Fe, Ni, Re, Al and Mg, and remains unchanged over Pt and Cu surfaces. If oxygen is pre-adsorbed on the metals, the formation of stable carbonate structures is favored.

The production of syngas, used for the synthesis of methanol from methane, occurs via its partial oxidation (Eq. 19), steam reforming (Eq. 20) and CO_2 reforming (Eq. 21), also called dry reforming:

$$CH_4 + \frac{1}{2}O_2 \rightarrow CO + 2\,H_2 \qquad \Delta H^0_{298} = -36\ \text{kJ mol}^{-1} \tag{19}$$

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \qquad \Delta H^0_{298} = 206\ \text{kJ mol}^{-1} \tag{20}$$

$$CO_2 + CH_4 \rightarrow 2\,CO + 2\,H_2 \qquad \Delta H^0_{298} = 247\ \text{kJ mol}^{-1} \tag{21}$$

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H^0_{298} = 131\ \text{kJ mol}^{-1} \tag{22}$$

$$CO + H_2O \rightarrow CO + H_2 \qquad \Delta H^0_{298} = -41\ \text{kJ mol}^{-1} \tag{23}$$

Only the partial oxidation of methane (Eq. 19) is exothermic, and can, also if only partially, compensate the endothermic reactions (20) and (21).

The combination of the three reactions (19)–(21) is known as “tri-reforming” [132] that produces the proper CO/H_2 ratio (1.7) for methanol or higher hydrocarbons synthesis [133]. CO_2 reforming of methane produces syngas with lower residual CH_4 with respect to steam reforming, which leaves up to 2% of unreacted methane. The great existing interest in dry reforming is justified by the fact that it can be used in remote natural gas fields to convert on site CO_2-rich LNG streams into liquid fuels [gas-to-liquid (GTL) fuels], which are more easily transportable than gas and require less energy. Tri-reforming can advantageously be integrated into the direct re-use of flue gas from carbon-based power plants. The recent discovery of catalysts (Ni-La_2O_3) that prevent coke formation may push forward the exploitation of the process. An innovative approach is the utilization of catalysts under cold-plasma conditions for methane dry reforming [134] that can also be used for the direct synthesis of oxy-fuels [135]. In 2002, a pilot plant for the conversion of natural GTL fuel under plasma conditions began to be operated in Alberta, Canada [136]. The so called “tri-reforming” seems to be a good option for CO_2 and methane co-utilization [137]. Such technology converts two “greenhouse gases” into useful chemicals. CO_2 can be also used for the synthesis of ethanol (C_2) or higher (C_n) alcohols, for which there is a need for clean selective technologies. Efficient catalysts for ethanol formation from H_2/CO_2 have been developed [138] and higher alcohols can be produced in the same way [139]. Nevertheless, the yield is lower than using H_2/CO and the technology requires further development for practical application.

The catalytic hydrogenation of CO_2 has been applied to the selective synthesis of C_{5+} olefins using iron carbide (Fe_5C_2) as catalyst (Exxon Corporation process) and C_2–C_4 olefin synthesis using a Fe-K/alumina catalyst. A selectivity of about 44% at a CO_2 conversion of 68% under 2 MPa at 400 °C has been reported [140]. Alternatively, in a two-stage reactor, C_2–C_4 olefins are produced with over 90% overall selectivity by first making methanol using a Cu-ZnO catalyst, which is then converted using a solid acid catalyst in a second stage [141].

Another interesting use of CO_2 is as selective oxidant towards hydrocarbons. CO_2 is conveniently used as dehydrogenating agent in the conversion of $C_6H_5CH_2CH_3$ into styrene, $C_6H_5CH{=}CH_2$ [142]. The reaction is represented as:

$$C_6H_5CH_2CH_3 + CO_2 \rightarrow C_6H_5CH{=}CH_2 + CO + H_2O \tag{24}$$

An aspect of this reaction that deserves attention is that the coproducts CO and H_2O can be converted into CO_2 and H_2 by using a water-gas-shift catalyst:

$$H_2O + CO \rightarrow H_2 + CO_2 \tag{25}$$

In this way, the net result would be the use of CO_2 as mild oxidant with production of the unsaturated hydrocarbon and hydrogen, a process of great interest for a selective dehydrogenation of hydrocarbons.

Production of Methanol Remarkable progress has been made in the last 10 years in terms of catalyst development for the hydrogenation of CO_2 to methanol, such that 100% selectivity and high TOF have been observed. The excellent performance, most likely due to a different reaction mechanism [139] than with CO, compensates for the extra amount of dihydrogen needed for CO_2 reduction (Eq. 27) with respect to CO (Eq. 26), that is currently used:

$$CO + 2\,H_2 \rightarrow CH_3OH \tag{26}$$

$$CO_2 + 3\,H_2 \rightarrow CH_3OH + H_2O \tag{27}$$

CO_2 is currently added (up to 30% of total C) to syngas that is converted using Cu-ZnO-based oxide at 250–300 °C and 5–10 MPa (ICI process). Interestingly, the addition of CO_2 to the H_2/CO feed significantly improves the methanol yield and the energy balance. In such a system, one could imagine that CO_2 may be converted into CO by the water-gas-shift reaction and the latter is then converted into methanol that would still be a production of methanol based on syngas. That this is not the case has been demonstrated by tracer analysis [143]. The direct methanol synthesis from a CO_2/H_2 feed has been reviewed by several authors [144]. Experimental results show a higher yield of methanol from H_2/CO_2 at 260 °C, with respect to H_2/CO, with a further improvement when Pd modified Cu-ZnO [145] is used. The first pilot plant (50 kg day^{-1}) has been built in Japan [146], using a SiO_2^- modified Cu-ZnO catalyst. Recycling the feed produces a space–time yield of methanol of around 600 g/L h, with 99.9% selectivity during 8000 h operation at 250 °C and 5 MPa. Such a performance is several times that of conventional catalysts for syngas conversion. As a matter of fact, the methanol production from H_2/CO_2 is technically competitive with the industrial production from syngas, albeit economically still less convenient.

The synthesis of methanol from CO_2 and water can be carried out by using a cascade of enzymes that allow the conversion of CO_2 into $HCOO^-$ (formate dehydrogenase), CH_2O (formaldehyde dehydrogenase) and CH_3OH (methanol dehydrogenases) [122, 123]. All enzymes are easily available and can be used either separately or co-encapsulated into a unique system that makes the one-pot-three-step conversion of CO_2 into methanol [123b]. The limiting factor is the electron source: the $NADPH^+/NADP$ couple has been used so far. Cheap reducing agents or solar energy should be used to generate the electrons necessary for the reduction of CO_2 to methanol. This process would be of great importance as the production of methanol under such conditions would represent the solution to recycling CO_2 and using it as source of carbon in the energy and chemical industry.

1.4.2.1.3 **Photoelectrochemical Reduction**

Transition metal complexes have been used as catalysts in photochemical conversions of CO_2 since they can absorb a significant part of the solar spectrum, have long-lived excited states, and can promote the activation of small molecules. Co complexes with N-macrocycles and $Ru(bpy)_2(CO)X_n$ complexes (X = CO, Cl, H) have shown quite interesting activity [147].

It is noteworthy that the potential for the reduction of CO_2 to the radical anion $CO_2^{\bullet-}$ is –2.2 V versus normal hydrogen electrode (NHE) in strictly anhydrous, aprotic solvents, making the one-electron reduction highly unfavorable. There is a large kinetic “overvoltage” because of the structural differences between linear CO_2 and bent $CO_2^{\bullet-}$. This causes the yield of photochemical conversion under transition metal catalysis to be low. In contrast, proton-assisted multielectron reductions are much more favorable as shown in Table 1.9. Therefore, multielectron reduction to any reduced form of CO_2 requires a considerably lower potential than the one-electron reduction to the radical anion. Consequently, electrolysis in the presence of catalysts can be carried out at reasonable voltages, as shown in Table 1.9.

Table 1.9 One-electron versus multielectron reduction of CO_2 assisted by protons (pH 7 in aqueous solution versus NHE) [147]

$CO_2 + e^- = CO_2^{\bullet-}$	$E^0/V = -2.1$
$CO_2 + 2H^+ + 2e^- = HCO_2H$	–0.61
$CO_2 + 2H^+ + 2e^- = CO + H_2O$	–0.53
$CO_2 + 4H^+ + 4e^- = C + 2H_2O$	–0.20
$CO_2 + 4H^+ + 4e^- = HCHO + H_2O$	–0.48
$CO_2 + 6H^+ + 6e^- = CH_3OH + H_2O$	–0.38
$CO_2 + 8H^+ + 8e^- = CH_4 + 2H_2O$	–0.24

Since the early work of Lehn and Ziessel [148] several metal complexes have been used with the aim of developing an effective photocatalyst for CO_2 reduction. In general, only low light efficiencies have been reached that are often coupled with low selectivity, which leaves open the need of research for developing effective systems that may find viable applications. Among the tested transition metals, encouraging results have been obtained with Co and Ru complexes. $CoHMD_2^+$ [147b] has been used successfully as a catalyst for photochemical reduction of CO_2 because of the small $Co^{II}HMD^{2+}/Co^{I}HMD^+$ reorganization energy, the fast CO_2 binding to $Co^{I}HMD^+$ ($1.7\times10^8\ M^{-1}\ s^{-1}$) and the large K_{CO_2} (HMD = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene). X-ray absorption near edge structure studies suggest that the Co(I) species can promote the two-electron transfer to the bound CO_2 with formation of CO_2^{2-} and a consequent easy reduction of CO_2. The slow step in the photoreduction of CO_2 has been suggested to be the C–O bond rupture of the bound carboxylic acid, produced by protonation of $[S\text{-}Co^{III}HMD(CO_2^{2-})]^-$. This hypothesis could not be tested because the UV-Vis spectrum of $[S\text{-}Co^{III}HMD(CO_2^{2-})]^-$ lacks features amenable to the study of the proton dependence of the reduction process [147b]. Interestingly, it has been found that the doubly reduced species $[Ru^{I}(bpy)(bpy^{\bullet-})(CO)]$ is able to react with CO_2 in CH_3CN to produce $[Ru(bpy)_2(CO)(COO)]$ together with $[Ru(bpy)_2(CO)(COOH)]^-$ stabilized by a Group 1 metal cation [147b]. Re systems have also been tested [147c, d] that are much slower than the Co and Ni systems, most probably because of Re–Re bond formation.

Alternatively to homogeneous catalysts, semiconductors have been used in an attempt to reduce CO_2 in water under sunlight irradiation. HCOOH, HCHO and CH_3OH are produced by reduction of CO_2 with H_2O under solar irradiation of an aqueous suspension of a variety of semiconductors such as TiO_2 and $SrTiO_3$ [149]. The barrier to the exploitation of this reaction is the low quantum yield [144 c], that may be improved by using sacrificial hole traps or electron donors, such as *n*-propanol, tertiary amines or ethylenediaminetetraacetic acid. This solution is not economically convenient as the organic materials may be more valuable than the CO_2 reduction products. An interesting photocatalytic system for the reduction of CO_2 with H_2O has been reported [150] that has a selectivity of 30% for ethanol production using a Ti-modified mesoporous silica catalyst, compared to 1.4% over bulk TiO_2. This area is of great interest for carbon recycling and warrants further investigation.

1.5
Conclusions

CO_2 is a suitable source of carbon in many synthetic applications or can be used as a technological fluid with great advantage over other possible solutions that have a high greenhouse gas potential. In the short term, the use in carboxylation processes (synthesis of carbonates, carbamates and carboxylates, including cyclic compounds) appears to be the most promising synthetic application. Addition to CO for making methanol and use as a mild oxidant are other interesting applications. All such uses, in addition to recycling CO_2, reduce CO_2 emissions, in part because they are more efficient than existing technologies.

Currently, some 130 Mt_{CO_2} $year^{-1}$ are used in several applications: for a correct estimate of the amount of CO_2 not emitted into the atmosphere, LCA methodology must be applied. A fair estimate of the amount of CO_2 that may be avoided in the short-medium term is 300 Mt_{CO_2} $year^{-1}$, should all options of CO_2 utilization be implemented, including the use in air conditioners [151]. The photochemical reduction of CO_2 in water under solar light irradiation is an option that would greatly enlarge carbon recycling. A key point is the cost of CO_2 that does not have a natural origin, but should be recovered from industrial or power plants. The existing separation techniques are quite expensive, while large amounts of very pure CO_2 are vented. However, should the capture of CO_2 be implemented on a large scale, large amounts of CO_2 would be available for utilization. Concerted policies are necessary that make less random the research, and focus science and technology upon fields that may better contribute to reducing the CO_2 emission. As a matter of fact, the utilization of CO_2 is the only technology that may produce profit out of recovered CO_2, while contributing to reducing its global emission.

References

1 (a) The first report was by Bassarov in 1870, see D. Fromm, D. Lutzov, *Chem Uns Zeit* **1979**, *13*, 78; (b) H. Kolbe, E. Lautemann, *Ann* **1869**, *113*, 125; (c) R. Schmitt, E. Burkard, *Ber* **1877**, *20*, 2699.

2 (a) M. Aresta, G. Forti (Eds.), *Carbon Dioxide as a Source of Carbon: Chemical and Biochemical Uses*, NATO-ASI Series, Reidel, Dordrecht, **1987**, C206; (b) M. Aresta, J. Schloss (Eds.), *Enzymatic and Model Reduction and Carboxylation Reactions for Carbon Dioxide Utilization*, NATO-ASI Series, Kluwer, Dordrecht, **1990**, C314; (c) A. Behr (Ed.), *Carbon Dioxide Activation by Metal Complexes*, VCH, Weinheim, **1988**; (d) C. Song, A.M. Gaffney, K. Fujimoto (Eds.), *CO_2 Conversion and Utilization, ACS Symp Ser 809*, ACS, Washington, DC, **2002**; (e) M. Aresta (Ed.), *Carbon Dioxide Recovery and Utilization*, Kluwer, Dordrecht, **2003**; (f) C.J. Liu, R. Mallinson, M. Aresta (Eds.), *Utilization of Greenhouse Gases, ACS Symp Ser 852*, ACS, Washington, DC, **2003**.

3 M. Aresta, J.N. Armor, M.A. Barteau, E.J. Beckman, A.T. Bell, J.E. Bercaw, C. Creutz, E. Dinjus, D.A. Dixon, K. Domen, D.L. Dubois, J. Eckert, E. Fujita, D.H. Gibson, W.A. Goddard, D.W. Goodman, J. Keller, G.J. Kubas, H.H. Kung, J.E. Lyons, L.E. Manzer, T.J. Marks, K. Morokuma, K.M. Nicholas, R. Periana, L. Que, J. Rostrup-Nielsen, W.M.H. Sachtler, L.D. Schmidt, A. Sen, G.A. Somorjai, P.C. Stair, B.R. Stults, W. Tumas, *Chem Rev* **2001**, *101*, 953–996.

4 R.J. Allam, R. Bredesen, E. Drioli, in *Carbon Dioxide Recovery and Utilization*, M. Aresta (Ed.), Kluwer, Dordrecht, **2003**, pp. 53–118.

5 (a) A. Mathisen, in *Proc ICCDU VIII*, June 20–23, **2005**, p. 2; (b) H. Kongsjordan, O. Karstad, T.A. Torp, *Waste Manag* **1997**, *17*, 303–308.

6 J. De Simone, in *Proc ICCDU VI*, September 9–14, **2001**, p. 33.

7 J. Vansant, in *Recovery and Utilization of Carbon Dioxide*, M. Aresta (Ed.), Kluwer, Dordrecht, **2003**, pp. 3–50.

8 B. Mertz, O. Davidson, R. Swart, J. Pan (Eds.), *The Third Assessment Report of Intergovernmental Panel on Climate Change*, Cambridge University Press, Cambridge, **2001**.

9 M. Ricci, in *Recovery and Utilization of Carbon Dioxide*, M. Aresta (Ed.), Kluwer, Dordrecht, **2003**, pp. 395–402.

10 J. Gale, Y. Kaya (Eds.), *Greenhouse Gases Technologies*, Pergamon Press, Oxford, **2002**.

11 M. Aresta, M. Galatola, *J Cleaner Prod* **1999**, *7*, 181–193.

12 M. Aresta, A. Caroppo, A. Dibenedetto, M. Narracci, in *Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century*, M. Maroto Valer, C. Song, Y. Soong (Eds.), Kluwer, Dordrecht, **2002**, pp. 331–347.

13 M. Aresta, A. Dibenedetto, in *CO_2 Conversion and Utilization, ACS Symp Ser 809*, C. Song, A.M. Gaffney, K. Fujimoto (Eds.), ACS, Washington, DC, **2002**, pp. 54–70.

14 J.W. Rabalais, J.M. McDonald, V. Scherr, S.P. McGlynn, *Chem Rev* **1971**, *71*, 73–108 and references therein.

15 M. Aresta, E. Quaranta, I. Tommasi, P. Giannoccaro, A. Ciccarese, *Gazz Chim Ital* **1995**, *125*, 509–539 and references therein.

16 D.E. Shemansky, *J Chem Phys* **1972**, *56*, 1582–1587.

17 G. Liger-Belair, E. Prost, M. Parmentier, P. Jeandet, J.-M. Nuzillard, *Agric Food Chem* **2003**, *51*, 7560–7563.

18 D.R. Lide, *Handbook of Chemistry and Physics*, 74th edn, CRC Press, Boca Raton, FL, **1993/1994**.

19 K.S. Lackner, C.H. Wendt, D.P. Butt, E.L. Joyce, D.H. Sharp, *Energy* **1995**, *20*, 1153–1170.

20 M. Aresta, C.F. Nobile, V.G. Albano, E. Forni, M. Manassero, *Chem Commun* **1975**, *15*, 636–637.

21 D.H. Gibson, *Chem Rev* **1996**, *96*, 2063–2095.

22 (a) T. Herskovitz, *J Am Chem Soc* **1977**, *99*, 2391–2392; (b) J.C. Calabrese, T. Herskovitz, J.B. Kinney, *J Am Chem Soc* **1983**, *105*, 5914–5915.

23 I. Castro-Rodriguez, H. Nakai, L. Zakharov, A.L. Rheingold, K. Meyer, *Science* **2004**, *305*, 1757–1759.

24 (a) M. Aresta, C.F. Nobile, *Dalton Trans* **1977**, *7*, 708–711; (b) M.G. Mason, J.A. Ibers, *J Am Chem Soc* **1982**, *104*, 5153–5157; (c) A. Doehring, P.W. Jolly, C. Krueger, M. Romao, *Z Naturforsch* **1985**, *40B*, 484–488.

25 (a) M. Aresta, C.F. Nobile, *Inorg Chim Acta* **1977**, *24*, L49–L50; (b) M. Aresta, E. Quaranta, I. Tommasi, *New J Chem* **1994**, *18*, 133–142.

26 (a) H.H. Karsch, *Chem Ber* **1977**, *110*, 2213; (b) S. Komiya, M. Akita, N. Kasuga, M. Hirano, A. Fukuoka, *Chem Commun* **1994**, *9*, 1115–1116.

27 M. Sakamoto, L. Shimizu, A. Yamamoto, *Organometallics* **1994**, *13*, 407–409.

28 (a) S.M. Tetrick, F.S. Thom, A.R. Cutler, *J Am Chem Soc* **1998**, *119*, 6193–6194; (b) S.M. Tetrick, C. Xu, J.R. Pinkes, A.R. Cutler, *Organometallics* **1998**, *17*, 1861–1867.

29 T.A. Hanna, A.M. Baranger, R.G. Bergman, *J Am Chem Soc* **1995**, *117*, 3292–3293.

30 J.D. Audett, T.J. Collins, B.D. Santarsiero, G.H. Spies, *J Am Chem Soc* **1982**, *104*, 7352–7353.

31 C.P. Kubiak, C. Woodcock, R. Eisenberg, *Inorg Chem* **1982**, *21*, 2119–2126.

32 (a) J.S. Field, R.J. Haines, J. Sundermeyer, S.F. Woollam, *Chem Commun* **1990**, *14*, 985–988; (b) J.S. Field, R.J. Haines, J. Sundermeyer, S.F. Woollam, *Dalton Trans* **1993**, *18*, 2735–2748.

33 C.T. Tso, A.R. Cutler, *J Am Chem Soc* **1986**, *108*, 6069.

34 (a) J.C. Vites, B.D. Steffey, M.E. Giuseppetti-Dery, A.R. Cutler, *Organometallics* **1991**, *10*, 2827–2834; (b) J.R. Pinkes, B.D. Steffey, J.C. Vites, A.R. Cutler, *Organometallics* **1994**, *13*, 21–23.

35 D.R. Senn, J.A. Gladysz, K. Emerson, R.D. Larsen, *Inorg Chem.* **1987**, *26*, 2737–2739.

36 D.H. Gibson, M. Ye, B.A. Sleadd, J.M. Mehta, O.P. Mbadike, J.F. Richardson, M.S. Mashuta, *Organometallics* **1995**, *14*, 1242–1255.

37 (a) C.R. Eady, J.J. Guy, B.F.G. Johnson, J. Lewis, M.C. Malatesta, G.M. Sheldrick, *Chem Commun* **1976**, 602; (b) G.R. John,

B. F. G. Johnson, J. Lewis, K. C. Wong, *J Organomet Chem* **1979**, *169*, C23.

38 B. K. Balbach, F. Helus, F. Oberdorfer, M. L. Ziegler, *Angew Chem* **1981**, *93*, 479–480.

39 (a) C. Floriani, G. Fachinetti, *Chem Commun* **1974**, *15*, 615–616; (b) G. Fachinetti, C. Floriani, P. F. Zanazzi, *J Am Chem Soc* **1978**, *100*, 7405–7407; (c) S. Gambarotta, F. Arena, C. Floriani, P. F. Zanazzi, *J Am Chem Soc* **1982**, *104*, 5082–5092.

40 (a) D. H. Gibson, *Coord Chem Rev* **1999**, *185–186*, 335–355; (b) D. H. Gibson, *Comp Coord Chem II* **2004**, *1*, 595–602.

41 E. G. Lundquist, J. C. Huffman, K. Folting, B. E. Mann, K. G. Caulton, *Inorg Chem* **1990**, *29*, 128–134.

42 J. Mascetti, M. Tranquille, *J Phys Chem* **1988**, *92*, 2177–2184.

43 J. Mascetti, F. Galan, I. Papai, *Coord Chem Rev* **1999**, *190–192*, 557–576.

44 (a) M. Aresta, E. Quaranta, I. Tommasi, *Chem Commun* **1988**, *7*, 450–452; (b) K. Tanaka, D. Ooyama, *Coord Chem Rev* **2002**, *226*, 211–218.

45 T. Yoshida, D. Thorn, T. Okano, J. A. Ibers, A. Yamamoto, *J Am Chem Soc* **1979**, *101*, 4212–4221.

46 J. C. Calabrese, T. Herskovitz, J. B. Kinney, *J Am Chem Soc* **1983**, *105*, 5914–5915.

47 J.-C. Tsai, M. Khan, K. M. Nicholas, *Organometallics* **1989**, *8*, 2967–2970.

48 (a) B. Demerseman, G. Bouquet, M. Bigorgne, *J Organomet Chem* **1978**, *145*, 41–48; (b) H. Felkin, P. J. Knowles, B. Meunier, *J Organomet Chem* **1978**, *146*, 151–153.

49 (a) K. M. Nicholas, *J Organomet Chem* **1980**, *188*, C10–C12; (b) C. Bianchini, A. Meli, *J Am Chem Soc* **1984**, *106*, 2698–2699.

50 (a) T. Tsuda, S. I. Sanada, T. Saegusa, *J Organomet Chem* **1976**, *116*, C10–C12; (b) D. L. Delact, R. Del Rosario, P. E. Fanwick, C. P. Kubiak, *J Am Chem Soc* **1987**, *109*, 754–755; (c) J. Wu, P. E. Fanwick, C. P. Kubiak, *Organometallics* **1987**, *6*, 1805–1807.

51 (a) J. Chatt, M. Kubota, G.-J. Leigh, F. C. March, R. Mason, D. J. Yarrow, *Chem. Commun.* **1974**, *24*, 1033–1034; (b) H. H. Karsch, *Chem Ber* **1977**, *110*, 2213; (c) G. Fachinetti, C. Floriani, A. Chiesi-Villa, C. Guastini, *J Am Chem Soc* **1979**, *101*, 1767–1775; (d) C. Burkhart, H. Hoberg, *Angew Chem Int Ed* **1982**, *21*, 76; (e) C. Bianchini, C. Mealli, A. Meli, M. Sabat, *Inorg Chem* **1984**, *23*, 2731–2732; (f) G. Fachinetti, G. Fochi, T. Funaioli, P. F. Zanassi, *Chem Commun.* **1987**, *2*, 89–90; (g) G. R. Lee, J. M. Maher, N. J. Cooper, *J Am Chem Soc* **1987**, *109*, 2956–2962; (h) K. A. Belmore, R. A. Vanderpool, J.-C. Tsai, M. A. Kahn, K. M. Nicholas, *J Am Chem Soc* **1988**, *110*, 2004–2005; (i) J. Ruiz, V. Guerchis, D. Astrc, *Chem Commun* **1989**, 812.

52 M. Aresta, A. Dibenedetto, in *CO_2 Conversion and Utilization, ACS Symp Ser 809*, C. Song, A. M. Gaffney, K. Fujimoto (Eds.), ACS, Washington, DC, **2002**, pp. 54–70.

53 J. V. Schloss, G. H. Lorimer, *J Biol Chem* **1982**, *257*, 4691–4694.

54 T. Akazawa, A. Incharoensakdi, T. Takabe, in *Carbon Dioxide as a Source of Carbon: Chemical and Biochemical Uses*, M. Aresta, G. Forti (Eds.), NATO-ASI Series, Reidel, Dordrecht, **1987**, pp. 83–91.

55 (a) T. J. Andrews, G. H. Lorimer, *FEBS Lett* **1978**, *90*, 1–9; (b) M. K. Morell, K. Paul, H. J. Kane, T. J. Andrews, *Aust J Bot* **1992**, *40*, 431–441; (c) Z. Swab, P. Hjdukiewicz, P. Maliga, *Proc Natl Acad Sci USA* **1990**, *87*, 8526–8530; (d) M. P. Reynolds, M. van Ginkel, J. M. Ribaut, *J Exp Bot* **2000**, *51*, 459–473; (e) T. J. Andrews, S. M. Whitney, *Arch Biochem Biophys* **2003**, *414*, 159–169; (f) M. A. J. Parry, P. J. Andralojc, R. A. C. Mitchell, P. J. Magdwick, A. J. Keys, *J Exp Bot* **2003**, *54*, 1321–1333; (g) M. W. Finn, F. R. Tabita, *J Bacteriol* **2004**, *186*, 6360–6366.

56 H. Wu, S. Huang, Z. Jiang, *Catal Today* **2004**, *98*, 545–552.

57 (a) T. Yatsuka, A. Ito, O. Manabe, M. Dehara, H. Hiyama, *Yuki Gosei kagaku kyokai Shi* **1972**, *30*, 1030–1034; (b) W. Bachmann, C. Gnabs, K. Janecka, E. Mudlos, T. Papenfuhs, G. Waese, *Ger Offen 2,426,850*, **1976**; (c) F. Mutterer, C. D. Weis, *J Hetero-cycl Chem* **1976**, *13*, 1103–1104; (d) Z. Weglinski, T. Talik, *Rocz Chem* **1977**, *51*, 2401–2409; (e) R. Ueno, M. Kitayama, R. Otsuka, T. Shirai, *Pat Appl WO-JP2554 20040302*, **2004**; (f) S. Muradov, B. N. Khamidov, Ch. Sh. Kadyrov, *O'zbekiston Kimyo Jurnali* **2004**, 25–29.

58 M. Aresta, A. Dibenedetto, *Rev Mol Biotechnol* **2002**, *90*, 113–128.

59 M. Aresta, A. Lack, I. Tommasi, G. Fuchs, *Eur J Biochem* **1991**, *197*, 473–479.

60 K. Schuehle, G. Fuchs, *J Bacter* **2004**, *186*, 4556–4567.

61 M. Aresta, E. Quaranta, R. Liberio, C. Dileo, I. Tommasi, *Tetrahedron* **1998**, *54*, 8841–8846.

62 M. Aresta, A. Dibenedetto, C. Pastore, R. Lonoce, *Environ Chem Lett* **2006**, *3*, 145–148.

63 (a) G. Bottaccio, G.P. Chiusoli, *Chem Commun* **1966**, *17*, 618; (b) G. Bottaccio, G.P. Chiusoli, M. Marchi, *Ger Offen 2514571*, **1975**.

64 (a) M. Aresta, I. Tkatchenko, I. Tommasi, in *Ionic Liquids as Green Solvents: Progress and Prospects, ACS Symp Ser 856*, R.D. Rogers, K.R. Seddon (Eds.), ACS, Washington, DC, **2003**, 93–99; (b) I. Tommasi, F. Sorrentino, *Tetrahedron Lett* **2005**, *46*, 2141–2145.

65 L.-H. Yin, Z.-H. Gao, W. Huang, K. Xie, *Taiyuan Ligong Daxue Xuebao* **2004**, *35*, 318–320.

66 (a) H. Hoberg, D. Schaefer, *J Organomet Chem* **1982**, *236*, C28–C30; (b) H. Hoberg, D. Schaefer, *J Organomet Chem* **1983**, *251*, C51–C53; (c) E. Dinjus, D. Walther, H. Schueltz, *Z Chem* **1983**, *23*, 408–409; (d) D. Walther, E. Dinjus, J. Sieler, L. Andersen, O. Lindqvist, *J Organomet Chem* **1984**, *276*, 99–107; (e) H. Hoberg, Y. Peres, A. Michelreit, *J Organomet Chem* **1986**, *307*, C41–C43; (f) H. Hoberg, Y. Peres, A. Michelreit, *J Organomet Chem* **1986**, *307*, C38–C40; (g) H. Hoberg, Y. Peres, C. Krueger, Y.-H. Tsai, *Angew Chem Int Ed* **1987**, *99*, 799–800.

67 S.A. Cohen, J.E. Bercaw, *Organometallics* **1985**, *4*, 1006–1014.

68 H. Hoberg, K. Jenni, K. Angermund, C. Krueger, *Angew Chem Int Ed* **1987**, *26*, 153.

69 R. Alvarez, E. Carmona, D.J. Cole-Hamilton, A. Galindo, E. Gutierrez-Puebla, A. Monge, M.I. Poveda, C. Ruiz, *J Am Chem Soc* **1985**, *107*, 5529–5531.

70 M. Aresta, E. Quaranta, *J Organomet Chem* **1993**, *463*, 215–221.

71 G. Schubert, I. Papai, *J Am Chem Soc* **2003**, *125*, 14847–14858.

72 I. Papai, G. Schubert, I. Mayer, G. Besenyei, M. Aresta, *Organometallics* **2004**, *23*, 5252–5259.

73 (a) S. Pitter, E. Dinjus, *J Mol Catal A* **1997**, *125*, 39–45; (b) F. Koster, E. Dinjus, E. Dunach, *Eur J Org Chem* **2001**, *18*, 3575; (c) F. Gassner, V. Haack, A. Janssen, A. Elsagir, E. Dinjus, *EP Appl 103297 20000218*, **2000**.

74 (a) A. Doehring, P.W. Jolly, *Tetrahedron Lett* **1980**, *21*, 3021–3024; (b) M. Aresta, E. Quaranta, A. Ciccarese, *C1 Mol Chem* **1985**, *1*, 283–295; (c) P. Albano, M. Aresta, *J Organomet Chem* **1980**, *190*, 243–246.

75 M. Aresta, A. Dibenedetto, I. Papai, G. Schubert, *Inorg Chim Acta* **2002**, *334*, 294–300.

76 A. Behr, G. Thelen, *C1 Mol Chem* **1984**, *1*, 137–153.

77 (a) M. Aresta, D. Ballivet-Tkatchenko, M.C. Bonnet, R. Faure, H. Loiseleur, *J Am Chem Soc* **1985**, *107*, 2994–2995; (b) M. Aresta, D. Ballivet-Tkatchenko, D. Belli Dell'Amico, M.C. Bonnet, D. Boschi, F. Calderazzo, R. Faure, L. Labella, F. Marchetti, *Chem Commun* **2000**, 1099–1100.

78 K. Masuda, Y. Ito, M. Horiguchi, H. Fujita, *Tetrahedron* **2005**, *61*, 213–229.

79 M. Aresta, E. Quaranta, *ChemTech* **1997**, *27*, 32–40.

80 J. Barthelemy, *Lyon Phar* **1986**, *37*, 249–263.

81 (a) T.-T. Wu, J. Huang, N.D. Arrington, G.M. Dill, *J Agric Food Chem* **1987**, *35*, 817–823; (b) K. Suzuki, T. Kato, J. Takahashi, K. Kamoshita, *Nippon Noyaku Gakkaishi* **1984**, *9*, 497–501; (c) U. Romano, F. Rivetti, G. Sasselli, *EP 125726*, **1985**.

82 M.H. Chisholm, M.W. Extine, *J Am Chem Soc* **1977**, *99*, 782–792.

83 (a) M. Aresta, E. Quaranta, *Tetrahedron* **1992**, *48*, 1515–1530; (b) M. Aresta, E. Quaranta, *Ital Pat 1237208*, **1993**.

84 W.D. McGhee, D.P. Riley, *Organometallics* **1992**, *11*, 900–907.

85 (a) F. Porta, S. Cenini, M. Pizzotti, C. Crotti, *Gazz Chim Ital* **1985**, *115*, 275; (b) R. Garcia Deleon, A. Kobayashi, T. Yamauchi, J. Ooishi, T. Baba, S. Masaki, F. Hiarata, *Appl Catal A* **2002**, *225*, 43–49; (c) M. Curini, F. Epifano, F. Maltese, O. Rosati, *Tetrahedron Lett* **2002**, *43*, 4895–4897; (d) C. Calderoni, F. Mizia, F. Rivetti,

U. Romano, *EP 391473*, **1990**; (e) S. Carloni, D.E. De Vos, P.A. Jacobs, R. Maggi, G. Sartori, *J Catal* **2002**, *205*, 199–204; (f) T. Baba, A. Kobayashi, T. Yamauchi, H. Tanaka, S. Aso, M. Inomata, Y. Kawanami, *Catal Lett* **2002**, *82*, 193–197.

86 (a) M. Aresta, E. Quaranta, *Ital Pat 1198206*, **1988**; (b) M. Aresta, E. Quaranta, *Tetrahedron* **1991**, *47*, 9489–9502; (c) M. Aresta, E. Quaranta, *Ital Pat 1237207*, **1993**; (d) M. Aresta, C. Berloco, E. Quaranta, *Tetrahedron* **1995**, *51*, 8073–8078; (e) M. Aresta, A. Bosetti, E. Quaranta, *Ital Pat 002202*, **1996**; (f) M. Aresta, A. Dibenedetto, E. Quaranta, *Tetrahedron* **1998**, *54*, 14145–14156; (g) M. Aresta, A. Dibenedetto, E. Quaranta, *Green Chem* **1999**, *1*, 237–242; (h) M. Aresta, A. Dibenedetto, *Chem A Eur J* **2002**, *8*, 685–690; (i) M. Distaso, E. Quaranta, *Tetrahedron* **2004**, *60*, 1531–1539; (j) M. Distaso, E. Quaranta, *J Catal* **2004**, *228*, 36–42.

87 (a) S. Carloni, D.E. De Vos, P.A. Jacobs, R. Maggi, G. Sartori, R. Sartorio, *J Catal* **2002**, *205*, 199–204; (b) S.P. Gupte, A.B. Shivarkar, R.W. Chaudari, *Chem Commun* **2001**, 2620–2621; (c) I. Vauthey, F. Valot, C. Gozzi, F. Fache, M. Lemaire, *Tetrahedron Lett* **2000**, *41*, 6347–6350; (d) Z.-H. Fu, Y. Ono, *J Mol Catal* **1994**, *91*, 399–405; (e) T. Baba, M. Fujiwara, A. Oosku, A. Kobayashi, R.G. Deleon, Y. Ono, *Appl Catal A* **2002**, *227*, 1–6.

88 (a) G. Gattow, W. von Behrendt, *Angew Chem Int Ed* **1972**, *11*, 534–535; (b) A. Dibenedetto, M. Aresta, P. Giannoccaro, C. Pastore, I. Pàpai, G. Schubert, *Eur J Inorg Chem* **2006**, *5*, 908–913.

89 D.J. Darensbourg, M.W. Holtcamp, *Coord Chem Rev* **1996**, *153*, 155–174.

90 (a) T. Sakai, N. Kihara, T. Endo, *Macromolecules* **1995**, *28*, 4701–4706; (b) M. Sone, T. Sako, C. Kamisawa, *Jpn Kokai Tokkyo Koho*, *JP 11335372*, **1999**.

91 (a) H. Yasuda, L.N. He, T. Sakakura, C.W. Hu, *J Catal* **2005**, *233*, 119–122; (b) Y. Du, F. Cai, D.L. Kang, L.N. He, *Green Chem* **2005**, *7*, 518–523.

92 (a) Y. Li, X.Q. Zhao, Y.J. Wang, *Appl Catal A* **2005**, *279*, 205–208; (b) X. Zhang, W. Wei, Y. Sun, in *Proc ICCDU VIII*, June 20–23, **2005**, p. 68.93

93 R.J. De Pasquale, *Chem Commun* **1973**, 157–158.

94 D.J. Darensbourg, M.S. Zimmer, *Macromolecules* **1999**, *32*, 2137–2140.

95 (a) T. Yano, H. Matsui, T. Koike, H. Ishiguro, H. Fujihara, M. Yoshihara, T. Maeshima, *Chem Commun* **1997**, 1129–1130; (b) K. Yamaguchi, K. Ebitani, T. Yoshida, H. Yoshida, K. Kaneda, *J Am Chem Soc* **1999**, *121*, 4526–4527; (c) M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore, *J Mol Catal A* **2003**, *204/205*, 245–252.

96 J. Sun, S.-I. Fujita, M. Arai, *J Organomet Chem* **2005**, *690*, 3490–3497.

97 (a) H. Sugimoto, S. Inoue, *J Pol Sci A Pol Chem* **2004**, *42*, 5561–5573; (b) H. Sugimoto, H. Ohtsuka, S. Inoue, *Stud Surf Sci Catal* **2004**, *153*, 243–246.

98 M. Super, E. Berluche, C. Costello, E. Beckman, *Macromolecules* **1997**, *30*, 368–372.

99 (a) D.J. Darensbourg, N.W. Stafford, T. Katsurao, *J Mol Catal* **1995**, *104*, L1–L4; (b) S. Mang, A.I. Cooper, M.E. Colclough, N. Chauhan, A.B. Holmes, *Macrocromolecules* **2000**, *33*, 303–308; (c) M. Van Schilt, M. Kemmere, J. Keurentjes, in *Proc ICCDU VIII*, June 20–23, **2005**, p. 54; (d) T. Endo, in *Proc ICCDU VIII*, June 20–23, **2005**, p. 60.

100 M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore, *J Mol Catal A* **2003**, *204/205*, 245–252.

101 M. Aresta, A. Dibenedetto, L. Gianfrate, C. Pastore, *Appl Catal A* **2003**, *255*, 5–11.

102 (a) S.J. Ainsworth, *Chem Eng News* **1992**, *2*, 9; (b) R.O. Kirk, T.J. Dempsey, in *Kirk–Othmer Encyclopedia of Chemical Technology*, M. Grayson, D. Eckroth, H.F. Mark, D.F. Othmer, C.G. Overberger, G.T. Seaborg (Eds.), Wiley, New York, **1982**, *19*, p. 46; (c) H.P. Wulff, F. Wattimenu, *US Patent 4,021,454*, **1977**, to Shell Oil Company; (d) N.W. Cant, W.K. Hall, *J Catal* **1978**, *52*, 81–87; (e) M.G. Clerici, P. Ingallina, *Catal Today* **1988**, *41*, 351–363 and references therein; (f) V. Duma, D. Honicke, *J Catal* **2002**, *191*, 93–104.

103 (a) G.F. Thiele, E. Roland, *J Mol Catal A* **1997**, *117*, 351–356; (b) M.G. Clerici,

G. Belussi, U. Romano, *J Catal* **1991**, *129*, 159–167.

104 (a) S.E. Jacobson, *EP 118248*; *EP 117147*, **1984**.

105 (a) M. Aresta, A. Ciccarese, E. Quaranta, *C1 Mol Chem* **1985**, *1*, 267–281; (b) M. Aresta, A. Ciccarese, E. Quaranta, *J Mol Catal* **1987**, *41*, 355–359; (c) M. Aresta, C. Fragale, E. Quaranta, I. Tommasi, *Chem Commun* **1992**, *4*, 315–317; (d) M. Aresta, A. Dibenedetto, I. Tommasi, *Eur J Inorg Chem* **2001**, 1801–1806.

106 (a) M. Aresta, A. Dibenedetto, I. Tommasi, *Appl Organomet Chem* **2000**, *14*, 799–802; (b) M. Aresta, A. Dibenedetto, *J Mol Catal* **2002**, *182/183*, 399–409; (c) M. Aresta, A. Dibenedetto, in *Proc ISHHC XII*, July 18–22, **2005**, p. 40.

107 M. Aresta, I. Tommasi, E. Quaranta, C. Fragale, J. Mascetti, M. Tranquille, F. Galan, M. Fouassier, *Inorg Chem* **1996**, *35*, 4254–4260.

108 S.W. Benson, N. Cohen, *Chem Rev* **1993**, *93*, 2419–2438.

109 T. Sakakura, Y. Saito, M. Okano, J.-C. Choi, T. Sako, *J Org Chem* **1998**, *63*, 7095–7096.

110 (a) T. Sakakura, Y. Saito, J.-C. Choi, T. Masuda, T. Sako, T. Oriyama, *J Org Chem* **1999**, *64*, 4506–4508; (b) T. Sakakura, Y. Saito, J.-C. Choi, T. Sako, *Polyhedron* **2000**, *19*, 573–576.

111 N.S. Isaacs, B. O'Sullivan, C. Verhaelen, *Tetrahedron* **1999**, *55*, 11949–11956.

112 M. Aresta, A. Dibenedetto, E. Amodio, C. Dileo, I. Tommasi, *J Sup Fluid* **2003**, *25*, 177–182.

113 M. Aresta, A. Dibenedetto, E. Fracchiolla, P. Giannoccaro, C. Pastore, I. Pápai, G. Schubert, *J Org Chem* **2005**, *70*, 6177–6186.

114 (a) M. Aresta, A. Dibenedetto, C. Pastore, in *Proc ICCDU VIII*, June 20–23, **2005**, p. 62; (b) M. Aresta, A. Dibenedetto, C. Pastore, *Topics Catal* **2006**, in press; (c) K. Tomishige, K. Kunimori, *Appl Catal A* **2002**, *237*, 103–106.

115 P. Ball, H. Fuellmann, W. Heitz, *Angew Chem* **1980**, *92*, 742–743.

116 M. Aresta, A. Dibenedetto, C. Devita, O.A. Bourova, O.N. Chupakhin, *Stud Surf Sci Catal* **2004**, *153*, 213–220.

117 (a) Q. Li, N. Zhao, W. Wei, Y. Sun, *Stud Surf Sci Catal* **2004**, *153*, 573–576; (b) Q. Li, W. Zhang, N. Zhao, W. Wei, Y. Sun, in *Proc ICCDU VIII*, June 20–23, **2005**, p. 164.

118 (a) G. Illuminati, U. Romano, R. Tesei (Snam Progetti SPA), *DE Patent 75-2528412*, **1985**; (b) G. Illuminati, U. Romano, R. Tesei (Snam Progetti SPA), *RO Patent 75-82648*, **1980**.

119 M. Aresta, A. Dibenedetto, C. Pastore, *Stud Surface Sci Catal* **2004**, *153*, 221–226.

120 (a) R.A. Schmitz, S.P.J. Albracht, R.K. Thauer, *FEBS Lett* **1992**, *309*, 78–81; (b) *Eur J Biochem* **1992**, *209*, 1013–1018; (c) R.A. Schmitz, M. Richter, D. Linder, R.K. Thauer, *Eur J Biochem* **1992**, *207*, 559–565; (d) J.J.G. Moura, C.D. Brondino, J. Trincão, M.J. Romão, *J Biol Inorg Chem* **2004**, *9*, 791–799.

121 (a) J.L. Kraft, *Biochemistry* **2002**, *41*, 1681–1688; (b) C.L. Drennan, T.I. Doukov, S.W. Ragsdale, *J Biol Inorg Chem* **2004**, *9*, 511–515.

122 R. Obert, B.C. Dace, *J Am Chem Soc* **1999**, *121*, 12192–12193.

123 (a) Z.Y. Jiang, H. Wu, S.W. Xu, S.F. Huang, *Chin J Catal* **2002**, *23*, 162; (b) Z. Jiang, S. Wu, H. Wu, *Stud Surf Sci Catal* **2004**, *153*, 475–480.

124 R.S. Wolfe, *Trends Biol Sci* **1985**, *10*, 396–399.

125 G. Fuchs, in *Carbon Dioxide as a Source of Carbon: Chemical and Biochemical Uses*, M. Aresta, G. Forti (Eds.), NATO-ASI Series, Reidel, Dordrecht, **1987**, pp. 263–274.

126 (a) S.W. Ragsdale, J.E. Clark, L.G. Ljungdahl, L. Lundie, H.L. Drake, *J Biol Chem* **1983**, *258*, 2364–2369; (b) M. Kumar, W.-P. Lu, S.W. Ragsdale, *Biochemistry* **1994**, *33*, 9769–9777.

127 D. Qiu, M. Kumar, S.W. Ragsdale, T.G. Spiro, *Science* **1994**, *264*, 817–819.

128 (a) M. Aresta, A. Dibenedetto, *Inorg Chim Acta* **1998**, *272*, 38–42; (b) M. Aresta, A. Dibenedetto, in *Proc ICCDU VIII*, June 20–23, **2005**, p. 4.

129 (a) S.W. Ragsdale, I. Tzanko, C.L. Drennan, *J Biol Inorg Chem* **2004**, *9*, 511–515; (b) S.W. Ragsdale, T. Craft,

Y.-C. Horng, *J Am Chem Soc* **2004**, *126*, 4068–4069.

130 (a) P.G. Jessop, T. Ikaryia, R. Noyori, *Nature* **1994**, *368*, 231–233; (b) P.G. Jessop, T. Ikaryia, R. Noyori, *Chem Rev* **1995**, *95*, 259–272; (c) P.G. Jessop, F. Joò, C.-C. Tai, *Coord Chem Rev* **2004**, *248*, 2425–2442; (d) F. Gassun, W. Leitner, *Chem Commun* **1993**, 1465; (e) P. Munshi, A.D. Main, J. Linehan, C.-C. Tai, P.G. Jessop, *J Am Chem Soc* **2002**, *124*, 7963–7971; (f) O. Krocker, R.A. Koppel, M. Froba, A. Baiker, *J Catal* **1998**, *178*, 284–298; (g) P.G. Jessop, H. Hsiao, T. Ikariya, R. Noyori, *J Am Chem Soc* **1994**, *116*, 8851–8852; (h) P. Munshi, D. Heldebrandt, E. McKoon, P.A. Kelly, C.-C. Tai, P.G. Jessop, *Tetrahedron Lett* **2003**, *44*, 2725–2726.

131 (a) F. Solymosi, G. Kliveny, *Surf Sci* **1994**, *315*, 255–268; (b) F. Solymosi, L. Bugyi, *Faraday Trans 1* **1987**, *83*, 2015–2033; (c) D.W. Goodman, D.E. Peably, J.M. White, *Surf Sci* **1984**, *140*, L239–L243.

132 C. Song, in *CO_2 Conversion and Utilization, ACS Symp Ser 809*, C. Song, A.M. Gaffney, K. Fujimoto (Eds.), ACS, Washington, DC, USA, **2002**, pp. 2–30.

133 (a) J.M. III Fox, *Catal Rev Sci Eng* **1993**, *35*, 169–212; (b) J.R. Rostrup-Nielsen, in *Natural Gas Conversion II*, H.E. Curry-Hyde, R.F. Howe (Eds.), Elsevier, Amsterdam, **1994**, p. 25; (c) J.R.H. Ross, A.N.J. van Keule, M.E.S. Hegarty, K. Seshan, *Catal Today* **1996**, *30*, 193–199.

134 B. Eliasson, U. Kogelschatz, *IEEE Trans Plasma Sci* **1991**, *19*, 1063–1077.

135 Y. Zhang, Y. Li, Yu Wang, C. Liu, B. Eliasson, *Fuel Process Technol* **2003**, *83*, 101–109.

136 A. Czernichowski, M. Czernichowski, P. Czernichowski, T.E. Cooley, *Fuel Chem Div Prepr* **2002**, *47*, 280–281.

137 M.M. Halmann, A. Steinfeld, in *Proc ICCDU VIII*, June 20–23, **2005**, p. 24.

138 M. Takagawa, A. Okamoto, H. Fujimura, Y. Izawa, H. Arakawa, in *Advances in Chemical Conversions for Mitigating Carbon Dioxide*, Elsevier, Amsterdam, **1998**, pp. 525–528.

139 R. Kieffer, M. Fujiwara, L. Udron, Y. Souma, *Catal Today* **1997**, *36*, 15–24.

140 (a) R.A. Fiato, S.L. Soled, G.B. Rice, S. Miseo, *US Patent 5140049*, **1992**; (b) M.J. Choi, K. Kikim, H. Lee, S.B. Kim, J.S. Nam, K.W. Lee, in *Proc 5th Int Conf on Greenhous Gas Control Technologies*, **2000**, pp. 607–612.

141 T. Inui, *Catal Today* **1996**, *29*, 329–337.

142 S.-E. Park, J.S. Yoo, *Stud Surf Sci Catal* **2004**, *153*, 303–314.

143 A. Rozovskii, *Russ Chem Rev* **1989**, *58*, 41–56.

144 (a) M. Saito, T. Fujitani, M. Takeuchi, T. Watanabe, *Appl Catal A* **1996**, *138*, 311–318; (b) H. Arakawa, in *Advances in Chemical Conversions for Mitigating Carbon Dioxide*, Elsevier, Amsterdam, **1998**, pp. 19–30; (c) M.M. Halmann, M. Steinberg (Eds.), *Greenhouse Gas Carbon Dioxide Mitigation Science and Technology*, Lewis, Boca Raton, FL, **1999**.

145 T. Inui, T. Takeguchi, K. Yanagisawa, M. Inoue, *Appl Catal A* **2000**, *192*, 201–209.

146 K. Ushikoshi, K. Mori, T. Watanabe, M. Takeuchi, M. Saito, in *Advances in Chemical Conversions for Mitigating Carbon Dioxide*, Elsevier, Amsterdam, **1998**, pp. 357–362.

147 (a) R. Ziessel, in *Carbon Dioxide as a Source of Carbon: Chemical and Biochemical Uses*, M. Aresta, G. Forti (Eds.), NATO-ASI Series, Reidel, Dordrecht, **1987**, pp. 113–138 and reference therein; (b) E. Fujita, *Coord Chem Rev* **1994**, *185/186*, 373–384; (c) Y. Heyashi, S. Kita, B.S. Brunschwig, E. Fujita, *J Am Chem Soc* **2003**, *125*, 11976–11987; (d) E. Fujita, J.T. Muckerman, *Inorg Chem* **2004**, *43*, 7636–7647.

148 T. Inoue, A. Fujisima, S. Konishi, K. Honda, *Nature* **1979**, *277*, 637–638.

149 A. Mackor, A.H.A. Tinnemans, T.P.M. Koster, in *Carbon Dioxide as a Source of Carbon: Chemical and Biochemical Uses*, NATO-ASI Series, M. Aresta, G. Forti (Eds.), Reidel, Dordrecht, **1987**, pp. 393.

150 M. Anpo, S.G. Zhag, Y. Fujii, H. Yamashita, K. Koyano, K.T. Tatsumi, *Chem Lett* **1997**, 659–660.

151 M. Aresta, A. Dibenedetto, *Catal Today* **2004**, *98*, 455–462.