Elsevier Editorial System(tm) for Journal of Catalysis
Manuscript Draft

Manuscript Number: JCAT-15-796R3

Title: State of the art and perspectives in catalytic processes for CO2 conversion into chemicals and fuels: the distinctive contribution of chemical catalysis and biotechnology.

Article Type: SI:CO2 conversion

Keywords: CO2 properties, coordination chemistry and reactions, CO2 conversion into chemicals, CO2 as source of carbon for energy products, Biotechnological uses of CO2

Corresponding Author: Prof. michele aresta,

Corresponding Author's Institution: NUS

First Author: michele aresta

Order of Authors: michele aresta; Eugenio Quaranta; Angela Dibenedetto

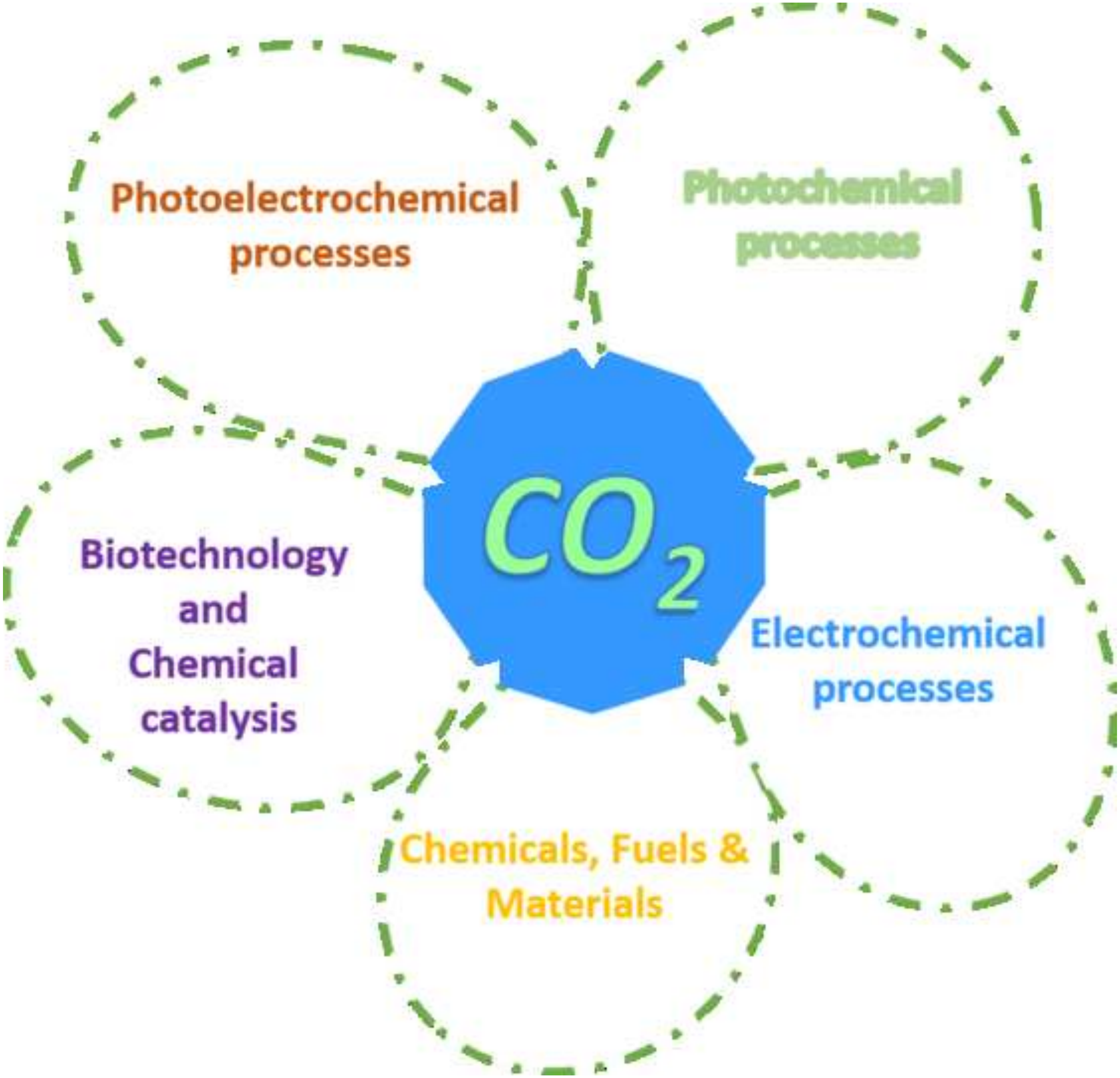
Manuscript Region of Origin: ITALY

Abstract: The need to reduce the emission of carbon dioxide into the atmosphere is pushing towards the use of "renewable carbon", so to avoid as much as possible burning "fossil carbon". Biomass is synonym of "renewable carbon", as it is re-generated from CO2, usually captured from atmosphere. A "close to zero emission" cycle can in principle be implemented that effectively reduces the emission of CO2. It would be possible to complement the natural "carbon cycle" by developing man-made industrial processes for "carbon recycling", converting, thus, "spent carbon" as CO2 into "working carbon", as that present in valuable chemicals or fuels. Such practice would fall again into the utilization of "renewable carbon", as the man-made process would perfectly mimic the natural process. An order of complexity higher would be represented by the integration of biotechnology and catalysis for an effective CO2 conversion, using selective catalysts such as enzymes, or even whole microorganisms, coupled to chemical technologies for energy supply to enzymes, using perennial sources as sun or wind or geothermal as primary energy.

These days all the above approaches are under investigation with an interesting complementarity of public-private investment in research. This paper aims at making the state of the art in CO2 conversion and giving a perspective on the potential of such technology.

Each atom of C we can recycle is an atom of fossil carbon left in the underground for next generations that will not reach the atmosphere today.

Graphical Abstract (for review)



Highlights

CO_2 properties, coordination chemistry and reactions
CO_2 as a C1-synthon for the synthesis of “intermediates and fine chemicals”
CO_2 as source of carbon for energy products
Biotechnological uses of CO_2: Integration of biotechnology and chemical catalysis

State of the art and perspectives in catalytic processes for CO_2 conversion into chemicals and fuels: the distinctive contribution of chemical catalysis and biotechnology.

Michele Aresta,[a,b] Angela Dibenedetto[b,c] and Eugenio Quaranta[b,c]

[a]Department of Chemical and Biomolecular Engineering, National University of Singapore, Engineering Drive 4, 117585 Singapore, SG, [b]CIRCC, via Celso Ulpiani 27, Bari 70126, Italy; [c]Department of Chemistry, Campus Universitario, University of Bari, 70126 Bari, Italy.

Content

1.0 Introduction

The need to reduce the emission of carbon dioxide into the atmosphere is pushing towards the use of "renewable carbon", so to avoid as much as possible burning "fossil carbon". Biomass is synonym of "renewable carbon", as it is re-generated from CO_2, usually captured from atmosphere. A "close to zero emission" cycle can in principle be implemented that effectively reduces the emission of CO_2. It would be possible to complement the natural "carbon cycle" by developing man-made industrial processes for "carbon recycling", converting, thus, "*spent carbon*" as CO_2 into "*working carbon*", as that present in valuable chemicals or fuels. Such practice would fall again into the utilization of "renewable carbon", as the man-made process would perfectly mimic the natural process. An order of complexity higher would be represented by the integration of biotechnology and catalysis for an effective CO_2 conversion, using selective catalysts such as enzymes, or even whole microorganisms, coupled to chemical technologies for energy supply to enzymes, using perennial sources as sun or wind or geothermal as primary energy.

These days all the above approaches are under investigation with an interesting complementarity of public-private investment in research.

This paper aims at showing the state of the art of CO_2 conversion and giving a perspective view of such technology.

Each atom of C we can recycle is an atom of fossil carbon left in the underground for next generations that will not reach the atmosphere today.

1.1 Where we are

The chemical utilization of CO_2 is not a new attitude. Industrial processes were developed as early as in the 1880-1893s, namely: the synthesis of urea [1], the soda Solvay process and the synthesis of hydrogen carbonates [2], the production of salycilic acid [3]. Interestingly, in the former process CO_2 recovered from the synthesis of NH_3 is used. In the 1900s there was not a great interest in developing new applications of CO_2. As a matter of fact, since the late 1800s the chemistry of CO (derived from fossil carbon) has been developed for the synthesis of chemicals and fuels that had its golden era in the 1900-1970s, and still today plays a key role in the production of chemicals and fuels. Only in the 1970s there was a revival in the exploitation of CO_2 as additive to CO in the synthesis of methanol [4] and as co-monomer in the pioneering production of organic carbonates from epoxides [5], *via* direct carboxylation. Table 1 gives the actual use of carbon dioxide in the synthesis of chemicals and the perspective use at 2030 [6], calculated considering the expected market growth for the listed chemicals and assuming that new technologies will be developed that ensure a large conversion of CO_2. Data reported in Table 1 show that in the best of cases the utilization of CO_2 will grow from 180 Mt/y in 2014 to 207 Mt/y in 2016 and 332 Mt/y in 2030: a drop in the ocean of the over 35 000 Mt/y emitted today. Such scenario validates the position of those who say that the conversion of CO_2 into chemicals will not contribute to the CO_2 emission reduction. We anticipate that what has value is the amount of avoided CO_2 more than the amount of used CO_2: the ratio avoided/used may span over a range 2-5, with a good average around 3. This gives a different weight to the utilization option as 1 Gt/y of avoided CO_2 may be a realistic goal in 2030. Should CO_2 be converted into fuels, a new perspective opens and the Carbon Capture and Utilization-CCU option may play a fundamental role in avoiding CO_2.

Table 1. Short and medium term perspective use of CO_2.

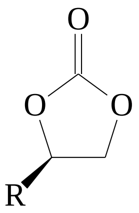
Compound	Formula	$C_{oxstate}$	Market 2016 Mt/y	CO_2 use Mt/y	Market 2030 Mt/y	CO_2 use Mt/y
Urea	$(H_2N)_2CO$	+4	**180**	132	**210**	154
Carbonate linear	$OC(OR)_2$	+4	>2	0.5	10	5
Carbonate cyclic		+4				
Polycarbonates	$-[OC(O)OOCH_2CHR]_n-$	+4	5	1	9-10	2-3
Carbamates	RNH-COOR	+4	>6	1	11	*ca.* 4
Acrylate	$CH_2=CHCOOH$	+3	5	1.5	8	5
Formic acid	HCOOH	+2	1	0.9	>10	>9
Inorganic carbonates	M_2CO_3 $M'CO_3$	+4	$CaCO_3$ **250**	70	**400**	100
Methanol	CH_3OH	-2	60	10	80	>28
Total				**207**		**>332**

Table 1 also shows the oxidation state of the carbon-atom in the various compounds listed. This is a key point as the energetics of any reaction depends on the variation of the C-oxidation state in the reaction. Figure 1 shows the Gibbs free-energy of formation of several C1 species.

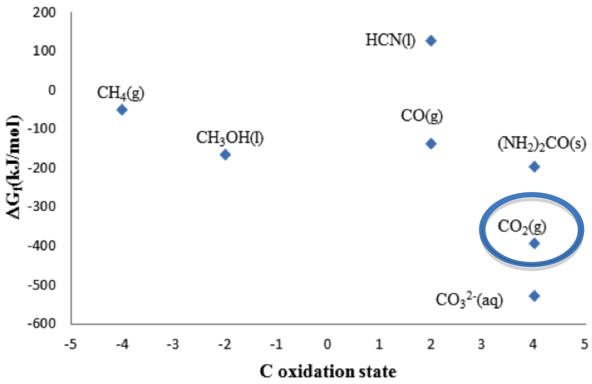


Figure 1. Gibbs free energy of formation of C1 species

It is quite evident that when the oxidation state of the carbon atom is reduced from +4 in CO_2 to 2 or lower, a significant amount of energy is needed, while when the oxidation state remains +4 or close to it (+3 in C2 species such as oxalic acid, HO_2C-CO_2H) the reaction is quasi-neutral (i.e., synthesis of organic carbonates and carbamates, located in the circle around CO_2) or even exothermic as in the synthesis of inorganic carbonates, which lie well below CO_2. On this basis, in the middle 1980s we have classified the CO_2 reactions in two classes [7], according to the fact that CO_2 is incorporated such as in the product (Class A) or it is converted into one of its reduced forms (Class B).

Class A: CO_2 fixation into inorganic carbonates-M_2CO_3, organic carbonates-$(RO)_2CO$, carbamates-$RR'N-CO_2R$, polycarbonates, polyurethanes, isocyanates-NCO^-.

Class B: CO_2 reduction to CO or hydrogenated products like methanol, methane, higher hydrocarbons.

Noticeably, the two classes are characterized by a distinct use of the products and a quite different size of their market. *Class A* species fall into the chemicals market, while *Class B* are fuels with a market that is some 12-14 times that of chemicals. Therefore, if one targets to convert large volumes of CO_2 one must pursue its conversion into fuels. And here a new issue arises about the necessary energy for the conversion (see Fig. 1) and the hydrogen for the production of hydrocarbons. It is obvious that H_2 cannot be derived from fossil C, but must come from water or organic waste, while energy must be supplied by perennial sources such as sun, wind, geothermal. A new approach must be developed for H_2 production with respect to the actual one based on the reforming (of coke or methane) at high temperature, a strongly endergonic process (Eq. 1-3).

$C + H_2O \rightarrow CO + H_2$ (Water Gas Reaction-WGR) $\Delta H^0_{298K} = 131.3$ kJ/mol (1)

$CH_4 + H_2O \rightarrow CO + 3H_2$ (Methane Wet Reforming) $\Delta H^0_{298K} = 206$ kJ/mol (2)

$CO + H_2O \rightarrow CO_2 + H_2$ (Water Gas Shift-WGS) $\Delta H^0_{298K} = -41$ kJ/mol (3)

1.2 Key issues in the conversion of CO_2

The conversion of CO_2 is a quite complex issue [8], complicated by the fact that if it targets carbon mitigation, the carbon balance must be kept under strict control, with the concept of "*avoided*" CO_2 winning on that of "*used*" CO_2. As a matter of fact, the use of CO_2 in new chemical processes can be quite interesting as it avoids the emission of large volumes of CO_2 (with respect to processes on stream), much larger that the amount of converted CO_2. Correct values of "*used*" and "*avoided*" CO_2 may be obtained by applying the LCA methodology. An early example is given by the use of LCA in the comparative analysis of different synthetic methodologies for the production of cyclic carbonates [9]. It is worth to emphasize that the correctness of the figures depends on the quality of available data. At the time of the above study very limited data were available. Today, more reliable data are loaded in continuously up dated data bases and figures obtained from pilot plants are more and more at the hand. This may assist to make a much better estimate of new processes based on CO_2. Figure 2 shows the amount of CO_2 emitted in processes based on the use

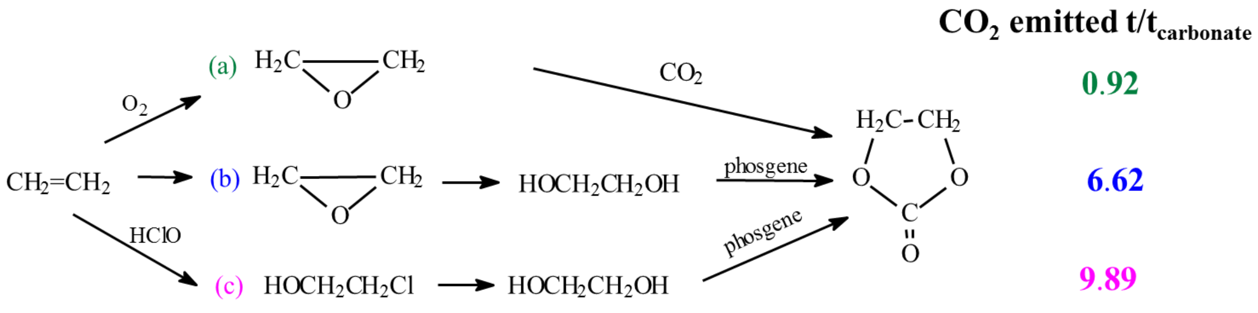


Figure 2. Amount of CO_2 emitted in the production ethene carbonate in synthetic routes based on CO_2 (a) or phosgene-$COCl_2$ (b, c).

of phosgene (on stream since the 1970s) *vs* the amount emitted in innovative processes based on the use of CO_2 [8]. It is clear that what really matters is not the amount of CO_2 *used* (0.5 t/t$_{carbonate}$) but the amount of CO_2 *avoided* (the amount of CO_2 emitted in the process based on phosgene minus the amount of CO_2 emitted in the direct carboxylation, almost *ca*. 6-9 $t/t_{carbonate}$). A parameter that can be used for the assessment of processes is the ratio CO_2 avoided/CO_2 used. For the carboxylation of propene oxide (similar to reaction (a) in Fig. 2) it is estimated to range around 3.5 today.

We come now to a key point: synthetic routes based on CO_2 *must* respond to a stringent requisite, namely: *the new process must minimize the CO_2 emission with respect to processes on stream.* In order to satisfy such condition, an immediate sub-condition is: *the CO_2-based process must be a consumer and not a producer of CO_2.*

1.3 Performance indicators in CO_2 conversion

Indicators which may help to assess a CO_2-based process are:

(a) the carbon utilization fraction (the percentage of reagent-C fixed into the products);
(b) the carbon-footprint (the CO_2 emission in the process per unit of product);
(c) the energy consumption factor (ratio of the input- to output-energy);
(d) the waste production factor (waste produced per unit of product, w/w);
(e) the "avoided" to "used" ratio.

The above indicators heavily depend on the reaction conditions. The reaction "*parameter space*" is defined by the following factors: *i.* Solvent; *ii.* Co-reagents; *iii.* Catalysts; *iv.* Temperature; *v.* Pressure; *vi.* Overall energy expenditure-time of reaction; *vii.* Conversion of reagents; *viii.* Formation of co-products/selectivity of the process; *ix.* Waste generation; *x.* End of process separation energy.

In order to maximize the benefit, the above parameters must respond to the conditions listed below:

i. The solvent can be one of the reagents. Solventless reactions can be a good solution. The use of sc-CO_2 may be beneficial.
ii. Co-reagents must be used in stoichiometric amount and be converted at their maximum. This is particularly true when H_2 is used. Any excess must be recovered.
iii. Catalysts must be simple and cheap (earth abundant elements), recoverable, reusable.
iv. The temperature must be as low as possible, and selected also taking into consideration the separation step. Temperature sweep must be avoided as the heat is not completely recovered and reused (especially at low temperature) and considerable energy loss occur.
v. The reaction pressure should be kept as low as possible. Pressurized liquid reaction mixtures and sc-conditions must be comparatively evaluated considering reaction rates, conversion yields and selectivities.
vi. The overall energy expenditure must be kept as low as possible.
vii. The conversion of reagents should be maximized.
viii. The formation of co-products should be minimized. Very active catalysts may favour the occurrence of several reactions at the same time, with increase of the conversion yield but lowering selectivity and increasing the post-process separation cost. Often such co-products are formed from co-reagents in equimolar amount with the target product. In case of large-scale (>Mt) chemicals such co-products must be either marketable or converted back into the original co-reagent.
ix. The waste generation (including waste solvents) must be minimized as waste will produce CO_2 during its final processing-burning.

x. The post-reaction process for product isolation may play a key role in the overall energy expenditure. Sometimes it is better to achieve a lower conversion with 100% selectivity than a high conversion with formation of several byproducts difficult to separate.

All the above issues are considered when a life cycle assessment-LCA study is performed. Such methodology is the one that can give a reliable answer to the question whether a particular use of CO_2 is avoiding CO_2 emission or increasing it. Having set such a frame to the objective of using CO_2 for the production of chemicals and fuels, we can face the aspect of how we can use CO_2 in profitable ways that contribute to the reduction of the CO_2-emission, trying to size the amount of recyclable carbon in man-made processes.

2. CO_2 properties, coordination chemistry and reactions

In this session we briefly discuss the electronic properties of CO_2 and the structural changes the cumulene undergoes upon co-ordination to a metal center. These concepts are relevant to any metal-driven conversion of CO_2.

2.1 Electronic properties of CO_2

CO_2 has a linear geometry ($D_{\infty h}$) in its ground state, with both the carbon-oxygen bonds being equivalent and displaying an equilibrium C–O distance of 1.1600 Å [10,11]. The valence electronic configuration of CO_2 (16 valence electrons) in the linear ground state, $^1\Sigma_g^+$, is $3\sigma_g^2 2\sigma_u^2 4\sigma_g^2 3\sigma_u^2 1\pi_u^4 1\pi_g^4$ [12]. Figure 3 shows a schematic and simplified representation of the molecular orbitals (MOs) of CO_2.

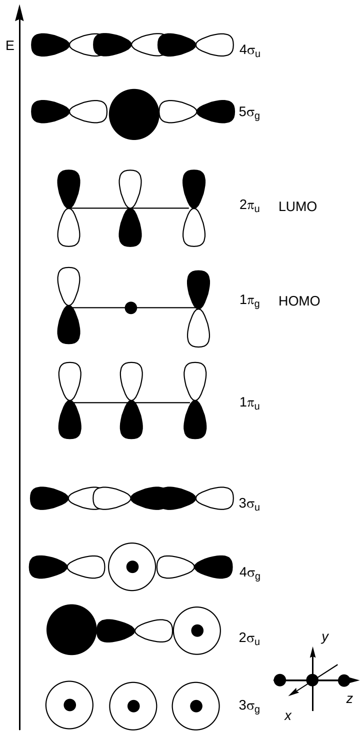


Figure 3. Molecular orbitals of CO_2 (only $1\pi_{uy}$, $1\pi_{gy}$ and $2\pi_{uy}$ are shown)

Combination of 2s and $2p_z$ of all the three atoms generates six σ molecular orbitals. Three couples of doubly degenerate reciprocally orthogonal π-orbitals ($1\pi_{ux}$ and $1\pi_{uy}$; $1\pi_{gx}$ and $1\pi_{gy}$; $2\pi_{ux}$ and $2\pi_{uy}$) are obtained from combining the remaining $2p_x$ and $2p_y$ orbitals of carbon and oxygens. The non bonding $1\pi_{gx}$ and $1\pi_{gy}$ MOs have null weight on the carbon atom and, therefore, are localized on the terminal oxygens, while the antibonding $2\pi_{ux}$ and $2\pi_{uy}$ MOs are mainly localized on the carbon atom, as they have a preponderant $2p_{xC}$ and $2p_y$ character, respectively. Of the eight occupied molecular orbitals, both $3\sigma_g$ and $2\sigma_u$ are responsible for the σ bonding skeleton of the molecule, while the $1\pi_u$ orbitals account for the C-O π bonds. By contrast, the electrons $4\sigma_g$, $3\sigma_u$ and $1\pi_g$ are, σ and π lone pairs, respectively.

Figure 4 reports the Walsh diagram [13] for the CO_2 molecule showing qualitatively the variation of the MOs energies with the change of OCO bond angle. The energies of the σ-orbitals increase or remain practically unaffected upon the change of molecular symmetry ($D_{\infty h} \rightarrow C_{2v}$). However, the energies of π-orbitals show more important changes. The degeneracy of the π-orbitals is lost in the bent geometry and the formerly degenerated π-orbitals separate in two non-equivalent orbitals with different energies. The splitting of the levels $1\pi_u$ and $1\pi_g$ is modest and the destabilization of $1\pi_u(5a_1)$ is roughly counterbalanced by the stabilization of $1\pi_u(1b_1)$. By contrast, the energies of both $1\pi_g$ orbitals increase upon bending, much faster for $1\pi_g(4b_2)$ than for $1\pi_g(1a_2)$. The energy of the $2\pi_u(2b_1)$ orbital is only slightly affected by the molecule bending. The rapid increase of the energy of $1\pi_g(4b_2)$ with diminution of the bond angle accounts for the linearity of the CO_2 molecule in the ground state. However, bending causes a marked decrease of the energy of the $2\pi_u(6a_1)$ MO, which can become even more stable than $1\pi_g(4b_2)$. The behavior of the $2\pi_u(6a_1)$ MO upon molecule bending suggests that *population of the $2\pi_u(6a_1)$ level is expected to produce a distortion of CO_2 molecule from linearity*. This statement finds several validations, for instance, when considering:

-the geometry of the CO_2 lowest excited states, related with the electronic configuration $1\sigma_u^2$ $1\sigma_g^2$ $2\sigma_g^2$ $3\sigma_g^2$ $2\sigma_u^2$ $4\sigma_g^2$ $3\sigma_u^2$ $1\pi_u^4$ $1\pi_g^3$ $2\pi_u^1$ [14];

- the geometry of CO_2^- radical anion (*vide infra*);

- the geometry of CO_2 acting as ligand in metal-complexes, when the cumulene interacts with the metal center through the C-atom, as observed both η^1-C adducts and η^2-C,O (side-on) mononuclear and polynuclear complexes (*vide infra*).

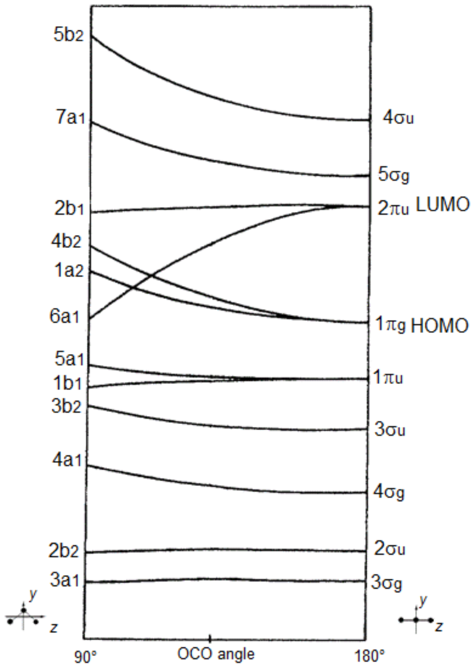


Figure 4. Qualitative Walsh diagram for CO_2

Upon addition of an extra electron the CO_2 molecule converts into the radical anion CO_2^- (eq. 4). The latter species, generated in many ways and trapped in solid matrices, shows a bent equilibrium geometry (C_{2v} symmetry) in the $^2A_1$ ground state ($(1a_1)^2(1b_2)^2(2a_1)^2(3a_1)^2(2b_2)^2(4a_1)^2(3b_2)^2(1b_1)^2(5a_1)^2(1a_2)^2(4b_2)^2(6a_1)^1$; see also Fig. 4), with elongated CO bonds and the value of OCO angle ranging around 130° [15].

$$CO_2 + e^- \rightarrow CO_2^{\cdot -} \qquad (4)$$

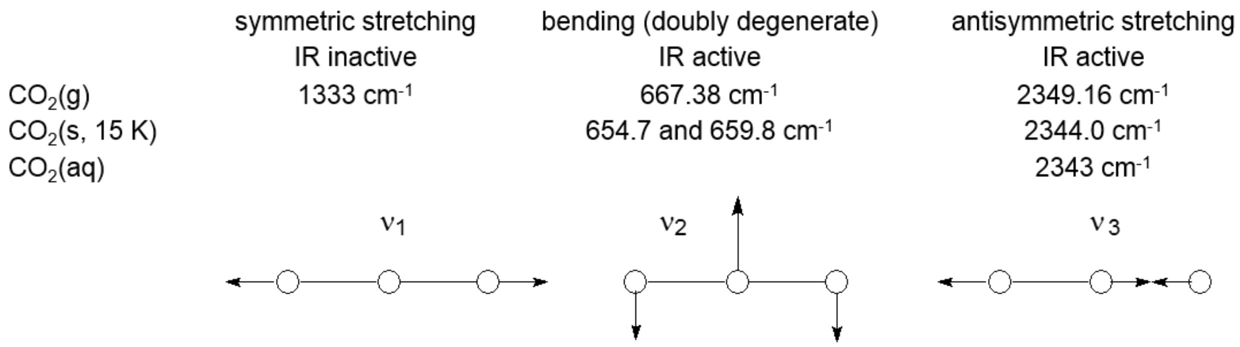
Reaction 4 is an endergonic process. A value of −0.6±0.2 eV has been measured for the adiabatic electron affinity (EA_{ad}) of the CO_2 ground state [16]. In the gas phase CO_2^- is metastable against electron autodetachment. The reason for the metastability of the anion (lifetimes in the range of 30-90 μs) is ascribed to the fact that the change of the molecular geometry from the $^2A_1$ state of CO_2^- to the ground state of CO_2, has a barrier of 0.4 eV [17]. Conversion of CO_2 to CO_2^- anion is regarded as an important mode of activating the molecule and represents the first of the reactive steps leading to the partial or full reduction of the heterocumulene. The change of geometry upon e^- transfer to CO_2 may affect the rate of the process. Such features are relevant to the electrochemical reduction of CO_2 as discussed in paragraph 4.2.

Removal of a $1\pi_g$ electron from CO_2 molecule to afford the CO_2^+ radical cation in the $^2\Pi_g$ ground state requires an energy of 13.79 eV [18], by far larger than that needed for the formation of the radical anion CO_2^- [16] or for the dissociation of neutral CO_2 to CO and atomic oxygen [19]. Spectroscopic measurements [20] show that CO_2^+ in its $^2\Pi_g$ ground state is a linear molecule with $D_{\infty h}$ point group symmetry: the two C-O bonds are equivalent with a length, which is only slightly longer (1.1769 Å) than that measured in the neutral molecule. The above features are relevant to the states of CO_2 coordinated in different ways to various metal systems (Fig. 4).

2.2 Spectroscopic (IR, UV, NMR) properties of CO_2

IR and NMR spectroscopies have been widely employed as diagnostic tools of the state of the CO_2 molecule and even for quantitative determinations. UV-visible spectroscopy has found less extensive use. However, the spectroscopic properties of CO_2 in the UV region are of fundamental importance for understanding the photochemistry of this molecule [19].

Figure 5 summarizes the spectroscopic properties of CO_2 in the IR region [21-23].



	symmetric stretching IR inactive	bending (doubly degenerate) IR active	antisymmetric stretching IR active
CO_2(g)	1333 cm^{-1}	667.38 cm^{-1}	2349.16 cm^{-1}
CO_2(s, 15 K)		654.7 and 659.8 cm^{-1}	2344.0 cm^{-1}
CO_2(aq)			2343 cm^{-1}

Figure 5. Normal vibration modes and frequencies of carbon dioxide molecule in its ground state

Table 2 compares the IR fundamental frequencies of gaseous CO_2 with those measured for gaseous CO_2^+ [24] and for CO_2^- isolated in solid neon [25,26] where the radical anion is free from interactions with metal cations. In the IR spectrum of CO_2^-, because of the bent geometry (C_{2v}) of the anion, all the three normal vibration modes are IR active. The stretching frequencies are shifted to lower values, which reflects a reduced average CO bond order (1.5 in CO_2^- *vs* 2 in CO_2).

As it will be discussed later, the formation of CO_2 metal complexes or, more generally, CO_2-adducts can originate large modifications in the IR spectrum of the CO_2 moiety [27]. The antisymmetric stretching mode, ν_a(OCO), falls in the range 2250-1400 cm^{-1}, the symmetric stretching mode, ν_s(OCO), becomes IR-active and can absorb in the region 1400-1100 cm^{-1}, the bending mode δ(OCO) is shifted from 667 cm^{-1}. Additional vibrational modes, such as metal-carbon and/or metal-oxygen stretching modes, C=O out-of-plane deformation, may be observed in the low-frequency region (down to 300 cm^{-1}). The latter spectroscopic features can provide useful informations on the bonding mode of the heterocumulene in the adduct, so that IR is quite diagnostic for understanding the state of CO_2 interacting with metal systems (atoms or complexes).

Table 2. Vibrational normal modes and related frequencies (cm^{-1}) for CO_2, CO_2^+, and CO_2^-

	ν_1 (ν_s(OCO))	ν_2 (δ(OCO))	ν_3 (ν_a(OCO))	Notes	Refs.
CO_2	1333	667.38	2349.16	gas state	[21]
CO_2^+	1244.3	511.4	1423.08	gas state	[24]
CO_2^-	1253.8	714.2	1658.3	Ne matrix	[25,26]

Carbon dioxide is transparent in the visible and near-to-middle ultraviolet regions, at least down to 210 nm (*hv* < 5.91 eV), both in the liquid phase and in the gas phase [20]. Only weak absorptions can be observed below 11 eV, in the vacuum ultraviolet region, at 147.5 (8.41 eV), 133.2 (9.31 eV) and 112.1 nm (11.08 eV), respectively. Above 11 eV there are several Rydberg series converging to the various states of CO_2^+.

CO_2 dissolved in a nonpolar solvent (benzene, toluene) displays only one ^{13}C NMR signal around 124 ppm. In aqueous solutions, the resonance is close to 125 ppm and can be used for the quantification of free CO_2. ^{13}C-NMR has proved to be a very useful spectroscopic technique for identifying the “CO_2“ moiety incorporated into a metal-compound (metal complexes, metal-carbamates $L_nM(O_2CNR_2)$, metal-hemicarbonates $L_nM(O_2COR)$, metal-carboxylates $L_nM(O_2CR)$, metallacarboxylic acids $L_nM(CO_2H)$, metallaesters $L_nM(CO_2R)$)[28] or organic products, such as carbamic acids or carbamates (150-160 ppm), carbonates (145-165 ppm), acids (160-180 ppm), esters (160-170 ppm).

2.3 Main features of carbon dioxide reactivity

The MOs most relevant to the chemical reactivity of carbon dioxide are the doubly occupied non-bonding $1\pi_g$ orbitals (HOMOs), mainly localized on the end oxygen atoms, and the empty antibonding $2\pi_u$ orbitals (LUMOs), mostly centered on the carbon (Fig. 3). Therefore, CO_2 can be considered an amphoteric molecule, as it can act as an acceptor of electrons at the C-atom (through the LUMOs) and a donor of electrons *via* the O-atoms (through the HOMOs).

Electron poor centers (electrophiles such as the proton, metal centers in high oxidation state, electron deficient molecules, etc.) are expected to attack CO_2 at the O-atom. Noteworthy, CO_2 displays a weak basic character, as demonstrated by the value of proton affinity of this molecule (eq. 5). The commonly accepted value of 540.5 ± 2 kJ/mol [29] is markedly lower than those found for other O containing molecules, such as H_2O, MeOH, Me_2O, H_2CO, MeCHO, Me_2CO, HCO_2H, $MeCO_2H$.

$$CO_2 + H^+ \rightarrow HOCO^+ \tag{5}$$

The electrophilic character of carbon dominates over the weak nucleophilic properties of the oxygen atoms. Consequently, CO_2 is a better acceptor than donor of electron density. Electrons and electron rich species will easily interact with CO_2 at the C-atom. This reactivity is exemplified by the direct non metal-mediated reactions of CO_2 with electron rich anionic or neutral species such as, for instance, H^- (eq. 6), OH^- (eq. 7), amines (*vide infra*).

$$H^- + CO_2 \rightarrow HCO_2^- \tag{6}$$
$$OH^- + CO_2 \rightarrow HOCO_2^- \tag{7}$$

Reaction of ionic (Group 1 or 2) hydrides with CO_2 to afford the relevant formate (eq. 5), albeit known since long time, has never found any practical application for the synthesis of formates, which are more conveniently synthesized by reaction of CO and the metal hydroxides.

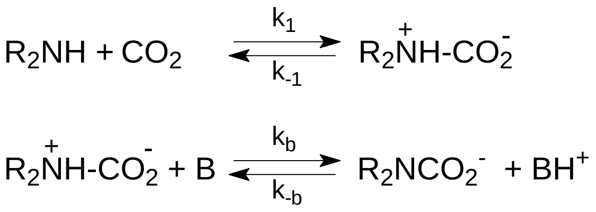
The reaction of CO_2 with ionic metal hydroxides $[M(OH)_n]$ (eq. 7) involves the nucleophilic attack of the anion (OH^-) to the electrophilic carbon of CO_2 [30]. The interest for this reaction is linked to its utilization for the separation of CO_2 from flue gases[31] or for the fixation of CO_2 into inorganic carbonates (eq. 8) that are under consideration for the safe long-term storage of CO_2 [32,33].

$$CaO + H_2O \rightarrow Ca^{2+}\ 2OH^- \xrightarrow{CO_2} Ca^{2+} + 2HCO_3^- \rightarrow CaCO_{3(s)} + H_2O + CO_2 \tag{8}$$

The *reaction of CO_2 with basic amines* is of particular interest, being exploited not only for up-taking CO_2 from a gas stream, but also for synthetic purposes [34-36]. The reactivity of amines with CO_2 depends on their nature and the working conditions. Under strictly anhydrous conditions, tertiary aliphatic amines do not absorb CO_2, but aliphatic primary and secondary amines do and form the corresponding ammonium carbamates (eq. 9)[34,35] or the relevant carbamic acid (eq. 10) which may be stabilized in a dimeric form through intermolecular hydrogen bonding, both in solution[37] and in the solid state [38]. Carbamic moieties play a key role as intermediates in several biological processes, such as carboxylations by biotin enzymes and photosynthetic activation of CO_2 promoted by RuBisCO (ribulose 1,5-biphosphate carboxylase-oxidase) [39].

$$2RR'NH + CO_2 \rightleftarrows RR'N\text{-}CO_2^-\,RR'NH_2^+ \tag{9}$$
$$RR'N\text{-}CO_2^-\,RR'NH_2^+ \rightleftarrows 1/2[RR'N\text{-}COOH]_2 + RR'NH \tag{10}$$

Different mechanisms have been proposed for the conversion of amine and CO_2 into alkylammonium carbamate [40], which may involve the intermediate formation of a zwitterionic species (Scheme 1) [41], or take place through a termolecular single step (Scheme 2) [42]. Base B in Schemes 1 and 2 is the amine itself under anhydrous conditions, but in an aqueous medium such role may be played by H_2O or OH^-. Whatever may be the working mechanism, the key feature of the carbamation process is the attack of the electron rich amine to the C-atom of CO_2.

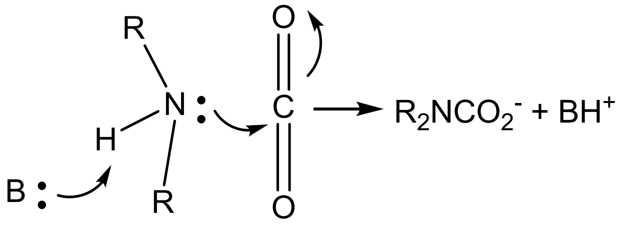


$$R_2NH + CO_2 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} R_2\overset{+}{N}H\text{-}CO_2^-$$

$$R_2\overset{+}{N}H\text{-}CO_2^- + B \underset{k_{-b}}{\overset{k_b}{\rightleftharpoons}} R_2NCO_2^- + BH^+$$

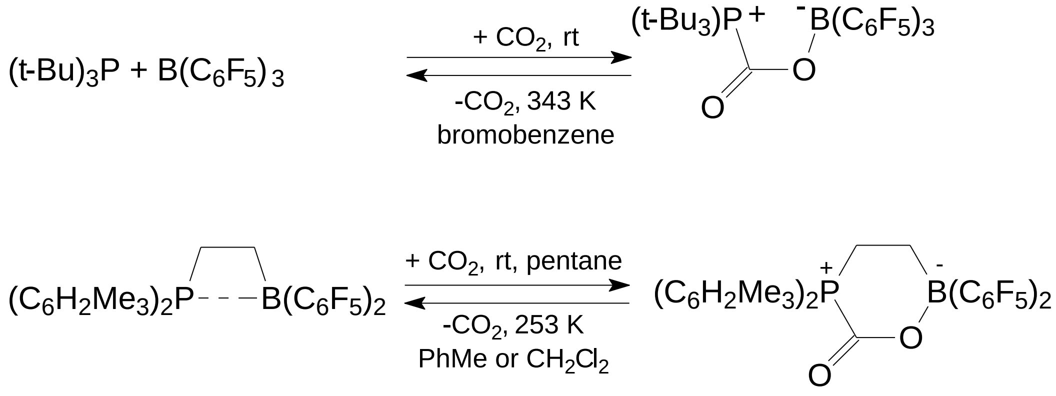
R_2NH = I or II amine; B = R_2NH, H_2O, OH^-

Scheme 1. Reaction of amines and carbon dioxide: zwitterion mechanism



Scheme 2. Reaction of amines and carbon dioxide: termolecular mechanism

CO_2 displays its *amphoteric character* in the reactions with frustrated Lewis pairs (FLPs) (Scheme 3) [43,44,45,46].



Scheme 3. Reactions of frustrated Lewis pairs (FLPs) with CO_2

The interest for FLPs as potential systems for activating the heterocumulene has markedly grown in the last few years [47]. Remarkably, B/N, B/P, or Al/P based FLPs can also effect the stoichiometric or catalytic reduction of the activated CO_2 moiety upon treatment with an appropriate reducing agent such as hydroboranes or hydrosilanes [48,49,50]. Hydroboration and hydrosilylation of CO_2 to methoxyboranes and methoxysilanes, respectively, are of significant academic interest, but remain costly processes without industrial utility. Of greater interest, in this context, may be the use of a reducing agent such as H_2 [51], which is known to be heterolytically activated by several FLPs. To date, this intriguing field is still poorly investigated, but requires greater attention as it may open perspectives towards the metal-free (or organic) catalytic reduction of the heterocumulene.

2.4 Interaction of carbon dioxide with metal centers

The reactivity patterns outlined above can be recognized easily when considering the behavior of *CO_2 as a ligand* or, more generally, the interaction of CO_2 with metal centers. Despite the significant advances achieved since the isolation and X-ray characterization of the first metal-CO_2 complex [52], this field still represents a challenging research area. Basic studies on this topic are welcome and new knowledge may be of fundamental importance for potential exploitation. In fact, most reactions based on the utilization of CO_2 are driven by metal systems. Understanding the interaction of the cumulene with metal centers, as well as the reactivity of coordinated CO_2, may be of great help in developing new catalysts for CO_2 conversion.

2.4.1 CO_2 coordination to metal centers

The basic *coordination modes of CO_2* to a single metal center are shown in Fig. 6 [53,54].

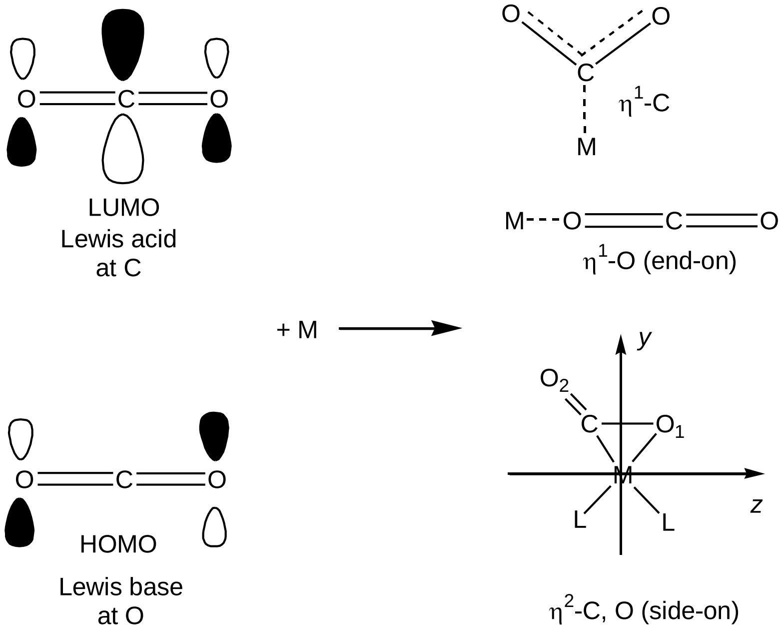


Figure 6. Basic coordination modes of CO_2 to a single metal center

They reflect in a clear way the ability of CO_2 to act as a pure C-electrophile, (η^1-C coordination), or O-nucleophile, linking the metal through oxygen (η^1-O or end-on coordination), or also to act as an acceptor and donor of electron density, interacting, thus, with the metal centre through the C and O atoms, as in the case of side-on (η^2-C,O) coordination. The mode of bonding of CO_2 to metal centres has been extensively reviewed [52-54], therefore we discuss here only selected cases, which can be relevant to catalytic processes.

Side-on coordination represents by far the most common bonding mode of CO_2. In $[Ni(CO_2)(PCy_3)_2]$ (Cy = cyclohexyl) [55], the first crystallographically characterized metal-CO_2 complex, the Ni-C and Ni-O_1 bond distances are, respectively, 1.84 and 1.99 Å, showing that both carbon and one of the oxygen atoms are bound to the nickel center, which exhibits a planar coordination. The coordinated CO_2 molecule looses the original $D_{\infty h}$ symmetry, typical of the free ligand: the measured lengths for the C-O_1 and C-O_2 bonds (Fig. 7) are, respectively, 1.22 and 1.17 Å, while the value of the OCO angle is 133°. The deviation of the coordinated CO_2 molecule from linearity is well in accordance with the features foreseen considering the Walsh diagram.

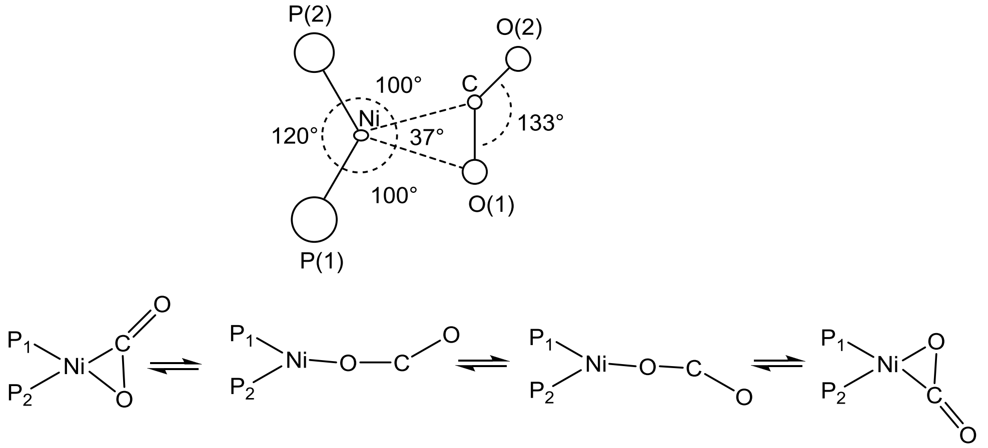


Figure 7. Top: XRD-Structure of solid $Ni(CO_2)(PCy_3)_2$. Bottom: Fluxionality of $Ni(CO_2)(PCy_3)_2$ in solution. The two phosphines are averaged.

Examples of bis(carbon dioxide) side-on complexes are also known, but only with molybdenum. An example is provided by *trans*-$Mo(CO_2)_2HN(CH_2CH_2PMe_2)_2(PMe_3)$ [56]. The complex has a distorted octahedral geometry with two staggered CO_2 ligands η^2-C,O-coordinated to Mo. The CO_2 ligands show C-O lengths ranging from 1.199 to 1.284 Å and OCO angles of 131°.

The dinuclear complex $[(IPr)Ni]_2(\mu{-}CO)(\mu{-}\eta^2,\eta^2{-}CO_2)$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene) documents an interesting case of a $\mu_2{-}\eta^2,\eta^2$–coordination, in which each C=O bond of the bridging CO_2 ligand is, respectively, side-on coordinated to a Ni atom [57] (Fig. 8).

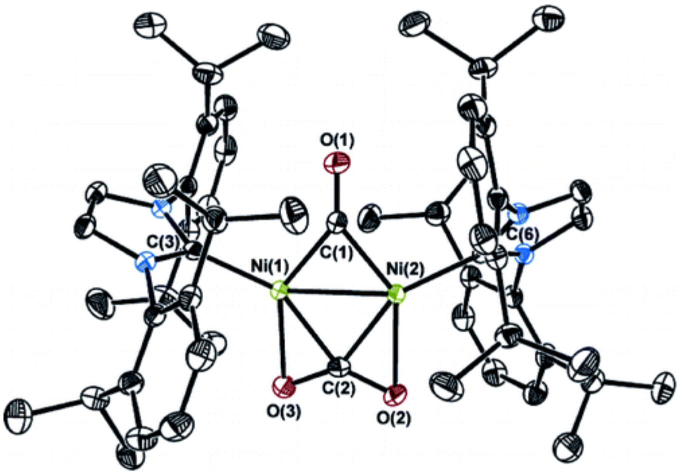
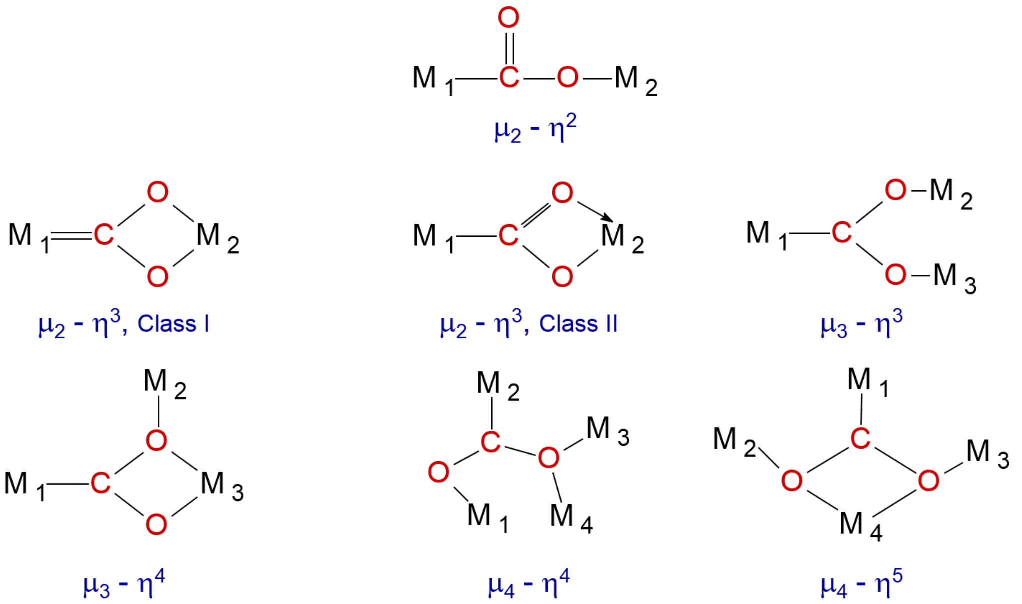


Figure 8. $[(IPr)Ni]_2(\mu_2{-}CO)(\mu_2{-}\eta^2,\eta^2{-}CO_2)$ (IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene). The bridged CO_2 is bent at 133.4° and the CO bond lengths are 1.255 and 1.257 Å

In principle, side-on adducts may be considered as three-membered oxametallacycles resulting from a formal oxidative addition of one of the π-bonds of the CO_2 ligand to the metal center or as π-complexes, wherein the metal-CO_2 interaction involves both electron donation from the O-centered $1\pi_{uy}(5a_1)$ and $1\pi_{gy}(4b_2)$ orbitals of CO_2 to empty d-orbitals of M and, at a greater extent, electron back-donation from a filled d-orbital of metal to the empty C-centered $2\pi_{uy}(6a_1)$ orbital of the ligand [58]. This point is relevant to the definition of the oxidation state of the metal center M: is it zero, one or two? However, whatever model may be followed, in these systems the CO_2 ligand always acts simultaneously as electron-donor through an end oxygen and electron-acceptor at the central carbon. The ability of CO_2 to act as a bifunctional system is further documented by the plethora of

CO_2 complexes in which the cumulene bridges two or more metal centers through carbon and one or both oxygens [52-54]. Scheme 4 summarizes the *CO_2 bonding modes in multinuclear complexes* with the metal centers bound to O and C.



Scheme 4. CO_2 bonding modes in multinuclear complexes with the metal centers bound to O and C

η^1-C(CO_2) transition metal complexes are less common. Rh(diars)$_2$(Cl)(CO_2) (diars = *o*-phenylene-bis(dimethyl)arsine) provides an example of the behavior of CO_2 ligand acting as a only-C-electrophile (Fig. 9) [59]. Rh is essentially octahedral with the CO_2 ligand *trans* to chlorine and interacting with the nucleophilic metal center through the central carbon (η^1-C coordination). In the adduct, the C-O distances, 1.20(2) and 1.25(2) Å respectively, are longer than in the free cumulene, while the OCO angle is 126°. The above structural data indicate an important pouring of electron density from metal into the empty antibonding $2\pi_u$(6a1) orbital, which weakens the C-O bonds and causes a remarkable bending of the coordinated CO_2 molecule (Fig. 4).

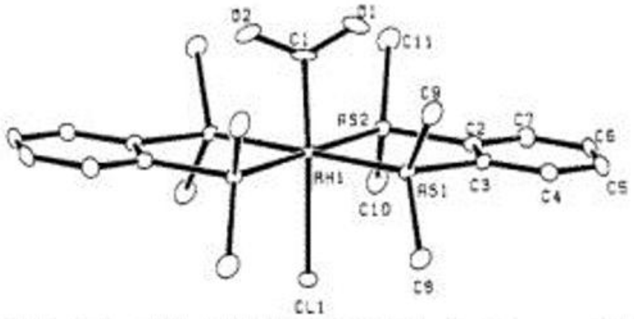


Figure 9. Structure of the η^1-C complex Rh(diars)$_2$(Cl)(CO_2)

η^1-C coordination has been claimed or demonstrated also in a few other Rh, Ir and Ru complexes [60-62]. Generally, η^1-C complexes are less stable than η^2-C,O complexes and are regarded as *reversible carriers of carbon dioxide*. The stability of the M-C bond strongly depends on the donor properties of the metal center. Often η^1-C complexes can be further stabilized by an intramolecular hydrogen bonding interaction between the O-atom of CO_2 ligand and hydrogen donor centers [63]. As discussed below, the interaction with external Lewis centers may also occur. It is worth noting that such an interaction may play a key role in stabilizing adducts of CO_2 also with non-metal species. In 1,3-dimethylimidazolium-2-carboxylate, obtained by reaction of 1-methylimidazole with dimethyl carbonate [64], the imidazolium C-carbene binds CO_2 at C by using the free couple of electrons. The resulting $C \rightarrow CO_2$ moiety is formally similar to the $M \rightarrow CO_2$ system: in the solid adduct, the carboxylate moiety is stabilized through the interaction of the nucleophilic O-atoms with the imidazolium-ring hydrogens. In the last two decades, the chemistry of N-heterocyclic carbenes (NHCs) with CO_2 has received great attention and NHCs and related complexes offer interesting perspectives as potential systems for capture, fixation, and activation of CO_2 [65].

End-on (η^1-O) coordination mode has remained elusive for a long time. Only more recently, a few genuine examples of isolated and structurally characterized adducts in which CO_2 acts exclusively as an O-nucleophile (η^1-O or end-on coordination) have been described in the literature [66-69].

The uranium-complex $(^{Ad}ArO)_3tacnU(\eta^1\text{-OCO})$ ($(^{Ad}ArO)_3tacn$ = 1,4,7-tris(adamantyl-5-*tert*-butyl-2-hydroxybenzyl)1,4,7-triazacyclononane), obtained by reacting the complex $(^{Ad}ArO)_3tacnU^{III}$ with CO_2 has provided the first evidence of (η^1-O) coordination [66,70]. The OCO moiety is almost linear (OCO angle = 178°) with the terminal CO bond length (1.277(4) Å) longer than the internal CO bond distance (1.122(4) Å). The structural data show that, when CO_2 behaves exclusively as an O-nucleophile, the coordinated CO_2 molecule essentially retains its original linear geometry or undergoes only slight distortion from linearity, as expected when there is not a significant back-donation of electron density into the $2\pi_u$ orbitals of the heterocumulene.

Examples of μ-η^1(O),η^1(O) coordination have been also described and structurally characterized [68,69]. In these systems the CO_2 molecule bridges two distinct metal centers through the end O atoms as shown in Fig. 10. Systems of particular applicative interest are represented by a few polyoxometalate anions, such as for instance $(H_2PMo_{11}CoO_{40})^{5-}$, which reacts with aqueous CO_2 affording the CO_2-adduct $(C_3H_5N_2)_3(C_3H_4N_2)(PMo_{11}CoO_{38}(CO_2))\cdot 4H_2O$, where CO_2 is (μ-η^1,η^1) coordinated through the end oxygen atoms [69]. This compound consists of $(PMo_{11}CoO_{38})_n$ polymeric chains bridged by the almost linear CO_2 ligand (OCO angle: 158 °) in an axial direction. Such behaviour is of great interest as it opens an intriguing perspective on the use of polyoxometalates as CO_2 capturing agents in aqueous medium.

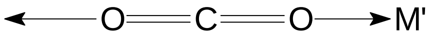


Figure 10. μ-O,O' coordination: M = M' = Mg [68]; M = Mo, M' = Co [69]

Further insight in understanding the reactivity of CO_2 with metal centers comes from the study of the interaction of the CO_2 molecule with *"naked" metal atoms in a gas matrix* at low temperature (< 20 K). FTIR spectroscopy and density functional theory (DFT), are helpful in discovering their behaviour [71], the most frequently observed reactions being the formation of a metal complex and the insertion into one the C=O bonds, depending on the nature of the metal [72], i.e. its oxophilicity. For instance, early transition metals (strong oxophiles) exhibit a different behavior relative to late transition metals [71,72]. Ti, V and Cr (or early transition metals, in general) insert spontaneously into one of the C=O bonds yielding oxo-carbonyl species OM(CO) even without energy barrier (Ti), while Fe, Co, Ni, Ag and Cu (late transition metals)] form 1:1 $M(CO_2)$ adducts in which the cumulene may display different coordination modes, depending on metal. A side-on bonding was found for Ni, an O-end-on for Cu, a η^1-C for Fe and Co. Noteworthy, in a few cases, the same coordination modes were found for "naked atoms" and the relevant metal complexes, which is not a general rule as the ancillary ligands L may significantly influence the behaviour of the metal center towards CO_2, influencing the electron density and governing the space availability [70].

2.4.2 Reactivity of coordinated CO_2

Coordination of carbon dioxide to a metal center produces marked changes of the structural and spectroscopic (IR, ^{13}C NMR) properties of the cumulene (loss of linearity; elongation of C=O bonds; shift of the IR frequencies and ^{13}C NMR resonance) [73]. The question rises whether coordinated CO_2, in whatever form in metal-complexes, can be considered an activated form with respect to the free molecule, and, thus, which are the effects of coordination on the reactivity of the cumulene and if there is a preferred mode of bonding for the conversion of CO_2. Also, one can ask whether spectroscopic data can be informative about the mode of bonding of the cumulene and can, thus, be used for predicting its reactivity. The rationalization of the whole matter is far from having been accomplished and further fundamental studies are still necessary. Another intriguing issue that must be addressed when investigating the reactivity of CO_2-metal complexes in solution is relevant to the "fluxionality" of the bonded cumulene: does CO_2 maintain the same mode of bonding in solution as in the solid state for a given adduct? This key aspect has been addressed only in a very few cases. For instance, ^{31}P and ^{13}C VT-NMR studies carried out on $[Ni(CO_2)(PCy_3)_2]$ have allowed to conclude that in solution, at 173 K, carbon dioxide is bonded to Ni as in the solid state, but at room temperature carbon dioxide is fluxional with an intramolecular motion that, most likely, involves the disanchorage of the carbon atom from nickel (Fig. 7, bottom) to afford an η^1-O intermediate [74]. Such fluxionality makes the two phosphines equivalent in solution at room temperature, which are not equivalent in the solid state (Fig. 7).

In principle, coordinated carbon dioxide can undergo either *electrophilic or nucleophilic attack*. In general, the C-atom of CO_2 bound to a metal in the η^1-C or η^2-C,O-coordination mode is expected to be less prone to react with nucleophilic species than the free molecule. However, if η^1-O-coordination of cumulene is considered, then the nucleophilic attack at C should be a more likely process. However, reactions of CO_2 complexes with nucleophiles are poorly documented in the literature and knowledge in this field is very lacunose. A nucleophilic attack has been proposed to be working in the Wittig-like reaction of $(PCy_3)_2Ni(\eta^2\text{-}CO_2)$ with $Me_3P{=}CH_2$ ylide to give the ketene complex $(Cy_3P)_2Ni(\eta^2\text{-C,O})\text{-}CH_2CO$ and Me_3PO [75]. This reactivity is relevant to the formation of C-C bonds and opens a question about about the necessity to have a co-ordinated CO_2 because a C-C coupling may occur.

Electrophilic attack is better documented. Both η^1-C and side-on coordinated CO_2 have been shown to display an enhanced reactivity at oxygen towards electrophiles and electrophilic attack is the prevalent reactivity of CO_2-bridged complexes with alkali cations [60, 76-78].

Of great interest is the *protonation of coordinated CO_2*, which may occur under very mild conditions (< 273 K) and affords CO as product. The electrons required for the reduction of CO_2 to CO are provided by the metal (eq. 11), which is oxidized, or may be furnished by an external source. The

$$LnM(CO_2) + 2H^+ \rightarrow LnM^{2+} + CO + H_2O \qquad (11)$$

utilization of PhSH as source of protons and electrons in the reaction with $(PCy_3)_2Ni(\eta^2\text{-}CO_2)$ has been demonstrated, providing an interesting biomimetic system [79]. Unfortunately, in this system

CO remains tightly bound to Ni and diphenyldisulphide adds oxidatively to Ni(0) to give $P_2Ni(SPh)_2$ (eqs. 12-14). These events prevent the reduction process to proceed catalytically with respect to nickel.

$PhSH \rightarrow PhS^{\cdot} + H^{+} + e^{-}$ (12)
$2\ PhS^{\cdot} \rightarrow PhS\text{-}SPh$ (13)
$P_2Ni(CO_2) + 2H^{+} + 2e^{-} \rightarrow \text{“}P_2Ni(CO)\text{”} + H_2O$ (14)

The above process (eq. 11) is strictly related to the more general reaction of “dissociative reduction of CO_2 to CO” (eq. 15). This is the simplest way to convert CO_2. The process is very energy

$CO_2 \rightarrow CO + 0.5\ O_2 \quad \Delta G_{(1000\ K)} = 190.5\ kJ/mol$ (15)

intensive, and, can be carried by a thermal (a high T > 1200 K) or a radiative route (using high energy radiations, <160 nm). As shown in Fig. 11a, this process is of great applicative interest if energy from natural sources other than fossils fuels (for instance concentrators of solar power, CSP) are used, as the formed CO, in turn, is both an energy source and a synthetically exploitable source of carbon.

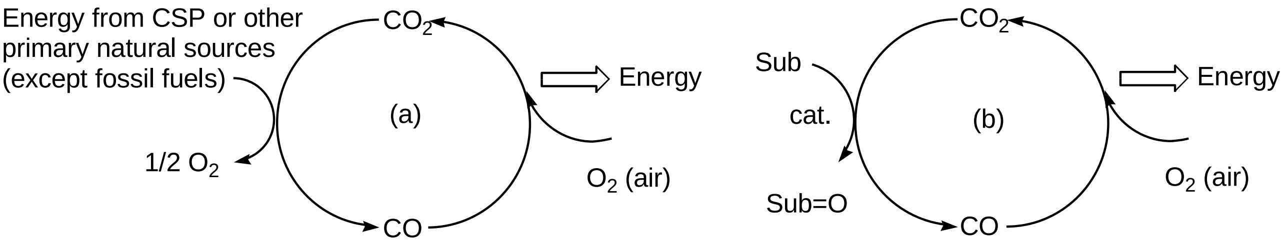


Figure 11. (a) Solar driven cyclic interconversion CO_2-CO-CO_2 with production of thermal energy. (b) Cyclic process with utilization of CO_2 as an oxidant and production of energy.

A cyclic process that runs on CO_2-CO couple and makes use of perennial energy sources (solar energy) as energy input is very appealing. Metal oxides (eq. 16 and 17) are under consideration as catalysts for such reaction using concentrators of solar power (CSP) that allow to operate at high temperature. When *CO_2 splitting* is coupled with *water splitting* using CSP, it is possible to produce

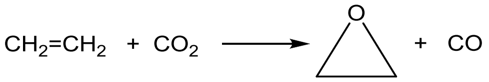
$MO_x + \text{Energy} \rightarrow MO_{x-1} + 1/2O_2$ (16)
$MO_{x-1} + CO_2 \rightarrow MO_x + CO$ (17)

Syngas (plus oxygen) from CO_2 and water, and, thus, liquid fuels by Fisher Tropsch. This high-temperature catalytic splitting is of great importance for the exploitation of CO_2 and H_2O as source of Syngas for the production of “solar liquid fuels” (methanol, DME, gasoline, diesel).
C-O bond cleavage with consequent formation of CO and O transfer to an “oxophile” is a reaction frequently observed for η^2- and η^1-C CO_2-complexes. The effect of coordination to a metal is evident as the “deoxygenation” of CO_2 can be performed even at room temperature using the suited metal centre and an “oxophile”. Formed CO is often found coordinated to the metal center. The oxophile acts as oxygen sink. Both these features contribute to drive the dissociative reduction of CO_2 to the right. The role of O-sink may be played by the metal atom itself (eq. 18) [80], or with

less oxophilic metals (late transition metals, for instance) by CO_2 itself (eq. 19) [81] with conversion of two CO_2 molecules into CO e CO_3^{2-}, or by a ligand. For instance, phosphines, PR_3 [55], can be converted by this way into their oxides ($O{=}PR_3$) (eq. 20), products of very limited utility and difficult to reduce back to the parent compounds if not using energy intensive reducing agents (metals) which cancel out the benefit of having the CO_2 splitting running at room temperature.

$$\text{“M-CO}_2\text{”} \rightarrow \text{“O=M(CO)”} \qquad (18)$$
$$\text{“M”} + 2\,CO_2 \rightarrow \text{“M(CO)(CO}_3\text{)”} \qquad (19)$$
$$\text{“M(CO}_2\text{)”} + PR_3 \rightarrow OPR_3 + \text{“M(CO)”} \qquad (20)$$

In principle, the deoxygenation process can be coupled with the production of useful chemicals, for instance by using as the oxophile a suitable organic substrate (“Sub”, in Fig. 11b). Such application may be limited by the market of the species “Sub=O” that can be generated. Suitable O-acceptors may be olefins (eq. 21) as their “oxidized” forms (epoxides) may have wide market as monomers for polymers. Equation 21 is not a straightforward process and may occur if mediated by metal oxides as catalysts in a two-step process: transfer of O-atom from a metal oxide to the olefin [82] and reoxidation of the reduced oxide with CO_2.



(21)

The epoxide can react with CO_2 to afford a cyclic carbonate. To date, this process, although of interest, has been demonstrated only at the laboratory scale.

The use of *CO_2 as soft and selective oxidant* has been demonstrated in the dehydrogenation of ethylbenzene to afford styrene (eq. 22) [83]. As H_2O and CO can be processed to afford H_2 and CO_2 (WGS) (eq. 23), the net reaction is represented in eq. 24 in which CO_2 acts as “promoter” of the dehydrogenation of ethylbenzene favouring milder conditions and higher selectivity with respect to pure dioxygen.

$$C_6H_5\text{-}CH_2CH_3 + CO_2 \rightarrow C_6H_5\text{-}CH{=}CH_2 + CO + H_2O \qquad (22)$$
$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (23)$$
$$C_6H_5\text{-}CH_2CH_3 \rightarrow C_6H_5\text{-}CH{=}CH_2 + H_2 \qquad (24)$$

Currently the role of CO_2 as a soft oxidant has been extended to oxidative coupling of methane to ethane and ethylene and oxidative dehydrogenation of various hydrocarbons (such as propane to propene) and there is still a lot of scope for its use in other reactions [83].

2.4.3. Relevance of CO_2 coordination to chemical utilization of CO_2. Synthesis of formic acid.

The use of *CO_2 as synthon in chemical synthesis* for manufacturing bulk or fine chemicals has been pursued since the 1980s. A key issue is the relevance of CO_2 coordination in such processes: is CO_2 coordination a strict prerequisite for its conversion? An answer can be given only by mechanistic studies on reactive systems. Any a priori attempt to foresee the behaviour of reactive systems is a pure guess. The thermal lability of CO_2 complexes and their tendency to dissociate coordinated CO_2

may add complexity and uncertainty to the problem. As an example, let us consider the reaction of $(PCy_3)_2Ni(CO_2)$ with dioxygen: the product would be the peroxocarbonate $(PCy_3)_2Ni(CO_4)$ (eq. 25) and one would foresee that reaction 25 may proceed *via* O_2 insertion into the Ni-C bond of the η^2-C,O form.

$$(PCy_3)_2Ni(CO_2)_{(s)} + O_{2\,(g)} \rightarrow (PCy_3)_2Ni(CO_4)_{(s)} \qquad (25)$$

Detailed mechanistic studies have shown that it proceeds instead through carbon dioxide decoordination, dioxygen coordination to Ni, and CO_2 insertion into the O-O bond of the newly formed, reactive $(PCy_3)_2Ni(O_2)$ complex [84]. Interestingly, using the $(PPh_3)_3RhCl(O_2)$ complex and labeled O_2 and CO_2 species ($^{16}O_2$, $^{18}O_2$, $^{16}O_2{}^{12}C$, $^{18}O_2{}^{12}C$, $^{16}O_2{}^{13}C$) it has been confirmed using FTIR and NMR studies that the formation of the peroxocarbonate moiety occurs *via* CO_2 insertion into the O-O bond more than into the Rh-O bond of the dioxygen-Rh complex [85].

However, whether or not the coordination of CO_2 is a prerequisite for further reaction depends on the kind of reaction CO_2 has to undergo. For sure, coordination to a metal center is necessary if the reduction of CO_2 to CO is considered (via O-transfer or protonation at O). In other cases, CO_2 pre-coordination to metal centers may not be necessary, as discussed later on.

The *insertion reactions of CO_2 into M-E* (E = H, C, N, O, etc) bonds are key steps of stoichiometric processes and catalytic cycles implying CO_2 incorporation into organic substrates with the generation of a new E-C bond. Often these reactions are initiated by nucleophilic attack of E (in M-E) at the electrophilic carbon of CO_2 and assisted by weaker interactions between the metal center and the lone pairs of one of the O-atoms of the cumulene.

This is the case of the insertion of CO_2 into M-O bond of metal-hydroxo (L_nM-OH) and metal alkoxo (L_nM-OR) complexes. The insertion reaction of CO_2 into a covalent polar M-OH bond affords a hydrogen carbonate species (eq. 26) that can be stable or can react further. This reaction is strictly related to the conversion of CO_2 into anionic or coordinated HCO_3^- and the elusive acid H_2CO_3, a transformation that plays a key role in the respiratory process of humans and animals. The Zn-enzyme Carbonic Anhydrase (CA) can accelerate the reaction of hydration-dehydration of CO_2, facilitating, thus, CO_2 up-take at cellular level and elimination in lungs from where it is expulsed [86]. It is now recognized that this enzymatic process implies the nucleophilic attack of a Zn^{2+}-bound hydroxyl group at free CO_2, which is held in place by hydrogen bonds within the pocket of the active site of the enzyme.

The *reaction of CO_2 with M-OR* (R = alkyl, aryl) bonds affords a metal-alkylcarbonate moiety (eq. 27) and has an industrial interest as it is related to the synthesis of molecular organic carbonates and polycarbonates based on the direct carboxylation of substrates such as alcohols, polyols and epoxides. A variety of L_nM-OR complexes have been investigated and also tested as catalysts in synthetic chemistry and co-polymerization processes [87,88,89]. The transition state of such reaction can be represented as in Fig. 12 and implies the interaction of the electrophilic C of CO_2 with the oxygen of the OR group [90,91]. Preliminary coordination of CO_2 to the metal center is not necessary in this class of reactions.

$$L_nM\text{-}OH + CO_2 \rightarrow L_nM\text{-}OC(O)OH \qquad (26)$$

$$L_nM\text{-}OR + CO_2 \rightarrow L_nM\text{-}OC(O)OR \qquad (27)$$

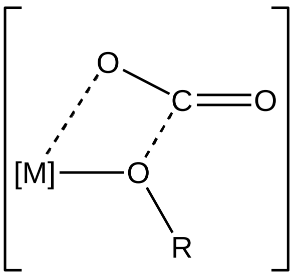


Figure 12. Insertion of CO_2 into the M-OR bond

The *insertion of CO_2 into the M-N* bond of metal-amido complexes ($L_nM\text{-}NR_2$) generates a new C-N bond and affords metal-carbamato complexes, which are important intermediates in the synthesis of carbamate esters, isocyanates, amides [34,35,92]. Also this process does not require, as a preliminary step, the coordination of CO_2. In fact, the reaction can proceed *via* attack of free CO_2 to the nitrogen atom of metal-amido-complex [93]. However, because of the aptitude of metal-amides and metal-carbamates to hydrolyze, it is possible also an amine-catalyzed mechanism summarized by reactions 29 and 30 [94]. Trace amounts of amine can be fortuitously present in solutions of $M(NMe_2)_n$ compounds as a result of $M(NMe_2)_n$ hydrolysis due to adventitious water. Under the working conditions (CO_2 in excess relative to amine), the free amine can interact with the heterocumulene to produce carbamic acid R_2NCO_2H, which reacts as shown in eq. 30.

$$L_nM\text{-}(NR_2) + CO_2 \rightarrow L_nM\text{-}O_2CNR_2 \qquad (28)$$

$$CO_2 + R_2NH \rightleftharpoons R_2NCO_2H \qquad (29)$$

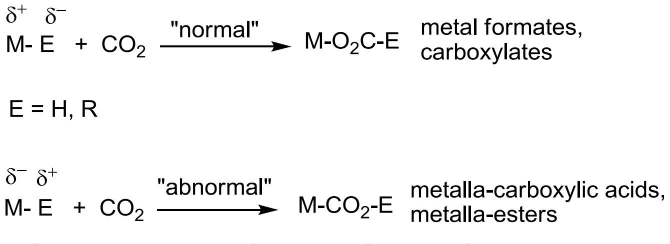
$$M\text{-}NR_2 + R'_2NCO_2H \rightleftharpoons MO_2CNR'_2 + R_2NH \qquad (30)$$

According to the above mechanism the formation of the metal carbamate complex should be better regarded as a ligand substitution, rather than a true insertion process. This reaction pathway has been largely exploited from the synthetic point of view for the preparation of a great number of metal carbamate adducts (eq. 31) [34,35].

$$L_nM\text{-}X + CO_2 + R_2NH \rightarrow L_nMO_2CNR_2 + HX \qquad (31)$$

(X= H, Cl, alkyl, OR, ClO_4, etc)

The *CO_2 insertion into a M-H or M-C* bond can occur according to two different modes, which are usually designated as "*normal*" and "*abnormal*" mode (Scheme 5) [54,95,96].



Scheme 5. "*Normal*" and "*abnormal*" insertion of CO_2 into M-H and M-R bonds

The observed insertion mode depends on the charge separation in the M-E bond (E = H, C), which may be critically affected by the nature of the metal itself and the ancillary ligands. The "*normal*" insertion mode affords metal-formates (E = H) or, more generally, metal-carboxylates (E = C), while the "*abnormal*" mode generates a metalla-carboxylic acid (E = H) or a metalla-ester (E = C). Such insertion reactions are important steps in stoichiometric or catalytic processes leading to the synthesis of carboxylic acids and carboxylate esters.

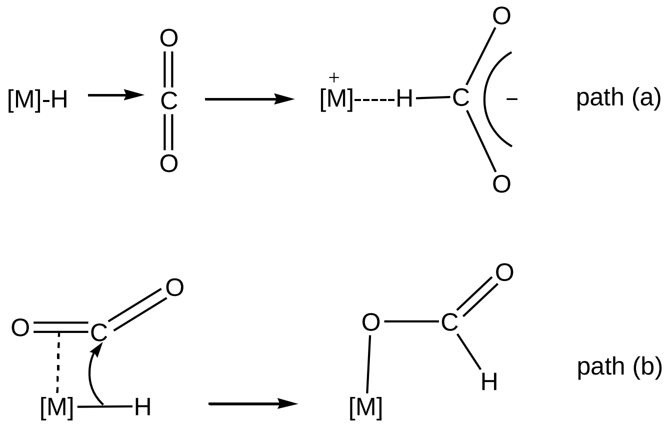
To date, very little is known about the "*abnormal insertion*" path for which only a few claims exist [54,95,96]. The M-CO_2H species is proposed [97] to be present and active in several processes implying MH-species and CO_2, but a clear-cut demonstration of CO_2 insertion into the M-H bond of a transition metal complex to afford M-CO_2H is not found in the literature. Conversely, M-CO_2H species have been generated by chemical or electrochemical protonation of M-CO_2 complexes, either η^2-C,O or η^1-C.

The *reactivity of "M-H/CO_2"* systems has reached high levels of attention because of its relevance to reactions that may have industrial interest such as the hydrogenation of CO_2 to afford *formic acid* (eq. 32) and the electrochemical reduction of CO_2 to other C1 or C1+ molecules.

$$CO_{2(g)} + H_{2(g)} \rightarrow HCOOH_{(l)} \qquad \Delta G° = 33\ \text{kJ mol}^{-1} \tag{32}$$

What is the role of CO_2 coordination in this insertion process (Scheme 5, (a); E =H) has been matter of several theoretical and experimental studies. Both paths represented in Scheme 6 are possible, depending on the nature of the metal center [98-100]. The nature of the reaction medium may also play a key role in influencing the mechanistic pathway [100]. However, the whole matter still wait for a full rationalization.

The *direct synthesis of HCO_2H from CO_2 and H_2* catalyzed by transition metal systems has much been investigated in the last twenty years. The interest towards such a process is mainly due to the potential of formic acid as hydrogen-carrier, as the two reactions, (i) carbon dioxide hydrogenation using molecular dihydrogen and (ii) decomposition of formic acid into the starting carbon dioxide and dihydrogen, give a quasi-CO_2-neutral cycle. Currently, worldwide production of formic acid, obtained from the combination of methanol and carbon monoxide with a strong base, is in the order of 0.8 Mt/y and is used in the textile industry, cleaning and as a preservative. Demand could increase markedly due to the development of efficient formic acid dehydrogenation catalysts that could find widespread application within the context of a hydrogen economy [101].



Scheme 6. Possible paths for "normal" insertion of CO_2 into a M-H bond

A limitation of the approach is the unfavorable thermodynamics of reaction 32. However, the formation of formic acid is more favourable in a condensed medium such as water (eq. 33, $\Delta G° = -4$ kJ mol^{-1}), where the $CO_2/H_2CO_3/HCO_3^-$ equilibrium as well as the second deprotonation to CO_3^{2-} must be taken into account, or if a base is used that produces formate salts instead of free formic acid, (eq. 34, $\Delta G° = -35$ kJ mol^{-1}) [102]. Under the latter conditions the actual substrate is HCO_3^- or CO_3^{2-} rather than CO_2.

$$CO_{2(aq)} + H_{2(aq)} \rightarrow HCO_2{}^-{}_{(aq)} + H^+{}_{(aq)} \quad (33)$$

$$H_{2(aq)} + CO_{2\,(aq)} + B_{(aq)} \rightarrow HCOO^-{}_{(aq)}\ BH^+{}_{(aq)} \quad (34)$$

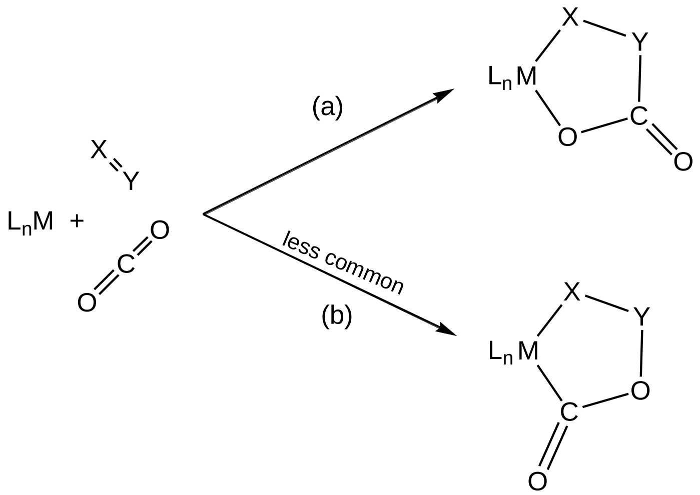
Another drawback is the kinetic stability of the intermediate hydrido-formate species $L_nMH(OCHO)$: breaking of the M-O and M-H bonds can represent the real kinetic barrier to the process. Overcoming the above kinetic and thermodynamic barriers requires the use of a "*shuttle*". Either Group 1 metal cations are used for the extraction of the formate moiety, or amines which are able to extract H. This has for long time prevented the exploitation of carbon dioxide hydrogenation as a catalytic direct route to free HCO_2H despite catalysts have been developed that have a high TON (several millions) and TOF [103,104] towards the salt. In fact, either the ammonium- or the Group 1 metal-formate that are produced need treatment with inorganic acid (such as H_2SO_4) for the production of the free acid. Such acid treatment produces equimolar (relative to HCO_2H) amounts of waste inorganic salts.

Very recent reports have opened interesting perspectives about the possible exploitation of the direct synthesis of *free formic acid from* CO_2 *and* H_2 in acidic media, without the need of any bases, amines or buffers. Lawrenczy has shown that it is possible to produce free formic acid by hydrogenation of carbon dioxide by carrying out the reaction in water or DMSO, without using any additive, in the presence of Ru-catalysts ($RuCl_2$(1,3,5-triaza-7-phosphaadamantane) and other related ligands) [102].This finding represents a breackthrough in this field and can open the way to an exploitation of the reaction.

Oxidative coupling reactions of CO_2 with unsaturated molecules X=Y (Scheme 7), such as olefins, dienes, cumulenes, alkynes, η^2-aryne, nitroso- or diaza-compounds and hetero-olefins (imines, carbodiimides, azadienes or aldehydes) [7,54,73,105-113], are key steps towards the functionalization of the above substrates.

These reactions generate a new C-Y bond (Y = C, N, O), and open an alternative route, in addition to the insertion reactions, to the incorporation of the heterocumulene into a variety of new carboxylated products (acids, esters, lactones, pyrones, etc), often characterized by complex molecular structures largely used in the production of pharmaceuticals, cosmetics, *etc.*

The coupling reaction is promoted by a low-oxidation state transition metal center (Ni, Mo, Fe, Mn, Pd, Rh, Pt, etc), which undergoes oxidation, and affords a five-membered metallaheterocycle, as shown in Scheme 7(a). Remarkably, in the known examples, the oxygen of carbon dioxide more than the C-atom binds to the metal (Scheme 7(b).



Scheme 7. Oxidative coupling with CO_2

The relevance of CO_2 coordination in such processes is another open issue, which has been addressed in detail only in a few cases. In principle, the above couplings can take place through one of the routes (i)-(iii) below:

(i) *the substrate reacts with co-ordinated CO_2 (pathway a)*;

$L_nM + CO_2 \longrightarrow L_nM(CO_2)$ (35a)

$L_nM(CO_2) + X{=}Y \longrightarrow L_n\overline{M(X\text{-}Y\text{-}C(O)O})$ (35b)

(ii) *free CO_2 reacts with a co-ordinated substrate/ligand (pathway b)*;

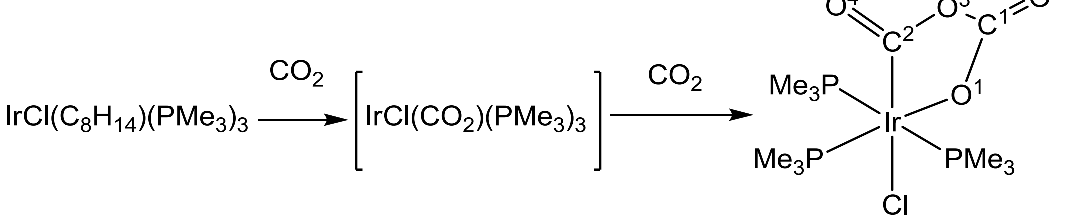
$L_nM + X{=}Y \longrightarrow L_nM(X{=}Y)$ (36a)

$L_nM(X{=}Y) + CO_2 \longrightarrow L_n\overline{M(X\text{-}Y\text{-}C(O)O})$ (36b)

(iii) *a three-center mechanism implying CO_2, the substrate and the metal center (pathway c).*

$LnM + CO_2 + X{=}Y \longrightarrow L_n\overline{M[X\text{-}Y\text{-}C(O)O})]$ (36c)

The head-to-tail CO_2 homocoupling at the Ir center of $IrCl(C_2O_4)(PMe_3)_3$ (Scheme 8) necessarily implies the intermediacy of a CO_2-Ir adduct and may follow pathway (a) [81]. However, the mechanistic details are not known. The reaction is believed to be initiated by the nucleophilic addition of $IrCl(C_8H_{14})(PMe_3)_3$ to CO_2 (O(3)C(2)O(4)), with the resultant more nucleophilic oxygen (O(3)) binding a second CO_2 molecule (O(2)C(1)O(1)) through C(1). Cyclization *via* Ir-O(1) bond formation affords the product.

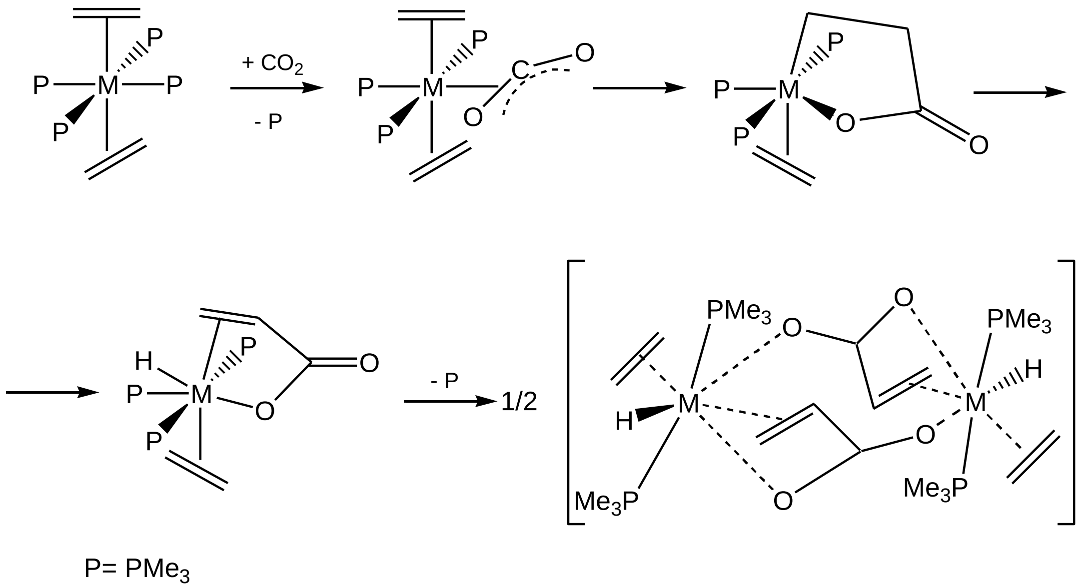


Scheme 8. Head-to-tail homocoupling of CO_2 promoted by $IrCl(C_8H_{14})(PMe_3)_3$

Pathway (b) has been documented experimentally for the oxidative coupling CO_2/propionaldehyde [112] (X = C, Y = O; Scheme 7) and CO_2/isoprene (X = Y = C; Scheme 7) [113] at a Ni(0) center for which the activation parameters have been measured ($\Delta H^{\ddagger}$=43±6 kJ/mol and $\Delta S^{\ddagger}$=-129±19 J/mol K [112]; $\Delta H^{\ddagger}$=25±7 kJ/mol; $\Delta S^{\ddagger}$=-184±24 J/mol K [113], respectively).

Several examples of *oxidative coupling* CO_2/olefin or CO_2/alkyne have been reported [7,105,106,114,115]. To date, the hypothesis that coordinated CO_2 might react with free alkene/alkyne to generate a metalla-lactone has not found sound experimental support. For instance, despite Ni(0)-complexes are very effective in promoting the oxidative coupling of CO_2/olefin, Aresta *et al.* found that $Ni(CO_2)(PCy_3)_2$, in the solid state, did not react with gaseous ethene even after three hours at room temperature. In solution, a substitution reaction occurred easily with formation of $Ni(PCy_3)_2(C_2H_4)$ [7,74,116], showing that ethene is more tightly bound to "$Ni(PCy_3)_2$" than CO_2. Accordingly, earlier DFT calculations carried out for the systems ethene/CO_2 [117] and alkyne/CO_2 [118,119] in the presence of Ni(0) bearing N-donor ligands, ruled out that the oxidative coupling of CO_2 with the above substrates (alkene/alkyne) at Ni(0) may involve the interaction of a Ni-CO_2 complex with the unsaturated substrate used (eq. 35b) or proceed through an associative mechanism involving the intermediate formation of a "mixed" substrate-carbon dioxide Ni-complex (eq. 36c). The calculations indicate that the coupling reaction involves the activation of the olefin by coordination at the metal center and the subsequent reaction of the activated substrate with an incoming CO_2 molecule (eq. 36b), as shown by previous experiments [116].

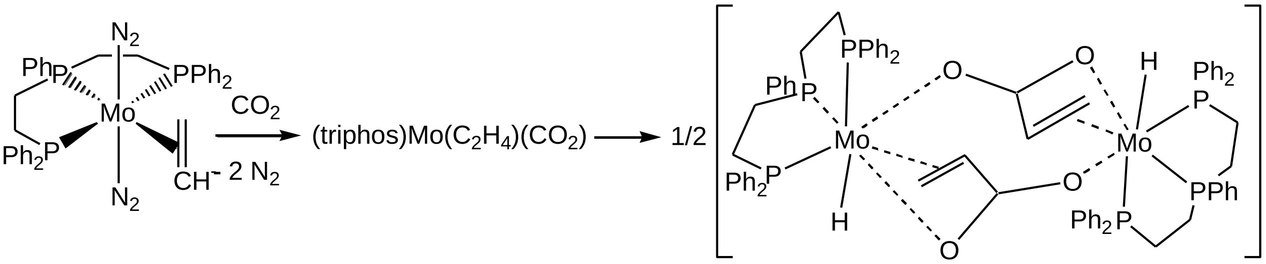
However, suitably changing the nature of ancillary ligands or metal center may open new mechanistic pathways and, for instance, shift the mechanism of olefin/CO_2 oxidative coupling towards pathway (c) (eq. 36c). For instance, a theoretical work supports that oxidative coupling ethene-CO_2 at nickel centers bearing bidentate phosphorous ligands can proceed through sequential coordination of ethene and CO_2 to Ni with formation of an ethene-CO_2-Ni-complex $LNi(C_2H_4)(CO_2)$, wherein, however, CO_2 is only weakly bound to Ni [120]. Pathway (c) was originally postulated by Carmona for the reaction of *trans*-$M(C_2H_4)_2(PMe_3)_4$ with CO_2 affording the binuclear hydrido-acrylate complex μ-$(CH_2{=}CHCOO)_2[HM(C_2H_4)(PMe_3)_2]_2$ (Scheme 9) [121].



Scheme 9. Proposed mechanism for the formation of μ-$(CH_2{=}CHCOO)_2[HM(C_2H_4)(PMe_3)_2]_2$

DFT calculations (carried out for M = Mo) have confirmed the consistency of the mechanism illustrated in Scheme 9 [122]. Coordination of CO_2 molecule to the metal center with formation of the CO_2-bis-ethene complex $Mo(C_2H_4)_2(CO_2)(PMe_3)_3$ is a necessary step to achieve the CO_2-alkene coupling, because the formation of the new C-C bond is promoted by a simultaneous metal→CO_2 and metal→C_2H_4 electron donation mechanism. The formation of the metalla-lactone species is, thermodynamically, allowed and the activation barrier has been estimated to be 11 kcal/mol. The five-membered metallacycle converts into a metal-hydride species through an exothermic β-hydrogen transfer step showing a calculated energy barrier of 10 kcal/mol. The hydrido-acrylate monomer is already well below the energy of the reactants, but further stabilization is achieved through the dimerization process.

The mechanism of *ethene carboxylation* at a Mo center has been investigated also experimentally [123], following the conversion of *trans*-(triphos)$Mo(C_2H_4)(N_2)_2$ (triphos = $(Ph_2PCH_2CH_2)_2PPh$) and CO_2 into the bridging acrylate hydride complex, [(triphos)Mo-(H)(OC(O)CH=CH_2)]$_2$ (Scheme 10). The observation of the intermediate complex (triphos)$Mo(C_2H_4)(CO_2)$ on the path to C-C bond formation (Scheme 10) provides the first experimental evidence that simultaneous coordination of both ethene and carbon dioxide at a metal center is a prerequisite for coupling the two unsaturates. This behavior is somewhat different from what described to occur at nickel centers. It has been suggested that the requirement of precoordination of both CO_2 and olefin, while being less stringent for late transition metal centers like Ni, may be more likely for early transition metal centers.



Scheme 10. Ethene carboxylation at the Mo center of trans-(triphos)$Mo(C_2H_4)(N_2)_2$

However, at present, generalizations may be rash. Knowledge in this field is still lacunose and further studies are required to fully elucidate, for a given M/X=Y/CO_2 system, the role of the metal center and ancillary ligands in marking the mechanistic pathway of the coupling reaction.

3.0 Conversion of CO_2 into chemicals

3.1 CO_2 as a C1-synthon for the synthesis of “intermediates and fine chemicals”

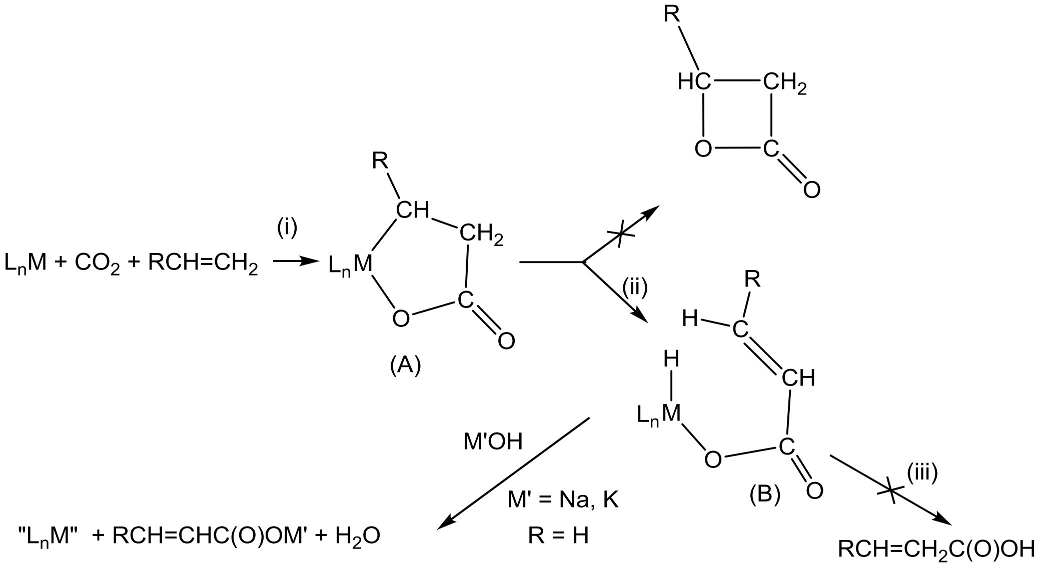
The *incorporation of carbon dioxide* into organic substrates tells in a clear way the huge potential of the cumulene as *C_1-synthon* for the synthesis of fine and commodity chemicals [36,124-130]. These reactions allow to build up new C-CO_2-H, C-CO_2-C, E-CO_2 (E=N, O) moieties and lead to the direct carboxylation of the organic substrate with formation of new products such as carboxylic acids, esters, lactones, carbamates, carbonates. Such synthetic approach is of great importance from the industrial point of view as the target products have a large market of the order of several Mt/y. Moreover, the exploitation of such synthetic methodology would allow the implementation of more direct or safer synthetic routes in place of those on-stream that do not respond to the energy- or atom-economy principles or make use of toxic and harmful starting materials such as phosgene, opening thus, and intriguing new perspectives of development of a more sustainable chemistry. In fact, with respect to processes on stream, the utilization of CO_2 for the synthesis of carboxylated compounds bears several benefits such as: reduce the production of waste, recycle carbon, and make less use of solvents if supercritical CO_2 ($scCO_2$) is used as solvent and reagent. Because of the more direct synthetic approach, there may also be a lower energy consumption. Such benefits may be accurately evaluated by using the LCA methodology, applied to the CO_2-based process and to the process that is being substituted [131].

One can foresee that in general, the energetics of the carboxylation processes will be acceptable, the energy required for CO_2 conversion being contributed by the co-reagent, which is an electron-rich species. This is the case of carboxylation reactions in which the carbon atom maintains the formal +4 oxidation state, as in carbamation or carbonation reactions (Fig. 1). To such processes, those bearing to the formation of carboxylates RCOOH(R) (e.g., acids, esters, and lactones), in which the C-atom has an oxidation state of +3, can be added. Also these reactions may be thermodynamically feasible but, at least in a few cases, they may show some thermodynamic or kinetic constraints.

In the following sections special attention will be devoted to compounds such as carboxylic acids, esters, lactones, carbamates, isocyanates, ureas, carbonates, due to their industrial importance.

3.1.1 Oxidative coupling with olefins: synthesis of acrylic acids and acrylates

As previously emphasized (2.4.3), CO_2 and olefins can react in presence of a suitable metal center and form a metallacyclo-carboxylate (A) (Scheme 11.). Such species have been isolated and characterized in a number of cases [54,73,110]. Scheme 11 shows two possible ways through which, in principle, (A) may further react, once formed. Formation of β-lactone, which may form from $L_nM(CH_2CH_2C(O)O)$ by reductive elimination, has never been observed experimentally. On the other hand, the metalla-lactone may generate, through a β-H shift reaction, a metal-hydrido-acrylate species (B).



Scheme 11. Potential reaction pathways for $L_nNi(CH_2CH_2C(O)O)$

Species like (B), which have been isolated (M = Mo, W) and fully characterized [121,123], have drawn great attention for their potential as precursors of acrylic acids $RHC{=}CH_2C(O)OH$ which, in principle, might be generated by reductive elimination. *Acrylic acid* is the simplest unsaturated carboxylic acid and is a building block for hundreds consumer products. The global acrylic acid market was valued at \$11006.6 million in 2013, and it is estimated to reach \$18824.0 million by 2020, growing at a rate of 7.6% during the forecast period (from 2014 to 2020) [132]. The global consumption of acrylic acid is anticipated to reach 8169.0 kt by 2020. Acrylic acid, $CH_2=CHCO_2H$, is used in a number of industrial applications. The primary use of acrylic acid is in the production of acrylic esters and resins, which are used primarily in coatings and adhesives. A growing use of acrylic acid Group 1 metal derivatives is in the production of supersorbent polymers.

It is also used in oil treatment chemicals, detergent intermediates, water treatment chemicals, and water absorbent polyacrylic acid polymers. It is currently manufactured at an industrial scale by two-stage oxidation of propene (eq. 37), a byproduct of hydrocarbon cracking and naphtha refining. This process employs heterogeneous catalysts consisting of metal oxides such as vanadium and molybdenum to oxidize propene to acrolein in the first step.

$$CH_2{=}CHCH_3 + O_2 \rightarrow CH_2{=}CH\text{-}CHO + H_2O \xrightarrow{0.5\ O_2} CH_2{=}CHCO_2H \qquad (37)$$

$$CH_2{=}CH_2 + CO_2 \rightarrow CH_2{=}CHCO_2H \qquad (38)$$

The synthesis of acrylic acid based on the direct combination of ethene with CO_2 (eq. 38) is, in principle, a very attractive alternative as it is 100% atom economical as all the atoms of the reactants are found in the target product.

Hoberg [133], in the early 1980s, first reported the (sub)stoichiometric formation of cynnamic acid, $PhCH=CH_2C(O)OH$, from styrene and CO_2, in the presence of $Ni(cod)_2$ and DBU. Since then, the catalytic synthesis of acrylic acids by direct coupling of olefins with CO_2 has greatly attracted the interest of chemists. However, to date, this goal still remains unaccomplished. In fact, going back to Scheme 11, either (A) or (B) may be stable species which prevent spontaneous release of acrylic acid. Theroretical and/or experimental studies [122,123] support (see 2.4.3) that the conversion of the five-membered metallacycle (A) into the metal-hydride species (B) at a Mo or W center is a both thermodynamically and kinetically accessible step, but the hydrido-acrylate monomer (B) does not eliminate acrylic acid, probably because of the barrier of the cleavage of the M−H and M−O bonds. On the other hand, the body of experimental evidences suggests that in Ni(0) promoted CO_2-olefin coupling reactions the metallacycle structure (A) (Scheme 11) is a thermodynamic sink, as a nickela-lactone was usually found to be the final product. A more recent attempt to liberate acrylic acid from a nickelalactone was based on the use of a basic phosphane, such as 1,2-bis(diphenylphosphino)methane (dppm). However, a molecular rearrangement took place bearing the cleavage of P−C bonds and the formation of stable acrylato-complexes [134]. Aresta and coworkers have first modeled using DFT the reaction of ethene with CO_2 over “L_2Ni” and shown that the formation of the acrylic acid occurs in three main steps passing through the facile formation of the pentaatomic metallacycle ring, which is in a well of energy that prevents on Ni a facile last step, i.e. the β-H shift. Moreover the elimination of acrylic acid has also a barrier [117]. Later on, Buntine and coworkers [135] have investigated the reactivity of $Ni(cod)(DBU)_2$ using DFT. The calculations showed again three main steps for the process: exothermic formation (-17.2 kJ/mol) of the five-membered nickelacycle by oxidative coupling; endothermic β-H shift (+21.3 kJ/mol) resulting in a nickel-hydrido-acrylate species; endergonic reductive elimination of acrylic acid; (see also Scheme 11). The three steps exhibited substantial energy barriers (respectively: 121.8

kJ/mol; 147.4 kJ/mol; 104.1 kJ/mol), but in the opinion of the authors, not so large that would prohibit the overall catalytic process. Thermodynamic in addition to kinetic constraints may also prevent the overall reaction from taking place at a significant extent, in accordance with the solvation-corrected Gibbs free energy of the coupling reaction in question, which was calculated to be unfavorable by +42.7 kJ/mol [135]. In this regard, it may be of interest to note that acrylic acid has been reported to react with “$Ni(cod)_2$” (1 equiv) in the presence of PCy_3 (1 equiv) to give the nickela-lactone species $Cy_3PNi(CH_2CH_2C(O)O)$ [136].

The *reductive elimination of acrylic acid* from a hydrido-acrylate metal complex closely resembles the previously discussed elimination of formic acid from hydrido-formate metal complexes $L_nM(H)O_2CH$. In the latter case, the elimination process is facilitated by using an appropriate "*shuttle*" of the formate anion (amine or Group 1 metal cations). The use of $K^+(Na^+)$ shuttle has been investigated by Limback [137,138] who has reported the first catalytic (also limited to a few cycles) formation of CH_2=CHCOOM (M = K, Na) by using Ni(0) catalysts in presence of M’OH (Scheme 11). A variation to this approach has been proposed by using excess Zn-powder to reduce Ni [139]. This process uses more than $2e^-$ per mol of acrylic acid (considering the loss of Zn used in excess), being less effective than the electrochemical generation of acrylates carried out in the 1993s [140]. The role of Lewis acids has been also investigated [141,142], and the activity of Pd systems has been explored [143].

Recent advances have opened new perspectives in this research area. The topic of coupling ethene-CO_2 has recently been faced following a new synthetic approach aimed at avoiding the contemporary formation of M-H and M-O bonds and driving the system towards the formation of a metallorganic species of the type $MCH_2CH_2CO_2R$, which easily eliminates the acrylato ester CH_2=CH-CO_2R via a β-H shift with generation of a M-H species. With the use of a Pd catalyst it has been shown that the elimination of the acrylate ester is an easy reaction and the catalytic formation of such ester was described, however limited to a few cycles [144]. The correctness of such strategy is further supported by a few recent results which describe the formation of methyl acrylate by methylation of nickela-lactones with MeI [145,146]. The latter results merit attention as they confirm that alkyl esters of acrylic acids can be released more easily than the corresponding acids from nickela-lactones.

A question may come to the mind of the reader: can CO_2 be co-polymerized with olefins to afford polyesters (eq. 39)? If one considers the skeleton of the product (A) obtained by coupling an olefin with CO_2 (Scheme 11), under which circumstances would it be possible to insert an olefin molecule into the M-O bond of (A), followed by another CO_2 molecule and so on?

$$nCO_2 + nRCH{=}CHR \rightarrow -[CHR\text{-}CHR\text{-}C(O)O]_n- \qquad (39)$$

Such alternate insertion of olefin and CO_2 has not been documented so far. It is useful to recall that alkynes are able to insert a second alkyne in the skeleton of the product of oxidative coupling of CO_2 and the alkyne (Scheme 12 and 18; *vide infra* 3.1.4). The insertion does not give an ester linkage as it occurs on the M-C bond rather than on the M-O bond. The product of coupling is then eliminated as a pyrone. The coupling of the olefin with CO_2 is more difficult than the coupling of the alkyne. Such reaction may have a large industrial interest and is worth investigating also if it is foreseeable that a perfect alternate insertion will not be easily reached, and the insertion of CO_2 will be statistical and will not reach the level of insertion of CO as in the case of ethene/CO.

3.1.2 Synthesis of other carboxylic acids by oxidative coupling CO_2 and olefins

The formation of a *terminal "carboxylic moiety"* C-CO_2 is achieved through a variety of routes such as: oxidation of hydrocarbons or aldehydes (obtained from olefins by hydroformylation), base catalyzed dehydrogenation of alcohols, carbonylation reactions often coupled with H_2O addition (Koch reaction; Reppe chemistry), oxidative cleavage of olefins by ozonolysis or using H_2O_2 or even O_2, potassium permanganate or potassium dichromate oxidation, hydrolysis of nitriles, esters, or amides with acid- or base-catalysis, carbonation of a Grignard or organolithium reagents. In some cases the synthetic methods are poorly selective or not quantitative, in other cases they may imply multistep procedures with production of wastes and loss of carbon [116]. In this ambit the development of direct catalytic carboxylation of organic substrates would be of great value and applicative interest.

As previously noted, unsaturated substrates such as olefins, alkynes, [54,73,105,106,109,110, 147,148] allenes [106,149] and conjugated dienes [73,105,106,118,119,150-155] can react with CO_2 in the presence of a suitable metal center in a low oxidation state through an oxidative coupling reaction, which provides an entry into a variety of metal-carboxylated species. Although most of such reactions at the moment are stoichiometric, they can play a significant role from the synthetic point of view as they are direct and clean routes to functionalized unsaturated carboxylic acids or alkyl esters, which can be released stoichiometrically upon simple protonolysis or acidolysis in the presence of alcohols.

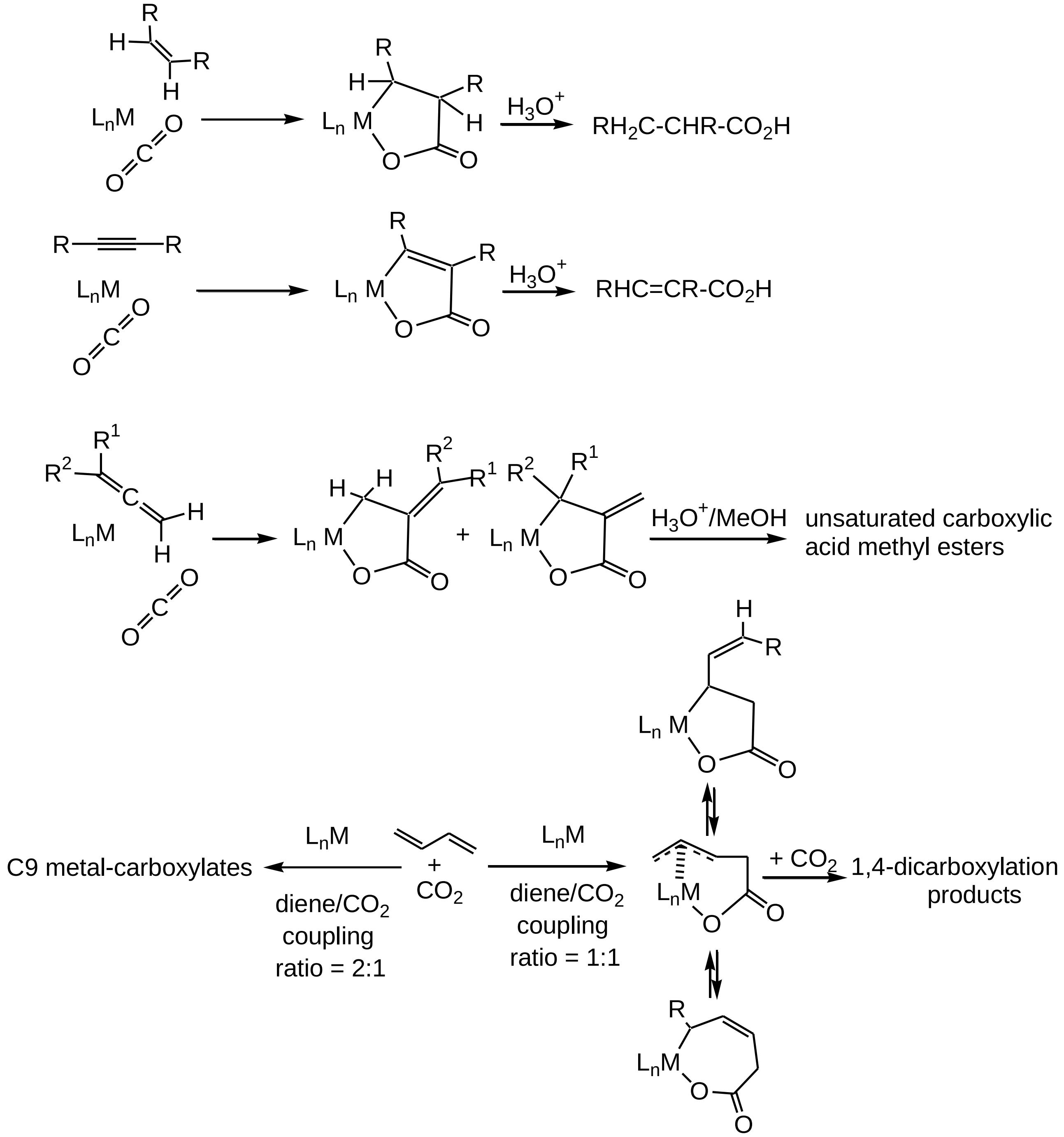
Functionalization of alkynes, allenes and conjugated dienes

Ni(0) is very effective in promoting the *oxidative coupling of alkynes or allenes with CO_2*. Scheme 12 shows the formation of carboxylic acids produced by hydrolysis of the metallacycle. Such route uses catalysis for the coupling of the unsaturated substrate with CO_2, but the metallacycle does not undergo spontaneous elimination, as already seen with acrylates. Acidolysis is necessary for recovering the carboxylic acid. Such syntheses have been achieved in the 1993s by electrocatalysis [156,157], which again is not catalytic as sacrificial electrodes were used and the carboxylated product was recovered as Mg-salt, in general. Making such processes catalytic would be of great importance.

Stoichiometric carboxylation of conjugated dienes with CO_2 has been carried out in the presence of both late and early transition metal complexes. Depending on the nature of the metal center, ancillary ligands, diene substrate, and, more generally, working conditions, the carboxylation reaction may evolve in different ways and afford metal-carboxylic products implying 1:2 or 1:1 or 2:1 CO_2/1,3-diene coupling, which are useful synthones for further reactions with electrophiles. For instance, in the presence of monodentate P-ligands, Ni(0) promotes the CO_2/1,3-diene coupling in a 1:2 ratio to yield a Ni(II)-C_9-carboxylate. This behavior reflects the well recognized ability of Ni(0)-complexes bearing labile phosphane ligands to promote olefin oligomerization. In this carboxylation reactions the dimerization of the diene to form a bis-allyl-C_8 chain is followed by CO_2 insertion into a Ni-allyl σ-bond to afford Ni(II)-carboxylates, which may undergo further rearrangement reactions. CO_2/diene coupling in a 1:1 ratio to give η^3-allyl-C_5-carboxylate Ni-complexes (Scheme 12) has been shown to be promoted in the presence of P- or N-chelating ligands [106,154]. Although η^3-coordination of the allyl moiety is thermodynamically more stable compared to the η^1-bonding mode, an η^3-η^1 rearrangement of the oxo-π-allyl intermediate formed by diene-CO_2 oxidative coupling is also possible and can be envisaged to account for the formation of α,ω-dicarboxylate complexes, which have been reported in a few cases (Scheme 12; M = Fe

[151], Zr [152], Ni [153]). Remarkably, only 1,4- and no 1,2-dicarboxylation have been observed. More recently, this stoichiometric chemistry has received new impulse [158-160] and has, for instance, been applied to the synthesis of *highly functionalized carboxylic acids*, such as α-methylene-γ-hydroxy carboxylic acids [158] and their derivatives, or exploited for the preparation of β-hydroxycarboxylic acid derivatives [159].

The synthetic valence of the reactions described above is out of discussion, but their stoichiometric character may represent a limitation to their exploitation. The moment being they can be applied on a small scale or for the synthesis of high added value chemicals of complex structure. The stoichiometric nature of these processes can be related with the thermodynamic and/or kinetic stability of metalla-lactones or C_n-carboxylate metal-complexes intermediate products as discussed above (Scheme 12).

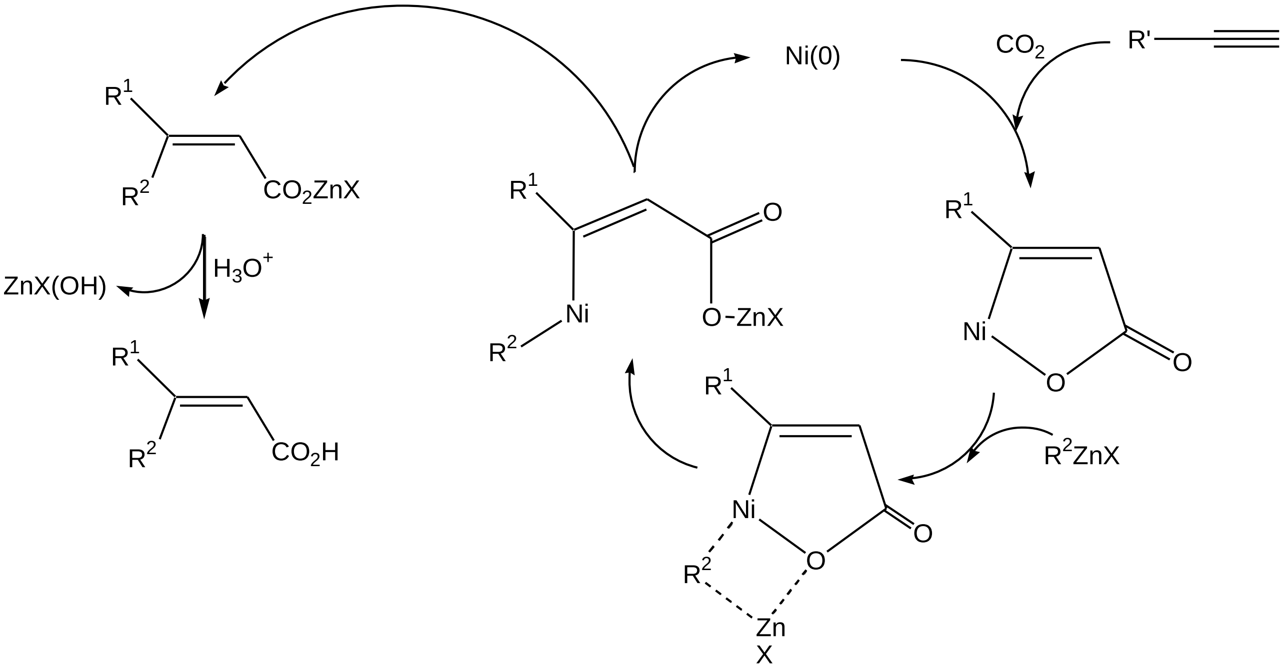


Scheme 12. Oxidative coupling of CO_2 with unsaturated organic substrates.

Driving catalytically the carboxylation of the above substrates is not an easy task. This goal may be achieved through a judicious choice of the metal center, the ancillary ligands and the experimental conditions. For instance, in the presence of Ni(0), switching from PPh_3 to less basic P(O-*i*-Pr)$_3$ ancillary ligand allowed to obtain 2-methylene-3-vinylcyclopentanecarboxylic acid from butadiene and CO_2 even catalytically, albeit in low yield and with a low turnover (TON = 29) [153]. Unfortunately, to date, this remains a rare example of such an approach.

Nowadays, new synthetic strategies have given new impulse to the research in this area opening new perspectives in the use of the heterocumulene as carboxylating agent of unsaturated organic substrates. These approaches exploit the reactivity of a suitable co-reagent able to reduce back the catalyst from Ni(II) to Ni(0). At the end the catalytic centre can be recycled, but a reduced form of a metal (Zn, Al) is oxidized. Such approach may have sense if the catalyst is a precious metal, less with Ni. The fact that another metal is in any case oxidized in stoichiometric amount leaves doubts about the correctness of using the term “catalytic” in such applications, and leaves on such reaction the label of “transmetalations” or “syntheses assisted by metals”.

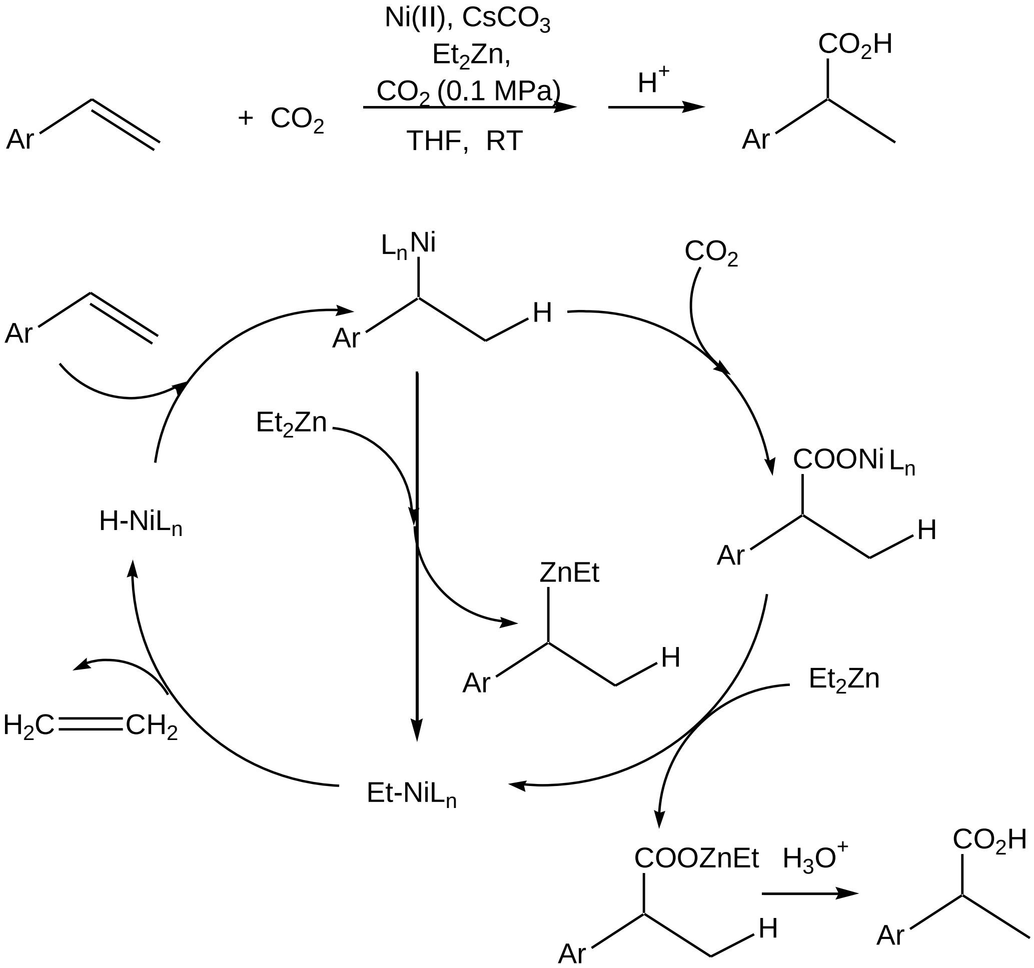
Alkyl- or aryl-zinc reagents, acting as alkylating(arylating)/transmetalating agents, have been used to push catalytically (in the sense discussed above) the carboxylation of alkynes [161] (Scheme 13) or bis 1,3-dienes[162,163] in the presence of Ni(0). The unsaturated carboxylic acids can be liberated from the relevant Zn carboxylated salt by protonolysis.



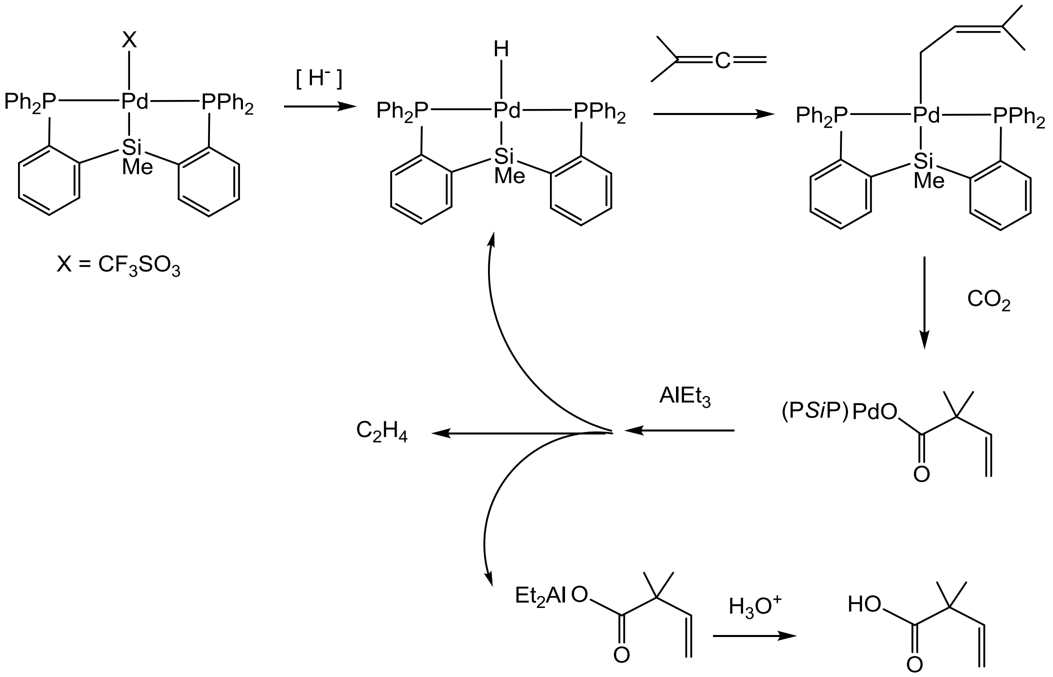
Scheme 13. Alkylative or arylative carboxylation of alkynes

According to a different approach organozinc reagents have been used as reducing/transmetalating agents for addressing catalytically the carboxylation of unsaturates, such as styrenes (Scheme 14) [164] or internal alkynes [165], in the presence of Ni(0) catalysts, through a hydrocarboxylative pathway which allows to bypass the formation of a classic Hoberg- type oxanickelacycle.

Such *hydrocarboxylative* approach has been successfully applied to the carboxylation of internal alkynes by using Cu catalysts and hydrosilanes as hydride transfer agents [166], and for the synthesis of β,γ-unsaturated carboxylic acids from allenes [167,168] or 1,3-dienes [169] and CO_2. A new hydrocarboxylating system has been used, based on a tridentate silyl pincer palladium catalyst precursor (X = trifluoromethanesulfonate in Scheme 15) and $AlEt_3$ (or $ZnEt_2$).



Scheme 14. Nickel-catalyzed hydrocarboxylation of styrenes



Scheme 15. Hydrocarboxylation of allenes with CO_2 catalyzed by a silyl pincer-type Pd complex

A mild and user-friendly Ni-catalyzed regioselective hydrocarboxylation of alkynes with CO_2 (0.1 MPa) has been also described which uses Mn as reducing agent and simple alcohols as proton sources [170].

A common feature of the carboxylation reactions discussed above is the utilization of a coreactant (ZnR_2, $HSiR_3$, AlR_3, etc; usually used in excess with respect to the unsaturated substrate), which is consumed to regenerate the catalytically active species ($L_nNi(0)$; L_nM-H) after each cycle. Therefore, as already discussed above, all these processes are catalytic with respect to the transition metal (Ni, Cu, Pd, etc), but not with respect to the co-reagent, which is used in excess and generates waste at the end of the process. Features like the energetic cost of the species used in transmetalation (metal alkyls are quite intensive in energy) and the metal waste generated in the final step of acidolysis, contribute to increasing the E-factor and decreasing the environmental sustainability of these syntheses. Nevertheless these reactions provide a powerful versatile tool for the direct synthesis of complex organic molecules functionalized with carboxylic acid moieties, which, otherwise, would be produced through multistep procedures. Further progresses in this area are expected through the definition of cheaper and cleaner reducing agents and enlarging the portfolio of used unsaturated substrates. LCA should be used for an environmental assessment of the process and for identifying the key issues in the reaction so to find a remedy and make such interesting reactive systems suitable for the direct carboxylation of organic substrates.

3.1.3 Carboxylic acids by CO_2 incorporation into C-H bonds

The *direct C−H carboxylation* with CO_2 provides another potential route to carboxylic acids (eq. 40). The process formally involves the insertion of CO_2 into a C-H bond. The enthalpy of such a reaction can be easily calculated as it is given by the following quantities: $\Delta H_r = [H_{(C\text{-}C)} + H_{(O\text{-}H)}] - H_{(C\text{-}H)}$. For different substrates major differences can be found in the values of $H_{(C\text{-}H)}$ and minor for $H_{(C\text{-}C)}$. The entropic content of the reaction is due mainly to the fact that gaseous CO_2 is at the end found in a liquid or solid form. The ΔS will be negative so that the term $-T\Delta S$ will be positive. The ΔG will depend mainly on the entropic content and the overall reaction will have a positive Gibbs free energy change, making the concentration of the acid quite low at the equilibrium. The carboxylation of methane or benzene (eqq. 41 and 42) exemplifies the situation at 298 K.

$$\text{R-H} + CO_2 \rightarrow \text{R-}CO_2H \qquad (40)$$

$$CH_{4\,(g)} + CO_{2\,(g)} \rightarrow CH_3COOH_{\,(l)} \qquad (41)$$

$\Delta H = -16.6$ kJ/mol; $\Delta G_{298K} = +54.8$ kJ/mol

$$C_6H_{6\,(l)} + CO_{2\,(g)} \rightarrow C_6H_5COOH_{\,(s)} \qquad (42)$$

$\Delta H = -40.7$ kJ/mol; $\Delta G_{298K} = +57.3$ kJ/mol

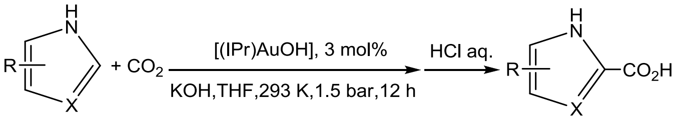
Various metallorganic reagents, usually obtained by the direct metalation of a C−H bond (as well as by reacting an organic halide with a metal compound), have been used for a stoichiometric carboxylation of organic substrates [171,172]. Also phenoxide anion ($C_6H_5O^-$) η^5-coordinated to transition metal centers, such as Mn(II) [173] or Rh(I) [174], has been shown to selectively activate the para-C−H bond of the aromatic ring and, upon CO_2 fixation, convert into the 4-OH-benzoic acid. Such carboxylation reactions are reminiscent of the for long time known carboxylation of Grignard's reagents and are stoichiometric processes as they require 1 mol of metal per mol of organic product and should be regarded as "metal-assisted" carboxylations. This feature represents a limitation making unlikely the application of these processes on a large scale.

Catalytic carboxylation of C-H bonds has been claimed to occur in presence of an active C−H bond. However, 2-dialkyl-imidazolium-carboxylates bearing CO_2 bonded at the heterocarbene moiety have been shown to be able to act as CO_2-carrier and transfer CO_2 to activated C−H bonds (eq. 43) [175]. The catalytic carboxylation of C−H bonds of heteroaromatics HetH has been carried out in presence of the system [(IPr)AuOH]/KOH (IPr = (1,3-bis(diisopropyl)-phenylimidazol-2-ylidene) (Scheme 16) [176].

$$R'R''Im{=}CO_2 + \text{Substrate-H} + MX \rightarrow R'R''ImH^+X^- + \text{Substrate-}CO_2M \qquad (43)$$

Substrate-H = $PhC(O)CH_3$, CH_3OH; MX = $NaBPh_4$, $NaBF_4$, KPF_6

Regeneration of the [(IPr)AuOH] catalyst from the intermediate gold carboxylate [(IPr)Au(O_2CHet)] is accomplished by K^+ cation acting as a shuttle of the carboxylate moiety. NHC−Cu complexes have also been used [177,178]. When common aromatic compounds (benzene derivatives) are used, the carboxylation occurs quite efficiently only if electron deficient groups are present in the ring, indicating that the C−H bond must be strongly activated (acidic C−H bonds) in order that the carboxylation may occur [179].

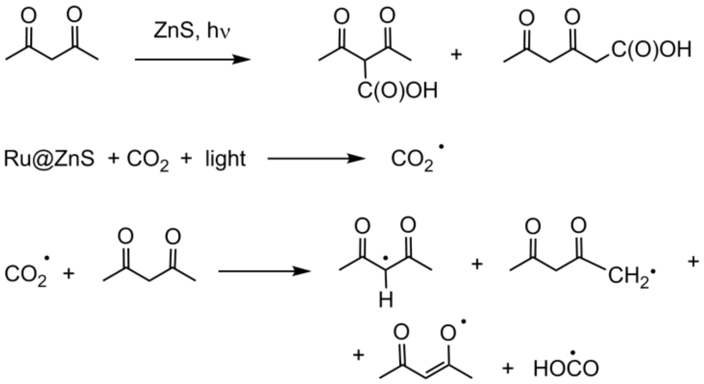


Scheme 16. Carboxylation of N-heterocycles promoted by Au(I). X=N, O

Therefore, the acidity of the C-H bond of the substrate represents a limitation in these processes, although it can be modulated by controlling the substituents in the organic substrate. However, this constrain may limit the number of potentially usable substrates which can afford carboxylated products that may not be of general use.

In principle, the interaction of the substrate with a suitable "activating system", such as a metal system, may provide another way to enhance the activity of a C−H moiety. This approach is by far more appealing as it can lead to several products of industrial use. Such direct functionalization might be very useful with short chain HCs (C1−C4) that do not find a convenient use today. Recently, direct carboxylation of simple arenes under atmospheric pressure of CO_2 has been achieved through a rhodium-catalyzed C–H bond activation without the assistance of a directing group, using $AlMe_2(OMe)$ [180] or $AlMe_{1.5}(OEt)_{1.5}$ [181] as reductant. Various arenes such as benzene, toluene, xylene, electron-rich or electron-deficient benzene derivatives, and heteroaromatics have been directly carboxylated with high TONs [181]. Also in this case the catalytic center (Rh) is regenerated at expenses of Al, another less expensive and more common metal, but the E-factor of such synthesis is quite high making it suitable for limited applications.

Photocatalysis may offer interesting perspectives in this area. Recently, the direct insertion of CO_2 into the C-H bond of acacH (actylacetone) has been shown to occur under photocatalysis (Scheme 17) [182]. The species identified as the initiator of the reaction is the $CO_2^{\cdot-}$ radical anion. It extracts a H-atom either from the enolic form or from acacH itself. Coupling of COOH with the acac-radical affords the acid. Interestingly, under photocatalysis two different isomeric acids are obtained that imply the CO_2 insertion into the activated methylenic C-H bond but also into the more inert C-H bond of the terminal -CH_3 moiety, that under chemical catalysis is not affected [183].



Scheme 17. Photocatalytic C-H activation and CO_2 insertion

Such approach has been used also for the photocarboxylation of 2,3-dihydrofuran (2,3-DHF) to afford 25% yields 2,3-DHF-2-COOH [184]. Noteworthy, the photocatalytic approach works in water and affords the free acid and not the salts as seen in other cases above. This feature makes the photocatalytic approach of great interest.

To date, *catalytic carboxylation of CH bonds* still remains a challenging research area, which deserves more research efforts. The only industrial exploitation of reaction 40 is still provided by the Kolbe-Schmitt synthesis of hydroxybenzoic acids [185] carried out by reacting CO_2 with Group 1 salts of phenol under severe conditions. Noteworthy, also this industrial synthesis is not a catalytic process as 1 mol of Group 1 metal (Na or K) is used per mol of phenol. It would be interesting to convert it into a catalytic process using phenol more than phenolates. The direct carboxylation reactions are of great importance, and their exploitation may have favorable impact on the chemical industry allowing the synthesis of several large market products (for instance, acetic acid, benzoic acid, long chain fatty acids, dicarboxylic acids) through less tortuous and more C-efficient routes.

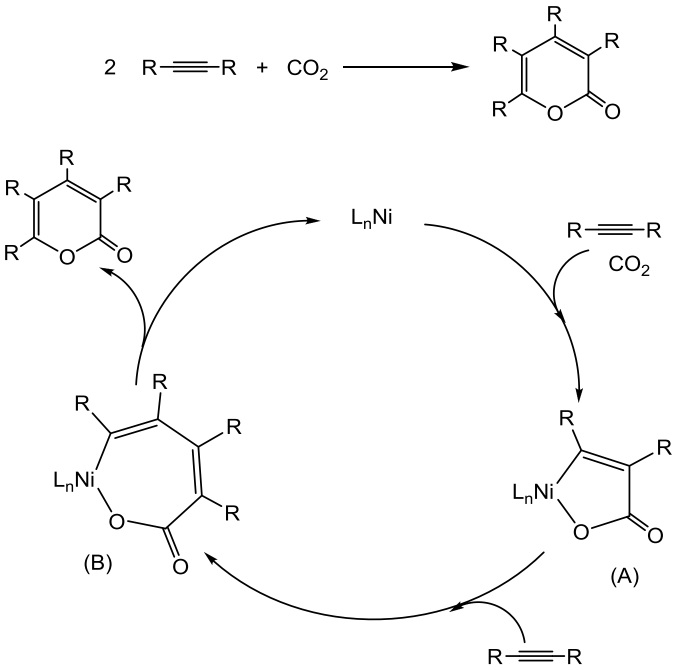
3.1.4 Synthesis of linear and cyclic esters from unsaturated hydrocarbons

Under suitable conditions, CO_2 and unsaturated organic substrates (alkynes, allenes, conjugated dienes and others) can be cooligomerized catalytically. These processes open new perspectives in the synthesis of industrially relevant classes of compounds, such as cyclic and linear esters, by direct reaction of CO_2 and unsaturated substrates. Nevertheless, so far, these transformations have not been widely developed and in most cases are still far from exploitation.

3.1.4.1 Catalytic cooligomerization of alkynes and CO_2.

The *cooligomerization of CO_2 with internal or terminal alkynes* affords 2-pyrones. This reaction is effectively promoted by phosphine-Ni(0) complexes as catalysts (Scheme 18) [108,186-189]. Ni(0)/NHC (NHC = N-heterocyclic carbene) systems have been also developed for the synthesis of pyrones from CO_2 and diynes under mild conditions (room temperature, 0.1 MPa CO_2 pressure) [190, 191]. 2-Pyrones are used in organic synthesis and medicinal chemistry as a building block for more complex chemical structures because they may participate in cycloaddition reactions to form bicyclic lactones. Moreover, 2-pyrone structure is found in numerous natural products isolated from plants, animals, marine organisms, bacteria, fungi, and insects that exhibit a broad range of biological activities, such as antifungal, antibiotic, cytotoxic, neurotoxic and phytotoxic. A variety of synthetic methodologies of 2-pyrones have been developed and have been recently reviewed [192].

Scheme 18 summarizes the generally accepted mechanism of the Ni-catalyzed formation of pyrone.The first step of the catalytic cycle is the formation of oxanickelacyclopentenone **A,** as already discussed. This intermediate can insert another alkyne molecule into the Ni-C(sp^2) bond to afford the oxanickelacycloheptadienone **B**, from which the pyrone product is liberated by reductive elimination. Dedicated studies have ruled out the hypothesis that pyrone formation might imply the preliminary coupling of two alkyne molecules to form a nickelacyclopentadiene complex, followed by CO_2 insertion into the Ni-C bond or [4+2] cycloadditon to a CO_2 molecule. On the contrary, nickelacyclopentadiene species are involved as intermediates only in the undesired side-reaction of alkyne cyclotrimerization. In this area Ni-based systems still continue to be among the most effective catalysts. Other metal catalysts (Co [193] and Rh [194] complexes) are less active and less selective because of collateral substrate cyclo-oligomerization. Heterogeneous catalysts have been explored only sparingly [195].

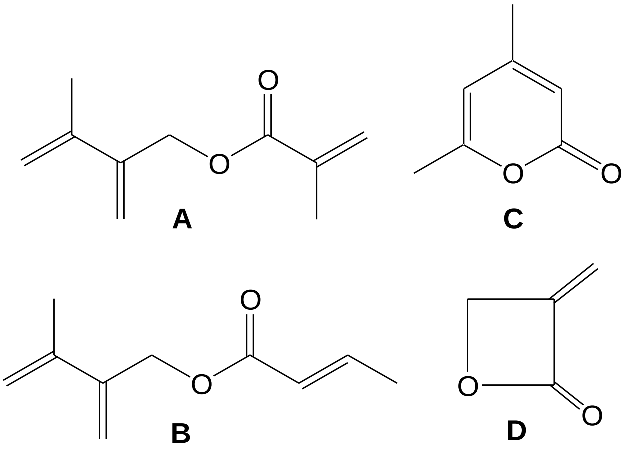


Scheme 18. Ni-catalyzed formation of 2-pyrones

3.1.4.2 Catalytic cooligomerization of allenes and CO_2

Also allenes, CO_2-like molecules, can be cooligomerized with CO_2 in the presence of transition metal (Pd, Rh, Ni) catalysts [196-200]. To date, this topic has received only moderate attention. Yields in carboxylated products are generally low to modest because of significant incidence of the undesired oligo- and polymerization of the substrate.

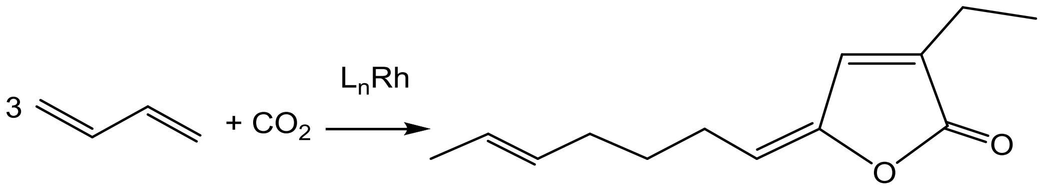
The reaction of allene with CO_2 in the presence of Pd [196] or Rh [197] catalysts yields linear and cyclic esters (A-C; Scheme 19). An unprecedented reaction has been observed by reacting allene with carbon dioxide in the presence of *trans*-$[RhCl(C_2H_4)P(i\text{-}Pr)_3]_2$ as catalyst and controlled amounts of H_2, used to repress the allene head-to-tail polymerization side-reaction [200]. In fact, under strictly controlled experimental conditions, $[RhCl(C_2H_4)P(i\text{-}Pr)_3]_2$ promoted, albeit in low yield, the formation of four-membered lactone 3-methylene-2-oxetanone (D, Scheme 19), which is the product of formal [2+2] addition of allene to CO_2 [201]. This product has never been observed when allene is reacted with CO_2 in absence of H_2. Such four membered systems are usually obtained by converting acrylates with singlet O_2 in the presence of PPh_3 as acceptor of unrequired oxygen [202]. The synthesis of the four membered lactone by direct reaction of allene and CO_2 is noteworthy and remains a unique evidence of coupling to afford the isomeric form of ketene.



Scheme 19. Carboxylated products from cooligomerization of allene with CO_2

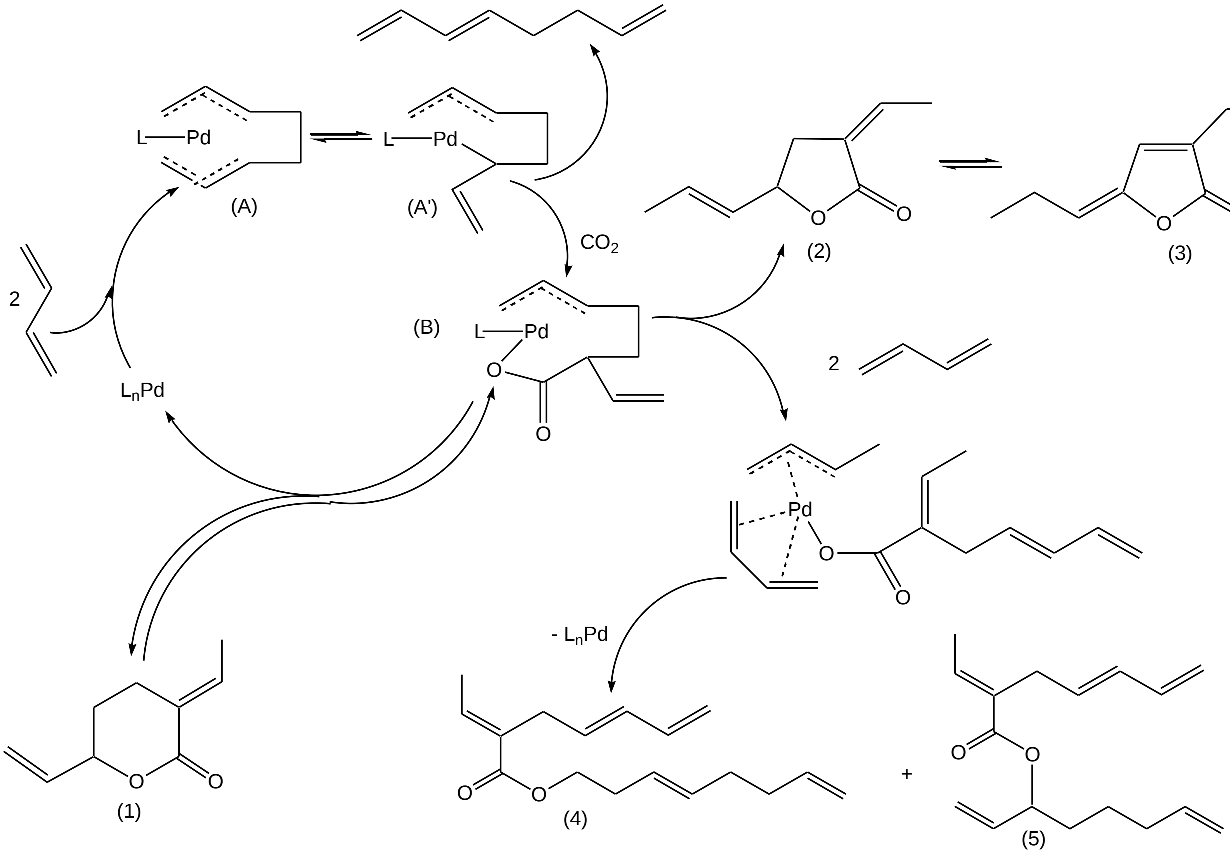
3.1.4.3 Catalytic cooligomerization of conjugated dienes and CO_2

Conjugated dienes can be cooligomerized with carbon dioxide in the presence of various transition metal (Pd, Ni, Ru, Rh) catalysts [110,203,204]. Most studies have concerned 1,3-butadiene as the reference substrate. The telomerization of 1,3-butadiene with CO_2 can afford a variety of carboxylated products in addition to products of substrate homocoupling. In the presence of Pd, Ru, Ni catalysts δ- and γ-lactones such as 2-ethylidene-6-heptene-5-olide, 2-ethylidene-5-heptene-4-olide and its conjugated isomer 2-ethyl-2,4-heptadiene-4-olide can be obtained together with smaller amounts of linear esters (Scheme 20). Carboxylic acids may also be found among the products, depending on the experimental conditions. The formation of these species requires, as a preliminary step, the coupling of two butadiene molecules before carboxylation occurs [110, 205]. However, Rh-catalysts promote, albeit with low yield (5-8%) and TON, the formation of γ-lactone 2-ethyl-2,4,9-undecatriene-4-olide in which three molecules of butadiene are coupled before CO_2 insertion occurs (eq. 44) [206,207].



(44)

Many efforts have been devoted to shed light on the conditions favoring the formation of δ-lactone 2-ethylidene-6-heptene-5-olide (Scheme 20) [110,207]. Interesting yields and selectivities to the δ-lactone have been obtained by using catalytic systems based on $Pd(acac)_2$ and phosphines with good σ-donor properties and bulky substituents, such as $P(i\text{-}Pr)_3$ or PCy_3. The presence of nitrile groups in the reaction medium (nitrile solvents) markedly facilitates the formation of the δ-lactone. Nitrile ligands may stabilize the catalytically active Pd(0)/phosphine system through the formation of a labile $Pd(NCR)_x(PR_3)_y$ complex that can more easily generate free coordination sites for the coordination of diene. Based on this "nitrile-effect", new hemi-labile phosphino-nitrile ligands, $R_2P(CH_2)_n\text{-}CN$, have been designed and prepared which increase the versatility of the catalytic system allowing to carry out the catalytic process in solvents other than nitriles or also in solvent-free conditions ("CO_2-expanded" butadiene, that ensures an easier recoverability of the products and a lower environmental impact of the process) [208].

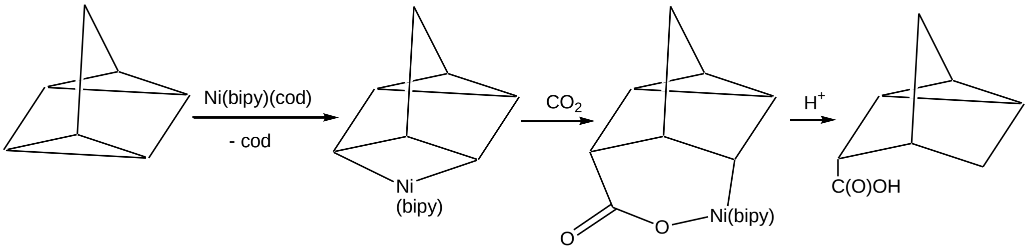


Scheme 20. Pd-catalyzed cooligomerization of butadiene with CO_2. The cycle applies also to less effective Ni and Ru-based catalysts.

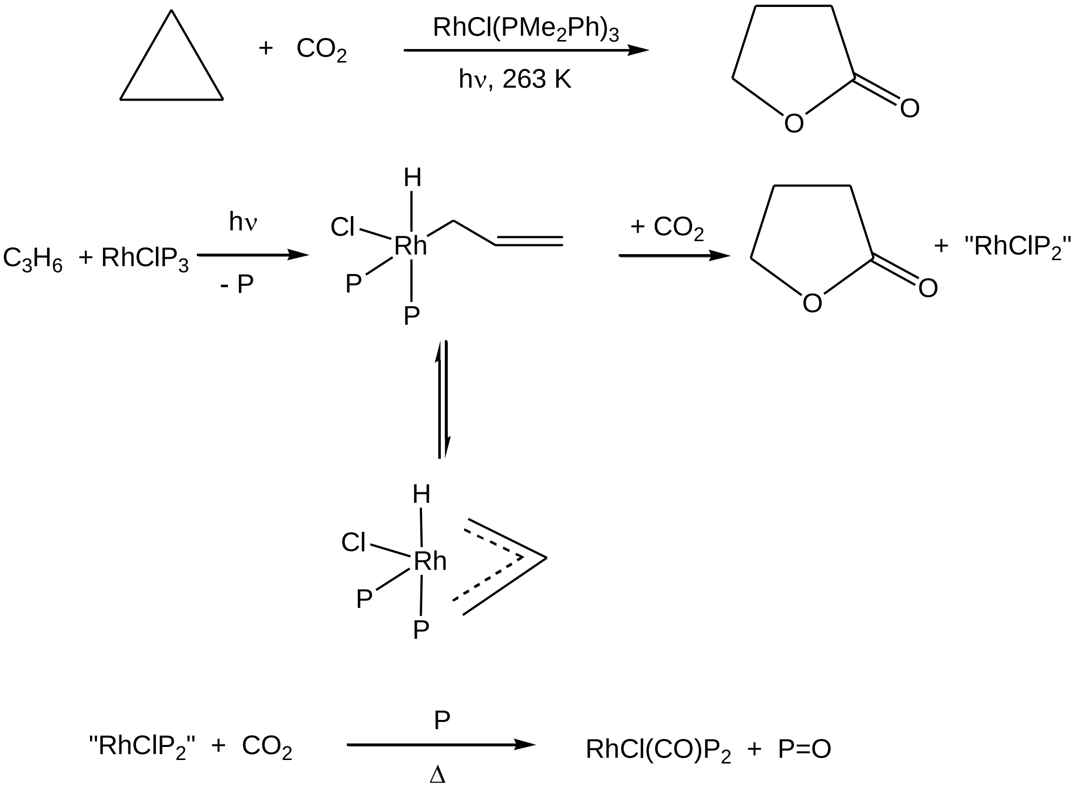
Organic carbonates have also been investigated as solvent alternative to acetonitrile [209]. Cyclic carbonates, such as ethene carbonate, propene carbonate, butene carbonate and glycerol carbonate, facilitate the formation of δ-lactone much more than linear carbonates, such as dimethyl- or diethyl carbonate, with selectivities depending on the structure of the carbonate. Strategies have been developed for catalyst recovery using 1,2,4-butanetriol or employing immobilized catalysts that show conversions and selectivities close the homogeneous systems [209-211]. To date, the synthesis of δ-lactone has been developed to miniplant scale [210]. The selectivity to the δ-lactone has been increased above 95% by recycling of by-products, reaching an overall butadiene conversion of 45%. Moreover, also solvent, unreacted starting materials, and catalyst can be recycled affording a stable process which is ready for industrial exploitation. The δ-lactone is a richly functionalized molecular system which may find practical utilization in numerous synthetic applications [212] of acids, alcohols or diols, aldehydes, amino acids or amines, esters, silanes and even polymers.

3.1.4.4 Carboxylation of strained rings: insertion into a C-C bond

Strained rings can be carboxylated in the presence of transition metal systems to give different products, which formally involve the insertion of CO_2 into a C-C bond. The reactivity depends on the size of the ring, the metal used and the reaction conditions. The carboxylation reaction proceeds stoichiometrically with Ni(0) systems [213,214], as illustrated, for instance, in Scheme 21 for the carboxylation of quadricyclane promoted by Ni(bpy)(cod) (bpy = 2,2'-bipyridine; cod = 1,4-cyclooctadiene). The 2-oxa-3-nickelacyclohexanone complex, which can be isolated, is too much stable to liberate the corresponding lactone in a subsequent reductive elimination step, and crystalline *endo*-nortricyclane-3-carboxylic acid can be obtained upon acid hydrolysis [214]. In these cases, 1 mol of metal is consumed per mol of carboxylated product formed, which is a serious drawback to the exploitation of the process. Other cyclic three-membered hydrocarbons less strained than quadricyclane, such as cyclopropane and norcarane, were not carboxylated in the presence of Ni(0).



Scheme 21. Ni(0)-promoted carboxylation of quadricyclane



Scheme 22. UV-Vis driven rhodium-catalyzed carboxylation of cyclopropane

Catalytic incorporation of CO_2 into a C-C bond of strained cyclic hydrocarbons, such as cyclopropane and methylenecyclopropanes, has been accomplished only in a few cases using Pd(0)- or Rh(I)-based catalysts [215-217]. Although TONs are still very low, these studies deserve attention as they open new perspectives in the direct synthesis of lactones and furanones a class of products, which find interesting applications in pharmaceutical, cosmetics, and foodstuff industry.

The Rh-promoted carboxylation of cyclopropane to γ-butyrolactone (Scheme 22) is a light-driven reaction [217]. Noteworthy, the lactone is not produced thermally, probably because the reduction of CO_2 to CO with phosphine oxidation is favored at higher temperatures. Formation of the carbonyl complex $RhCl(CO)(PMe_2Ph)_2$ corresponds to the deactivation of the catalyst.

3.1.5 Synthesis of carbamates

The interaction of CO_2 with amines, mediated or not by metal or non-metal species, affords the carbamate moiety,"$RR'NCO_2$", either ionic or covalently bound to an electrophilic center [34,35,218-222]. Direct interaction of CO_2 with primary or secondary amines affords carbamic acids or alkylammonium carbamates (eqq. 9 and 10) [34,35,37,38]. In the presence of metals, metal salts (eq. 45) [220,221] or metal-complexes (eq. 31), amines and CO_2 can afford metal carbamates [34,35]. Formally, metal or p-block carbamates can be obtained also by insertion of the heterocumulene in the M-N bond of metal- or p-block-amides [35,218,222] (eq. 28).

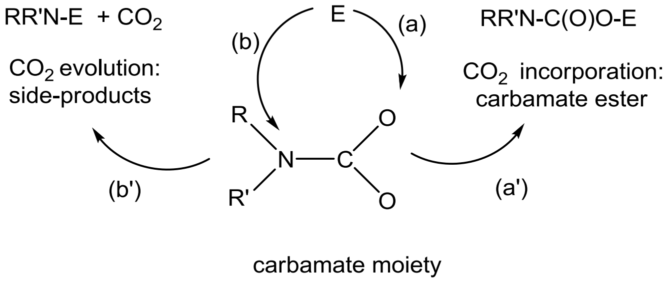
$$RR'NH + L + MBPh_4 + CO_2 \longrightarrow M(O_2CNRR') + [HL]BPh_4 \qquad (45)$$

R' = H, alkyl, L = RR'NH; R = aryl, R' = H, L = NR''_3 (R" = alkyl); M= Li, Na, K

Nowadays, this chemistry arouses great interest being relevant not only to chemical syntheses but also to several technological applications implying gaseous-CO_2 [34-36], being the process reversible. Amines (MEA, DEA, TEA, MDEA, etc) and polymer-bound amines are reusable "CO_2 scrubbers", used for removing carbon dioxide from industrial exhaust streams [36]. To this purpose, multiple amine-containing dendrimers [223] and ionic liquids [224] or MOF (Metal Organic Framework) incorporating $-NH_2$ groups in their structure are also under evaluation [225,226]. Organogels [227] and supramolecular polymers have also been prepared [228]. Computational studies have been carried out to evaluate the parameters of the reaction [229]. More recently, amine-CO_2 systems have been employed for molecular imprinting of polymers [230] and for preparing switching-polarity solvents [231].

The reaction of CO_2 with amines opens new perspectives to the utilization of CO_2 as a substitute of phosgene in organic synthesis. In fact, the carbamate moiety "$RR'NCO_2$", once generated (see above), can be transferred to a suitable organic substrate for the synthesis of carbamate esters or also used as precursor of ureas and/or isocyanates, providing an appealing eco-friendly alternative route to the conventional synthetic technologies based on phosgenation methods [34,219,232]. Carbamate esters find application in pharmacology as drugs or prodrugs [233] or as agrochemicals [234]. Organic carbamates also play a key role in synthetic chemistry as suitable intermediates and for protecting amino-groups [235], or as linkers in combinatorial chemistry [236], or as precursors of ureas, isocyanates and polymers [237-239].

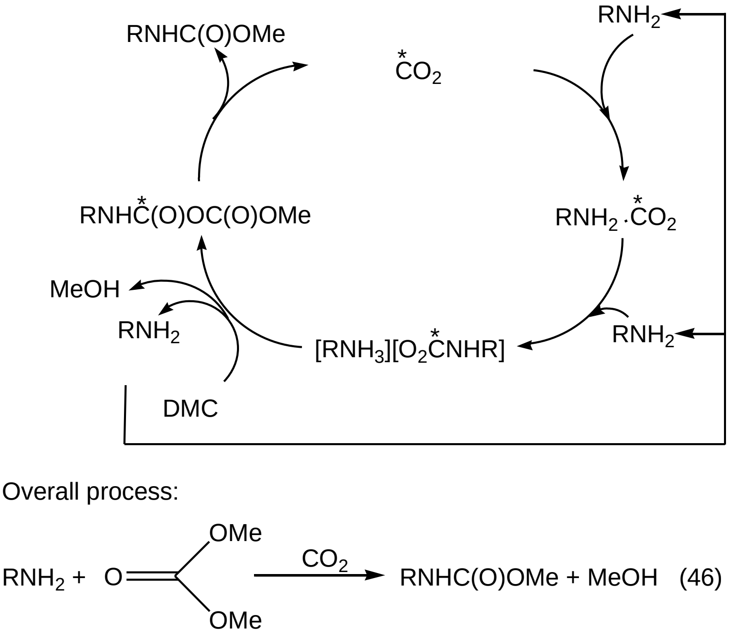
The development of CO_2-based routes to carbamates is not an easy task. Carbamate moiety "$RR'NCO_2$" is an example of ambident nucleophile, at the O- and N-atoms. Carbamation of an electrophile E (Scheme 23) requires the electrophilic attack by E to be addressed onto one of the O-atoms (Scheme 23; (a)). Electrophilic attack to the nitrogen atom (Scheme 23; (b)) causes elimination of CO_2 from the carbamic moiety and formation of undesired alkylated amines as side-products (Scheme 23; (b')).



Scheme 23. Reaction of carbamate group with an electrophile E

The transfer of carbamate anion from a metal ion, p-block element or an alkylammonium cation, to alkylating agents as alkyl halides or dialkyl sulphates has been achieved only in a few cases [34,35]. The reactivity of metal or ammonium carbamates can be addressed towards O-alkylation by enhancing the O-nucleophilicity of the anion through the use of a suitable complexing agent (crown-ether, cryptand) able to coordinate the countercation [240,241]. Carbamate esters have been synthesized, under mild conditions, from amine, CO_2 and alkylating agents also in the presence of sterically hindered strong bases, such as amidines, pentaalkylguanidines, phosphazenes [242,243,244]. Basic systems have also been studied [245,246]. The base can be generated even electrochemically by cathodic reduction of O_2 to superoxide in the presence of CO_2 [247]. The electrochemical activation of CO_2 to radical anion $CO_2^{\bullet -}$ in conventional solvents, or in ionic liquids, also promotes the formation of carbamate esters from aromatic or aliphatic amines and alkyl halides under mild conditions [248]. A variety of heterogeneous catalysts in the synthesis of urethanes from aliphatic and aromatic amines, CO_2, and alkyl halides have been explored only quite recently [249-252].

Dimethyl carbonate (DMC) has successfully been used for the selective synthesis of carbamate methyl esters by reaction with aliphatic primary amines and CO_2 [253-255]. Mechanistic studies have shown that DMC behaves as a methoxycarbonylating rather than as a methylating agent of the carbamate anion, which initially forms by direct reaction of amine and CO_2 (Scheme 24).



Scheme 24. Reaction of aliphatic primary amines and DMC in the presence of CO_2. Catalytic role of carbon dioxide.

Labelling experiments with $^{13}CO_2$ have allowed to demonstrate that the resulting mixed anhydride, RNHC(O)OC(O)OMe, converts into the carbamate product by releasing the $^{13}CO_2$ molecule originally fixed by the starting amine that is not incorporated in the final product. Therefore, CO_2 in this process acts as a catalyst of the methoxycarbonylation reaction of amine (eq. 46) [256,257,258]. With respect to the synthesis from amines, CO_2 and alkyl halides, the synthesis of carbamates from amines, CO_2 and alcohols (eq. 47) is not only a phosgene-free, but also a halogen-free process. Moreover, water forms as the only reaction co-product. These features make this route to carbamates very attractive from the point of view of environmental sustainability. Nevertheless, the studies in this field are still very few [259-264]. Also, reaction 47 requires a water tolerant catalyst in order to avoid deactivation. The use of suitable technique able to sequestrate the coproduced water may be a useful strategy to prolong the life of catalyst.

$$RNH_2 + CO_2 + R'OH \overset{\text{cat.}}{\leftrightarrows} RNHCO_2R' + H_2O \qquad (47)$$

Recently, the one pot synthesis of organic carbamates from amines, CO_2, and alcohols has been achieved with high yield, in the absence of dehydrating agents, using CeO_2 as a recyclable catalyst, even in the absence of any additive [262].

The reaction of CO_2 with 1,2–aminoalcohols is a transformation closely related to reaction (47) and provides a synthetic route to cyclic urethanes, such as oxazolidin-2-ones [265-269]. This reaction can take place even in the absence of any catalyst, but under severe conditions of temperature and CO_2 pressure [265]. Cyclic carbamates can be obtained also by incorporation of carbon dioxide molecule into the aziridine ring [270,271]. This reaction represents a valuable example of insertion reaction of the heterocumulene into a C-N bond. The cycloaddition reaction can be promoted by a variety of catalysts, such as alkali or tetraalkylammonium halides [272,273], Lewis acids [274,275,276], = (R)N···HX (X = N, O) hydrogen bond donors (for instance, polymer supported diol functionalised ionic liquids or amino acids) [277,278,279]. Other catalysts include 1,3-bis-(2,6-diisopropylphenyl)imidazol-2-ylidene (IPr) functionalized MCM-41 (MCM-41-IPr) [280], Pd(0)-complexes [281], or $Ni(Br)_2$(cyclam) under electrochemical conditions [282]. The use of sc-CO_2 [283] has also been explored.

The transfer of carbamate moiety to epoxides may provide a suitable entry into carbamic esters of 1,2-diols [284] or also oxazolidinones [285].

Electrophilic activation of alkynes towards nucleophilic adducts of CO_2 with amines allows the catalytic incorporation of the heterocumulene into enol carbamates [286]. The search of catalysts able to promote the carbamation process selectively relative to oligomerization of alkyne and with high stereoselectivity is a challenging task. Mononuclear Ru complexes have been shown to be effective catalysts for the activation of terminal alkynes towards ammonium *N*,*N*-dialkyl carbamates [287,288], even in sc-CO_2 [289].

The reaction of functionalized alkynes such as propargyl alcohols with carbon dioxide and secondary aliphatic amines opens the way to the one step synthesis of *O*-β-oxoalkyl-*N,N*-dialkyl carbamates (eq. 48). Reaction (48) can be actively promoted by Ru-complexes [293,291] (R^3 = H), lanthanide metal chlorides [292] (R^3 = H), iron-carbonyls [293] (R^3 = H), cationic copper(I) [294] (R^3 = H), AgO_2CCH_3/DBU (R^3 = alkyl) [295] and can occur effectively in sc-CO_2 even without any catalyst [296].

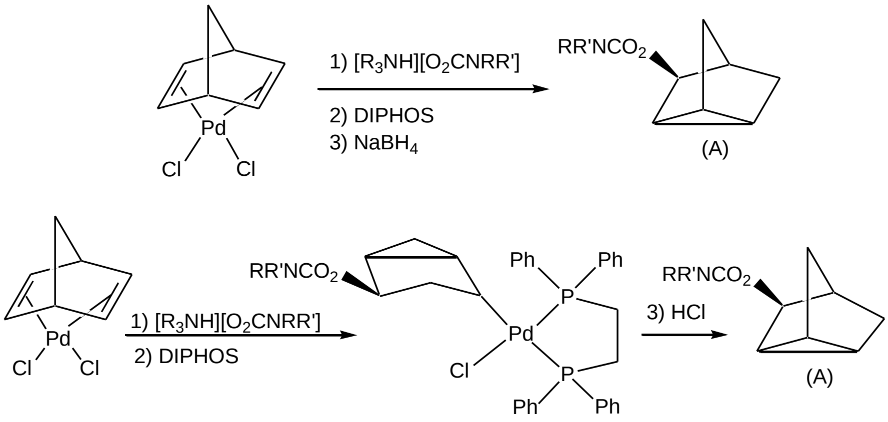
$$R_2NH + CO_2 + R^3C{\equiv}C\text{-}C(R^1)(R^2)OH \rightarrow R_2NCO_2C(R^1)(R^2)C(O)CH_2R^3 \qquad (48)$$

Primary amines react with propargylic alcohols and CO_2 in a different way to give cyclic carbamates, as oxazolidin-2-ones. The process can be catalyzed by Cu(I) derivatives [297-299] or by a tertiary phosphine such as tri-*n*-butylphosphine [300], or by silver salts [301]. Cyclic carbamates such as 5-methylene-2-oxazolidinones can be obtained also by reaction of propargylamines with CO_2 under metal (Cu [297], Ru [302], Pd [303], Ag [304,305]), PIL (protic ionic liquid) [306] or base catalysis[307,308]. In sc-CO_2’ 5-methylene-1,3-oxazolidin-2-ones have been prepared in good yields from *N*-alkylprop-2-ynylamines and carbon dioxide even in the absence of any metal or base catalyst [309]. An efficient solvent free synthesis of oxazolidin-2-ones via the cycloaddition of cheaper terminal alkynes, primary amines, and CO_2 has been recently achieved under the catalysis of copper (I) iodide [310].

Carbamation of alkenes provides an appealing 100% atom economical route to carbamic esters. Nevertheless, this reaction has received very little attention. The transfer of carbamate moiety to the C=C bond of olefins has been documented only in very few cases, using activated unsaturated substrates, such as ethyl vinyl ethers (eq. 49) [311], allylamines (to give oxazolidin-2-ones) [312], or allenylamines [313], or a few diolefins in the presence of a suitable metal center (Pd) able to activate the unsaturated substrate through coordination (Scheme 25) [314].

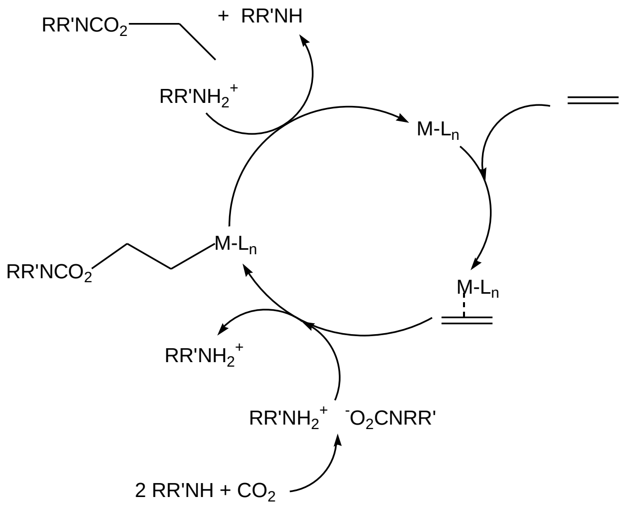
$$R_2NH + CO_2 + CH_2{=}CHOEt \rightarrow R_2NCO_2CH(CH_3)OEt \qquad (49)$$

In the latter case, however, the carbamate ester is obtained stoichiometrically relative to Pd and was liberated from the metal after a final quenching step involving reductive cleavage with $NaBH_4$ or H_2 or also protonolysis with anhydrous HCl, as observed for (DIPHOS)Pd(Cl)(nortricyclo urethane) (Scheme 25).



Scheme 25. Metal-assisted carbamation of olefins.

The latter result indicates that the Pd-C bond in (DIPHOS)Pd(Cl)(nortricyclo urethane) is too strong for protonolysis by ammonium ion, but its cleavage can be more easily accomplished by a stronger acid such as HCl. The body of these findings deserves attention as they suggest the possibility that, with a proper choice of the metal-ligand environment, carbamation of olefin may be carried out catalytically, as illustrated in Scheme 26.



Scheme 26. Metal-catalyzed carbamation of olefins: a potential catalytic pathway.

3.1.6 Synthesis of isocyanates

Isocyanates, RNCO, are industrially relevant compounds, which find application in several fields [315,316,317]. Many isocyanates are starting materials for the manufacture of plant protection agents, pesticides, dyes, resins and plastics, textile waterproofing agents, detergents, bleaches and adhesives. They are also widely used in surface coatings such as paints, sealants and finishes, and in the manufacture of rubbery plastics such as those used to coat wires. Traditionally, diisocyanates are the primary feedstock for the production of polyurethanes. The global market for diisocyanates in year 2000 was 4.4 Mt, of which 61.3% was methylene diphenyl diisocyanate (MDI), 34.1% toluene diisocyanate (TDI), 3.4% the total for hexamethylene diisocyanate (HDI) and isophorone diisocyanate (IPDI), and 1.2% was the total for various others. Currently, the global isocyanate capacity amounts to 8.8 Mt and is scheduled to increase by more than 3 Mt until 2020. The market is in expansion by, on average, 4.5% per year [318]. The isocyanates market value will grow to $38729 million by 2019, at a significant CAGR from 2014 to 2019 [319]. Isocyanates may be prepared via a number of routes, but, to date, only amine phosgenation is practiced on a significant industrial scale [320].

The direct synthesis of isocyanates from carbon dioxide is a challenging task. Building up of isocyanate group from CO_2 requires the de-oxygenation of the heterocumulene [35,321]. The reaction with isonitriles (eq. 50), in which carbon dioxide acts as an oxidant of the organic substrate, represents an interesting approach which, however, is limited by the availability of the substrate and the low TON observed so far [322,323].

$$RNC + CO_2 \rightarrow RNCO + CO \qquad (50)$$

Direct synthesis from amines and CO_2 (eq. 51a) is, in principle, a more appealing and versatile route to isocyanates, if suitable methods are developed to drive this thermodynamically not favoured reaction to the right [324].

$$RNH_2 + CO_2 \rightleftarrows RNCO + H_2O \qquad (51a)$$
$$RNH\text{-}CO_2R' \longrightarrow RNCO + R'OH \qquad (51b)$$

Researchers at Monsanto have studied in depth this process using as coreagent a tertiary organic co-base (guanidines, phosphazene, triethylamine) in the presence of dehydrating agents ($POCl_3$, PCl_3, P_4O_{10}, SO_3, $SOCl_2$) [325]. In general, the reaction proceeds fast, with high yield, under mild conditions. However, the use of large amounts of co-base and the production of large quantities of waste makes the exploitation of this process on a large industrial scale difficult.

A clean route to isocyanates is the thermal treatment of primary amines carbamates (eq. 51b) produced from amines and CO_2. Such route already finds some industrial exploitation when $R'=CH_3$.

3.1.7 Synthesis of ureas

Interest for ureas derives from their application in a wide variety of fields, as pharmaceuticals, petrochemicals and agrochemicals [238,239]. Ureas are used as dyes for cellulose fibre, antioxidants in gasoline, corrosion inhibitors, plant growth regulators, agroprotectives (pesticides and insecticides), tranquillizing and anticonvulsant agents. Unsymmetric ureidic group characterizes several biologically active compounds, with activity as inhibitors of HIV-1 protease or p38 kinase. Ureas are also useful intermediates for the production of carbamates [326].

While the industrial synthesis of urea $(NH_2)_2CO$ is based on the reaction of ammonia with CO_2 by dehydration of intermediate ammonium carbamate [324], the conventional way to the synthesis of symmetrically N,N'-substituted ureas is based on the reaction of amines with phosgene [320,327]. The latter approach is less efficient for the synthesis of unsymmetrical ureas because of important side formation of symmetrical ureas. Addition of amines to isocyanates provides the main route to the synthesis of unsymmetrical substituted ureas. In the last few years, harmful phosgene and isocyanates have been increasingly replaced with safer phosgene equivalents, such as triphosgene, activated carbonates, carbonyldiimidazole, carbamoyl chlorides, chloroformates or also carbamates [320]. However, most of them are still usually prepared from $COCl_2$.

The utilization of CO_2 in the synthesis of substituted ureas is an intriguing alternative to classical phosgenation methods [34,328], also if the attempts made so far have poor applicative interest.

The reaction of amines with carbon dioxide provides a direct synthetic approach to ureas (eq. 52). This reaction is a reversible process [329], which implies elimination of water (eq. 52). Exploitation of reaction 52, without using auxiliary reagents (such as condensating reagents), would have a great practical significance.

$$2\ RR'NH + CO_2 \rightleftharpoons (RR'N)_2CO + H_2O \qquad (52)$$

Very few catalytic systems have been explored so far. Interesting results, mostly limited to the synthesis of symmetric or cyclic ureas, have been obtained using $RuCl_3{\bullet}H_2O/Bu_3P$ [330], base catalysts (CsOH/BMImCl[331]; [BMIm]OH [332]; CsOH, CsF, Cs_2CO_3 [329]), KOH/ PEG1000 [333], MCM-41 and HMS-type mesoporous silica [334], polymer supported nanogold particles [335] and, more recently, Mg-Al LDHs (Mg-Al layered double hydroxides) [336] and CeO_2 [337].

3.1.8 Synthesis of acyclic carbonates

Molecular acyclic (Fig. 13a) and cyclic (Fig. 13b) organic carbonates will experience a great expansion of their market during coming years, due to their use in the chemical- (as solvent and reagent [338]), pharmaceutical [339] and polymer-industry [340] (Fig. 14).

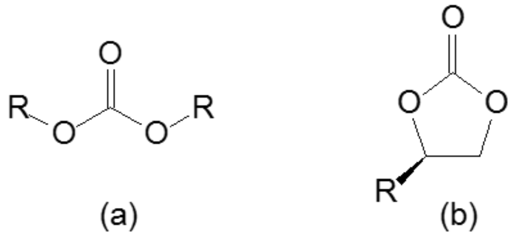


Figure 13. Linear (a) and cyclic (b) molecular organic carbonates

Also, the lower members of the acyclic carbonate family, namely dimethyl-carbonate (DMC), diethylcarbonate (DEC) or dibutylcarbonate (DBC) have been evaluated as components of gasoline [341], to which they can be added up to 5-10 %, depending on their O-content. It is, thus, foreseeable that their free market (most of the DMC produced nowadays is for captive use in the industry of polycarbonates: only *ca*. 10% reaches the free market) may grow of more than two orders of magnitude from actual 0.1 Mt/y.

The direct carboxylation of alcohols (eq. 53) and the reaction of alcohols with urea (used as an active form of CO_2) (eq. 54) represent appealing alternatives to the use of phosgene or to more recent synthetic methodologies based on the oxidative carbonylation of alcohols, mainly confined to methanol, or on the use of less conventional techniques (high speed ball milling, HSBM) [342]. Of the syntheses based on CO_2, the former (eq. 53) has some kinetic and thermodynamic barriers, the latter rises the issues relevant to NH_3 recovery and product separation.

$$2ROH + CO_2 \rightarrow (RO)_2CO + H_2O \tag{53}$$

$$R = Me, Et, Allyl$$

$$2ROH + H_2NCONH_2 \rightarrow (RO)_2CO + 2NH_3 \tag{54}$$

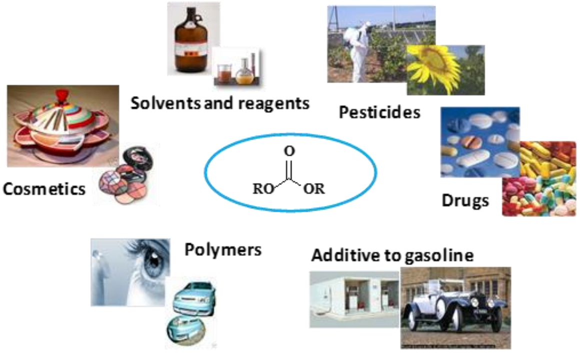


Figure 14a. Uses of dialkylcarbonates

Figure 14b. Uses of cyclic carbonates

Eq. 53 formally implies the following elementary reactions:

- i. breaking of two O-H bonds in two alcohol molecules
- ii. formation of two O-H bonds in water
- iii. breaking of two C-O bonds in CO_2
- iv. formation of two CO bonds in the carbonate.

The ΔH change is shown in eq. 55 where the affected bonds are in italics:

$$\Delta H_r = [2\Delta H_f(O\mathit{C}\text{-}\mathit{O}R) + 2\Delta H_f(\mathit{H}\text{-}\mathit{O})] - [2\Delta H_d(R\mathit{O}\text{-}\mathit{H}) + \Delta H_d(\mathit{C}{=}\mathit{O})] \tag{55}$$

A enthalpy change close to zero can be foreseen for most aliphatic alcohols, or positive for aromatic derivatives, such as phenols. The O-H energy in alcohols and the O-R energy in the resulting carbonates will thus influence the enthalpy of the reaction, while the entropic content is mainly driven by CO_2, which goes from the gas phase into a liquid or solid product.

As a result of the unfavorable thermodynamics (Table 3), the equilibrium concentration of the formed carbonate is quite low, often around 1% or even less, depending on the reaction temperature that usually is in the range 400-450 K for the metal-catalyzed reaction, or as lower as 335 K for peculiar systems (*vide infra*).

Table 3. $\Delta H°$ and $\Delta G°$ for the synthesis of organic carbonates from alcohols and CO_2 [343].

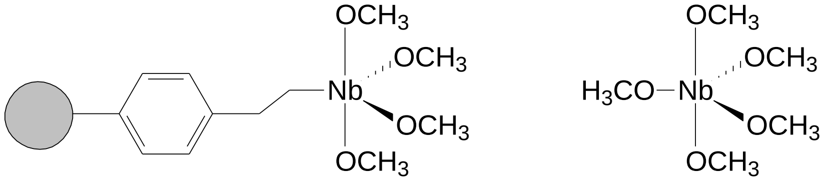
R Group	**ΔH at 298 K kcal mol^{-1}**	**ΔG° at 298 K kcal mol^{-1}**
CH_3	**- 4.0**	**6.0**
C_2H_5	**- 3.8**	**6.2**
CH_2=CH-CH_2	**- 3.9**	**6.1**
C_6H_5	**12.1**	**22.1**

In the direct carboxylation, alcohols undergo, *a priori*, two distinct elementary reactions, as categorized in Scheme 27. In *(i)* an alcohol molecule is converted by a *base* into an alkoxo-moiety that interacts *(ii)* with CO_2, affording the hemi-carbonate, RO-C(O)O^-. A second molecule of alcohol is activated by an acid *(iii)* and produces the alkyl cation moiety that reacts with the hemi-carbonate (*iv*) and generates the dialkylcarbonate.

$$\mathrm{ROH + base \rightarrow RO^- + base\text{-}H^+} \qquad \text{(i)}$$
$$\mathrm{RO^- + CO_2 \rightarrow RO\text{-}CO_2^-} \qquad \text{(ii)}$$
$$\mathrm{ROH + acid \rightarrow R^+ + acidOH^-} \qquad \text{(iii)}$$
$$\mathrm{RO\text{-}CO_2^- + R^+ \rightarrow (RO)_2CO} \qquad \text{(iv)}$$
$$\mathrm{Base\text{-}H^+ + acid\text{-}OH^- \rightarrow base + acid + H_2O} \qquad \text{(v)}$$

Scheme 27. Putative reaction path for the carboxylation of alcohols

Homogeneous [343-347], immobilized [348-351] (Fig. 15), heterogeneous catalysts [352-357] and organic catalysts [358] have been used to drive eq. 53. Each class presents its own *pros* and *cons*. Immobilized catalysts are more easily recoverable than the parent homogeneous compounds, but the choice of the support requires attention. In Fig. 15 the Nb active center is bonded to the polymeric matrix through a C2-tether: its direct link to the aromatic ring would deactivate the catalyst.



1 2

Figure 15. Structural analogies between the heterogenized Nb catalyst supported on a polymeric matrix and its free form.

The reaction mechanism [359] has been studied for a few homogeneous catalysts and shown to be dependent on the metal used. Route A in Fig. 16 is followed by Nb-complexes, for which the pathway depicted in Scheme 27 holds, while Sn-complexes follow an intramolecular Me-transfer (Fig. 16, middle route) not found for Nb.

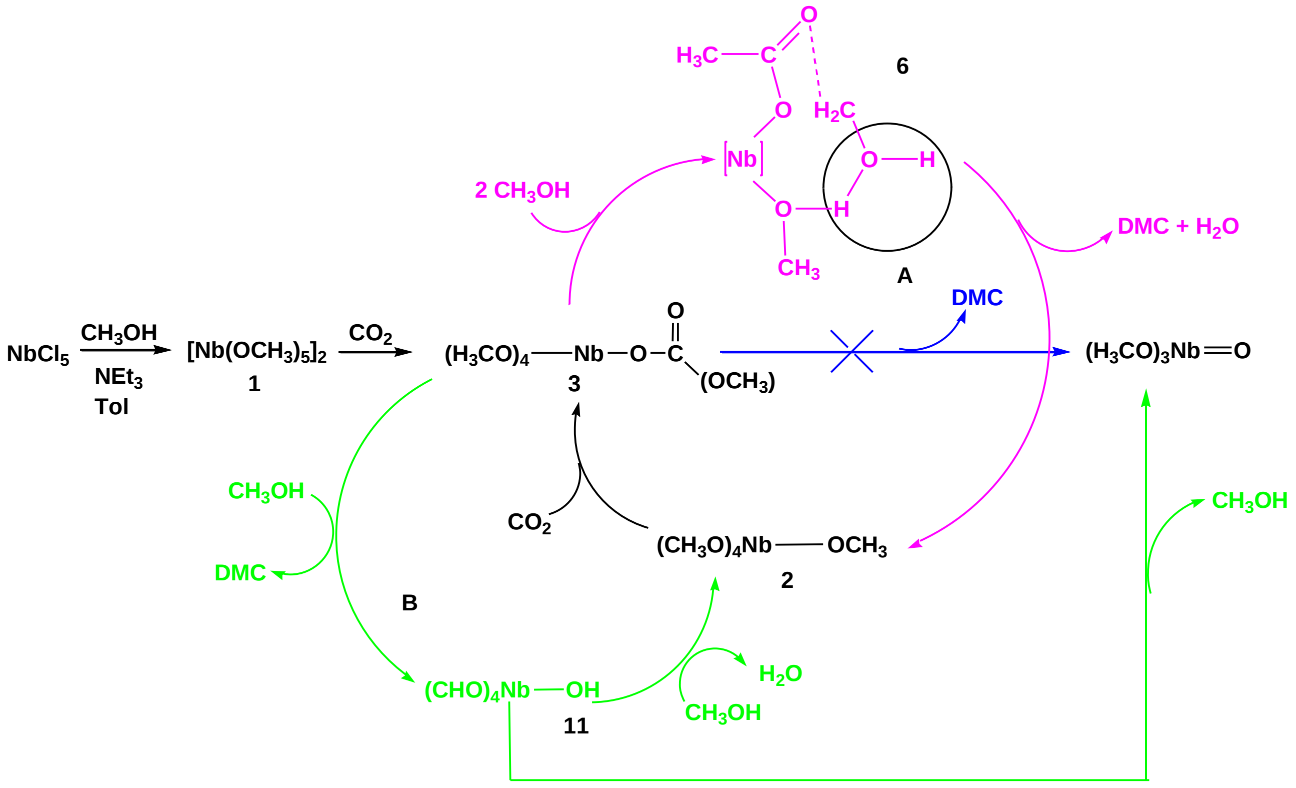


Figure 16. Putative reaction pathways for the carboxylation of methanol on Nb. The upper route is active.

Interestingly, the key step in the formation of DMC with Nb is the reaction of the hemicarbonate moiety with two moles of methanol (Fig. 16, upper part) that allows the formation of water to take part out of the inner co-ordination sphere of the metal. In this way the active monomeric form of the catalyst is reformed. Conversely, $nBu_2Sn[OR](OC(O)OR]$ undergoes intramolecular Me-transfer with formation of $[nBu_2Sn{=}O]_n$ that needs re-activation [360-363].

Water removal for shifting equilibrium 53 to right and preserving the catalyst has been attempted using both chemical and physical means. Chemical traps are easily hydratable organic species (acetals [364], ketals [365], cyanides [366] and imides) or inorganic materials (zeolite-based materials). Zeolites need to be used at low temperature (e.g., 240 K) [367] otherwise their acidic surface may decompose the carbonates at the reaction temperature of >400 K. This makes their use energetically questionable, as the temperature swing (>400 K → 240 K → >400 K) requires energy not always (completely) recoverable and usable.

Moreover, zeolites need to be dehydrated with energy consumption and possible loss of materials. Organic water traps have the advantage that can be used at the same temperature of the reaction and, as their hydration is exergonic by *ca*. -35 kcal/mol, the overall reaction ΔG is negative, allowing the reaction of carboxylation of alcohols to occur at lower temperature with respect to the metal catalyzed reaction (even room temperature) and with much better yields. On the other hand, organic water traps suffer several drawbacks, such as: *i.* they are used in excess with respect to

alcohol, *ii.* themselves and their hydrated forms are soluble in the reaction medium that increases the post-reaction separation processing with energy loss, *iii.* they need to be recovered from the reaction mixture and regenerated for re-use, otherwise their stoichiometric use would make the entire process economically non acceptable and the E-factor of the process would be very high.
Carbodiimides, e.g., CyN=C=NCy, have been used as water traps [368], but later on [358] their role

$$\mathrm{CyHNC(OCH_3){=}NCy} + \mathrm{HOCH_3} \rightarrow \mathrm{CyHNC^{+}(OCH_3)\text{-}NHCy}\ {}^{-}\mathrm{OC(O)OCH_3} \quad (56a)$$

$$\mathrm{CyHNC^{+}(OCH_3)\text{-}NHCy}\ {}^{-}\mathrm{OC(O)OCH_3} \rightarrow \mathrm{CyHNC(O)NHCy} + \mathrm{(CH_3O)_2CO} \quad (56b)$$

$$\mathrm{CyN{=}C{=}NCy} + 2\ \mathrm{CH_3OH} + \mathrm{CO_2} \rightarrow \mathrm{CyHNC(O)NHCy} + \mathrm{(CH_3O)_2CO} \quad (57)$$

as organic catalysts (Eq. 56, 57) was ascertained and their ability to carboxylate methanol and other alcohols at 335 K described. Their peculiarity is that their hydrated form (i.e., the urea RHNC(O)NHR, DCU) is insoluble in the reaction medium and can easily be recovered. Interestingly, the conversion of DCU into DCC has been achieved [369,370].
In order to avoid the complexity of chemical traps, a pervaporation membranȩ (Fig. 17) technology has been developed [357] for water removal, that is quite simple and avoids post-reaction complex operations. The unfavorable thermodynamics of the direct carboxylation of alcohols has pushed to find alternative routes, based on CO_2, for the conversion of alcohols into the relevant carbonates. Urea, formed from CO_2 and NH_3, can be considered an active form of CO_2 (Fig. 1).

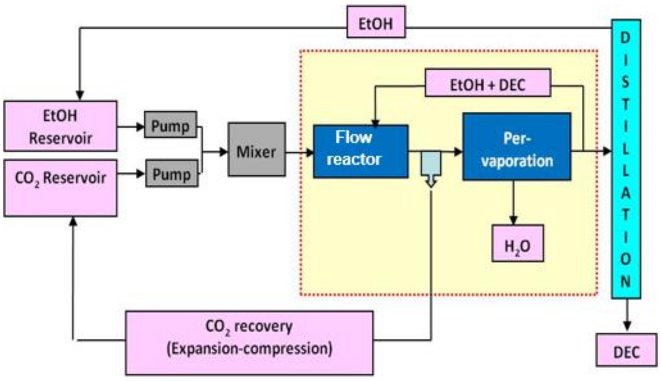
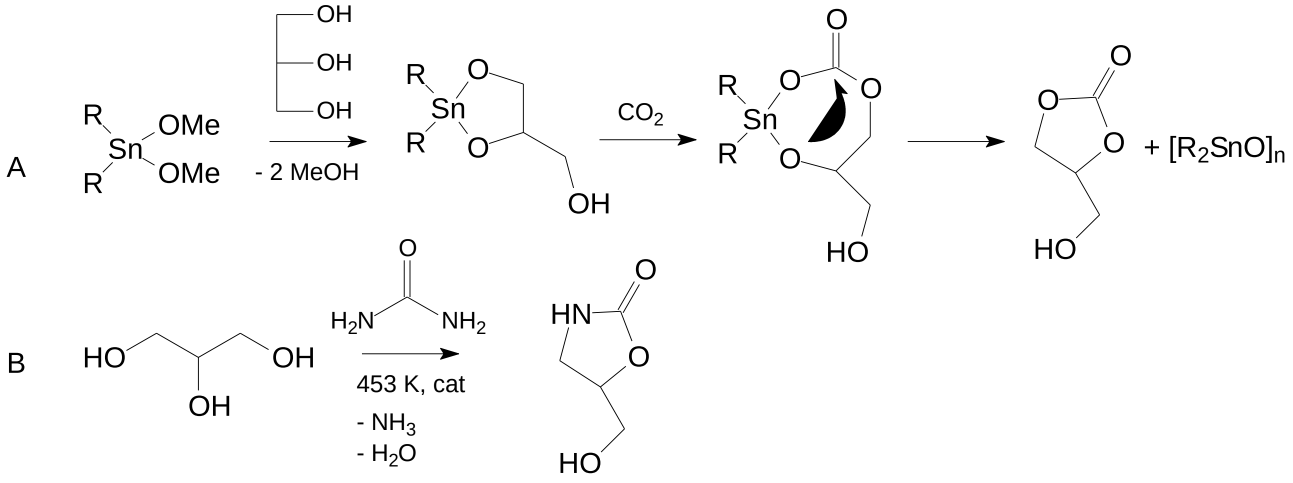


Figure 17. Laboratory scale mini-plant for water elimination using pervaporation membranes

Its formation ΔG is some 200 kJ/mol less negative than that of CO_2. However, the reaction of urea with alcohols would have a better thermodynamics than the reaction of CO_2 and, consequently, the equilibrium position should be shifted towards right, reaching higher conversion at the equilibrium. As a matter of fact, urea has been used in several applications bringing the synthesis of carbonates from alcohols to the demo-plant level. The reaction mechanism has been studied by several authors [371-373]. Further studies are still in progress for better understanding the potential of such methodology that requires the recovery of ammonia for reaching an economic acceptation [374]. The separation of the reaction mixture remains a key issue. This field has made progress in the last decade and fundamental knowledge has been acquired by combination of experimental and theoretical (DFT) studies. Nevertheless further research is necessary for the up-scale of processes to the industrial application.

3.1.9 Synthesis of cyclic carbonates

The direct carboxylation of diols and polyols has been attempted using a variety of synthetic techniques since long time with alternate success. Organic bases (15.3% conversion yield, 100 % selectivity. Catalyst: TBD, 1,5,7-triazabicyclo[4.4.0dec-5-ene]) in presence of ammonium carbonate and acetonitrile as water trap [375], and electrogenerated heterocyclic carbenes [376] have shown interesting properties. Also in this case, there are thermodynamic restrictions and water traps have been used to shift the equilibrium. Recently, CeO$_2$ has been used for the direct carboxylation of propanediol to afford propenecarbonate with yields >60% in presence of 2-CN-pyridine as water scavenger [377]. Glycerol (Scheme 28A) has also been carboxylated with 5.8% conversion yield at the equilibrium [378], close to the thermodynamic value 6% [379].



Scheme 28. A) Glycerol carboxylation; B) glycerolysis of urea

Also in this case the use of urea as CO$_2$ substitute has much improved the syntheses (Scheme 28B), reaching high conversion (over 93 %) with excellent selectivity (100 %) [380]. The reaction is very temperature sensitive: working above 408 K (Scheme 27B) causes urea decomposition with decrease of selectivity and formation of N-containing cycles such as oxazolidinones, which are cyclic carbamates and monomers for polymers. The mechanism has been fully elucidated [381].

Cyclic ethers are substrates of great interest for the synthesis of cyclic monomeric carbonates or even as co-monomers for the production of polymers through the ring-opening carboxylative polymerization. Their reactivity is driven by different parameters, such as:

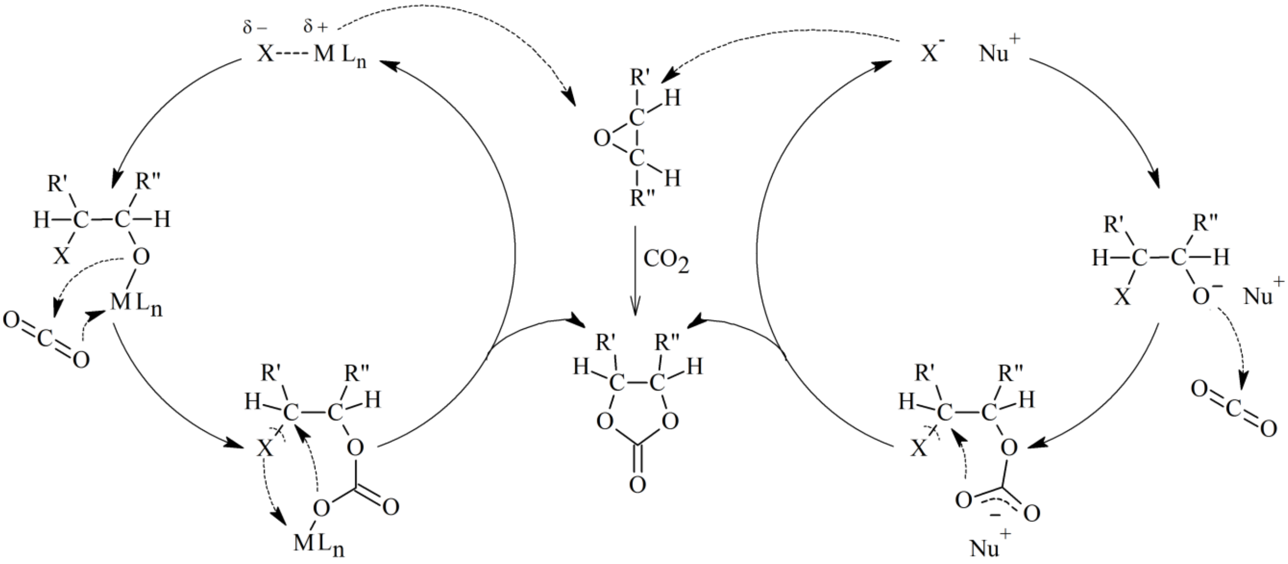
i) the ring size and the ring stress-energy: three-, four-, five-, six-membered ethers will have a quite different reactivity;

ii) the substituents on the ring: groups which may produce a different charge localization on O or ethereal Cs have an influence on the rate of opening of the ring;

iii) the ring backbone: an ethereal ring on a linear alkyl chain (e.g., propeneoxide) will have a different reactivity than the same size ring on a alicyclic structure (e.g., cyclohexeneoxide).

This field has been recently reviewed and the role and peculiarities of a large variety of catalysts described in the several papers cited [382,8]. The reaction mechanism has been studied and the pathways depicted in Scheme 29 are commonly accepted. The opening of the ring is promoted by either nucleophiles or electrophiles. This makes the reaction very sensitive to the medium in which it takes place. Adventitious species may deeply influence the reaction, making difficult the rationalization of the experimental data.

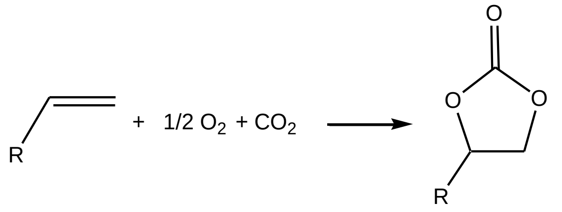
Optically active epoxides have been carboxylated with total retention of configuration [383,384] using heterogeneous catalysts, while racemic mixtures of epoxide show a moderate *ee* upon carboxylation, due to the low stability of the homogeneous catalysts (deanchoring of the optically active ligand) under the reaction conditions [383].



Scheme 29. Accepted mechanistic pathways for the synthesis of cyclic carbonates.

The limiting factors in such chemistry are: *i*) the production of epoxides, and *ii*) the availability of a large variety of structural motifs. The use of H_2O_2 represents the cleaner route to epoxides. The cost and the amount available on the market (ca. 600 kt/y) do not match well the parameters of commodity chemicals such as the carbonates: low cost and market of several Mt/y). Therefore, major improvements are necessary in this field concerning: i) the use of cheap oxidants (air, O_2) for the production of epoxides; ii) the availability of a larger number of structural motifs. Further mechanistic studies are necessary as the gained knowledge is still incomplete and does not allow to design the “perfect” catalyst.

The oxidative carboxylation of olefins appears to be an interesting approach to the synthesis of cyclic carbonates from cheap and easily available reagents such as olefins, non-O_2-free CO_2 and air (eq. 58). The reaction can be carried under homogeneous and heterogeneous catalysis. The latter assures a longer life of the catalysts.



(58)

The direct oxidative carboxylation of olefins [383,385,386] couples two processes, namely: i) the epoxidation of the olefins and ii) the carbonation of the epoxide, occurring in the same reactor. Moreover, the problem of water is eliminated as it is not formed in the system. Interestingly, it has been shown that CO_2 modulates the oxidant properties of O_2 [387]. Drawback in such process is the radical chemistry that may be induced by metals in presence of O_2. O_2 may attack the olefin with subsequent cleavage of the double bond, producing by-products and low selectivity. The best selectivity reached is 50% with respect to the olefin. An attempt has been done in decoupling the O-transfer to the olefin from O_2. Metal oxides have been used as O-transfer agents, which where subsequently re-oxidized with O_2 in absence of olefin [388-390]. Such approach avoids the radical reaction, but introduces another hurdle: depending on the mode of preparation of the metal oxide the epoxidation may be highly selective or a combustion of the olefin is observed.

4.0 CO_2 as source of C for energy products

4.1 Thermal chemical processes

In recent years, significant efforts have been made towards the utilization of CO_2 in high temperature catalyzed reactions, such as dry reforming of methane (MDR), oxidative coupling of methane (MOC), dehydrogenation of hydrocarbons (DH), in addition to the conversion of CO_2 into oxygen containing fuels such as CH_3OH and CH_3OCH_3 (DME) [382]. Transformation of CO_2 into hydrogen containing chemicals, typically requires hydrogen or electroreductive processes implying e^- and H^+ transfer [391-394]. The use of CO_2 as oxidant in selective processes as well as C-source in the synthesis of methanol or other energy rich species such as dimethylether are key reactions [395] that may substantially contribute to the conversions of large volumes of CO_2 with significant greenhouse gases (GHG) mitigation, besides having an economic value.

4.1.1 Synthesis of methanol, dimethylether and higher alcohols

Methanol is a common feedstock considered as a building block in the chemical industry due to its versatility in the synthesis of several important chemicals such as chloromethane, acetic acid, methyl *tert*-butyl ether (MTBE), alkyl halides and formaldehyde [4,396,397]. Methanol can be converted into dimethyl ether (DME) that is attracting a lot of attention as it can be used in fuel cells and diesel engines [398]. In addition, methanol is used for the production of higher hydrocarbons (through the *methanol-to-gasoline route*) or of unsaturated hydrocarbons (through the *methanol to olefins*-MTO or *methanol to propene*-MTP routes).

Even though hydrogenation of CO_2 to methanol has favorable thermodynamics, high activation energy barriers must be overcome and this requires the use of appropriate catalysts. Formation of other by-products during the CO_2 hydrogenation, such as CO, hydrocarbons and higher alcohols [393] requires highly selective heterogeneous catalysts with the important function of improving the process sustainability or tunable catalysts which can address the production of higher alcohols as an alternative. The reaction for methanol production *via* CO_2 hydrogenation is shown in eq. 59:

$$CO_2 + 3H_2 \rightarrow CH_3OH + H_2O \qquad \Delta H^\circ_{298K} = -49.5\ kJ.\ mol^{-1} \qquad (59)$$

Thermodynamically, a decrease of the reaction temperature or an increase of the reaction pressure can favour the synthesis of methanol. A reaction temperature higher than 513 K facilitates the CO_2 activation and, consequently, the methanol formation [393,394,399].

Despite the numerous theories on the mechanistic pathways for the methanol synthesis, and the extensive investigation, there is still uncertainty on the definition of the role of Cu°, Cu^+, Cu-Zn alloy and the carrier sites [400]. In the past, it has been assumed that CO hydrogenation is the main pathway for methanol synthesis. However, isotopic labelling experiments conducted by Chinchen *et al*. [401] have revealed that methanol is formed directly from CO_2, whilst CO scavenges the oxygen atoms which hinder the active metal sites [402,403].

According to earlier proposed mechanisms, formate hydrogenation on Cu/ZnO catalysts is the rate-determining steps (eq. 61). This was based on data reported by Fujitani *et al.* [404] who found that the formate coverage on Cu/ZnO catalysts is proportional to the turn over frequency for methanol formation. The proposed reaction pathway is shown in Eq. 60-62.

$CO_2 + ½ H_2 \leftrightarrow HCOO_{(a)}$ (60)

$HCOO_{(a)} + 2H_{(a)} \leftrightarrow CH_3O_{(a)} + O_{(a)}$ **(RDS)** (61)

$CH_3O_{(a)} + H_{(a)} \leftrightarrow CH_3OH$ (62)

Fig. 18 shows the species that more likely are present on the surface of a Cu/ZrO_2 catalyst and the distinct role of Cu and Zr centres.

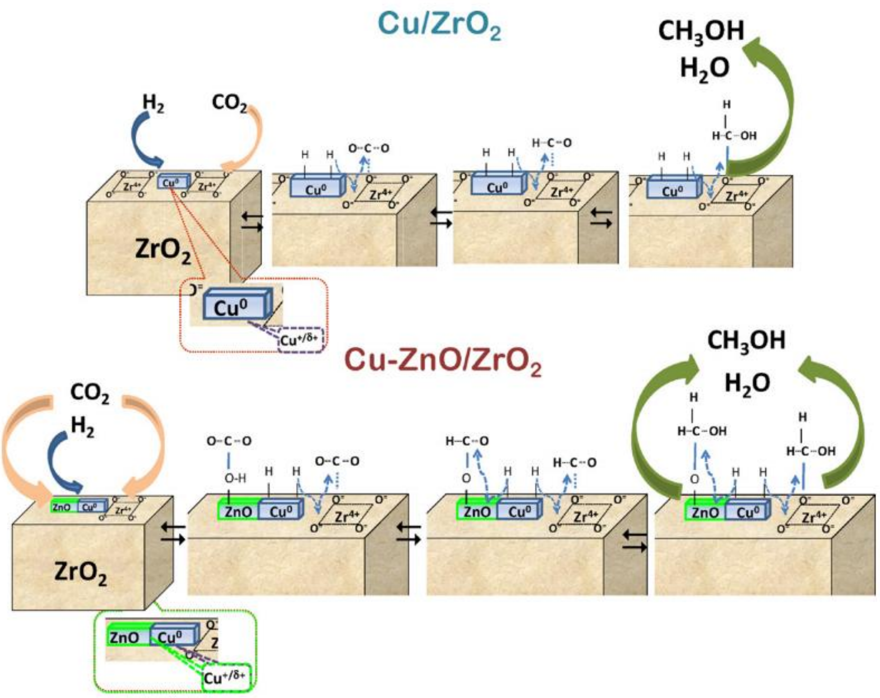
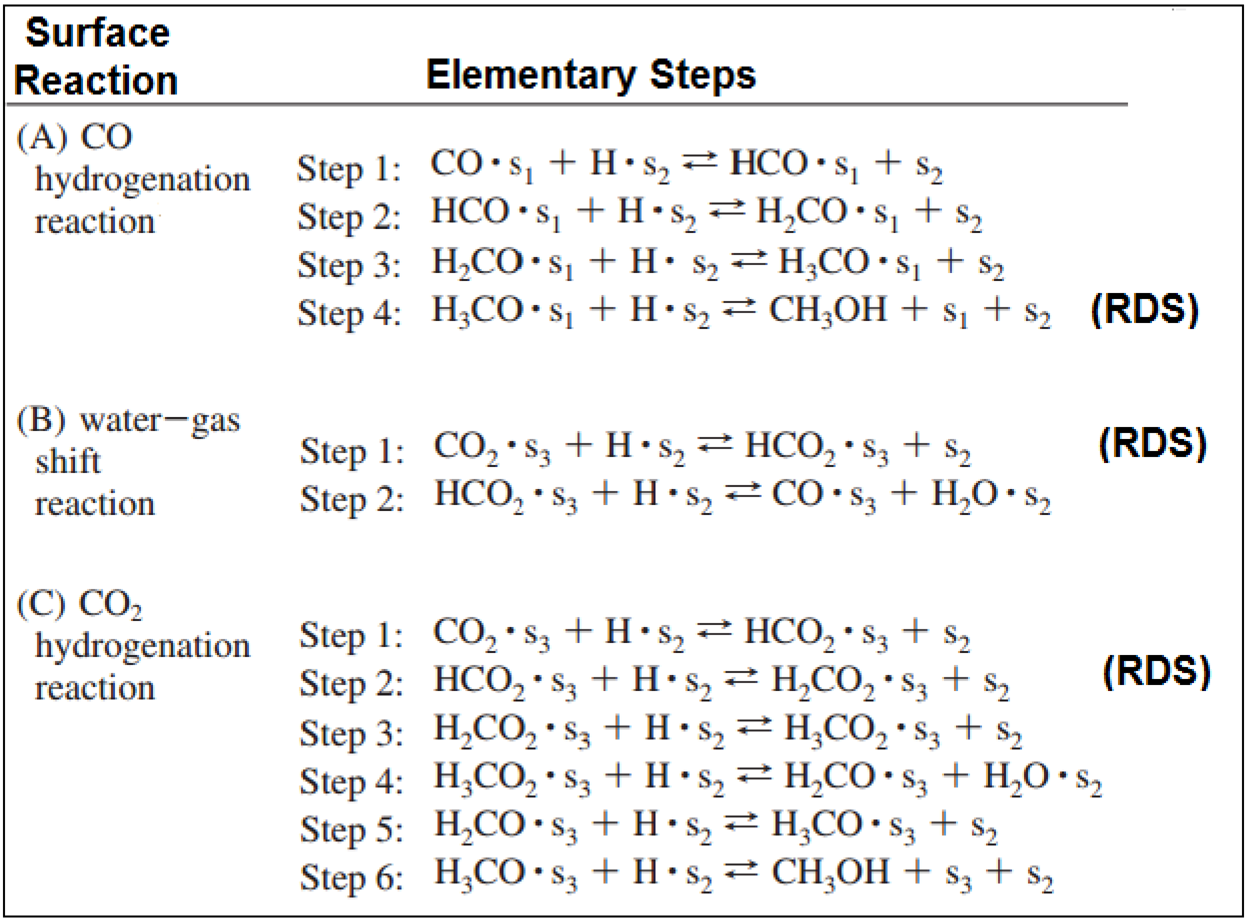


Figure 18. Formation of CH_3O on Cu supported on ZrO_2.

Scheme 30 compares the mechanism of CO *vs* CO_2 conversion into methanol. The CO_2 route implies different intermediates such as the formate species, not found in the CO conversion. These distinctive characters have ruled out that CO_2 is converted first *via* RWGS into CO which is then converted into methanol.



Surface Reaction	Elementary Steps		
(A) CO hydrogenation reaction	Step 1:	$CO\cdot s_1 + H\cdot s_2 \rightleftarrows HCO\cdot s_1 + s_2$	
	Step 2:	$HCO\cdot s_1 + H\cdot s_2 \rightleftarrows H_2CO\cdot s_1 + s_2$	
	Step 3:	$H_2CO\cdot s_1 + H\cdot s_2 \rightleftarrows H_3CO\cdot s_1 + s_2$	
	Step 4:	$H_3CO\cdot s_1 + H\cdot s_2 \rightleftarrows CH_3OH + s_1 + s_2$	**(RDS)**
(B) water−gas shift reaction	Step 1:	$CO_2\cdot s_3 + H\cdot s_2 \rightleftarrows HCO_2\cdot s_3 + s_2$	**(RDS)**
	Step 2:	$HCO_2\cdot s_3 + H\cdot s_2 \rightleftarrows CO\cdot s_3 + H_2O\cdot s_2$	
(C) CO_2 hydrogenation reaction	Step 1:	$CO_2\cdot s_3 + H\cdot s_2 \rightleftarrows HCO_2\cdot s_3 + s_2$	
	Step 2:	$HCO_2\cdot s_3 + H\cdot s_2 \rightleftarrows H_2CO_2\cdot s_3 + s_2$	**(RDS)**
	Step 3:	$H_2CO_2\cdot s_3 + H\cdot s_2 \rightleftarrows H_3CO_2\cdot s_3 + s_2$	
	Step 4:	$H_3CO_2\cdot s_3 + H\cdot s_2 \rightleftarrows H_2CO\cdot s_3 + H_2O\cdot s_2$	
	Step 5:	$H_2CO\cdot s_3 + H\cdot s_2 \rightleftarrows H_3CO\cdot s_3 + s_2$	
	Step 6:	$H_3CO\cdot s_3 + H\cdot s_2 \rightleftarrows CH_3OH + s_3 + s_2$	

Scheme 30. Surface reactions involved in the methanol synthesis from CO_2 (or CO) and the corresponding elementary and rate determining steps

Dimethyl ether (DME, CH_3OCH_3) is generally formed upon methanol dehydration but can be directly produced by CO_2 hydrogenation. DME is an efficient alternative to petroleum based transportation fuels (due to its high cetane number) and liquefied natural gas and has been found to lead to a low environmental impact since it does not generate sulfur oxide or soot [405,406]. In the chemical industry, DME is a useful intermediate for the synthesis of chemicals such as methyl acetate, dimethyl acetate and light olefins [407,408]. Even though methanol has been used in diesel engines, its low cetane number limits its application as a replacement for diesel fuel. On the contrary, DME has about 40% higher value in cetane number compared to diesel fuel and is, thus, far superior compared to methanol for such application. Two main pathways convert CO_2 into DME: i) a two-step process, i.e. methanol is synthesized on a suitable metal catalyst (eq. 63, Scheme 31), which is then dehydrated on an acid catalyst (eq. 64) and, ii) a single-step process, using a bifunctional catalyst that produces methanol and causes its dehydration in the same reactor, forming DME (eq. 65)[409].

Scheme 31 summarizes the thermodynamic properties of the conventional (CO based) synthesis of DME *via* the 2-step process [407,410,411] as compared to the one step synthesis based on CO_2.

The one step process, which integrates the methanol synthesis and its dehydration to DME, reduces the investment and operational cost since only one reactor is required [412].

The study on the mechanism for the one-step CO_2 hydrogenation to DME is still in its infancy as most studies are devoted to the optimization of the bifunctional catalyst. Chen *et al.* [407] have conducted a kinetic and thermodynamic study on the DME production *via* the direct synthesis route over a bifunctional Cu-ZnO-Al_2O_3/HZSM-5 catalyst at various pressures. Their studies reveal that DME production is governed by two different factors above or below 498 K. At the lower temperatures (<498 K), the reaction is dominated by chemical kinetics, whereas for the higher temperatures (>498 K), the thermodynamic equilibrium dominates the reaction.

Conventional 2-step synthesis of DME based on CO

(i) Methanol synthesis

$$CO + 2H_2 \rightarrow CH_3OH \qquad \Delta H^\circ_{298K} = -93.6\ kJ.mol^{-1} \qquad (63)$$

(ii) Methanol dehydration (in the presence of solid acid catalyst)

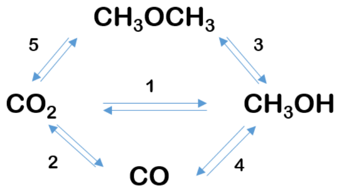
$$2CH_3OH \rightarrow CH_3OCH_3 + H_2O \qquad \Delta H^\circ_{298K} = -23.4\ kJ.mol^{-1} \qquad (64)$$

One-step reaction for the synthesis of DME from CO_2

$$2CO_2 + 6H_2 \rightarrow CH_3OCH_3 + 3H_2O \qquad \Delta H^\circ_{298K} = -122.2\ kJ.mol^{-1} \qquad (65)$$

Scheme 31. Conventional synthesis of DME *via* methanol production and dehydration (2-step) and direct synthesis *via* CO_2 hydrogenation (1-step)

Based on a recent study on Cu-ZnO-ZrO_2/H-ZSM-5 system, the reaction pathway is proposed to be a multi-site reaction, taking place with the primary formation of methanol and the consecutive production of DME on the acid sites of the zeolite framework from methanol dehydration [412]. According to Frusteri *et al*. [412], on the Cu-ZnO-ZrO_2/H-ZSM-5 system, H_2 is initially adsorbed and activated (H_2^*) on the Cu° sites, thus resulting in reduction of the Cu species, whereas CO_2 is bridge adsorbed on the basic surface sites of ZnO and ZrO_2 forming activated CO_2 (CO_2^*). Thereafter, the H_2^* spill-over to CO_2^* leads to formation of intermediate species (such as formate/dioxomethylene/methoxy) stabilized at the metal-oxide interface prior to evolving as methanol from the hydrogenation reaction.



1) $CO_2 + 3H_2 \rightarrow CH_3OH + H_2O$
2) $CO_2 + H_2 \rightarrow CO + H_2O$
3) $2CH_3OH \rightarrow CH_3OCH_3 + H_2O$
4) $CO + 2H_2 \rightarrow CH_3OH$
5) $2\ CO_2 + 6\ H_2 \rightarrow CH_3OCH_3 + 3\ H_2O$

Scheme 32. Reaction scheme for the direct CO_2 hydrogenation to DME [411].

Based on the thermodynamic evaluation by Bonura *et al*. [411], the conversion of methanol to DME on the acidic zeolite sites rapidly approaches the equilibrium level at all the investigated temperatures since it is a fast reaction. Moreover, they also observed a promoting effect of the reaction temperature on the relative rate of methanol synthesis from CO_2 rather than CO, on the basis of thermodynamics. Hence, based on their findings, the authors have proposed the reaction Scheme 32. It turns out that, apart from the methanol dehydration, reaction (3) in Scheme 32 takes place very fast at any temperature, reactions 1-2-4 (Scheme 32) affect the methanol formation in dependence of their relative reaction rate. The thermodynamic analysis of the main reaction paths involved in the synthesis of DME by CO_2 hydrogenation, reaction (5) in Scheme 32, reveals that, under kinetic conditions, the CO concentration dramatically increases with temperature; therefore, low reaction temperature and recycling unreacted CO_x/H_2 mixture could be a solution to improve the methanol/DME productivity.

4.1.2 Methanation and synthesis of higher hydrocarbons

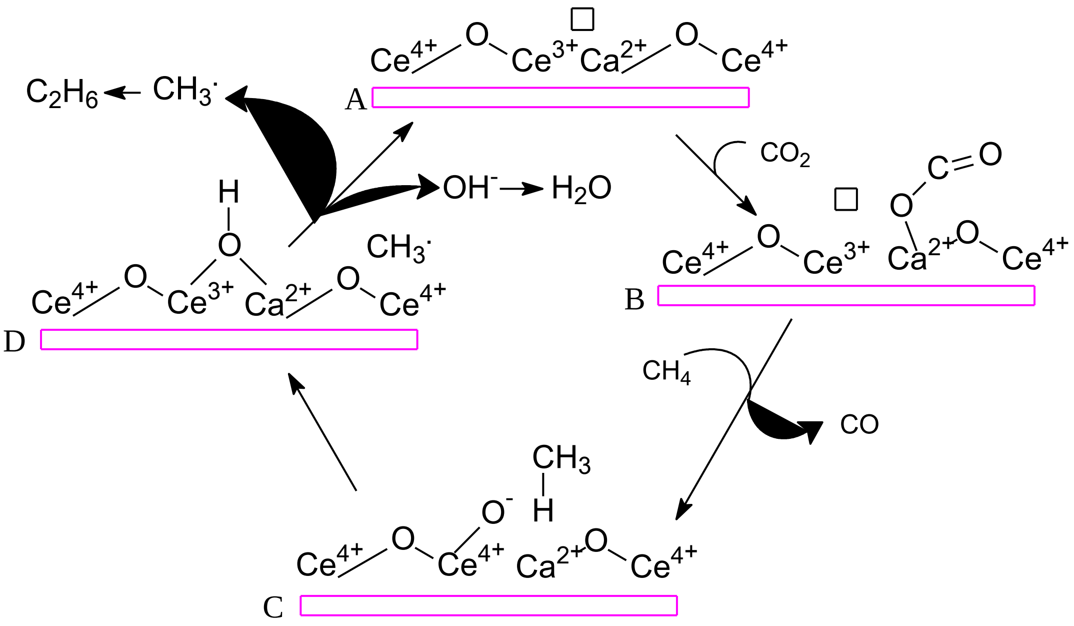
CO_2 methanation is thermodynamically favorable (X_e>95%) around 573 K and 0.1–3.0 MPa. The methane selectivity is close to 100% under these conditions. Interestingly, it has been demonstrated that coke formation is not favored for stoichiometric or H_2-rich feed compositions. Therefore, hydrogenation of CO_2 to CH_4 is thermodynamically feasible for improving the quality of CO_2-rich natural gases. Experimental data over a variety of catalyst systems support the above findings [413]. The thermodynamic simulation to obtain equilibrium CO_2 conversions and product compositions was performed in the range T=473–823 K, P=0.1–3.0 MPa and H_2/CO_2=1–8 mol/mol. Over the range of practical interest, the carbon dioxide conversion is very high, while the competitive reverse water gas shift is relatively insignificant. Consequently, the equilibrium selectivity to methane is also very high. Below 573 K, in most cases, complete conversion of CO_2 to methane with very high selectivity is thermodynamically feasible. The approach to equilibrium analysis of experimental data suggests that over Ni-based catalysts CO_2 methanation could occur *via* reverse water-gas-shift reaction. Methane formation from CO_2 has an interest for car industry as methane is a fuel already used today. Obviously such conversion has a meaning only for the environmental aspect of carbon-recycling. Considered the low price of shale gas, the production of methane from CO_2 using renewable H_2 is not economically comparable.

Methane has still a poor chemistry, due to the high energy of the C-H bond. Although it is easy to convert methane by burning the four hydrogens, it is very difficult to selectively substitute one or two Hs. Nevertheless studies on the coupling of methane to generate C2 or even Cn are ongoing (*vide infra*).

Catalytic conversion of CO_2 to high energy chemicals such as light olefins and liquid hydrocarbons can generally proceed *via* two routes: (i) conversion of CO_2 into liquid hydrocarbons *via* CO formation (F-T route), which is a combination of CO_2 hydrogenation by RWGS and further hydrogenation of CO to hydrocarbons, and (ii) direct (without CO formation) hydrogenation of CO_2 to methanol, dimethyl ether (DME), higher alcohols, methane and higher hydrocarbons. A common issue for such processes is the production of hydrogen from renewable sources if large volumes of CO_2 should be converted. Key issues are: i) the stability of the CO_2 molecule, ii) the amount of H_2 necessary to hydrogenate CO_2 iii) the kinetics of the reaction [414]. Hence, it is highly crucial to employ suitable catalysts which can decrease the energy barriers, thus resulting in lower energy states of the system. Exploring the mechanistic pathways of such reactions may help to gain a deeper insight into the feasibility of CO_2 conversion at lower temperatures.

4.1.3 CO_2 as dehydrogenating agent of hydrocarbons

By coupling kinetic studies and CO_2 chemisorption data, the mechanism shown in Scheme 33 is proposed for the oxidative coupling of methane to ethane.



Scheme 33. Proposed mechanism for CO_2-OCM reaction over CaO-CeO_2 catalyst [415]. Pink rectangles is support, black empty squares are vacant sites.

CO_2 adsorbs on the catalyst by interaction with the acid Ca^{2+} sites at the outermost layer via the O-atom (B). The Ce^{3+} sites present in ceria activate CO_2 forming CO and “active oxygen” species present most likely as subsurface oxygen (C), responsible for the conversion of methane to methyl radical (D). Hence, the cooperation of Ca^{2+} and Ce^{3+} sites in solid solution of the catalyst leads to a greater chemisorption and activation of CO_2 that produces more active oxygen species for selective C_2 formation. The incorporation of Ca^{2+} into CeO_2 lattice (proven by XPS analysis) generates defect sites, which can also promote redox interchange between Ce^{4+} and Ce^{3+} [415].

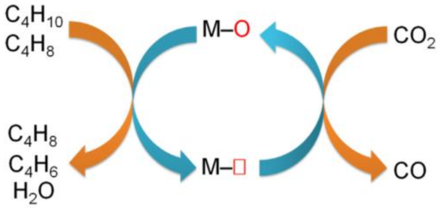
The utilization of CO_2 in the oxidative dehydrogenation (ODH) of alkanes has received considerable attention in recent years. CO_2 has the potential to act as both a hydrogen acceptor and a “soft” oxidant. As co-fed gas in the oxidative dehydrogenation of light alkanes it shifts the reaction equilibrium towards more olefin production [416,417]. The ODH reaction has a great interest as it represents a straightforward reaction for the production of olefins such as ethene, propene and butene from their respective saturated hydrocarbons. Such olefins are classified as building blocks in the petrochemical industry. Ethene, in particular, has a diversified derivatives portfolio and can be used for the production of plastics, polymers, fibers and packaging materials [418,419]. The dehydrogenation of light alkanes is reversible and, due to limitation by thermodynamics, the reaction is often carried out at high temperatures (>800 K). Industrially, steam cracking of hydrocarbons or naphtha is used for the synthesis of ethene, a very energy consuming technology and prone to severe catalyst deactivation due to coking [418]. Hence, it is desirable to utilize an oxidant capable of oxidizing, in the presence of a suitable catalyst the hydrogen produced so to shift the equilibrium. The use of molecular oxygen as oxidant can effectively reduce the reaction temperature. Nevertheless, undesirable factors affect this reaction such as: the low selectivity due to the production of CO_x species from HCs, the need to remove excess heat of reaction, and the undesired reaction mixture flammability [420]. On the other hand, CO_2 has been found to serve as a medium for heat supply for the endothermic dehydrogenation reaction, as a diluent to enhance equilibrium conversion of alkanes and as a coke removal agent from the catalyst [417]. In addition, CO_2 inhibits deep oxidation of the reaction products, thus improving the olefin selectivity [421]. Catalysts with redox properties, such as molybdenum-, chromium- and vanadia-based catalysts, show high activity in various oxidative dehydrogenation reactions of hydrocarbons [422-425]. Factors influencing the reaction also include acid-base bifunctionality, which plays an important role in CO_2-mediated dehydrogenation reactions [426]. Both basic sites and Lewis-acid vacant sites are important for hydrocarbons activation [427] In fact, an enhanced basicity results in an improved performance due to the rapid desorption of the electron-rich alkenes, whereas Lewis acid sites enhance the dehydrogenation process [428]. Also, in presence of CO_2 as feed, surface basicity favors the adsorption formation and reduction of active chromium sites.

Using Cr-based catalysts, CO_2 as oxidant (Scheme 34) is found to boost the regeneration of the reduced chromium sites formed during the dehydrogenation of propane (eq. 66) as well as the consecutive reduction with H_2 (eq. 68) [424], where CrO_x represents the oxidized form and CrO_{x-1} represents the reduced form of the catalyst).

$$C_3H_8 + CrO_x \leftrightarrows CrO_{x-1} + C_3H_6 + H_2O \tag{66}$$
$$CO_2 + CrO_{x-1} \leftrightarrows CO + CrO_x \tag{67}$$
$$H_2 + CrO_x \leftrightarrows CrO_{x-1} + H_2O \tag{68}$$
$$CO_2 + CrO_{x-1} \leftrightarrows CO + CrO_x \tag{69}$$

Scheme 34. CO_2-ODH of propane over chromium oxide catalytic sites

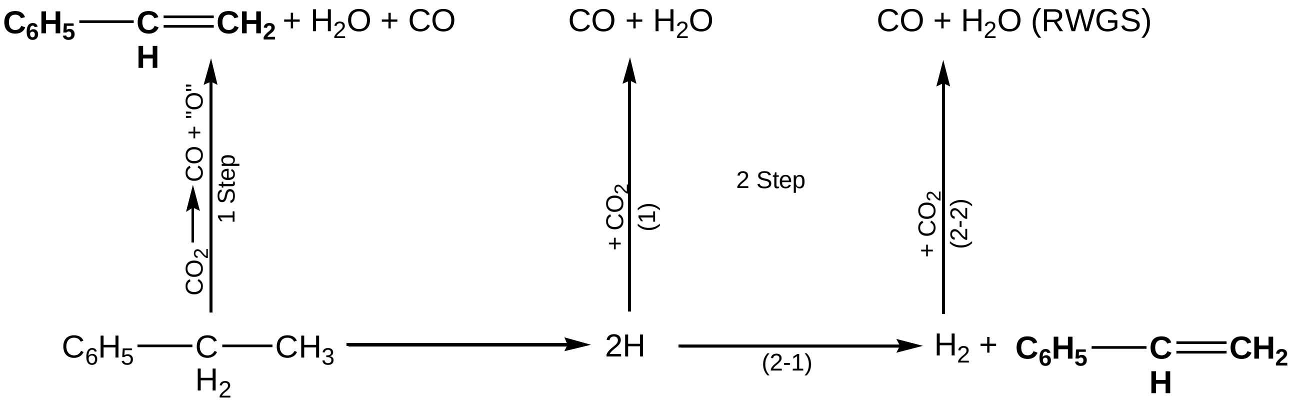
Scheme 35 shows the role of the metal in the dehydration of HC. The vacancy created by the dehydrogenation is filled by CO_2 converted into CO.



Scheme 35. Proposed reaction pathway (O, lattice oxygen and □ anion vacancy) for butane-ODH with CO_2

The oxidative dehydrogenation of ethylbenzene (ODE) to styrene is a promising alternative or complement to the current industrial technology based on steam that may contribute to meeting the growing demand of styrene and the strong market incentive [429,430]. Styrene is one of the most widely used feedstock in the production of high-value commercial products such as synthetic rubbers, polystyrene and styrene–acrylonitrile copolymers [429,431]. The global styrene annual production is 14.6 Mt, with US producing 4 Mt and Europe 3.4 Mt, respectively [432].

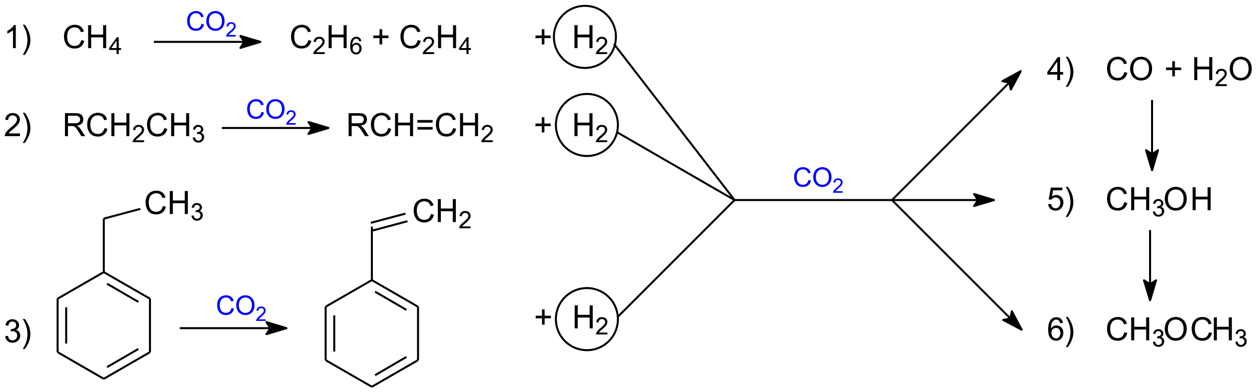
Several possible mechanisms have been identified by Sun *et al*. [433] taking into consideration that ethylbenzene (EB) is activated by acid base catalysts or lattice oxygen (*via* redox mechanism) in presence of CO_2. Based on the CO_2-ODE reaction over V and Fe supported catalysts, Sun *et al*. [434] found that a synergistic effect exists between EB dehydrogenation and the RWGS reaction. In fact, CO_2 can be either reduced to CO *via* interaction with redox sites (one-step mechanism) or by reaction with hydrogen formed in EB dehydrogenation (two-step pathway) as shown in Scheme 36 [434].



Scheme 36. Role of CO_2 in the CO_2-ODE process

Based on these two pathways, three vital mechanistic steps are proposed. Mechanism 1 (one step pathway) is redox based: vanadia or ceria type catalysts play an important role for activation of both CO_2 and EB. The C-H bond breaking proceeds *via* a Mars-van-Krevelen (redox) type mechanism and lattice oxygen of the catalyst is consumed during dehydrogenation process, producing styrene and water. The lattice oxygen however, is replenished by CO_2 dissociation to CO and surface oxygen species. Different types of V and Ce species act as oxygen carrier through their oxidized-reduced pairs [435].

In conclusion CO_2 can act as a "soft oxidant" in the dehydrogenation of HC to olefins or can be hydrogenated to afford methanol, higher alcohols, DME, or hydrocarbons. Such interesting network of reactions is represented in Scheme 37.



1) CO_2-OCM; 2) CO_2-ODH; 3) CO_2-ODE; 4) RWGS; 5) CO_2 to Methanol; 6) CO_2 to DME

Scheme 37. Network of reactions showing the role of CO_2 in dehydrogenation and hydrogenation reactions.

4.2 Electrochemical processes

The electron-transfer to CO_2 experiences both thermodynamic and kinetic hindrance. The Gibbs free energy change (ΔG) of formation of several C1 molecules is represented in Fig. 1. It says that if CO_2 has to be converted into species in which the C-oxidation state is lower than +4, energy is needed if not also hydrogen. With exception of CO that can be originated from CO_2 through routes that may or may not employ hydrogen (CO_2 splitting to afford CO and "O" does not require hydrogen), all other C1 molecules have a H/C ratio that is higher than the value in CO_2, where it is zero. This means that the reduction process requires “H” or “e^- plus H^+” transfer. The source of “H, H^+” must be water if the reduction of the heterocumulene must be performed on a large scale. Using water as source of hydrogen, in principle, the reduction of CO_2 can be performed following two quite different routes: i) electrolysis of water to afford H_2 and use of the latter in thermal catalytic reactions with CO_2 bearing to energy-rich C1 or C1+ molecules; ii) electro-co-processing of CO_2 and water to afford C-reduced species. The two routes are quite different, as the former requires production and possibly storage of H_2 for the production of CH_4, CH_3OH, DME, higher alcohols, etc., while the latter directly converts CO_2 into its reduced forms without any need of a preliminary production of H_2. The former option, which requires non-fossil-C derived hydrogen, is limited today by the higher cost (up to three times) of PV- or wind-H_2 with respect to reforming-H_2.

CO_2 can be reduced through a 1-e^- transfer to the radical anion $CO_2^{\cdot -}$. Any reduction of CO_2 to other C1 species is a “nx2e^-” reduction. A process that may be born from the transfer of “1e^-” to CO_2 is the synthesis of C-C bonds. For example, the C2 species oxalic acid (HO_2C-CO_2H), in which the oxidation state of C is +3, can be formed by coupling two $CO_2^{\cdot -}$ units followed by protonation; the direct carboxylation of hydrocarbons forming carboxylic acids (R-H + CO_2 → R-CO_2H), in which again the formal oxidation state of C in CO_2 is +3, is another interesting reaction. The 1e^- transfer to CO_2 can originate also a second species that is the carbonyl-carbonate, $^-$OC(=O)-OC(=O)$^-$, obtained upon coupling of CO_2 with $CO_2^{\cdot -}$ and subsequent transfer of a second electron to the product of coupling. However, several questions may be born to the mind of the reader, such as: are radical-anions $CO_2^{\cdot -}$ to be likely intermediates in the synthesis of other C1 molecules? Is such one-electron transfer thermodynamically more or less feasible than a multielectron process? Is the multielectron transfer a process occurring at different potentials per each e^--transfer? Or are possible iso-potential (iso-energetic) synchronous multiple e^--transfers? Also, when a metal interacts with the C-atom of CO_2, or electrons are transferred to the same atom, the molecular geometry of the latter is dramatically changed and the change requires the reorganization of the energy levels of the molecular orbitals. Does such geometry change represent an influential barrier to the reduction of CO_2? Therefore, does the co-ordination mode influence the 1e^- - 2e^- transfer? The electroreduction of CO_2 is not a trivial case. In this section, an answer will be attempted to such questions, and the state of our knowledge presented.

The potentials of the various reactions of reduction of CO_2 to other C1 molecules are shown in Table 4. It is quite evident that the one-electron transfer is a process that requires higher energy than the multi-electron transfers.

Table 4. Potential of reduction of CO_2 to other C1 molecules (da 1) *vs* the Standard Hydrogen Electrode (SHE)

Entry	Reaction		E° V (NHE)
1	$CO_2 + e^- = CO_2^{\cdot -}$	-2.21 in aprotic solvents;	-1.93 in water
2	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$		-0.53
3	$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$		-0.61
4	$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O$		-0.48
5	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$		-0.38
6	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$		-0.24

If the reductions are considered to take place in water, then it is useful to recall the Frost diagram built by correlating the number of electrons transferred in a process and the free energy change (or electrochemical potential) of that process (Fig. 19). If co-ordinated CO_2, more than free CO_2, has to be reduced, then a key step in the entire reduction process is the bonding of CO_2 to the metal centre. It has been shown that ligands may influence the mode of bonding of CO_2 to the metal centre. Moreover, carrying out the electro-reduction in water, requires that the metal centre is stabilized by ligands that have a good water affinity, proper donor properties and correct steric hindrance.

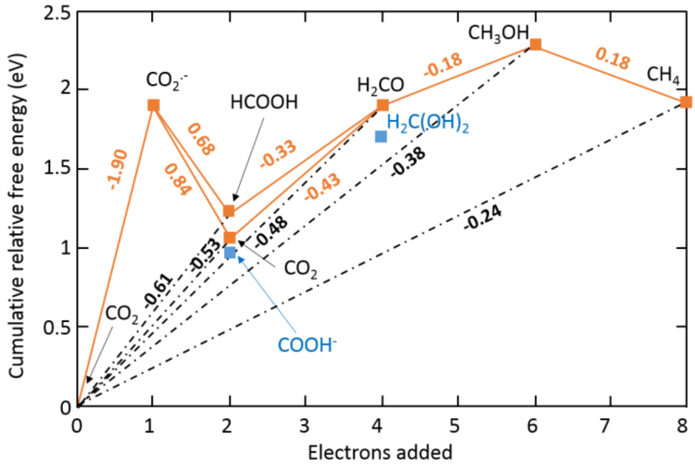


Figure 19. Frost diagram applied to the reduction of CO_2 through n(e^- + H^+) transfer processes

Consequently, N- or O-ligands are more frequently used than phosphines, unless the latter are conveniently functionalized (for example with sulphonic groups or other water soluble moieties) for enhancing their water solubility or mixed organic-water solvent media are used. Figure 20 presents a list of P, O, N-ligands, from the historical ones such as *cyclam* used in the first studies in this field, to more sophisticated ones.

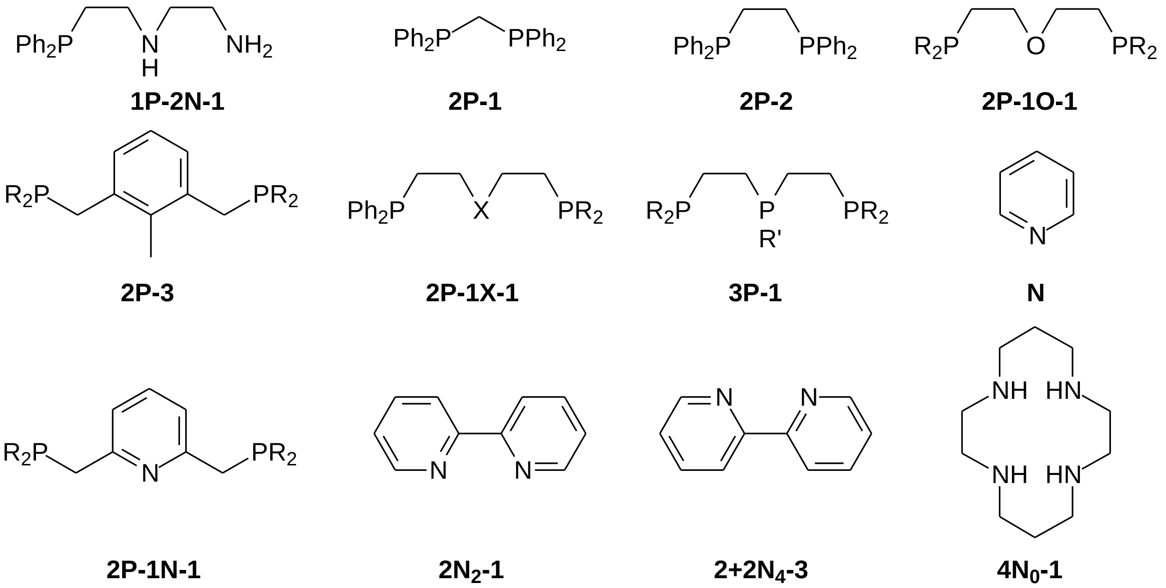


Figure 20. Selected N and P-ligands used in the electrochemical reduction of CO_2. X can be: As, S, O, N

A key note is that the electroreduction of CO_2 may take place at the electrode surface or be mediated by a catalyst attached to the electrode or soluble in the solvent (Scheme 38). In case (**A**) the reaction occurs at the surface of the electrode that directly transfers electrons to CO_2: this in general requires high overvoltage and may cause electrode deterioration or even consumption and scarce selectivity. In case (**B**), the electrode transfers electrons to the catalyst which then interacts with CO_2 causing its reduction. In such case, CO_2 is not in contact with the electrode, and this results in a better stability of the electrode and its longer life, that may be important in the overall cost determination of a process.

(**A**)

$$\text{Surface} + CO_2 + ne^- \longrightarrow \text{Surface-}CO_2(^{n-}) \longrightarrow \text{Surface} + CO_2\text{-reduction products} + \ldots.$$

(**B**)

$$\text{Surface} + \text{Catalyst} + ne^- \longrightarrow \text{Surface} + \text{Catalyst}(^{ne-})$$

$$\text{Catalyst}\ (^{ne-}) + CO_2 \rightarrow \text{Catalyst-}CO_2(^{ne-}) \xrightarrow{\text{substrate}} \text{Catalyst} + CO_2\text{-reduction products} + \ldots$$

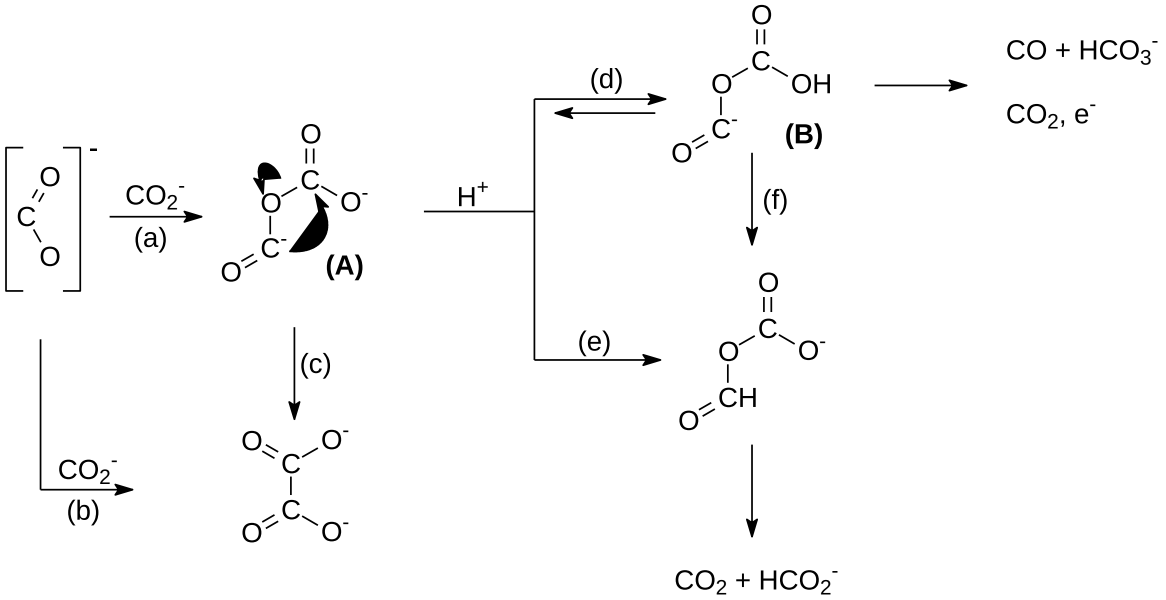
$$\text{Catalyst}\ (^{ne-}) + \text{substrate} \rightarrow \text{Catalyst-substrate}(^{ne-}) \xrightarrow{CO_2} \text{Catalyst} + CO_2\text{-reduction products} + \ldots$$

Scheme 38. Direct (**A**) and catalyst-mediated (**B**) electroreduction of CO_2 in solution

Another advantage of electrocatalysis is that overvoltages are reduced almost to zero and the electron transfer occurs near the thermodynamic potential of the reaction, e.g. E° (substrates/ products), one wishes to perform.

One-electron transfer to CO_2 vs multi-electron transfer

The one electron transfer to free CO_2 affords $CO_2^{\cdot-}$, as seen above. Table 4 shows that it is much more energy requiring than multielectron transfers. Moreover, the potential is dependent on the medium in which the electron transfer occurs: polar media (-1.9 V) or apolar media (-2.21 V). The one electron-transfer generates the $CO_2^{\cdot-}$ species that can evolve according to two different routes (Scheme 39).



Scheme 39. Reaction mechanisms for the conversion of the radical anion $CO_2^{\cdot-}$

The radical anion $CO_2^{\cdot-}$ has a life as short as 30-93 μs, as discussed above. It can be stabilized by interaction with the solvent or radical traps. It can attack a second CO_2 molecule *via* a *hetero* O-C coupling and generate the dianion (A) in Scheme 39 that can be the source of CO and carbonate, as already seen. However, by protonation, the following couple of products can be obtained: either CO and hydrogencarbonate HCO_3^-, or CO_2 and formate HCO_2^-.

Viceversa, the *homo* C-C coupling of two radical anions with antiparallel spin of the electron localized on C will produce the oxalate anion (B). The e^--transfer to "free" CO_2 has been attempted for the synthesis of oxalates, with alternate fortune [436]. If the homo-coupling or hetero-coupling are favoured will depend on several parameters such as: the solvent, the current density, the electrode.

All anions will need a cation for neutralization, which is provided by the electrode, in general, that is consumed. Such technology is not exploited at industrial level.

Competitive co-ordination of CO_2 and H^+ to a catalytic centre and their reduction

When the electron transfer implies CO_2 co-ordinated to a metal centre, then several factors determine both the kinetics and thermodynamics of the reaction. Such factors can be categorized as follows: the metal, the nature and structure of the ligand, the geometry of the metal-complex, the solvent: they may affect the electron-transfer process in many ways. Moreover, the addition of a proton to the metal centre and its consequent reduction to H_2 is a side-by-side process with CO_2 co-ordination-reduction. However, the reduction of CO_2 in water is not a simple process and the selectivity towards a target C1 or C1+ molecule containing CO_2 in a reduced form is quite variable with the system used, having the formation of either hydrogen or other C-species as a competing process. Some of the competitive reactions are shown in Scheme 40.

$$L_nM^{n+} + H^+ \rightarrow M\text{-}H^{(n+1)+}$$

$$L_nM^{n+} + CO_2 \rightarrow L_nM^{n+}(CO_2)$$

$$L_nM\text{-}H^{(n+1)+} + e^- \rightarrow L_nM^{n+} + \text{“H”} \rightarrow L_nM^{n+} + \mathbf{1/2H_2}$$

$$L_nM\text{-}H^{(n+1)+} + CO_2 \rightarrow L_nM\text{-}OC(O)H^{(n+1)+}$$

$$L_nM\text{-}OC(O)H^{(n+1)+} + e^- + H^+ \rightarrow L_nM^{n+} + \mathbf{HCO_2H}$$

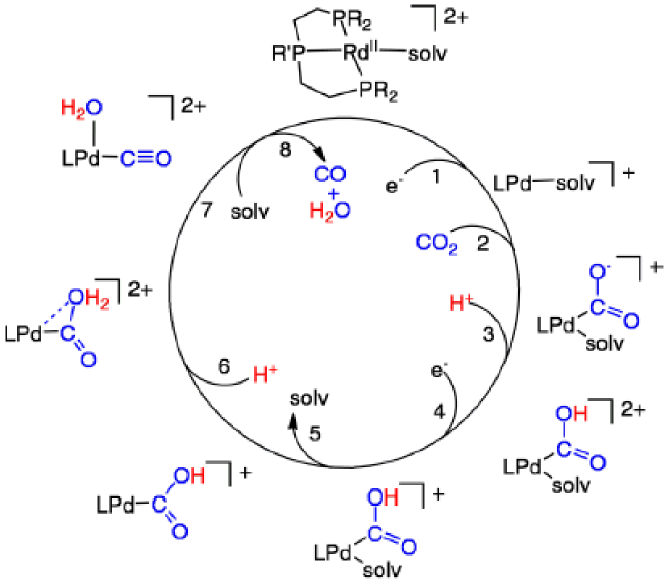
$$L_nM^{n+}(CO_2) + e^- \rightarrow L_nM^{n+}(CO_2)^-$$

$$L_nM^{n+}(CO_2)^- + H^+ \rightarrow L_nM^{n+}(CO_2H)$$

$$L_nM^{n+}(CO_2H) + e^- + H^+ \rightarrow L_nM(\mathbf{CO})^{n+} + \mathbf{H_2O}$$

Scheme 40. Competitive co-ordination to a metal centre and metal-catalyzed reduction reactions implying the proton and CO_2. The formation of H_2, CO and HCO_2H are highlighted.

A variety of metal systems have been used as catalysts in the electroreduction of CO_2, the most studied being Ni, Co, Pd, Ru. While in the photochemical or photoelectrochemical processes Ru and Re are mainly used. A different mechanism always based on a double consecutive (e^-+H^+) transfer has been proposed (Scheme 41) in which the formation of the "Pd-C(CO)OH_2" intermediate more than the hydroxyl-carbene is postulated.



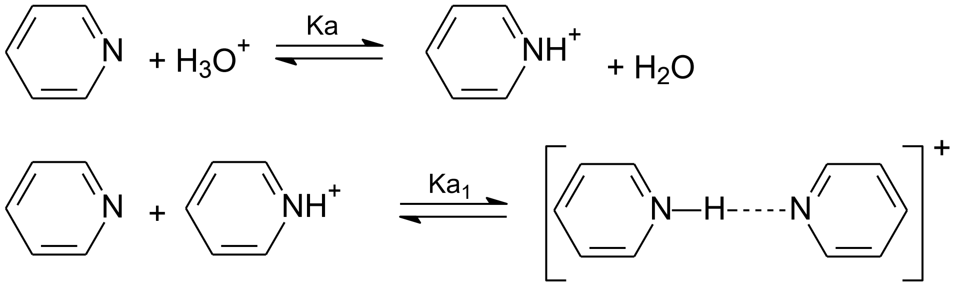
Scheme 41. Alternative mechanism for the Pd-electrocatalyzed reduction of CO_2

Very recently [437] a $2e^-$ reduction of N-heterocyclic carbene-carbonyl Mn(I) to Mn(-I) has been reported that occurs at the same potential (-1.35 V *vs* SCE) instead of two consecutive potential apart of a few hundreds mV as shown for analogous $MnBr(CO)_x(2N\text{-}1)$. Such Mn complexes catalyse very selectively the CO_2 to CO reduction with a Faradic efficiency of 34.6 %. All the above catalytic systems afford mainly CO, an interesting molecule as it may release energy in the combustion with air (see Fig. 11a), but more useful C1 or C1+ molecules can be produced.

Scheme 42 shows the multiple "e^-+H^+" transfer to afford methanol. Such a sequence is very interesting as it can be found in enzymatic reactions. (see Section 5).

$CO_2 + 2e^- + H^+ \rightarrow HCOO^-$
$HCOO^- + 2e^- + 3H^+ \rightarrow CH_2O + H_2O$
$CH_2O + 2e^- + 2H^+ \rightarrow CH_3OH$
Scheme 42. Triple $2e^- + H^+$ transfer to CO_2 for its conversion into CH_3OH.

The use of pyridine as an organic catalyst [438-440] has been proposed by Bocarsly and coworkers. The interesting aspect of such electrocatalysts is that they can promote several "$1e^- + H^+$" transfer steps affording several reduced species of CO_2, such as: HCO_2H, CH_2O, CH_3OH, but also C2 and C3 species. Quite recently, the authors have critically reviewed [441] the proposed mechanisms and report the possible role of H-bonded pyridinium-to-pyridine dimers in the electrocatalytic reduction of CO_2 (Scheme 43).



Scheme 43. H-bonded pyridine-pyridinium ion dimers as possible actors in the e^- -transfer

4.3 Photochemical and photoelectrochemical reduction of CO_2

Photochemical (PC) processes can be used for the reduction of CO_2 in which semiconductors produce excitons upon irradiation and generate electrons and holes used in the reduction of CO_2 and oxidation of an electron donor (water should be used, or waste organics that may also be oxidized in useful products), respectively. In addition, photoelectrochemical (PEC) reduction of CO_2 is playing a more and more important role. In PEC, a photoactive material is attached to the electrode surface and the excitons produced upon irradiation generate electrons used for the reduction process. All such methodologies have in common the "*electron plus proton*" transfer to CO_2. Recently, the use of solar energy for powering the reduction of CO_2 is much under consideration as this would represent a way to convert low-value CO_2 into useful chemicals and fuels mimicking Nature and natural photosynthesis. The use of PV as source of electrons in reduction reactions is considered today with much attention as it may represent an effective way to the conversion of large volumes of CO_2. As a matter of fact, the use of PV for CO_2 reduction using water as electron donor, already today is an attractive technology, although the cost may appear high. From the solar to chemicals/fuels (StC/F) energy conversion point of view, it must be pointed out that the most ready technology is based on the sequence shown in Scheme 44.

Solar **t**o **E**lectricity >>> **E**lectricity **t**o **H**ydrogen >>> **H**ydrogen (and CO_2) **t**o **F**uels
PV (water as H-source) (CH_3OH or CH_4)
StE **EtH** **HtF**$_{\text{l or g}}$
η=20% η=70% 70-80%
Overall "Solar to Fuel-StF" maximum efficiency = (20x70x80)%= 11.2%

Scheme 44. Efficiency in the conversion of solar energy, water and CO_2 into fuels

The use of solar energy and other perennial primary sources of energy (wind, geothermal, hydro) for the reduction of CO_2 has a great relevance to the conversion of large volumes of CO_2 to valuable chemicals and fuels. All such sources can be used in a indirect way, as they can generate electricity that can be used either, as indicated above, for the reduction of CO_2 in water, or for the electrolysis of water to afford hydrogen that can be used for CO_2 reduction. In the very short term the use of excess electric energy (out of peak electricity), especially if produced from perennial sources, is a suitable strategy, in the medium term the use of PV can results in a viable approach [442]. Today, the cost of PV is too high (Table 5) for a practical application.

This implies that the price of chemicals produced by using the PV-generated H_2 will be much higher than that of products obtained using H_2 produced by reforming of methane.

Table 5. Comparison of the cost of production of H_2 (1 kg) using different technologies.

Technology	**Gas Reforming**	**Electrolysis with nuclear**	**Electrolysis with oil as primary energy source**	**Electrolysis with PV**	**Electrolysis with wind**	**Electrolysis with SPC**
Cost €/kg	1.10 1.15	1.45 1.50	1.50 2.20	2.8 4.0	3.8 5.20	3.50

Anyway, if one considers the perspective increase of the efficiency of PV (from 20 to 40%) and the reduced cost of PV-materials, one can foresee that the price of PV-generated H_2 will decrease and get close to that of H_2 by reforming. So, in the short term H_2 generated *via* PV or wind- or geothermal- or hydro-electricity may compete with H_2 produced by methane reforming.

In such frame, the use of solar energy assumes a particular role as solar radiations can be used directly in photochemical-PC and photoelectrochemical-PEC processes. The former use either soluble (homogeneous) or insoluble (heterogeneous) compounds that may capture solar radiations that generate excitons (e^- + hole) used for the direct reduction of CO_2 and oxidation of the donor (water or waste organics to be converted into usable products) while in PEC electrons generated in photoreactions are used in conjunction with an electrode.

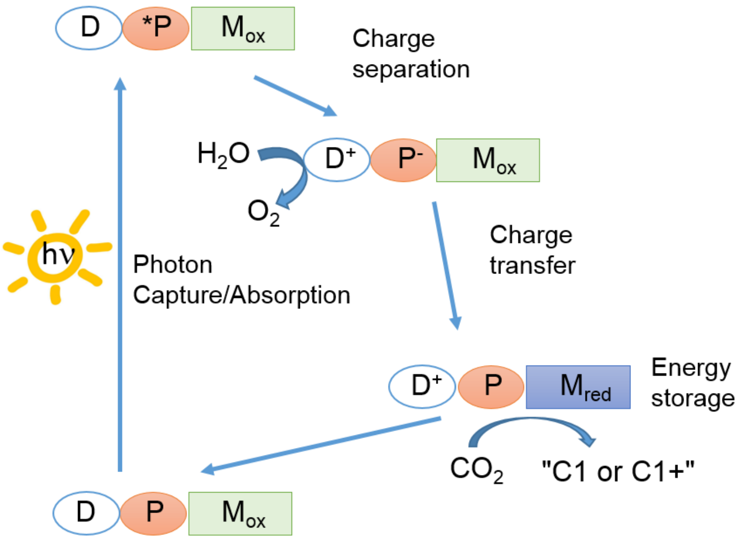


Figure 21. Elementary steps in the semiconductor driven photoreduction of CO_2 using solar light.

In a homogeneous photochemical process, (Fig. 21) the solar radiations are captured by a soluble sensitizer (P) in presence of a donor (D) while a solid photomaterial is used in heterogeneous photochemical processes (Fig. 22). The photosensitizer is excited to P* with production of an exciton (e^- + hole). The hole oxidizes the donor (water or a waste) while the negative charge is transferred to a metal centre (M_{red}) where the CO_2 is reduced to C1 or C1+ species with re-oxidation of the metal centre.

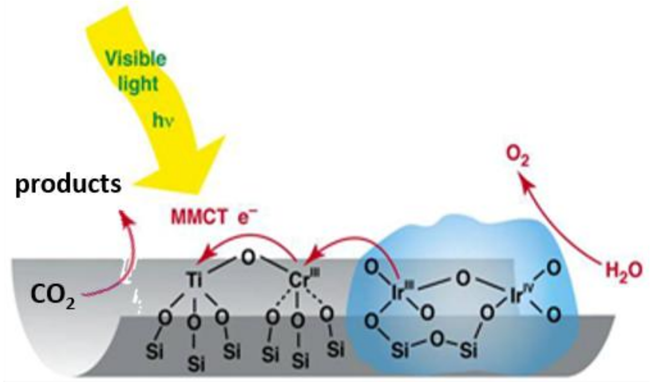


Figure 22. Inorganic photomaterials for CO_2 reduction in water

Several sensitizers have been used such as metal-complexes (Ru, Re) with the 2N-1 ligand and its derivatives or organic complex molecules. Solid inorganic materials [443] can also be used as heterogeneous photocatalysis.

Another approach to the use of solar energy is the hybrid system [182,444-447] formed by enzymes for the selective reduction of CO_2 and solar energy and photomaterials for the regeneration of co-factors (Fig. 23).

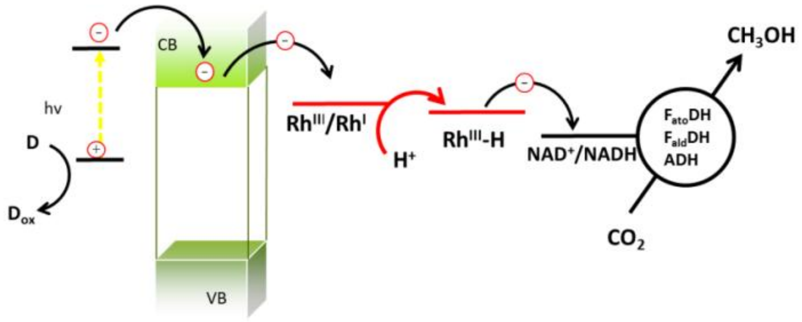


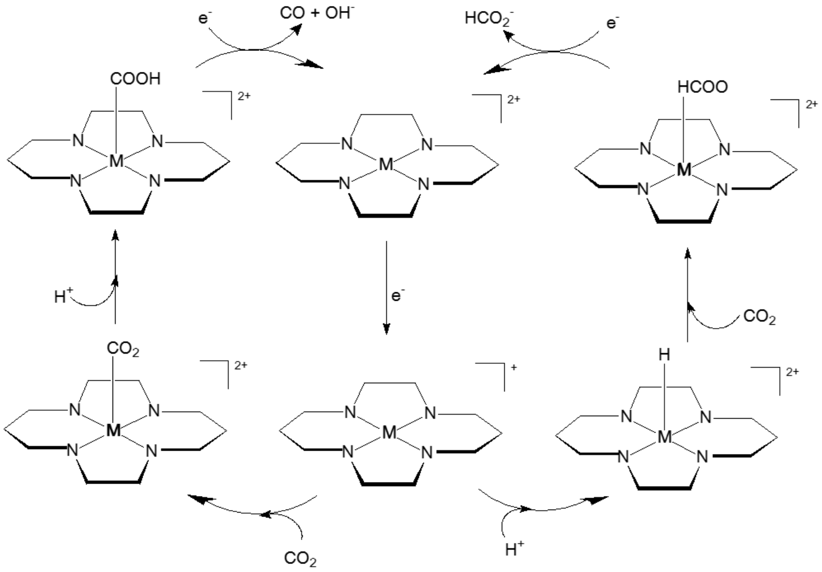
Figure 23. Hybrid systems for the reduction of CO_2 to methanol in water at room temperature.

In all above systems, a key parameter is the “quantum efficiency” expressed as (eq. 70) where ne^-

$$\Phi = (mol_{products}/n_{photons\ adsorbed})\ x\ \ ne^- \qquad (70)$$

is again the number of electrons transferred to CO_2. The quantum yield is a parameter somehow similar to the “Faradic Efficiency”.

Among homogeneous photocatalysts, it is worth citing metal complexes with ligands having an extended system of conjugated double-bonds able to adsorb solar light: phtalocyanins [448] corroles [449], corrins [450] or similar macrocyclic systems are typical ligands. The metal centres are Co or Fe or other metals. The negative point is that a low selectivity is observed with a large production of hydrogen, and this is true also for those systems, which under electrochemical conditions are quite effective for CO_2 reduction to C1 species (Scheme 45) .



Scheme 45. Products obtained from the reduction of CO_2 according to the insertion of CO_2 into the M-B bond: abnormal (left) vs normal (right).

In early studies of the 1980s [451-453] Ru(2N-1)$_3^{n+}$ was used as efficient photosensitizer and costly organic molecules as e$^-$-donors. The drawback was that the sacrificial reagents were more expensive than the products formed from CO_2, making such systems not economically viable. An interesting case in which a unique complex acts as sensitizer and catalyst is represented by Re(2N-1)$(CO)_3$X (X=Cl, Br) [451,454] able to selectively produce CO.
The semiconductor band gap must match the potential of reduction of CO_2 for a reaction to occur (Fig. 24), otherwise the absorption will not produce any conversion reaction.

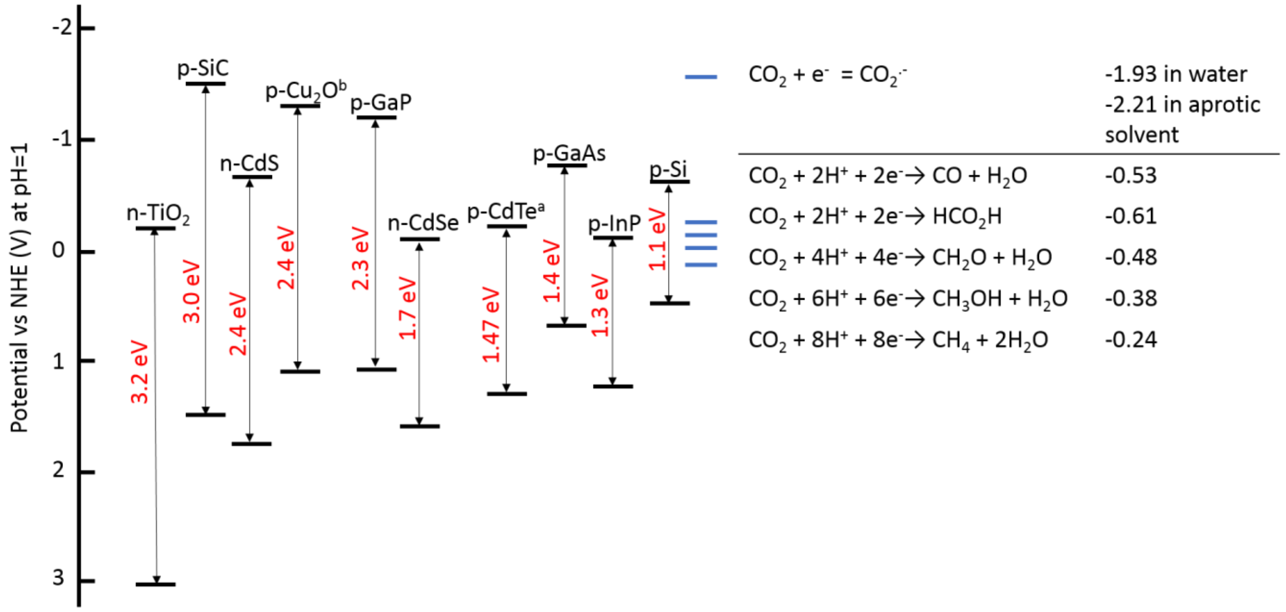


Figure 24. Comparison of the band-gap of some semiconductors with the reduction potential of CO_2 in acidic water (pH=1) in several one- and multi-electron transfer processes.

This problem can be solved by modifying the TiO_2 properties by deposition on its surface of materials which can influence the band gap by shifting it more towards the visible region or by increasing its ability in using the near UV radiations which constitute *ca*. 7% of the Visible Light. This is possible in several modes as shown in Fig. 25. [184]
The interesting aspect of PEC is that it is possible to use such technology with a single dual-face electrode (Fig. 26 in compact two-compartment single cell that allows simple product separation.

Such device needs a well-performing, fast and robust proton-exchange membrane. In principle, a cell designed for water splitting [455] under solar irradiation may serve also for CO_2-water co-processing. Therefore, work done for solar-driven water splitting [456] can be transferred to CO_2 conversion into chemicals/fuels under solar irradiation.
The interesting aspect is that, as it has been discussed above, different electrocatalysts may afford different CO_2-reduction product. Therefore, such technology may result in a flexible tool for the production of selected chemicals or fuels from CO_2 and water, implementing a "*CO_2-H_2O based economy*". Adaptation of the combinatorial approach to testing electrocatalysts [457] has been proposed as a route to shortening time-to-market for such devices. Miniaturization [458] or development of new concept photobioreactors [459] can be a way to solving the space issue, which is a predominant factor in the large scale development of CO_2 conversion. Coupling EC-PC-PEC with thermal processes and with enhanced biotechnological conversion of CO_2 [382] may shorten time to exploitation of carbon-recycling, mimicking natural photosynthesis.

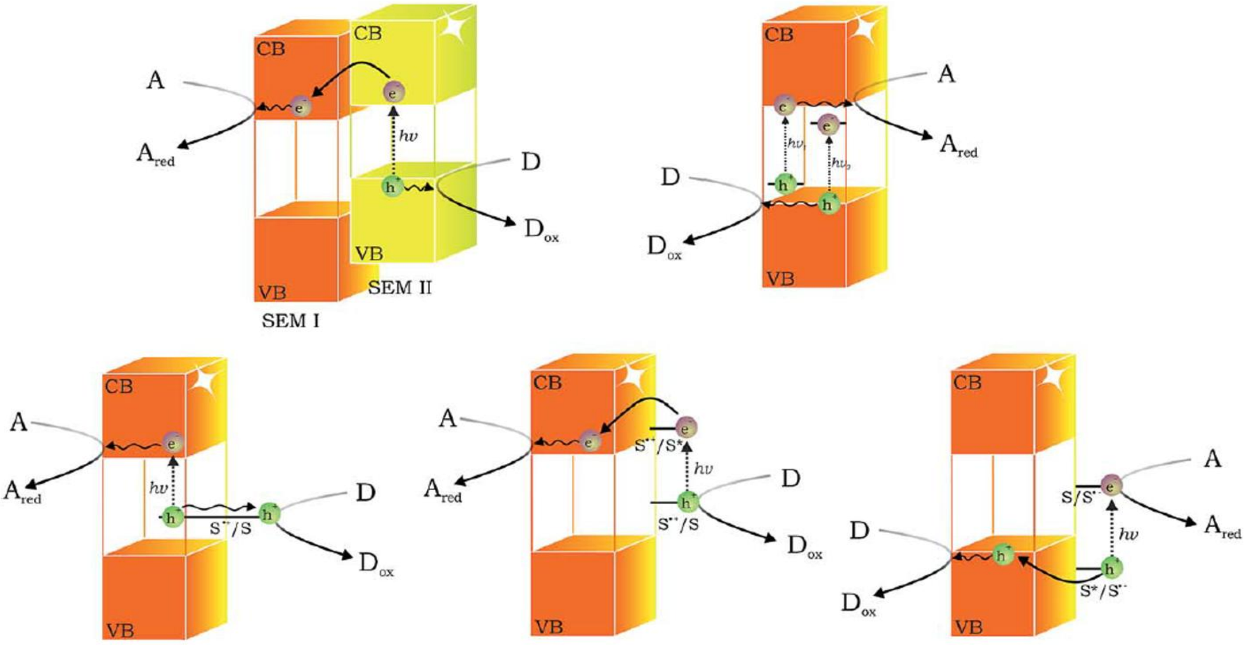


Figure 25. Mechanism of wide band gap semiconductors photosensitization. A – formation of composite semiconductors, B – bulk doping resulting in formation of acceptor or donor levels, C – direct photosensitization (optical charge transfer), D – dye-photosensitization involving an electron injection to the conduction band from the excited photosensitizer, E – dye-photosensitization involving a hole injection to the valence band from the excited photosensitizer.

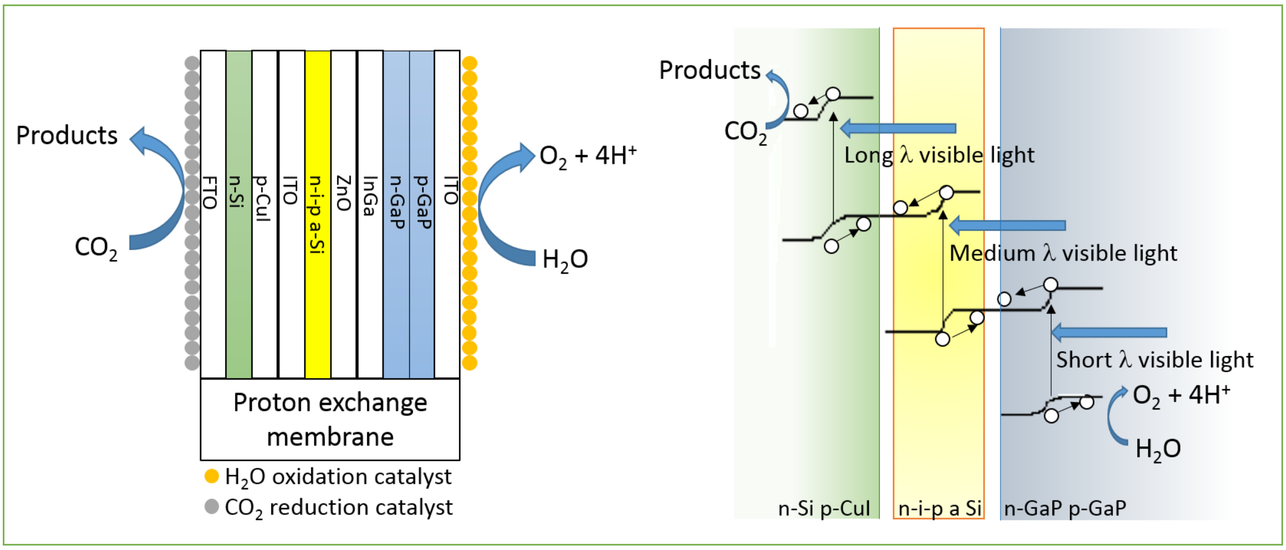


Figure 26. Dual-face electrode for the co-processing of CO_2 and water under solar irradiation.

5.0 Biotechnological uses of CO_2

Biotechnology may provide new opportunities for sustainable production of existing and new products and services. In contrast with chemical processes, the biocatalyst-based processes occur at low temperature, produce fewer emissions and by-products, and in general, less toxic waste if the microbial biomass itself is correctly managed.

Biotechnological routes to enhanced biological conversion of CO_2 involve the use of enzymes or (modified) organisms to convert CO_2 into useful products under optimized conditions. They can be categorized as follows.

1) **Aquatic biomass technologies**, where aquatic biomass, produced under "non natural" or "enhanced" conditions from CO_2 and sunlight, is used as source of chemicals or raw materials which are catalytically processed to afford useful products.

2) **Advanced biotechnological processes,** where the ability of cyanobacteria (a branch of microalgae) to use CO_2 as a *carbon source* and sunlight are merged with the metabolic pathways of known micro-organisms to produce fuels or chemicals,

3) **Bioelectrochemical systems**, where enzymes or micro-organisms use CO_2 as a carbon source and PV-electricity as an energy source for the synthesis of chemicals and fuels**,**

4) **CO_2 fermentation**, where CO_2 is fermented to a desired molecule using non-fossil hydrogen as an energy carrier,

5) **Man-made photosynthesis**, where CO_2 and water are converted into desired chemicals or fuels with the aid of a (bio)catalyst or through integrated biotechnological-chemical processes.

5.1 Integration of biotechnology and chemical catalysis

5.1.1 Aquatic biomass technologies

Aquatic biomass [460] (microalgae in particular [461,462]) can be grown using air enriched with carbon dioxide. The concentration of CO_2 in the gaseous phase can be increased up to 150 times the natural one, conditions referred as CO_2 enhanced fixation. By implementing the concept of biorefinery, aquatic biomass may be used as a source of raw materials catalytically converted into energy products (fuels), chemicals and new materials.

Aquatic biomass has a higher photosynthetic efficiency (6–8%) than terrestrial biomass (1.5–2.2%). The interesting aspect is that flue gases from power plants or streams from industries can in principle be pumped into a photobioreactor or into ponds under controlled conditions as a source of carbon [463], supposed that the concentration of toxic species such as NOx or SOy are kept below the threshold accepted by the algal pond (usually below 150 ppm [464]). Selected microalgae with a high biomass and lipid productivity such as, *Botryococcus braunii*, *Chlorella vulgaris,* and *Scenedesmus sp.* have been cultivated using either ambient air, or air enriched with 10% CO_2 or flue gas [463,465]. Some strains are appropriate for mitigating CO_2, due to their high biomass productivity and C-fixation ability.

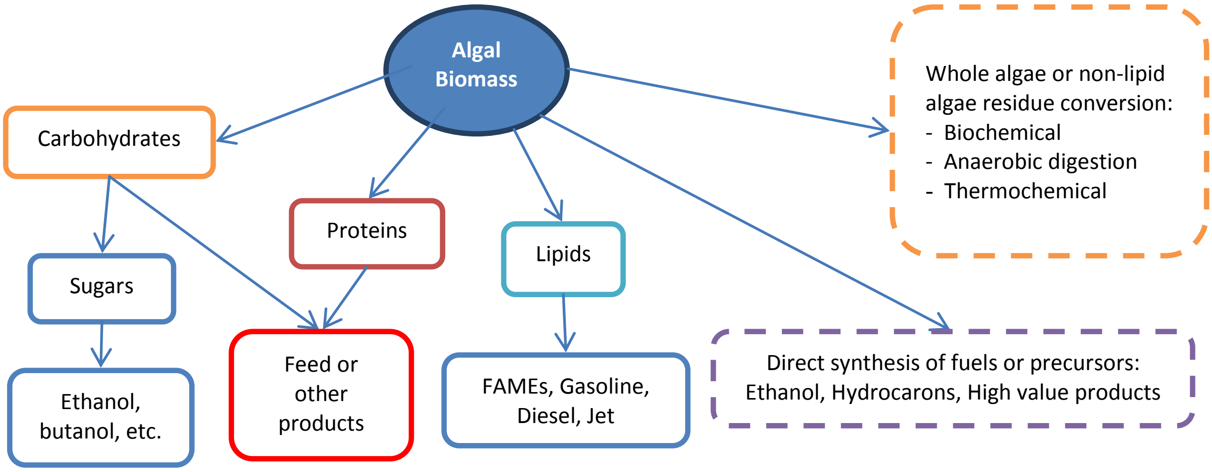


Figure 27. Production of algal biomass and the conversion to fuels and chemical products

Algal biomass contains three main components (Fig. 27), e.g.: carbohydrates, proteins and lipids, in addtition to minor amounts of essential vitamins [466] and omega-3 fatty acids (Table 6).

Table 6. Useful substances contained in algal biomass

Pigments/ carotenoids	ε-carotene, lycopene, γ-carotene and β-carotene, xanthophylls astaxanthin, canthaxanthin, β-cryptoxanthin, echinenone, myxoxanthophyll and oscillaxanthin
Poly-unsaturated fatty acids (PUFAs)	γ-linolenic acid (GLA-C18:3), arachidonic acid (AA-C20:4), eicosapentaenoic acid (EPA-C20:5) and docosahexaenoic acid (DHA-C22:6)
Antioxidants	Catalases, polyphenols, superoxide, dismutase, tocopherols
Vitamins	A, B1, B6, B12, C, E, Biotin, riboflavin, nicotinic acid, pantothenate, folic acid
Others	Antifungal, antimicrobial and antiviral agents, toxins, aminoacids, proteins, sterols

Some species can be engineered to produce a specific product: *Botryococcus braunii* has been engineered to produce the terpenoid C30 botryococcene, a hydrocarbon similar in structure to squalene [467,468].

Several companies produce microalgae for different uses, examples are listed in Table 7.

Table 7. Producers of microalgae and products

Microalgae species	Application/products	Company	Country
Nannochloropsis *Tetraselmis* *Pheodactrylum*	Cosmetics and aquaculture	Astaxa	Germany
Nannochloropsis *Haematococcus pluvialis* *Spirulina* *Chlorella*	PUFA, omega 3, EPA astaxanthin	Bluebiotech	Germany
Haematococcus pluvialis	Astaxanthin/human, fish and animal consumption	Alga Technologies	Israel
Nannochloropsis sp *Pheodactrylum tricornutum* *Amphora sp* *Navicular sp* *Dunaliella sp* *Chlorococcum sp* *Tetraselmis sp* *Nannochloris sp*	Food additives, animal and fish feed, biofuel	Seambiotic	Israel
Haematococcus pluvialis	Astaxanthin	Biogenic Co., Ltd.	Japan
Haematococcus pluvialis *Spirulina*	Astaxanthin	Cyanotech	USA
Chlorella	Biofuels, nutritional, health sciences, chemicals	Solazyme	USA
Spirulina *Chlorella* *Crypthecodinium Cohnii*	DHA/dietary supplements, aquaculture feeds, cosmetics	Femico	Taiwan

Biofuels such as biodiesel, bioethanol, bio-hydrogen and biogas can be produced from aquatic biomass. The quality and composition of the biomass will suggest the best option for the biofuel to be produced. A biomass rich in saturated lipids will be suitable for the production of biodiesel, while unsaturated lipids will be used for the production of chemicals and a biomass rich in sugars will be suited for the production of bioethanol. The anaerobic fermentation of residual biomass can be used for producing biogas. Fig. 28 gives an example of utilization of algal oil in the chemical and energy industry.

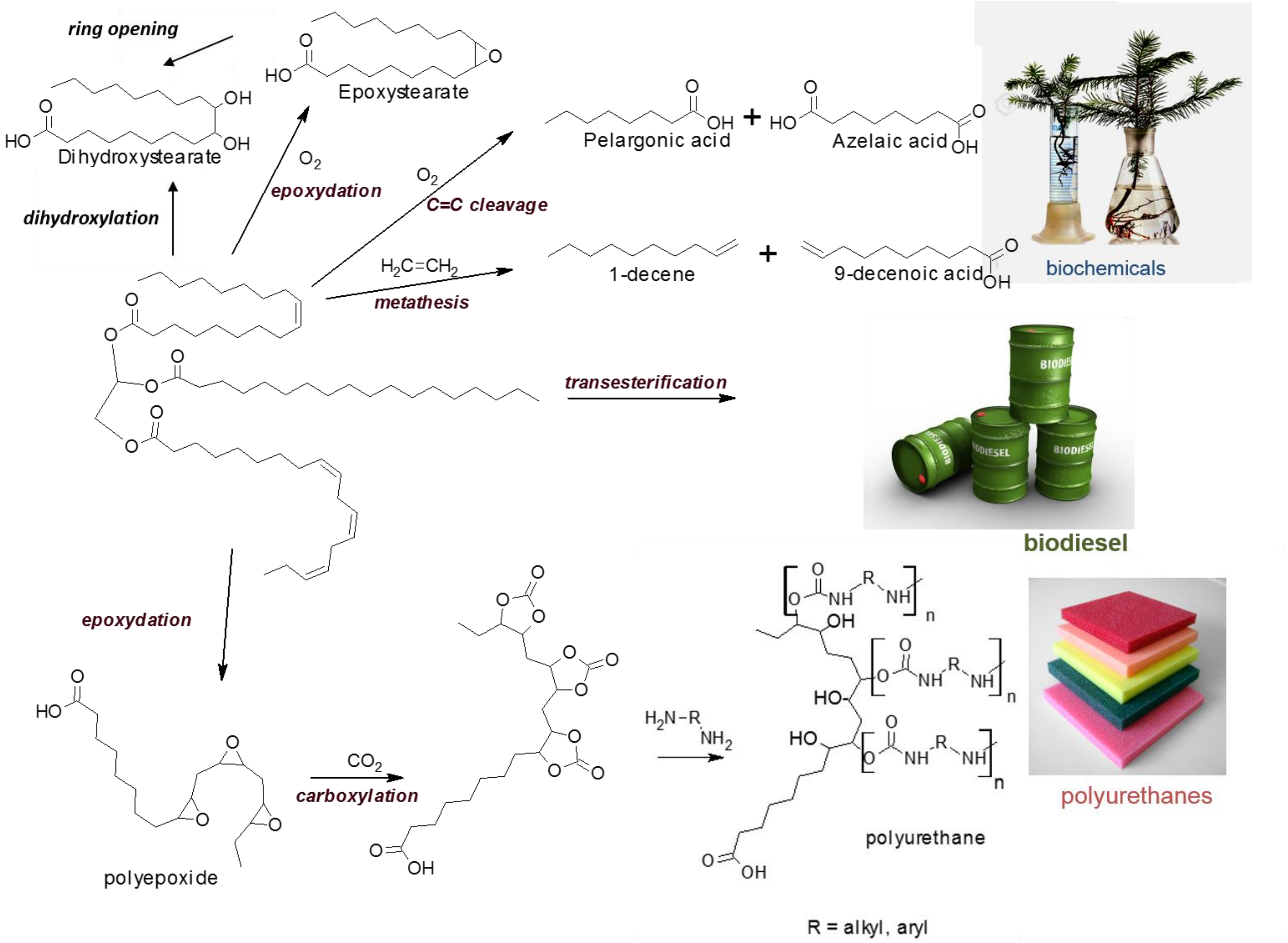


Figure 28. Example of utilization of algal oil in the chemical and energy industry

In a commercial culture what is of interest is the productivity of a pond that means the production per unit time. Often, fast growing algae are not the most specialized for a target product.

The use of process water that may contain nutrients (N- and P-compounds and trace elements) for the growth of the biomass is essential: the addition of nutrients (micro and macro) is not economical and does not make this technology useful for CO_2 reduction.
Synthetic biology and genomics can enhance the productivity and increase the use of algae to produce advanced plastics (collagen, gelatine, alginates, casein, elastin, and zein), hybrid co-polymers and chemicals from biomass generated from enhanced CO_2 fixation.

5.1.2 Advanced biotechnological processes

Cyanobacterial species are easier to genetically manipulate than eukaryotic algae and other photosynthetic organisms, and are being engineered for the production of chemicals or fuels directly from CO_2 [469,470]. Polyhydroxyalkanoate (PHA) is a type of biodegradable polymer for potential application in biomedical or pharmaceutical field. Several cyanobacteria such as *Aphanothece* sp. [471], *Oscillatoria limosa* [472], some species of the genus *Spirulina* [473,474], and the thermophilic strain *Synechococcus* sp. MA19 [475] are natural producers of PHA with a yield <10%. *Synechocystis* sp. PCC 6803 [476] genetically modified produces PHA with 14 wt%. High PHA accumulation of up to 52% dry cell weight was demonstrated in marine cyanobacterium *Synechococcus* sp. PCC 7002. The *Synechococcus* sp. was transformed with plasmid carrying *Cupriavidus necator* PHA biosynthetic genes using *recA* complementation as selection pressure for plasmid stability [477]. The ability of (*S*)- and (*R*)-3-hydroxybutyrate molecules synthesis and secretion from genetically engineered *Synechocystis* sp. PCC 6803 cells was also reported [478].

The modified *Synechococcus elongatus* PCC 7942 has been used for direct photosynthetic conversion of CO_2 into 3-hydroxypropionic acid (3HP) [479] or 1-butanol [480]. Cyanobacteria have been also engineered to produce isoprene and/or ethene. *Synechocystis sp*. PCC 6803 was modified to produce 50 μg g^{-1} dry cell weight per day of isoprene [481-483]. An increase in photosynthetic carbon partitioning towards production of isoprene (120 μg g^{-1}) was achieved by the heterologous expression of the mevalonic acid pathway in *Synechocystis*, which enriched the pool of precursors to isoprene, isopentenyl-diphosphate and dimethylallyl-diphosphate [484].

5.1.3 Bioelectrochemical systems

Bioelectrochemical systems (BES) have recently been proposed as a new and sustainable technology for energy generation and useful products from wastes: in a BES, bacteria interact with solid-state electrodes by exchanging electrons with them, either directly or via redox mediators [485]. A possible application is the electrochemical reduction of carbon dioxide to methane according to reaction 72:

$$CO_2 + 8\,H^+ + 8e^- \rightarrow CH_4 + 2H_2O \qquad (72)$$

Indeed, both the electrons and carbon dioxide released at the anode during the microbial oxidation of the organic matter contained in a waste stream can be in principle exploited for the cathodic generation of methane, according to the schematic drawing reported in Fig. 29. At standard conditions, this reaction requires a theoretical voltage of −0.244 V (vs. SHE) at pH 7, but it is usually affected by quite large overpotentials that, however, could be possibly reduced by using a microbial biocathode.

Another interesting example of bioelectrochemical systems is presented by the enzyme formate dehydrogenases that contains molybdenum or tungsten cofactors able to transfer the electrons from formate oxidation to an independent active site, to reduce quinone, protons, or NAD(P) [487,488]. These enzymes are suitable for adsorption onto an electrode, so that the electrode accepts the electrons from formate oxidation, and it may also donate electrons and drive CO_2 reduction. Therefore, they are potential electrocatalysts for the reduction of CO_2 (see Fig. 30). Two electrons are transferred from the electrode to the active site (buried inside the insulating protein interior) by the iron–sulfur clusters, to reduce CO_2 to formate, forming a C–H bond. Conversely, when formate is oxidized, the two electrons are transferred from the active site to the electrode.

One of the tungsten-containing formate dehydrogenases, namely FDH1, can be isolated from *Syntrophobacter fumaroxidans*, an anaerobic bacterium that oxidizes propionate to acetate, CO_2, and six reducing equivalents [489].

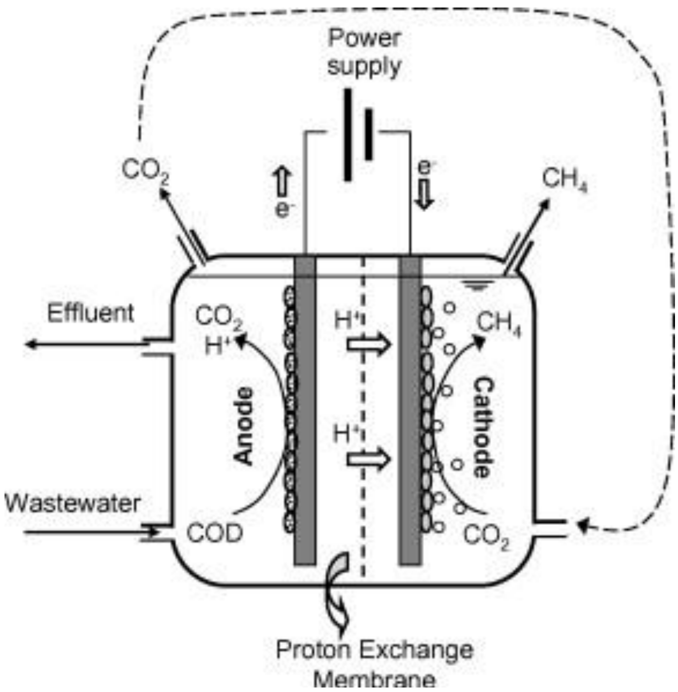


Figure 29. Schematic drawing of a bioelectrochemical system for wastewater treatment and simultaneous CH_4 production based on bioelectrochemical CO_2 reduction [486]

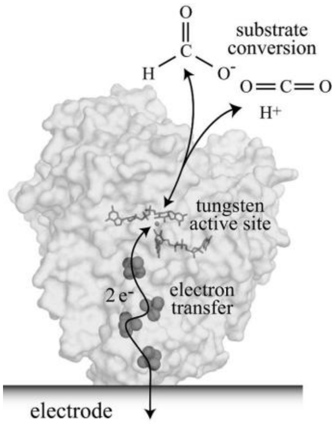


Figure 30. Electrocatalytic interconversion of CO_2 and formate by a formate dehydrogenase from *Desulfovibrio gigas* adsorbed on an electrode surface.

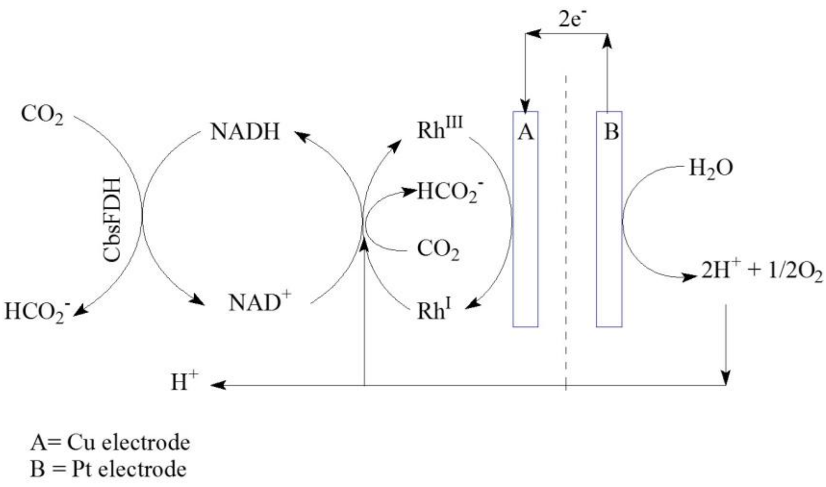


Figure 31. Electro-enzymatic CO_2 reduction using CbsFDH.

The reducing equivalents are used to reduce protons to hydrogen or CO_2 to formate. The NADH-independent FDH enzymes from *S. fumaroxidans* are highly unstable and inactive in the presence of O_2, limiting their practical application. Differently, the NADH-dependent FDH from *Candida boidinii* (CbsFDH) is sufficiently stable for commercial use and has been used to enzymatically regenerate NADH. CbsFDH requires NADH, protons and electrons to convert CO_2 into formate, the latter can be supplied by the electrochemical system of the Cu electrode (Fig. 31). The $[Cp^*Rh(bpy)Cl]^+$ complex has been used as catalyst for the conversion of NAD^+ into the active NADH with almost 100% selectivity [490, 491].

Although some enzymatic reaction systems have been reported that can interconvert CO_2 to formate electrochemically [492], these enzymes originate from strictly anaerobic microbes with extremely weak stability in the presence of oxygen, which could be a severe obstacle for the industrial application of enzymatic CO_2 reduction. Although one example of oxygen-tolerant formate dehydrogenase has been reported, this enzyme requires the expensive NADH cofactor with hydrogen gas as an electron donor [493]. In addition, the use of separated enzymes requires extra purification steps that may increase the cost of the reaction system.

Interestingly, in order to facilitate the process, microbial whole cell systems have been used that can be applied under aerobic conditions. *Methylobacterium* microbial were found to produce formate from CO_2 by using electrons supplied from cathode electrode [494,495].

Bioelectrochemical systems have been used also for the microbial electrosynthesis (MES) of acetate from the biocathodic reduction of carbon dioxide. Hydrogencarbonates (the dissolved form of CO_2) were the substrate for the bioelectrochemical production of acetate under mild applied cathodic potential of -400 mV (*vs* SHE) in single chamber electrochemical cells [496].

5.1.4 CO_2 fermentation

The idea to convert CO_2 and H_2 to biomethane (Eq. 72) through a chemoautotrophic conversion mediated by methanogenic *archaea* is still undeveloped because most of the H_2 production worldwide comes from steam reforming of CH_4 [497].

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \qquad (72)$$

However, if one considers the implementation of renewable energies and produces H_2 from wind and solar power through water electrolysis, the transformation of carbon dioxide into biomethane can make sense, which can be injected into natural gas (NG) grids or employed as fuel for vehicles [498]. CO_2 can be selectively fermented to specialty, commodity chemicals, food components or fuels using metabolically engineered biocatalysts with high product selectivity [499] in contrast with chemical syngas catalysis characterized by low selectivity. CO_2-rich syngas or captured CO_2 with added hydrogen can be completely fermented by engineered biocatalysts with zero CO_2 process emissions to target products if non-fossil H_2 sources are available (sea water electrolysis using electricity produced by high efficiency solar panels in situ) [499].

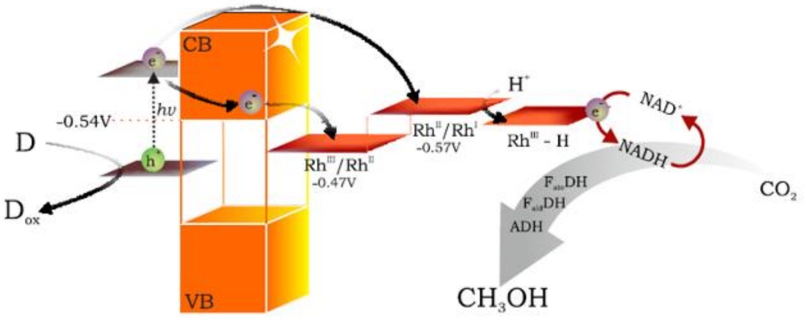
Acetogenic bacteria are used to produce alcohols and organic acids directly from CO_2 and H_2. In particular *Clostridium carboxidivorans* and *Clostridium ragsdalei* can metabolize syngas components to produce ethanol and acetic acid [500-503].

5.1.5 Man made photosynthesis

Nature, which generates up to 115 Gt [504] of biomass annually from the reduction of CO_2 using solar energy, provides inspiration to develop man-made systems able to capture solar energy and convert CO_2 and H_2O into value-added chemicals. Two classes of enzyme, carbon monoxide dehydrogenases (CODH) and formate dehydrogenases (FDH), catalyse two-electron reduction of CO_2, the first and crucial stage of its entry into organic chemistry. The enzymes avoid radical intermediates such as CO_2^{-} or COOH (−1.9 V *vs.* SHE at pH 7 [505]) proceeding instead *via* proton-coupled electron transfers (PCET) in single concerted steps to CO or HCOOH. Both CODH and FDH are reversible electrocatalysts when attached to graphite electrodes [506,507], suggesting their use as CO_2 reduction catalysts in (bench-scale) man made photosynthesis systems.

Of interest is also the hybrid bioinspired systems used for the enzymatic reduction of CO_2 to CH_3OH in water [445] that combines two processes: the enzymatic reduction of CO_2 to CH_3OH promoted by the reduced form of coenzyme NADH with the *in situ* efficient and selective photocatalytic regeneration of NADH from NAD^+, using semiconductors. A number of semiconducting materials that behave as photocatalysts under visible-light, such as: Cu_2O, $InVO_4$, TiO_2 modified either with the organic compound rutin, or with the inorganic complex $[CrF_5(H_2O)]^{2}$) [447] and the doped sulphide Fe/ZnS have been prepared and used for the reduction of NAD^+ to NADH. The expected mechanism of NADH regeneration is shown in Scheme 46.

Regeneration of the cofactor NADH from NAD^+ has been achieved by using visible light-active heterogeneous TiO_2-modified photocatalysts. The regeneration process is made more efficient by using a Rh^{III}-complex that facilitates the electron and hydride transfer from the H-donor (water or a water-glycerol solution) to NAD^+. In this way one mol of NADH was used for producing 100-1000 mol of CH_3OH, opening the way to a practical application [445].



Scheme 46. Expected mechanism of NADH regeneration and further carbon dioxide reduction to methanol [445, 447].

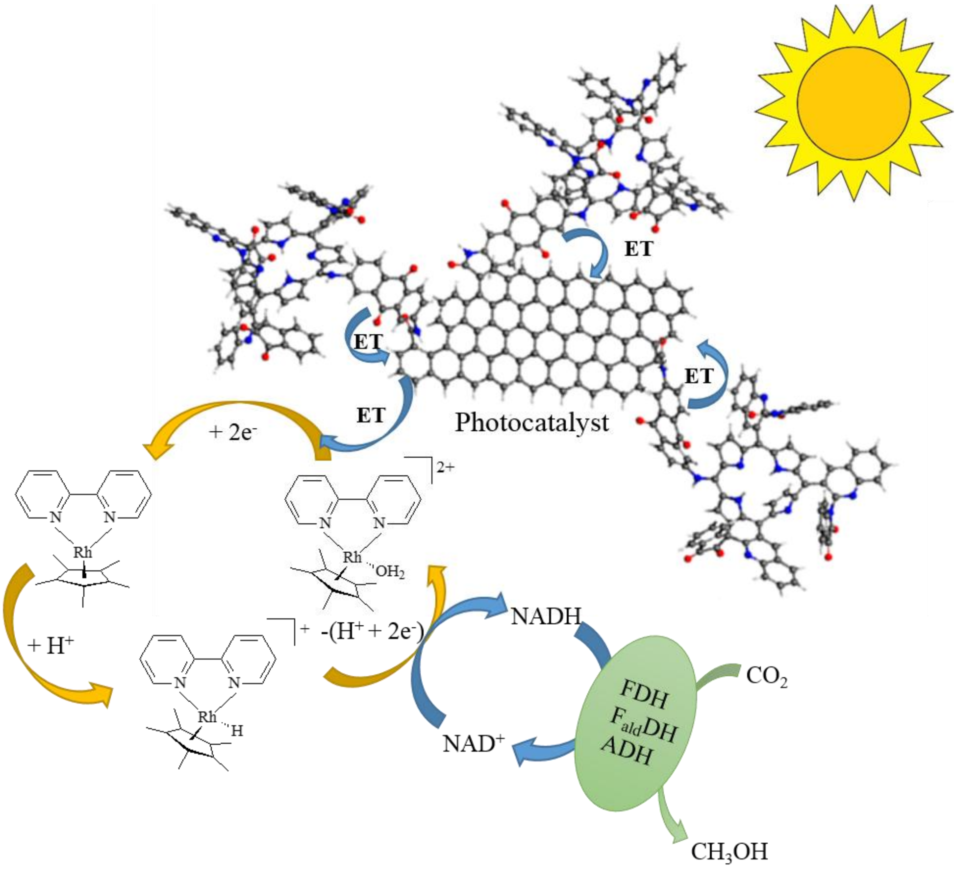
Of interest is also the graphene-based photocatalyst integrated sequentially with enzymes formate dehydrogenase, formaldehyde dehydrogenase, and alcohol dehydrogenase as depicted in Scheme 47 [508].

The above examples illustrate some options leading to a man-made hybrid photosynthetic device that uses solar energy for the conversion of CO_2 and water into chemicals and fuels, mimicking Nature. Another recent use of photocatalysis is the direct fixation of CO_2 into an organic substrate to afford acids (Scheme 17). Inorganic materials (semiconductors) have been engineered to use solar light for the reduction of CO_2 to C1 or Cn species [509]. Photoelectrochemistry [PEC] can represent an interesting tool for the conversion of CO_2 using solar energy (see section 4.3).

The challenge is, thus, open for a large scale CO_2 conversion mimicking Nature. Our future will be based on a “CO_2-water economy” if we will be good enough to make an integrated use of biotechnology and catalysis for the conversion of CO_2 into useful products.

6.0 Conclusions

Carbon dioxide can be used as synthon for several carboxylated products, or source of carbon for fuels. A few reactions are known since the late 1800s and industrial processes are run since more than a century that today use 180 Mt_{CO2}/y, to which 20 Mt_{CO2}/y as technological fluid must be added. The exploited processes do not require a high energy input as the carbon atom maintains the same +4 oxidation state in the product (mainly chemicals) as in free CO_2. In perspective, in a business as usual scenario, the amount of CO_2 that can be used may grow to *ca*. 330 Mt/y by 2030, that in terms of *avoided* CO_2 corresponds to *ca.* 1 Gt_{CO2}/y. Considered in terms of carbon mitigation, such use of CO_2 does not make a significant contribution to C-reduction. Conversely, the use of CO_2 as source of carbon for fuels may expand the amount of used CO_2 by one order of magnitude, as the market of fuels is 12-14 times larger than that of chemicals. Such new use requires energy and hydrogen, two requisites that have so far ruled out the production of fuels from CO_2 as both energy and H_2 are mainly (85-93 %) derived from fossil carbon. However, if perennial energies such as solar, wind and geothermal are used for running the conversion of CO_2 into fuels,



Scheme 47. Schematic illustration of photocatalyst/biocatalyst integrated system to reduce CO_2 to methanol [508].

the use of large volumes of CO_2 will be made possible and by 2050 several Gt_{CO2}/y would be converted into non-fossil carbon based products for the chemical or energy industry. This would make the carbon dioxide capture and utilization-CCU technology as one of the routes that may help to cut substantial emissions of CO_2. Recycling of carbon in CCU would complement the natural C-cycle making a step away from the actual linear C-economy, towards a circular C-economy.

Compared to the CO-chemistry, the CO_2 chemistry is very young as it has been developed after Aresta and coll. discovered in 1975 the first Ni-CO_2 complex and demonstrated that the co-ordination of CO_2 to a metal centre facilitates the splitting of the C-O bond, a reaction that for the free molecule requires high energy (thermal or radiative).

Since then, new reactions have been discovered for CO_2 conversion into fine chemicals or intermediates, some of which are catalytic processes while others are syntheses assisted my metals and consume one mol of metal per mol of CO_2 converted. This is not economically nor energetically acceptable, and is a heavy environmental burden. Making such processes catalytic is a must for their exploitation that would result in a considerable cut of CO_2 emissions as the CO_2-based processes are more direct than those on stream, use safer conditions, increasing the efficiency of energy and material use.

The reaction parameter space (T, P, solvent, catalyst, conversion yield, selectivity, separation techniques, *etc*) must be correctly managed to ensure that the new reaction is a net CO_2-consumer and not an emitter.

Several routes are possible for the conversion of CO_2 into fuels, a strong endergonic process, that can be run using perennial primary energy sources such as solar, wind or geothermal. Hydrogen necessary for the conversion of CO_2 into C1 or Cn energy-rich species, must be produced from water or waste organics. Electrochemical technologies for water electrolysis are commercial and used today. Excess electric energy is already used today with profit: using fossil carbon derived electricity for CO_2 conversion would not represent a wise solution as the whole process would not reduce the CO_2 emission. The use of excess electric energy (eventually produced also by nuclear plants) goes in the direction of a higher efficiency in the use of fossil carbon and makes the CO_2 conversion a way to store electricity, a problem so far not yet solved as batteries do not represent the best solution on a large scale. The use of PV for H_2 production, today not convenient from the economical point of view, may become convenient in the near future if the target of 40% efficiency in solar energy conversion into electricity is reached and cheap materials are developed for capture of solar energy. Also, the reduction of emissions in the production of PV materials must be targeted.

The photochemical and photoelectrochemical conversion of CO_2 are innovative technologies that may play a key role in supporting the conversion of large volumes of CO_2 into fuels or chemicals.

Integrating biotechnology and catalysis may push towards a better exploitation of biomass obtained in natural or enhanced processes, and mastering algae growing for fuels and chemicals may give a substantial contribution to CO_2 mitigation. The development of innovative technologies based on integrated biotech and catalysis as bioelectrochemical technologies or microbial fuel cells, may also give a strong push towards the exploitation of CO_2 as source of carbon.

Several new processes have been discovered that must be correctly mastered in order to make them net CO_2 consumers. The Life Cycle Assessment-LCA methodology must be used for assessing the real impact on CO_2 mitigation of the new synthetic routes.

Scientists and technologists have in their hands powerful tools for CO_2 reduction, financial support is necessary for their assessment and growth from actual TRL 3-5 to exploitation and this must jointly come from the public and private sectors.

Mimicking Nature in CO_2 conversion *via* photosynthetic processes will represent a move from the today linear carbon economy towards a circular carbon economy based on CO_2 and water, converting spent carbon into working carbon, saving natural resources for future generations and implementing the concept of sustainable chemistry.

Each atom of carbon recycled is an atom of carbon that does not reach the atmosphere today and stays in the ground for next generations.

References

1. A.I. Bazarov, J. Prakt. Chem. 2 (1870) 283.
2. G. Steinhauser, J. Cleaner Prod. 16 (2008) 833.
3. H. Kolbe, J. Prakt. Chem. 10 (1874) 89.
4. X.-M. Liu, G. Q. Lu, Z.-F. Yan, J. Beltramini, Ind. Eng. Chem. Res. 42 (2003), 6518.
5. T. Tsuda, Y. Chujo, T. Saegusa, J. Chem Soc. Chem. Commun. (1976) 415.
6. M. Aresta, A. Dibenedetto, L.N. He, Analysis of demand for captured CO_2 and products from CO_2 conversion, TCGR report 2013.
7. M. Aresta, E. Quaranta, I. Tommasi, P. Giannoccaro, A. Ciccarese, Gazz. Chim. Ital. 125 (1995) 509.
8. M. Aresta, A. Dibenedetto, E. Quaranta, Reaction Mechanisms in the conversion of CO_2, Springer-Verlag Berlin Heidelberg, 2015.
9. M. Aresta, M. Galatola, J. Cleaner Prod. 7 (1999) 181.
10. E. Hirota, T. Iijima, K. Kuchitsu, W.J. Lafferty, D.A. Ramsay, J. Vogt, in: K. Kuchitsu (Ed.), Structure data of free polyatomic molecules, Landolt-Börnstein, Springer, Berlin, 1992, Volume II/21, p. 151.
11. G. Graner, E. Hirota, T. Iijima, K. Kuchitsu, A.D. Ramsay, J. Vogt, N. Vogt, in: K. Kuchitsu (Ed.), Structure data of free polyatomic molecules, Landolt-Börnstein, Springer, Berlin, 1995, Volume II/23, p. 146.
12. M. Vučelić, Y. Ohrn, J.R. Sabin, J. Chem. Phys. 59 (1973) 3003.
13. A.D. Walsh, J. Chem. Soc. (1953) 2266.
14. C. Cossart-Magos, F. Launay, J.E. Parkin, Mol. Phys. 103 (2005) 629-641 and references therein.
15. G. Preda, G. Pacchioni, M. Chiesa, E. Giamello, J. Phys. Chem. 112 (2008) 19568 and references therein.
16. R. N. Compton, P.W. Reinhardt, C.D. Cooper, J. Chem. Phys. 63 (1975) 3821.
17. J. Pacansky, U. Wahlgren, P.S. Bagus, J. Chem. Phys. 62 (1975) 2740.
18. C. Cossart-Magos, M. Jungen, F. Launay, Molec. Phys. 61 (1987) 1077.
19. H. Okabe, Photochemistry of small molecules, John Wiley and Sons, Inc., New York, 1978.
20. G. Herzberg, Molecular spectra and molecular structure.III. Electronic spectra and electronic structure of polyatomic molecules, Van Nostrand-Reinhold, New York, 1966.
21. T. Shimanouchi, NSRDS-NBS (US) 39 (1972) 1.
22. F.A. van Broekhuizen, I.M.N. Groot, H.J. Fraser, E.F. van Dishoeck, S. Schlemmer, A&A 451 (2006) 723.
23. M. Falk, A.G. Miller, Vibr. Spectrosc. 4 (1992) 105.
24. M.E. Jacox, J. Phys. Chem. Ref. Data 19 (1990) 1388.
25. M.E. Jacox, W.E Thompson, J. Chem. Phys. 91 (1989) 1410.
26. M. Zhou, L. Andrews, J. Chem. Phys. 110 (1999) 2414.
27. C. Jegat, J. Mascetti, New J. Chem. 15, (1991) 17.
28. M. Aresta, A. Dibenedetto, E. Quaranta, Reaction Mechanisms in Carbon Dioxide Conversion, Springer-Verlag Berlin Heidelberg, 2015, Chapter 2.
29. E.P. Hunter, S.G. Lias, J. Phys. Chem. Ref. Data 27 (1998) 413.
30. L. Kucka, E.Y. Kenig, A. Gorak, Ind. Eng. Chem. Res. 41 (2002) 5952.
31. G. Astarita, D.W. Savage, A. Bisio, Gas treating with chemical solvents, J. Wiley and Sons, NY, 1983.
32. K. S. Lackner, C.H. Wendt, D.P. Butt, E.L. Joyce, D.H. Sharp, Energy 20 (1995) 1153.

33. G. Gadikota, J. Matter, P. Kelemenb, A.A. Park, Phys. Chem. Chem. Phys. 16 (2014) 4679.
34. E. Quaranta, M. Aresta, in: M. Aresta (Ed.), Carbon Dioxide as Chemical Feedstock, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010, p. 121.
35. D. Belli Dell'Amico, F. Calderazzo, L. Labella, F. Marchetti, G. Pampaloni, Chem. Rev. 103 (2003) 3857.
36. Z.-H. Yang, L.-N. He, J. Gao, A.-H. Liu, B. Yu, Energy. Environ. Sci. 5 (2012) 6602.
37. M. Aresta, E. Quaranta, Tetrahedron 48 (1992) 1515.
38. M. Aresta, D. Ballivet-Tkatchenko, D. Belli Dell'Amico, M.C. Bonnet, D. Boschi, F. Calderazzo, R. Faure, L. Labella, F. Marchetti, Chem. Comm. (2000) 1099.
39. W.W. Cleland, T.J. Andrews, S. Gutteridge, F.C. Hartmann, G.H. Lorimer, Chem. Rev. 98 (1998) 549.
40. G. Couchaux, D. Barth, M. Jacquin, A. Faraj, J. Grandjean, Oil & Gas Science and Technology - Rev. IFP Energies Nouvelles 69 (2014) 865.
41. P.V. Danckwerts, Chem. Eng. Sci. 34 (1979) 443.
42. J.E. Crooks, J.P. Donnellan, J. Chem. Soc. Perkin Trans. II (1989) 331 and references therein.
43. D.W. Stephan, G. Erker, Angew. Chem. Int. Ed., 49 (2010) 46.
44. G.Erker, D.W. Stephan (Eds), Frustrated Lewis Pairs I, Topics in Current Chemistry, Springer, Heidelberg Vol. 232 (2013).
45. G.Erker, D.W. Stephan (Eds), Frustrated Lewis Pairs II, Topics in Current Chemistry, Springer, Heidelberg Vol. 234 (2013).
46. C. Appelt, H. Westenberg, F. Bertini, A.W. Ehlers, J.C. Slootweg, K. Lammertsma, W. Uhl, Angew. Chem. Int. Ed. 50 (2011) 3925 and references therein.
47. S.A. Weicker, D.W. Stephan, Chem. Eur. J. 21 (2015) 13027.
48. M.-A. Courtemanche, M.-A. Légaré, L. Maron, F.-G. Fontaine, J. Am. Chem. Soc. 136 (2014) 10708.
49. R. Declercq, G. Bouhadir, D. Bourissou, M.-A. Légaré, M.-A. Courtemanche, K.S. Nahi, N. Bouchard, F.-G. Fontaine, L. Maron, ACS Catal. 5 (2015) 2513.
50. A. Berkefeld, W.E. Piers, M. Parvez, J. Am. Chem. Soc. 132 (2010) 10660.
51. M.-A. Courtemanche, A.P. Pulis, E. Rochette, M.-A. Légaré, W. Stephan, F.-G. Fontaine, Chem. Comm. 51 (2015) 9797.
52. M. Aresta, A. Angelini, Top. Organomet. Chem. 53 (2015) 1.
53. D.H. Gibson, Coord. Chem. Rev. 185-186 (1999) 335 and references therein.
54. X. Yin, J.R. Moss, Coord. Chem. Rev. 181 (1999) 27.
55. M. Aresta, C.F. Nobile, V.G. Albano, E. Forni, M. Manassero, J. Chem. Soc. Chem. Comm. (1975) 636.
56. L. Contreras, M. Paneque, M. Sellin, E. Carmona, P.J. Perez, E. Gutierrez-Puebla, A. Monge, C. Ruiz, New J. Chem. 29 (2005) 109 and references therein.
57. C.H. Lee, D.S. Laitar, P. Mueller, J.P. Sadighi, J. Am. Chem. Soc. 129 (2007) 13802.
58. S. Sakaki, Stereochemistry of Organometallic and Inorganic Compounds (Stereochem. Control, Bonding Steric Rearrange) 4 (1990) 95.
59. J.C. Calabrese, T. Herskovitz, J.B. Kinney, J. Am. Chem. Soc. 105 (1983) 5914.
60. R.L. Harlow, J.B. Kinney, T. Herskovitz, J. Chem. Soc. Chem. Commun. (1980) 813.
61. M. Aresta, C.F. Nobile, Inorg. Chim. Acta 24 (1977) L49.
62. K. Tanaka, D. Ooyama, Coord. Chem. Rev. 226 (2002) 211.
63. E. Fujita, C. Creutz, N. Sutin, B.S. Brunschwig, Inorg. Chem. 32 (1993) 2657.
64. J.D. Holbrey, W.M. Reichert, I. Tkatchenko, E.Bouajila, O. Walter, I. Tommasi, R.D. Rogers, Chem. Comm. 1 (2003) 28.
65. L. Yang, H.Wang, ChemSusChem 7 (2014) 962.
66. I. Castro-Rodriguez, H. Nakai, L.N. Zakharov, A.L. Rheingold, K. Meyer, Science 305 (2004) 1757.
67. P.D.C. Dietzel, R.E. Johnsen, H.Fjellväg , S. Bordiga, E. Groppo, S. Chavan, R. Blom, J. Chem. Soc. Chem. Comm. 5 (2008) 125.
68. C.-C. Chang, M.-C. Liao, T.-H. Chang, S.-M. Peng, G.-H. Lee, Angew. Chem. Int. Ed. 44 (2005) 7418.
69. G. Gao, F. Li, L.Xu , X. Liu, Y.Yang, J. Am. Chem. Soc. 130 (2008) 10838.
70. O.P. Lam, K. Meyer, Polyhedron 32 (2012) 1.
71. J. Mascetti, F. Galan, I. Papai, Coord. Chem. Rev. 190–192 (1999) 557.
72. J. Mascetti, in: M. Aresta (Ed.), Carbon Dioxide as Chemical Feedstock, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2010, pp. 55 and references therein.
73. W. Leitner, Coord. Chem. Rev. 153 (1996) 257.

74. M. Aresta, R. Gobetto, E. Quaranta, I. Tommasi, Inorg. Chem. 32 (1992) 4286.
75. J.K. Gong, C.A.Wright, M.Thorn, K. McCauley, J.W. McGill, A. Sutterer, S.M. Hinze, R.B. Prince, Advances in Chemical Conversions for Mitigating Carbon Dioxide 114 (1998) 491.
76. J.C.T. Sai, M. Khan, K.M. Nicholas, Organomet. 8 (1989) 2967.
77. M. Hirano, M. Akita, K.Tani, K. Kumagai, N. Kasuga, A. Fukuoka, S. Komiya, Organomet. 16 (1997) 4206.
78. P. Deglmann, E. Ember, P.Hofmann, S. Pitter, O. Walter, Chem. Eur. J. 13 (2007) 2864.
79. M. Aresta, E. Quaranta, I. Tommasi, J. Chem. Soc. Chem. Comm. (1988) 450.
80. I. Castro-Rodriguez, K. Meyer, J. Am. Chem. Soc. 127 (2005) 11242.
81. T. Herskowitz, L. Guggenberger, J. Am. Chem. Soc. 98 (1976) 1615.
82. M. Aresta, A. Dibenedetto, J. Mol. Catal. 399 (2002) 182.
83. M.B. Ansari, S.-E. Park, Energy Environ. Sci. 5 (2012) 9419.
84. M. Aresta, I. Tommasi, A. Dibenedetto, M. Fouassier, J. Mascetti, Inorg. Chim. Acta 330 (2002) 63.
85. M. Aresta, I. Tommasi, E. Quaranta, C. Fragale, J. Mascetti, M. Tranquille, F. Galan, M. Fouassier, Inorg. Chem. 35 (1996) 4254.
86. I. Bertini, C. Luchinat, in: I. Bertini, H.B. Gray, S.J. Lippard, J.S. Valentine (Eds.), Bioinorganic Chemistry, University Science Books, Mill Valley, 1994.
87. P.T. Altenbuchner, S. Kissling, B. Rieger, in: B.M. Bhanage, M. Arai (Eds.), Transformation and Utilization of Carbon Dioxide, Green Chemistry and Sustainable Technology, Springer-Verlag Berlin Heidelberg 2014, p. 163.
88. D.J. Darensbourg, A.D. Yeung, Polym. Chem. 5 (2014) 3949.
89. Y. Wang, J. Fan, D.J. Darensbourg, Angew. Chem. Int. Ed. 54 (2015)10206.
90. D.J. Darensbourg, K.M. Sanchez, J.H. Reibenspies, A.L. Rheingold, J. Am. Chem. Soc. 111 (1989) 7094.
91. R.D. Simpson, R.G. Bergman, Angew. Chem. Int. Ed. Engl. 31 (1992) 220.
92. S. Schenk, J. Notni, U. Kohn, K. Wermann, E. Anders, Dalton Trans. (2006) 4191.
93. J.F. Hartwig, R.G. Bergman, R.A. Andersen, J. Am. Chem. Soc. 113 (1991) 6499.
94. M.H. Chisolm, M. Extine, J. Am. Chem. Soc. 99 (1977) 792.
95. M.E. Vol'pin, I.S. Kolomnikov, Pure Appl. Chem. 33 (1973) 567.
96. K.K. Pandey, Coord. Chem. Rev. 140 (1995) 37.
97. D.L. DuBois, A.R. Miedaner, R.C. Curtis Haltiwanger, J. Am. Chem. Soc. 113 (1991) 8753.
98. H. Konno, A. Kobayashi, K. Sakamoto, F. Fagalde, N. Katz, H.Saitoh, O. Ishitani , Inorg. Chim. Acta 299 (2000) 155.
99. T. Matsubara, K. Hirao, Organomet. 20 (2001) 5759.
100. Y. Ohnishi, Y. Nakao, H. Sato, S. Sakaki Organomet. 25 (2006) 3352.
101. L. Schlapbach, A. Züttel, Nature 414 (2001) 353.
102. S. Moret, P. Dyson, G. Laurenczy, Nat. Commun. 5 (2014) 1.
103. C. Federsel, R. Jackstell, M. Beller, Angew. Chem. Int. Ed. 49 (2010) 6254.
104. R.Tanaka, M. Yamashita, K. Nozaki, J. Am. Chem. Soc. 131 (2009) 14168.
105. J. Louie, Curr. Org. Chem. 9 (2005) 605-623.
106. H. Hoberg in: M. Aresta, G. Forti (Eds.) D. Reidel Publishing Company, Dordrecht, 1987, p. 275 and references therein.
107. A. Graët, L. Sinault, M.B. Fusaro, A.-L. Vallet, C. Seu, J.L. Kilgore, M.M. Baum, Organomet. 29 (2010) 1997 and references therein.
108. T. Tsuda, Gazz. Chim. Ital. 125 (1995) 101.
109. D. Walther, Coord. Chem. Rev. 79 (1987) 135.
110. A. Behr, Carbon dioxide activation by metal complexes. VCH Verlagsgesellschaft mbH, Weinheim, 1988
111. L. Dahlenburg, C. Prengel, Inorg. Chim. Acta 22 (1986) 55.
112. C. Geyer, E. Dinjus, S. Schindler, Organomet. 17 (1998) 98 and references therein.
113. C. Geyer, S. Schindler, Organomet. 17 (1998) 4400.
114. K. Yamashita, N. Chatani, Synlett. (2005) 919.
115. M. Aresta, E. Quaranta, J. Organomet. Chem. 463 (1993) 215.
116. M. Aresta, A. Dibenedetto, ACS Symp Ser 809 (CO_2 Conversion and Utilization) (2002) 54.
117. I. Papai, G. Schubert, I. Mayer, G. Besenyei, M. Aresta, Organomet. 23 (2004) 5252.
118. J. Li, G. Jia, Z. Lin, Organomet. 27 (2008) 3892.

119. D.C. Graham, M.I. Bruce, G.F. Metha, J.H. Bowie, M.A. Buntine J. Organomet. Chem. 693 (2008) 2703.
120. G. Yang, B. Schaffner, M. Blug, E.J.M. Hensen, E.A. Pidko, ChemCatChem 6 (2014) 800.
121. A. Galindo, A. Pastor, P.J. Perez, E. Carmona, Organomet. 12 (1993) 4443.
122. G. Schubert, I. Papai, J. Am. Chem. Soc. 125 (2003) 14847.
123. W.H. Bernskoetter, B.T. Tyler, Organomet. 30 (2011) 520.
124. D. Yu, S.P. Teong, Y. Zhang, Coord. Chem. Rev. 293–294 (2015) 279.
125. A. Pinaka, G.C. Vougioukalakis, Coord. Chem. Rev. 288 (2015) 69.
126. C.S. Yeung, V.M. Dong, Top. Catal. 57 (2014) 1342.
127. A.-H. Liu, B. Yu, L.-N. He Greenhouse Gas Sci. Technol. 5 (2015) 17.
128. Q. Liu, L. Wu, R. Jackstell, M. Beller, Nature Commun. (2015) DOI: 10.1038/ncomms6933.
129. D. Chaturvedi, Tetrahedron 68 (2012) 15.
130. B. Yu, L.-N. He, ChemSusChem, 8 (2015) 52.
131. M. Aresta, A. Caroppo, A. Dibenedetto, M. Narracci, in: M. Maroto Valer, C. Song, Y. Soong (Eds.), Environmental Challenges and Greenhouse Gas Control for Fossil Fuel Utilization in the 21st Century, Kluwer, Dordrecht, **2002**, p. 331.
132. http://www.prnewswire.com/news-releases/acrylic-acid-market-all-set-to-grow-exponentially-during-the-forecast-2014-to-2020-big-market-research-294988401.html
133. H. Hoberg, Y. Peres, A. Milchereit, J. Organomet. Chem. 307 (1986) C38.
134. R. Fischer, J. Langer, G. Malassa, D. Walther, H. Gorls, G. Vaughan, Chem Comm. (2006) 2510.
135. D.C. Graham, C. Mitchell, M.I. Bruce, G.F. Metha, J.H. Bowie, M.A. Buntine, Organomet. 26 (2007) 6784.
136. T. Yamamoto, K. Igarashi, S. Komiya, A. Yamamoto, J. Am. Chem. Soc. 102 (1980) 7448.
137. M.L. Lejkowski, R.R. Lindner, T. Kageyama, G.E. Bódizs, P.N.N. Plessow, I.B. Müller, A. Schäfer, F. Rominger, P. Hofmann, C. Futter, S.A. Schunk, M. Limbach, Chem. Eur. J. 18 (2012) 14017.
138. N. Huguet, I. Jevtovikj, A. Gordillo, M.L. Lejkowski, R. Lindner, M. Bru, A. Y. Khalimon, F. Rominger, S.A. Schunk, P. Hofmann, M. Limbach, Chem. Eur. J., 20 (2014) 16858.
139. C. Hendriksen, E.A. Pidko, G. Yang, B. Schaffner, D. Vogt, Chem. Eur. J., 20 (2014) 12037.
140. S. Dérien, J.C. Clineth, E. Dunach, J. Périchon, Tetrahedron, 48 (1992) 5235.
141. D. Jin, P.G. Williard, N. Hazari, W.H. Bernskoetter, Chem. Eur. J. 20 (2014) 3205.
142. D. Jin, T.J. Schmeier, P.G. Williard, N. Hazari, W.H. Bernskoetter, Organomet. 32 (2013) 2152.
143. S. Chantal, E. Stieber, N.Huguet, T. Kageyama, S.A. Schunk, F. Rominger, P. Hofmann, M. Limbach, Chem. Comm. 51 (2015) 10907.
144. M. Aresta, C. Pastore, P. Giannoccaro, G. Kovacs, A. Dibenedetto, I. Papai, Chem. Eur. J. 13 (2007) 9028.
145. C. Bruckmeier, M.W. Lehenmeyer, R. Reichardt, S. Vagin, B. Rieger, Organomet. 29 (2010) 2199.
146. S.Y.T. Lee, M. Cokoja, M.Drees, Y. Li, J. Mink, W.A. Herrmann, F.E. Kühn, ChemSusChem 4 (2011) 1275.
147. S.A. Cohen, J.E. Bercaw, Organomet. 4 (1985) 1006.
148. I. Six, Eur. J. Org Chem., (2003) 1157.
149. H. Hoberg, B.W. Oster, J. Organomet. Chem. 266 (1984) 321.
150. S.N. Riduan, Y. Zhang, Dalton Trans. 39 (2010) 3347.
151. H. Hoberg, K. Jenni, C. Krüger, E. Raabe, Angew. Chem. Int. Ed. 98 (1986) 819.
152. H.Yasuda, T. Okamoto, Y. Matsuoka, A. Nakamura, Y.Kai, N. Kanehisa, N. Kasai, Organomet. 8 (1989) 1139.
153. H. Hoberg, S. Gross, A. Milchereit, Angew. Chem. Int. Ed. Engl. 26 (1987) 571.
154. A. Behr, U. Kanne, J. Organomet. Chem. 317 (1986) C41.
155. M. Takimoto, M. Mori, J. Am. Chem. Soc. 123 (2001) 2895.
156. S. Dérien, J.-C. C linet, E. Duñach, J. Périchon, J. Org. Chem. 58 (1993) 2578.
157. S. Dérien, E. Duñach, J. Périchon, J. Am. Chem. Soc. 113 (1991) 8447.
158. M. Aoki, M. Kaneko, S. Izumi, K. Ukai, N. Iwasawa, Chem. Comm. (2004) 2568.
159. M. Takimoto, M. Kawamura, M. Mori, Y.Sato, Synlett. (2011) 1423.
160. M. Aoki, S. Izumi, M. Kaneko, K. Ukai, J. Takaya, N. Iwasawa, Org. Lett. 9 (2007) 1251.
161. M. Mori, Eur. J. Org. Chem. (2007) 4981 and references therein.
162. M. Takimoto, M. Mori, J. Am. Chem. Soc. 124 (2002) 10008.
163. M. Takimoto, Y. Nakamura, K. Kimura, M. Mori, J. Am. Chem. Soc. 126 (2004) 5956.
164. C.M. Williams, J.B. Johnson, T. Rovis, J. Am. Chem. Soc. 130 (2008) 14936.

165. S. Li, W.Yuan, S. Ma, Angew. Chem. Int. Ed. 50 (2011) 2578.
166. T. Fujihara, T. Xu, K. Semba, J. Terao, Y.Tsuji, Angew. Chem. Int. Ed. 50 (2011) 523.
167. J. Takaya, N. Iwasawa, J. Am. Chem. Soc. 130 (2008) 15254.
168. M. North, Angew. Chem. Int. Ed. 48 (2011) 4104.
169. J. Takaya, K. Sasano, N. Iwasawa, Org. Lett. 13 (2011) 1698.
170. X. Wang, M. Nakajima, R. Martin, J. Am. Chem. Soc. 137 (2015) 4061.
171. K. Huang, C.-L.Sun, Z. Shi, Chem. Soc. Rev. 40 (2011) 2435.
172. J. Takaya, S. Tadami, K. Ukai, N. Iwasawa, Org. Lett. 10 (2008) 2697.
173. M. Aresta, I. Tommasi, C. Dileo, A. Dibenedetto, M. Narracci, J. Ziolkowski, A. Jezierski, Can. J. Chem. 79 (2001) 570.
174. M. Aresta, A. Dibenedetto, M. Pascale, E. Quaranta, I. Tommasi, J. Organomet. Chem. 605 (2000) 143.
175. M. Aresta, I. Tkatchenko, I. Tommasi in: R.D. Rogers and K.R. Seddon (Eds.), Ionic Liquids as Green Solvents: Progress and Prospects. Vol 856, ACS Symposium Series, ACS, Washington DC, 2003, p. 93.
176. I.I.F. Boogaerts, S.P. Nolan, J. Am. Chem. Soc. 132 (2010) 8858.
177. L. Zhang, J.Cheng, T. Ohishi, Z. Hou, Angew. Chem. Int. Ed. 49 (2010) 8670.
178. I.I.F. Boogaerts, G.C. Fortman, M.R.L. Furst, C.S.J. Cazin, S.P. Nolan, Angew. Chem. Int. Ed. 49 (2010) 8674.
179. S. Gaillard, A.M.Z. Slawin, S.P. Nolan, Chem. Comm. 46 (2010) 2742.
180. H. Mizuno, J. Takaya, N. Iwasawa, J. Am. Chem. Soc. 133 (2011) 1251.
181. T. Suga, H. Mizuno, J. Takaya, N. Iwasawa, Chem. Comm. 50 (2014) 14360.
182. T. Baran, A. Dibenedetto, M. Aresta, K. Kruczała, W. Macyk, ChemPlusChem 79 (2014) 708.
183. G. Bottaccio, G.P. Chiusoli, E. Alneri, M. Marchi, G. Lana, US4032555A (1977).
184. M. Aresta, A. Dibenedetto, T. Baran, W. Macyk, Far. Disc. 2015 DOI: 10.1039/C5FD00040H.
185. H. Kolbe, Just. Lieb. Ann. Chem. 113 (1860) 125-127.
186. Y. Inoue, Y. Itoh, H. Kazama, H. Hashimoto, Bull. Chem. Soc. Jpn. 53 (1980) 3329.
187. D. Walther, H. Schönberg, E. Dinjus, J. Sieler, J. Organomet. Chem. 334 (1987) 377.
188. P.J. Jessop, W. Leitner (Eds.), Chemical synthesis using supercritical carbon dioxide, Wiley-VCH Verlag GmbH, Weinheim (1999).
189. Y. Kishimoto, I. Mitani, Synlett. 14 (2005) 2141.
190. J. Louie, J.E. Gibby, M.V. Farnworth, T.N. Tekavec, J. Am. Chem. Soc. 124 (2002) 15188.
191. T.N. Tekavec, G. Zuo, K. Simon, J. Louie, J. Org. Chem. 71 (2006) 5834.
192. J.S. Lee, Mar. Drugs 2015, 13, 1581-1620
193. P. Diversi, G. Ingrosso, A. Lucherini, S. Malquori, J. Mol. Catal. 40 (1987) 267.
194. P. Albano, M. Aresta, J. Organomet. Chem. 190 (1980) 243-246.
195. S.M. Pillai, R. Ohnishi, M. Ichicawa, React. Kinet. Catal. Lett. 48 (1992) 201.
196. A. Dohring, P.M. Jolly, Tetrahedron Lett. 21 (1980) 3021.
197. M. Aresta, A. Ciccarese, E. Quaranta, C_1 Mol. Chem. 1 (1985) 283.
198. Y. Sasaki, J. Mol. Catal. 54. (1989) L9.
199. T. Tsuda, T. Yamamoto, T. Saegusa, J. Organomet. Chem. 429 (1992) C46.
200. M. Aresta, A. Dibenedetto, I. Papai, G. Schubert, Inorg. Chim. Acta 334 (2002) 294.
201. J. Cz. Dobrowolski, M.H. Jamroz, M.A. Borowiak, E. Quaranta, M. Aresta, Vibr. Spectrosc. 22 (2006) 19.
202. W. Adam, L. Hasemann, Angew. Chem., Int. Ed. Engl. 27 (1988) 1536.
203. Y. Inoue, Y. Sasaki, H. Hashimoto, J. Chem. Soc. Chem. Comm. (1976) 605.
204. A. Musco, J. Chem. Soc. Perkin Trans. 1 (1980) 693.
205. P. Braunstein, D. Matt, D. Nobel, J. Am. Chem. Soc. 110 (1988) 3207.
206. A. Behr, R. He, J. Organomet. Chem. 276 (1984) C69.
207. A. Behr, R. He, K.D. Juszak, C. Krueger, Y.H. Tsay, Chem. Ber. 119 (1986) 991.
208. K. Buchmüller, N. Dahmen , E. Dinjus , D. Neumann, B. Powietzka, S. Pitter, J. Schön, Green Chem. 5 (2003) 218.
209. A. Behr, P. Bahke, B. Klinger, M. Becker, J. Mol. Catal. A Chem. 267 (2007) 149.
210. A. Behr, M. Becker, Dalton Trans. (2006) 4607.
211. N. Holzhey, S. Pitter, E. Dinjus, (Forschungszentrum Karlsruhe GmbH, Germany) Patent Application WO 9857745, 1998.
212. A. Behr, H. Henze, Green Chem. 13 (2011) 25.

213. M. Murakami, N. Ishida, T. Miura, Chem, Comm. (2006) 643.
214. A. Behr, G. Thelen, C_1 Mol, Chem. 1 (1984) 137.
215. Y. Inoue, T. Hibi, M. Satake, H. Hashimoto, J. Chem. Soc. Chem. Commun. (1979) 982.
216. P. Binger, H.J. Weintz, Chem. Ber. 117 (1984) 654.
217. M. Aresta, E. Quaranta, A. Ciccarese, C_1 Mol. Chem. 2 (1985) 267.
218. M. Aresta, E. Quaranta, J. Chem. Soc. Dalton Trans. (1992) 1893.
219. M. Aresta, E. Quaranta, ChemTech 27 (1997) 32.
220. M. Aresta, A. Dibenedetto, E. Quaranta, J. Chem. Soc. Dalton Trans. (1995) 3359.
221. M. Aresta, E. Quaranta, J. Organomet. Chem. 488 (1995) 211.
222. M. Aresta, E. Quaranta, J. Org. Chem. 53 (1988) 4153.
223. B. Fadhel, M. Hearn, A. Chaffee, Micropor. Mesopor. Mat. 123 (2009) 140.
224. E. Bara, J.D.E. Camper, D.L. Gin, R.D. Noble, Acc. Chem. Res. 43 (2010) 152.
225. S. Choi, T. Watanabe, T.-H. Bae, D.S. Sholl, C.W. Jones, J. Phys. Chem. Lett. 3 (2012) 1136.
226. J.-R. Li., Y. Mab, M.C. McCarthyb, J. Sculleya, J. Yub, H.-K. Jeongb, P.B. Balbuena, H.-C.Zhoua, Coord. Chem. Rev. 255 (2011) 1791.
227. M. George, R.G. Weiss, Acc. Chem. Res. 39 (2006) 489.
228. V. Stastny, A. Anderson, D.M. Rudkevivh, J. Org. Chem. 71 (2006) 8696.
229. E.M. Mindrup, W.F. Schneider, ChemSusChem 3 (2010) 931.
230. C.D. Ki, C. Oh, S.-G. Oh, J.Y. Chang, J. Am. Chem. Soc. 124 (2002) 14838.
231. P.G. Jessop, S.M. Mercer, D.J. Eldebrant, Ener. Environ. Sci. 5 (2012) 7240.
232. M. Carafa, E. Quaranta, Mini-Rev. Org. Chem. 6 (2009) 168.
233. S. Ray, S.R. Pathak, D. Chaturvedi, Drugs Fut. 30 (2005) 161.
234. R.C. Gupta, in: R.C. Gupta (Ed.), Toxicology of Organophosphate and Carbamate Compounds, Elsevier Inc., Burlington, 2006, pp. 5.
235. T.W.Green, P.G.M. Wuts, Protective Groups in Organic Synthesis, 4rd ed., Wiley, New Jersey, 2007.
236. H.P. Buchstaller, Tetrahedron 54 (1998) 3465.
237. H. Ullrich, in: Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd ed., 1983, Vol. 23, p. 576.
238. G. Sartori, R. Maggi, Science of Synthesis 18 (2005) 665.
239. I. Gallou, Org. Prep. Proced. Intern. 39 (2007) 355.
240. M. Aresta, E. Quaranta, Ital. Pat. 1237206 (1993).
241. A. Belforte, F. Calderazzo, J. Chem. Soc. Dalton Trans. (1989) 1007.
242. W.D. McGhee, D. Riley, C. Kevin, Y. Pan, B. Parnas, J. Org. Chem. 60 (1995) 2820.
243. W.D. McGhee, D.P. Riley, M.E. Christ, K.M. Christ, Orgamomet. 12 (1993) 1429.
244. W.Z. Zhang, X. Ren, X.-B. Lu, Chinese, J. Chem. 33 (2015) 610.
245. D. Chaturvedi, S. Ray, Curr. Org. Chem. 11 (2007) 987.
246. T. Niemi, J.E. Perea-Buceta, I.Fernandez, S. Alakurtti, E. Rantala, T.Repo, Chem. Eur. J. 20 (2014) 8867.
247. M. Feroci, M. A.Casadei, M. Orsini, L.Palóombi, A. Inesi, J. Org. Chem. 68 (2003) 1548.
248. M. Feroci, M. Orsini, L.Rossi, G. Sotgiu, A.Inesi, J. Org. Chem. 72 (2007) 200.
249. R. Srivastava, M.D. Manju, D. Srinivas, P.Ratnasamy, Catal. Lett. 97 (2004) 41.
250. R. Srivastava, D. Srinivas, P. Ratnasamy, Appl. Catal. A. Gen. 289 (2005) 128.
251. R. Srivastava, D. Srinivas, P. Ratnasamy, Tetrah. Lett., (2006) 47 4213.
252. R. Srivastava, D. Srinivas, P. Ratnasamy, Micropor. Mesopor. Mater. (2006) 90, 314.
253. M. Aresta, E. Quaranta, Ital. Pat. 1237207 (1993).
254. M. Aresta, E. Quaranta, Tetrahedron 47 (1991) 9489.
255. M. Aresta, A. Dibenedetto, E. Quaranta, M. Boscolo, R. Larsson, J. Mol. Catal. 174 (2001) 7.
256. M. Distaso, E. Quaranta, J. Catal. 253 (2008) 278 .
257. E. Quaranta, A. Angelini, M. Carafa, A. Dibenedetto, V. Mele, ACS Catal. 4 (2014) 195.
258. M. Litwinowicz, J. Kijeński, Sustainable Chemical Processes 3 (2015) 1.
259. M. Abla, J.-C. Choi, T. Sakakura, J. Chem. Soc. Chem. Commum. (2001) 2238.
260. M. Abla, J.-C. Choi, T. Sakakura, Green Chem. 6 (2004) 524.
261. A. Ion, C. Van Doorslaer, V. Parvulescu, P. Jacobs, D. De Vos, Green Chem. 10 (2008) 111.
262. M. Honda, S. Sonehara, H. Yasuda, Y. Nakagawa, K. Tomishige, Green Chem. 13 (2011) 3406.
263. M. Tamura, M. Honda, K.Noro, Y. Nakagawa, K.Tomishige, J. Chem. Technol. Biotechnol. 89 (2014) 1553.
264. G. Fan, S. Luo, T. Fang, Q. Wu, G. Song, J. Li, J. Mol. Catal. A 404–405 (2015) 92.

265. B.M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, Green Chem. 5 (2003) 340.
266. H. Matsuda, A. Baba, R. Nomura, M. Kori, S. Ogawa, Ind. Eng. Chem. Prod. Res. Dev. 24 (1985) 239.
267. K. Tominaga, Y. Sasaki, Synlett. (2002) 307.
268. S. Fujita, H. Kanamaru, H. Senboku, M. Arai, Int. J. Mol. Sci. 7 (2006) 438.
269. M. Tamura, M, Honda, K.Noro, Y. Nakagawa, K. Tomishige, J. Catal. 305 (2013) 191
270. X.Y. Dou, L.N. He, Z.Z. Yang, J.L. Wang, Synlett. 14 (2010) 2159-2163.
271. C. Phung, R.M. Ulrich, M. Ibrahim, N.T.G. Tighe, D.L. Lieberman, A.R. Pinhas, Green Chem. 13 (2011) 3224.
272. Y.Wu, G. Liu, Tetrah. Lett. 52 (2011) 6450.
273. C. Phung, A.R. Pinhas, Tetrah. Lett. 51 (2010) 4552.
274. R.A. Watile, D.B. Bagal, Y.P. Patil, B.M. Bhanage, Tetrah. Lett. 52 (2011) 6383.
275. A.W. Miller, S.B. Nguyen Org. Lett. 6 (2004) 2301.
276. D. Adhikari, A.W. Miller, M.-H. Baik, S.T. Nguyen, Chem. Sci. 6 (2015) 1293
277. R.A.Watile, D.B. Bagal, Y.P. Patil, K.M. Deshmukh, K.P. Dhake, B.M. Bhanage, J. Mol. Cat. A 351(2011) 196.
278. A.C. Kathalikkattil, J.Tharun, R. Roshan, H.-G. Soek, D.-W. Park, Appl. Catal. A 447– 448 (2012) 107.
279. Y.-N. Zhao, Z.-Z.Yang, S.-H.Luo, L.-N. He, Catal. Tod. 200 (2013) 2.
280. H. Zhou, Y.M.Wang, W.Z. Zhang, J.P. Qu, X.B. Lu, Green Chem. 13 (2011) 644.
281. F. Fontana, C.C. Chen, V. Aggarwal, Org. Lett. 13 (2011) 3454.
282. P. Tascedda, R. Duñach, Chem. Commun. (2000) 449.
283. H. Kawanami, Y. Ikushima, Tetrah. Lett. 43 (2002) 3841.
284. F. Kojima, T. Aida, S. Inoue, J. Am. Chem. Soc. 106 (1986) 391.
285. B. Wang, E. H. M. Elageed, D.Zhang, S. Yang, S. Wu, G. Zhang, G. Gao, ChemCatChem, 6 (2014) 278.
286. P.H. Dixneuf, Catal. Lett., 145 (2015) 360.
287. C. Bruneau, P.H. Dixneuf, J. Mol. Catal. 74 (1992) 97.
288. R.A. Watile, B. M. Bhanage, RSC Adv. 4 (2014) 23022.
289. Y. Kayaki, T. Suzuki, T. Ikariya, Chem. Asian J. 3 (2008) 1865.
290. C. Bruneau, P.H. Dixneuf, Tetrahedron Lett. 28 (1987) 2005.
291. Y. Sasaki, P.H. Dixneuf, J. Org. Chem. 52 (1987) 4389.
292. S.C. Shim, J.O. Baeg, C.H. Doh, Y.Z. Youn, T.J. Kim, Bull. Korean Chem. Soc. 11 (1990) 467.
293. T.J. Kim, K.H. Kwon, S.C. Kwon, J.O. Baeg, S.C. Shim, J. Organomet. Chem. 389 (1990) 205.
294. H.S. Kim, J.W. Kim, S.C. Kwon, S.C. Shim, T.J. Kim, J. Organomet. Chem. 545-546 (1997) 337.
295. C.R. Qi, L.B. Huang, H.F. Jiang, Synthesis (2010) 1433
296. C.R. Qi, H.F. Jiang, Green Chem. 9 (2007) 1284.
297. P. Dimroth, H. Pasedach, E. Schefczik, Ger. Pat. 1151507 (1964).
298. Y. Gu, Q. Zhang, Z. Duan, J. Zhang, S. Zhang, Y. Deng, J. Org. Chem. 70 (2005) 7376.
299. H. Jiang, J. Zhao, A Wang, Synthesis (2008) 763.
300. J. Fournier, C. Bruneau, P.H. Dixneuf, Tetrah. Lett. 31 (1990) 1721.
301. H.-F.Jiang, J.-W. Zhao, Tetrah. Lett. 50 (2009) 60–62.
302. T. Mitsudo, Y. Hori, Y. Yamakawa, Y. Watanabe, Tetrah. Lett. 28 (1987) 4417.
303. M. Shi, Y.M. Shen, J. Org. Chem. 67 (2002) 16.
304. T. Ishida, R. Kobayashi, T. Yamada, Org. Lett. 16 (2014) 2430.
305. T. Ishida, S. Kikuchi, T. Tsubo, T. Yamada, Org. Lett. 15 (2013) 848.
306. J. Hu, J. Ma, Q.Zhu, Z. Zhang, C. Wu, B. Han, Angew. Chem. Int. Ed. 54 (2015) 5399.
307. M. Costa, G.P. Chiusoli, D. Taffurelli, G. Dalmonego, J. Chem. Soc. Perkin Trans. I (1998) 1541.
308. R. Maggi, C. Bertolotti, E. Orlandini, C. Oro, G. Sartori, M. Selva, Tetrahed. Lett. 48 (2007) 2131.
309. Y. Kayaki, M. Yamamoto, T. Suzuki, T. Ikariya, Green Chem. 8 (2006) 1019.
310. J. Zhao, H. Jiang, Tetrahedron Lett. 53 (2012) 6999.
311. Y. Yoshida, S. Inoue, Chem. Lett. (1977) 1375.
312. L. Soldi, C. Massera, M. Costa, N. Della Ca’, Tetrahedron Lett. 55 (2014) 1379.
313. K. Yamashita, S. Hase, Y. Kayaki, T. Ikari, Org. Lett. 17 (2015) 2334.
314. W.D. McGhee, D.P. Riley, Orgamomet. 11 (1992) 900.
315. P. Braunstein, Chem. Rev., 89 (1989) 1927.
316. D. Randall, S. Lee, The polyurethane book, Wiley, 2002.

317. O. Kreye, H. Mutlu, M. A. R. Meier Green Chem. 15 (2013) 1431.
318. http://www.ceresana.com/en/market-studies/plastics/pur-isocyanates/
319. http://www.marketsandmarkets.com/PressReleases/isocyanate.asp
320. L. Cotarca, H. Eckert, Phosgenations - A Handbook, Wiley-VCH,Weinheim, 2004.
321. A. Belforte, D. Belli Dell'Amico, F. Calderazzo, Chem. Ber. 121 (1988) 1891.
322. T. Tsuda, S. Sanada, T. Saegusa, J. Organomet. Chem. 116 (1976) C10.
323. W.Y. Kim, J.S. Chang, S.E. Park, C.P. Kubiak, Res. Chem. Intermed. 25 (1999) 459.
324. C.A. Tsipis, P.A. Karipidis, J. Phys. Chem. A 109 (2005) 8560.
325. W.D. McGhee, M. Paster, D. Riley, K. Ruettimann, J. Solodar, T. Waldmann, ACS Symposium Series (Benign by Design), 626 (1996) 49.
326. L. Rossi, Science of Synthesis 18 (2005) 461.
327. S. Kubik, Sciences of Synthesis, Knowledge updates 3 (2013) 217.
328. D. Carnaroglio, K. Martina, G. Palmisano, A. Penoni, C. Domini, G. Cravotto, Beilstein J. Org.Chem. 9 (2013) 2335.
329. A. Ion, V. Parvulescu, P. Jacobs, D. De Vos, Green Chem. 9 (2007) 158.
330. J. Fournier, C. Bruneau, P.H. Dixneuf, S.L. Lécolier, J. Org.Chem. 56 (1991) 4456.
331. F. Shi, Y. Deng, T. SiMa, J. Peng, Y. Gu, B. Qiao, Angew. Chem. Int. Ed. 42 (2003) 3257.
332. T. Jiang, X. Ma, Y. Zhou, S. Liang, J. Zhang, B. Han, Green Chem. 10 (2008) 465.
333. D.L. Kong, L.N. He, J.Q. Wang, Synlett. 8 (2010) 1276.
334. T. Seki, Y. Kokubo, S. Ichikawa, T. Suzuki, Y. Kayaki, T. Ikariya, Chem. Commun. (2009) 349.
335. F. Shi, Q. Zhang, Y. Na, Y. He, Y. Deng, J. Am. Chem. Soc. 127 (2005) 4182.
336. R. Zhang, L. Hua, L. Guo, B. Song, J. Chen, Z. Hou, Chin. J. Chem. 31 (2013) 381.
337. M. Tamura, K. Noro, M. Honda, Y. Nakagawa, K. Tomishige, Green Chem. 15 (2013) 1567.
338. D. Delledonne, F. Rivetti, U. Romano, Appl. Catal. A: Gen. 221(1-2) (2001) 241.
339. A.A.G. Shaikh, S. Sivaram, Chem. Rev. 96 (1996) 951 and references therein.
340. H.J. Buysch in Ullmann's Enciclopedia of Industrial Chemistry, Weinheim: VCH Publishers, A5 (1992) 197.
341. M.A. Pacheco, C.L. Marshall, Energy & Fuels 11(1) (1997) 2.
342. D.C. Waddell, I. Thiel, A. Bunger, D. Nkata, A. Maloney, T. Clark, B. Smith, J. Mack, Green Chem. 13 (2011) 3156.
343. M. Aresta, A. Dibenedetto, C. Pastore, Inorg. Chem. 42(10) (2003) 3256 and references therein.
344. K. Tomishige, T. Sakaihori, Y. Ikeda, K. Fujimoto, Catal. Lett. 58 (1999) 225.
345. J.-C. Choi, T. Sakakura, T. Sako, J. Am. Chem. Soc. 121 (1999) 3793.
346. D. Ballivet-Tkatchenko, O. Douteau, S. Stutzmann, Organomet. 19 (2000) 4563.
347. A. Dibenedetto, C. Pastore, M. Aresta, Cat. Tod. 115 (2006) 88.
348. M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, Inorg. Chimica Acta 361 (2008) 3215.
349. S.H. Zhong, L.L. Kong, H.S. Li, X.F. Xiao, Ranliao Huaxue Xuebao 30(5) (2002) 454.
350. M. Aresta, A. Dibenedetto, F. Nocito, A. Angelini, B. Gabriele, Appl. Catal. A: Gen. 387 (2010) 113.
351. B. Fan, J. Zhang, R. Li, W. Fan Catal. Lett. 121 (2008) 297.
352. K. Tomishige, Y. Yoshida, Y. Arai, S. Kado, K. Kunimori, Catal. Tod. 115 (2006) 95.
353. K. Tomishige, Y. Furusawa, Y. Ikeda, M. Asadullah, K. Fujimoto, Catal. Lett. 76 (2001) 71.
354. M. Aresta, A. Dibenedetto, C. Pastore, C. Cuocci, B. Aresta, S. Cometa, E. De Giglio, Catal. Tod. 137 (2008) 125.
355. M. Aresta, A. Dibenedetto, C. Pastore, A. Angelini, B. Aresta, I. Pápai, J. Catal. 269 (2010) 44.
356. E. Finocchio, M. Daturi, C. Binet, J.C. Lavalley, G. Blanchard, Catal. Tod. 52 (1999) 53.
357. A. Dibenedetto, M. Aresta, A. Angelini, J. Ethiraj, B.M. Aresta, Chem.-A Eur. J. 18(33) (2012) 10324.
358. M. Aresta, A. Dibenedetto, E. Fracchiolla, P. Giannoccaro, C. Pastore, I. Pàpai, G. Schubert, J. Org. Chem. 70(16) (2005) 6177.
359. M. Aresta, A. Dibenedetto, A. Angelini, I. Pàpai, Top. Catal. 58 (2015) 2.
360. D. Ballivet-Tkatchenko, S. Chambrey, R. Keiski, R. Ligabue, L. Plasseraud, P. Richard, H. Turunen, Catal. Tod. 115 (2006) 80.
361. K. Kohno, J.-C. Choi, Y. Ohshima, A. Yili, H. Yasuda, T. Sakakura, J. Organomet. Chem. 693 (2008) 1389.
362. D. Ballivet-Tkatchenko, H. Chermette, L. Plasseraud, O. Walter, Dalton Trans. (2006) 5167.
363. T. Sakakura, Y. Saito, J.-C. Choi, T. Sako, Polyhedron 19 (2000) 573.
364. T. Sakakura, Y. Saito, J.-C. Choi, T. Masuda, T. Sako, T. Oriyama, J. Org. Chem. 64 (1999) 4506.

365. M. Aresta, A. Dibenedetto, C. Di Leo, I. Tommasi, E. Amodio, J. Supercrit. Fluids 25 (2003) 177.
366. M. Honda, S. Kuno, S. Sonehara, K. Fujimoto, K. Suzuki, Y. Nakagawa, K. Tomishige, ChemCatChem 3(2) (2011) 365.
367. K. Tomishige, K. Kunimori, Appl. Catal. A: Gen. 237 (2002) 103.
368. N.S. Isaacs, B. O'Sullivan, C. Verhaelen, Tetrahedron 55 (1999) 11949.
369. M. Aresta, A. Dibenedetto, P. Stufano, B. M. Aresta, S. Maggi, I. Papai, T.A. Rokob, B. Gabriele, Dalton Trans. 39 (2010) 6985.
370. M. Aresta, A. Dibenedetto, P. Stufano, IP MI 2009A001221 (2009).
371. W. Zhao, F. Wang, W. Peng, N. Zhao, J. Li, F. Xiao, W. Wei, Y. Sun, Ind. Eng. Chem. Res. 47 (2008) 5913.
372. Y. Gaoa, W. Penga, N. Zhaoa, W. Wei, Y. Sun, J. Mol. Catal. A Chem. 35 (2011) 29.
373. A. Dibenedetto, A. Angelini, S. Fasciano, I. Papai, F. Curulla, M. Aresta, J. CO_2 Util. 8 (2014) 27.
374. J.L. Dubois, EP Patent 2137133B1 (2011).
375. S. Huang, J. Ma, J. Li, N. Zhao, W. Wei, Y. Sun, Catalysis Commun. 9 (2008) 276.
376. L.X Wu, H. Wang, Z.-Y. Tu, B.-B. Ding, Y. Xiao, J.-X. Lu, Int. J. Electrochem. Sci. 7 (2012) 11540.
377. M. Honda, M. Tamura, K. Nakao, K. Suzuki, Y.Nakagawa, K. Tomishige, ACS Catal. 4 (2014) 1893.
378. M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, J. Mol. Cat. 257 (2006) 149.
379. C. Vieville, J.W. Yoo, S. Palet, Z. Mouloungui, Catal. Lett. 56 (1998) 245.
380. M. Aresta, A. Dibenedetto, F. Nocito, J.L. Dubois, WO Patent WO2010040786 A3 (2010)
381. A. Dibenedetto, F. Nocito, I. Papai, A. Angelini, R. Mancuso, M. Aresta, Chemsuschem, 6(2), (2013) 345.
382. M. Aresta, A. Dibenedetto, A. Angelini, Chem. Rev. 114 (2014) 1709.
383. M. Aresta, A. Dibendetto, L. Gianfrate, C. Pastore, Appl. Cat. A Gen. 255 (2003) 5.
384. M. North, R. Pasquale, C. Young, Green Chem. 12 (2010) 1514.
385. M. Aresta, E. Quaranta, A. Ciccarese J. Mol. Cat. 41 (1987) 355.
386. M. Aresta, A. Dibendetto, L. Gianfrate, C. Pastore, J. Mol. Cat. A Gen. 204-205 (2003) 245.
387. M. Aresta, C. Fragale, E. Quaranta, I. Tommasi, J. Chem. Soc. Chem. Commun. (1992) 315.
388. M. Aresta, A. Dibenedetto, F. Nocito, C. Pastore, A. M. Venezia, E. Chirykalova, V. I. Kononenko, V.G. Shevchenko, I.A. Chupova, Catal. Tod. 115 (2006) 117.
389. A. Dibenedetto, M. Aresta, C. Pastore, F. Nocito, Preprints - ACS, Division of Petroleum Chemistry 52(2), (2007) 273.
390. A. Dibenedetto, M. Aresta, M. Distaso, C. Pastore, A. M. Venezia, C.-J. Liu, M. Zhang, Catal. Tod. 137 (2008) 44.
391. P. Styring, K. Armstrong, Chem. Tod. 29 (2011) 28.
392. W.C. Chueh, C. Falter, M. Abbott, D. Scipio, P. Furler, S.M. Haile, A. Steinfeld, Science 330 (2010) 1797.
393. W. Wang, S. Wang, X. Ma, J. Gong, Chem. Soc. Rev. 40 (2011) 3703.
394. J.J. Zou, C.J. Liu, in: M. Aresta (Ed.) Carbon Dioxide as Chemical Feedstock, 2010, p. 267.
395. M. Aresta, A. Dibenedetto, Catal. Tod. 98 (2004) 455.
396. B.A.V. Santos, J.M. Loureiro, A.M. Ribeiro, A.E. Rodrigues, A.F. Cunha, Can. J. Chem. Eng. 93 (2015) 396.
397. D.H. Mei, L.J. Xu, G. Henkelman, J. Catal. 258 (2008) 44.
398. G.A. Olah, Angew. Chem. Int. Ed., 52 (2013) 104.
399. J. Ma, N.N. Sun, X.L. Zhang, N. Zhao, F.K. Mao, W. Wei, Y.H. Sun, Cat. Tod. 148 (2009) 221.
400. M.K. Gnanamani, G. Jacobs, V.R.R. Pendyala, W. Ma, B.H. in: Centi G and Perathoner S. (Eds.), Green Carbon Dioxide: Advances in CO_2 Utilization, First Edition, John Wiley & Sons, Inc., 2014, p 99.
401. G.C. Chinchen, K.C. Waugh, D.A. Whan, Appl. Catal. 25 (1986) 101.
402. F. Arena, G. Mezzatesta, G. Zafarana, G. Trunfio, F. Frusteri, L. Spadaro, J. Catal. 300 (2013) 141.
403. I. Melian-Cabrera, M.L. Granados, J.L.G. Fierro, J. Catal. 210 (2002) 273.
404. T. Fujitani, I. Nakamura, T. Uchijima, J. Nakamura, Surface Science 383 (1997) 285.
405. G.A. Olah, A. Goeppert, G.K. Surya Prakash, J. Org. Chem. 74 (2009) 487.
406. I.H. Kim, S. Kim, W. Cho, E.S. Yoon, Computer Aided Chem. Eng. 28 (2010) 799.
407. W.H. Chen, B.J. Lin, H.W. Lee, M.N. Huang, Appl. Ener. 98 (2012) 92.
408. S.W. Kang, J.W. Bae, K.W. Jun, H.S. Potdar, Catal. Commun. 9 (2008) 2035.
409. S. Wang, D. Mao, X. Guo, G. Wu, G. Lu, Catal. Commun. 10 (2009) 1367.
410. L.A. Pellegrini, G. Soave, S. Gamba, S. Lange, Appl. Ener. 88 (2011) 4891.

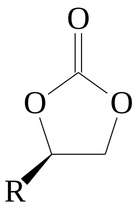
411. G. Bonura, M. Cordaro, L. Spadaro, C. Cannilla, F. Arena, F. Frusteri, Appl. Catal. B: Environm. 140-141 (2013) 16.
412. F. Frusteri, M. Cordaro, C. Cannilla, G. Bonura, Appl. Catal. B: Environm. 162 (2015) 57.
413. S. Sahebdelfar, M.T. Ravanchi, J. Petrol. Sci. Eng. 134 (2015) 14.
414. D. Cheng, F.R. Negreiros, E. Apra, A. Fortunelli, ChemSusChem 6 (2013) 944.
415. Y. Wang, Y. Takahashi, Y. Ohtsuka, J. Catal. 186 (1999) 160.
416. G. Raju, B.M. Reddy, S.E. Park, J. CO_2 Util. 5 (2014) 41.
417. F. Urlan, I.C. Marcu, I. Sandulescu, Catal. Commun. 9 (2008) 2403.
418. A. Qiao, V.N. Kalevaru, J. Radnik, A. Düvel, P. Heitjans, A.S. Hari Kumar, P.S. Sai Prasad, Ind. Eng. Chem. Res. 53(49) (2014) 18711.
419. V.N. Cavaliere, M.G. Crestani, B. Pinter, M. Pink, C. Chen, M. Baik, D.J. Mindiola, J. Am. Chem. Soc. 133 (2011) 10700.
420. M.d.C. Rangel, A.P.d.M. Monteiro, M. Oportus, P. Reyes, M.d.S. Ramos, S.B. Lima, in: Liu G. (Ed.), Greenhouse Gases-Capturing, Utilization and Reduction, 2012, p 117.
421. H. Liu, Z. Zhang, H. Li, Q. Huang, J. Nat. Gas Chem. 20 (2011) 311.
422. B. Grzybowska, Appl. Catal. A: Gen., 157 (1997) 409.
423. F. Solymosi, R. Nemeth, A. Oszko, Stud. Surf. Sci. Catal. 136 (2001) 339.
424. P. Michorczyk, P. Pietrzyk, J. Ogonowski, Microp. Mesop. Mat. 161 (2012) 56.
425. M. Geske, O. Korup, R. Horn, Catal. Sci. Technol. 3 (2013) 169.
426. S. Sato, M. Ohhara, T. Sodesawa, F. Nozaki, Appl. Catal. 37 (1988) 207.
427. S. Deng, H. Li, S. Li, Y. Zhang, J. Mol. Catal. A: Chem. 268 (2007) 169.
428. O.R. Evans, A.T. Bell, T.D. Tilley, J. Catal., 226 (2004) 292.
429. F. Cavani, F. Trifiro, Appl. Catal. A: Gen. 133 (1995) 219.
430. A.J.R. Castro, J.M. Soares, J.M. Filho, A.C. Oliveira, A.C. Edwin, R.C. Milet, Fuel 108 (2013) 740.
431. B.S. Liu, G. Rui, R.Z. Chang, C.T. Au, Appl. Catal. A: Gen. 335 (20) 88.
432. http://www.essentialchemicalindustry.org/polymers/polyphenylethene.html
433. A. Sun, Z. Qin, J. Wang, Appl. Catal. A: Gen. 234 (2002) 179.
434. A. Sun, Z. Qin, S. Chen, J. Wang, J. Mol. Catal. A: Chem. 210 (2004) 189.
435. C.N. Satterfield, (1980) Heterogeneous Catalysis in Practice, McGraw-Hill, New York, p. 460.
436. C. Amatore, J.-M. Savéant, J. Am. Chem. Soc. 103 (1981) 5021.
437. J. Agarwal, T.W. Shaw, C.J. Stanton III, G.F. Majetich, A.B. Bocarsly, H.F. Schaefer III, Angew. Chem. Int. Ed. 53 (2014) 5152.
438. C.E. Barton, P.S. Lakkaraju, D.M. Rampulla, A.J. Morris, E. Abelev, A.B. Bocarsly, J. Am. Chem. Soc. 132 (2010) 11539.
439. K.W. Jr Frese, D. Canfield, J. Electrochem. Soc. 131 (1984) 2518.
440. Y. Yan, E.L. Zeitler, J. Gu, Y. Hu, A.B. Bocarsly, J. Am. Chem. Soc. 135 (2013) 14020 and references to same authors.
441. Y. Yan, J. Gu, A.B. Bocarsly, Aerosol and Air quality Research 14 (2014) 515.
442. M. Aresta, A. Dibenedetto, A. Angelini, Phil. Trans. A Math. Phys. Eng. Sci. 371 (2013) 20120111.
443. http://www2.lbl.gov/mfea/assets/docs/posters/14_Artificial_Photosynthesis.pdf
444. A. Dibenedetto, P. Stufano, W. Macyk, T. Baran, C. Fragale, M. Costa, M. Aresta, ChemSusChem 5 (2012) 373.
445. M. Aresta, A. Dibenedetto, T. Baran, A. Angelini, P. Łabuz, W. Macyk, Beilstein J. Org. Chem. 10 (2014) 2556.
446. M. Aresta, A. Dibenedetto, W. Macyk in: "From Molecules to Materials-Pathways to Artificial Photosynthesis" E. A., Rozhkova, K. Ariga (Eds.) (Springer) 2015, V, p. 400.
447. M. Aresta, A. Dibenedetto, W. Macyk, T. Baran MI2013A001135 (2013).
448. J. Grodkowski, T. Dhanasekaran, P. Neta, P. Hambright, B.S. Brunschwig, K. Shinozaki, E. Fujita, J. Phys. Chem. A, 104 (2000) 11332.
449. J. Grodkowski, P. Neta, E. Fujita, A. Mahammed, L. Simkhovich, Z. Gross, J. Phys. Chem. A 106 (2002) 4772.
450. J. Grodkowski, P. Neta, J. Phys. Chem. A 104 (2000) 1848.
451. J. Hawecker, J.-M. Lehn, R. Ziessel, J. Chem. Soc. Chem. Commun. 9 (1983) 536.

452. A.H.A. Tinnemans, T.P.M. Koster, D.H.M.W. Thewissen, A. Mackor, Recl. Trav. Chim. Pays.-Bas. 103 (1984) 288.
453. M. Ulman, A.H.A. Tinnemans, A. Mackor, B. Aurian-Blajeni, M. Halmann, Intern. J. Solar Energy 1(3) (1982), 213.
454. J. Hawecker, J.-M. Lehn, R. Ziessel, Helv Chim Acta 69 (1986) 1990.
455. S. Yamane, N. Kato, S. Kojima, A. Imanishi, S. Ogawa, N. Yoshida, S. Nonomura, Y. Nakato, J. Phys. Chem. C 113 (2009) 14575.
456. M.G. Walter, E.L. Warren, J.R. McKone, S.W. Boettcher, Q. Mi, E.A. Santori, N.S. Lewis, Chem. Rev. 110 (2010) 6446.
457. T. Dang, R. Ramsaran, S. Roy, J. Froehlich, J. Wang, C.P. Kubiac, Electroanalysis 23 (2011) 2335.
458. Y. Yamada, N. Matsuki, T. Ohmori, H. Mametsuka, M. Kondo, A. Matsuda, E. Suzuki, Int. J. Hydrog. Energy 28 (2003) 1167.
459. T.V. Nguyen, J.C.S. Wu, Appl. Cat. A 335 (2008) 112.
460. K. Gao, K.R. McKinley, J. Appl. Phycol. 6, 1994, 45
461. E.W. Wilde, J.R. Benemann, Biotech. Adv. 11 (1993) 781.
462. K.L. Kadam, Energy Convers. Mgmt. 38 (1997) 505.
463. S. Buono, A. Dibenedetto, A. Colucci, A.L. Langellotti, M. Morana, V. Fogliano, M. Aresta, ICCDU XIII, Singapore 2015.
464. K.G. Zeiler, D.A. Heacox, S.T. Toon, K.L. Kadam, L.M. Brown, Energy Convers. Mgmt. 36 (1995) 707.
465. C. Yoo, S.-Y. Jun, J.-Y. Lee, C.-Y. Ahn, H.-M. Oh, Biores. Technol. 101 (2010) S71.
466. W. Becker, in A. Richmond (Ed.), Handbook of microalgal culture Blackwell, Oxford, 2004, 312
467. C. Arnaud, Chemical & Engineering News (2008) 45.
468. T.D. Niehaus, S. Okada, T.P. Devarenne, D.S. Watt, V. Sviripa, J. Chappell, PNAS 108(30) (2011) 12260.
469. Y. Wang, F. Tao, J. Ni, C. Li, P. Xu, Green Chem. 17 (2015) 3100.
470. Y. Xue, Y. Zhang, D. Cheng, S. Daddy, Q. He, Proc. Natl. Acad. Sci.U.S.A. 111 (2014) 9449.
471. R.J. Capon, R.W. Dunlop, E.L. Ghisalberti, P.R. Jefferies, Phytochem. 22(5) (1983) 1181.
472. L.J. Stal, H. Heyer, G. Jacobs, Novel Biodeg. Micr. Pol. (1990) 435.
473. J. Campbell III, S.E. Stevens Jr., D.L. Balkwill, J. Bacteriol. 149(1) (1982) 361.
474. M. Vincenzini, C. Sili, R. de Philippis, A. Ena, R. Materassi, J. Bacteriol. 172(5) (1990) 2791.
475. M. Miyake, M. Erata, Y. Asada, J. Fermen. Bioeng. 82(5) (1996) 512.
476. N.-S. Lau, C. P. Foong, Y. Kurihara, K. Sudesh, M. Matsui, PLoS ONE 9(1) (2014).
477. H. Akiyama, H. Okuhata, T. Onizuka, S. Kanai, M. Hirano, S. Tanaka, K. Sasaki, H. Miyasaka, Biores. Technol. 102(23) (2011) 11039.
478. B. Wang, S. Pugh, D. R. Nielsen, W. Zhang, D. R. Meldrum, Metab. Eng. 16(1) (2013) 68.
479. E.I. Lan, D.S. Chuang, C.R. Shen, A. M. Lee, S.Y. Ro, J.C. Liao, Metab. Eng. 31 (2015) 163.
480. E.I. Lan, J.C. Liao, Metab. Eng. 13 (2011) 353.
481. P. Lindberg, S. Park, A. Melis, Metab. Eng. 12 (2010) 70.
482. A. Melis, Energy Environ. Sci. 5 (2012) 5531.
483. J.E. Chaves, H. Kirst, A. Melis J. Appl. Phycol. 27(3) (2015) 1089.
484. F.K. Bentley, A. Zurbriggen, A. Melis, Mol. Plant 7 (2014) 71.
485. K. Rabaey, R.A. Rozendal, Appl. Ind. Microbiol. 8 (2010) 706.
486. M. Villano, F.A.C. Ciucci, T. Ferri, A. Giuliano, M. Majone, Biores. Technol. 101(9) (2010) 3085.
487. J.C. Boyington, V.N. Gladyshev, S.V. Khangulov, T.C. Stadtman, P.D. Sun, Science 275 (1997) 1305.

488. H. Raaijmakers, S. Macieira, J.M. Dias, S. Teixeira, S. Bursakov, R. Huber, J.J.G. Moura, I. Moura, M.J Romão, Structure 10 (2002) 1261.
489. F.A.M. de Bok, P.-L. Hagedoorn, P.J. Silva, W.R. Hagen, E. Schiltz, K. Fritsche, A.J.M. Stams, Eur. J. Biochem. 270 (2003) 2476.
490. S. Kima, M.K. Kimb, S.H. Leeb, S. Yoonc, K.-D. Junga, J. Mol. Catal. B: Enzymatic, 102 (2014) 9.
491. M. Aresta, A. Dibenedetto, G. Giannoccaro, P. Stufano, CRS International Conference, St. Petersburg, Tsars Village, 2010.
492. F.A. Armstrong, J. Hirst Proc. Natl. Acad. Sci. U.S.A., 108 (2011) 14049.
493. T. Hartmann, S. Leimkühler FEBS J. 280 (2013) 6083.
494. H. Hwang, Y.J. Yeon, S. Lee, H. Choe, M.G. Jang, D.H. Cho, S. Park, Y.H. Kim, Biores. Technol. 185 (2015) 35.
495. A. Alissandratos, H.-K. Kim, C.J. Easton, Biores. Technol. 164 (2014) 7.
496. M. Gunda, J.S. Seelam, K. Vanbroekhoven, D. Pant, Paper ID: 170, ICCDU XIII, 2015 Singapore.
497. F. Ullmann, Ullmann’s Encyclopedia of Industrial Chemistry, (seventh ed.) Wiley-VCH, Weinheim (2000).
498. D. Deublein, A. Steinhauser, Biogas from Waste and Renewable Resources: An Introduction, Wiley, 2011, p. 578.
499. V. Berzin, M. Kiriukhin, M. Tyurin, Lett. Appl. Microbiol. 55 (2012) 149.
500. M.N. Ukpong, H.K. Atiyeh, M.J.M. Delorme, K. Liu, X. Zhu, R.S. Tanner, M.R. Wilkins, B.S. Stevenson, Biotechnol. Bioeng. 109 (2012) 2720.
501. R.P. Datar, R.M. Shenkman, B.G. Cateni, R.L. Huhnke, R.S. Lewis, Biotechnol. Bioeng. 86 (2004) 587.
502. K.D. Ramachandriya, M.R. Wilkins, M.J.M. Delorme, X.G. Zhu, D.K. Kundiyana, H.K. Atiyeh, R.L. Huhnke, Biotechnol. Bioeng. 108 (2011) 2330.
503. K.D. Ramachandriya, D.K. Kundiyana, M.R. Wilkins, J.B. Terrill, H.K. Atiyeh, R.L. Huhnke, Appl. Ener. 112 (2013) 289.
504. C.B. Field, M.J. Behrenfeld, Randerson, P. Falkowski, Science 281 (5374) (1998) 237.
505. B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, C.P. Kubiak, Annu. Rev. Phys. Chem. 63 (2012) 541.
506. T. Reda, C.M. Plugge, N.J. Abram, J. Hirst, Proc Natl Acad Sci USA 105 (2008) 10654.
507. A. Parkin, J. Seravalli, K.A. Vincent, S.W. Ragsdale, F.A. Armstrong, J. Am. Chem. Soc. 129 (2007) 10328.
508. R.K. Yadav, G.H. Oh, N.-J. Park, A. Kumar, K-J. Kong, J.-O. Baeg, J. Am. Chem. Soc. 136 (2014) 16728.
509. W. Kim, G. Yuan, B.A. McClure, H. Frei, J. Am. Chem. Soc. 136 (31) (2014) 11034.

Table

Table 1. Short and medium term perspective use of CO_2.

Compound	Formula	$C_{oxstate}$	Market 2016 Mt/y	CO_2 use Mt/y	Market 2030 Mt/y	CO_2 use Mt/y
Urea	$(H_2N)_2CO$	+4	**180**	132	**210**	154
Carbonate linear	$OC(OR)_2$	+4	>2	0.5	10	5
Carbonate cyclic		+4				
Polycarbonates	$-[OC(O)OOCH_2CHR]_n-$	+4	5	1	9-10	2-3
Carbamates	RNH-COOR	+4	>6	1	11	*ca.* 4
Acrylate	$CH_2=CHCOOH$	+3	5	1.5	8	5
Formic acid	HCOOH	+2	1	0.9	>10	>9
Inorganic carbonates	M_2CO_3 $M'CO_3$	+4	$CaCO_3$ **250**	70	**400**	100
Methanol	CH_3OH	-2	60	10	80	>28
Total				**207**		**>332**

Table

Table 2. Vibrational normal modes and related frequencies (cm^{-1}) for CO_2, CO_2^+, and CO_2^-

	ν_1 (ν_s(OCO))	ν_2 (δ(OCO))	ν_3 (ν_a(OCO))	Notes	Refs.
CO_2	1333	667.38	2349.16	gas state	[21]
CO_2^+	1244.3	511.4	1423.08	gas state	[24]
CO_2^-	1253.8	714.2	1658.3	Ne matrix	[25,26]

Table

Table 3. ΔH° and ΔG° for the synthesis of organic carbonates from alcohols and CO_2 [343].

R Group	**ΔH at 298 K kcal mol^{-1}**	**ΔG° at 298 K kcal mol^{-1}**
CH_3	**- 4.0**	**6.0**
C_2H_5	**- 3.8**	**6.2**
CH_2=CH-CH_2	**- 3.9**	**6.1**

Table 4. Potential of reduction of CO_2 to other C1 molecules (da 1) *vs* the Standard Hydrogen Electrode (SHE)

Entry	Reaction		E° V (NHE)
1	$CO_2 + e^- = CO_2^{\cdot -}$	-2.21 in aprotic solvents;	-1.93 in water
2	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$		-0.53
3	$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$		-0.61
4	$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O$		-0.48
5	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$		-0.38
6	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$		-0.24

Table

Table 5. Comparison of the cost of production of H_2 (1 kg) using different technologies.

Technology	**Gas Reforming**	**Electrolysis with nuclear**	**Electrolysis with oil as primary energy source**	**Electrolysis with PV**	**Electrolysis with wind**	**Electrolysis with SPC**
Cost €/kg	1.10	1.45	1.50	2.8	3.8	3.50
	1.15	1.50	2.20	4.0	5.20	

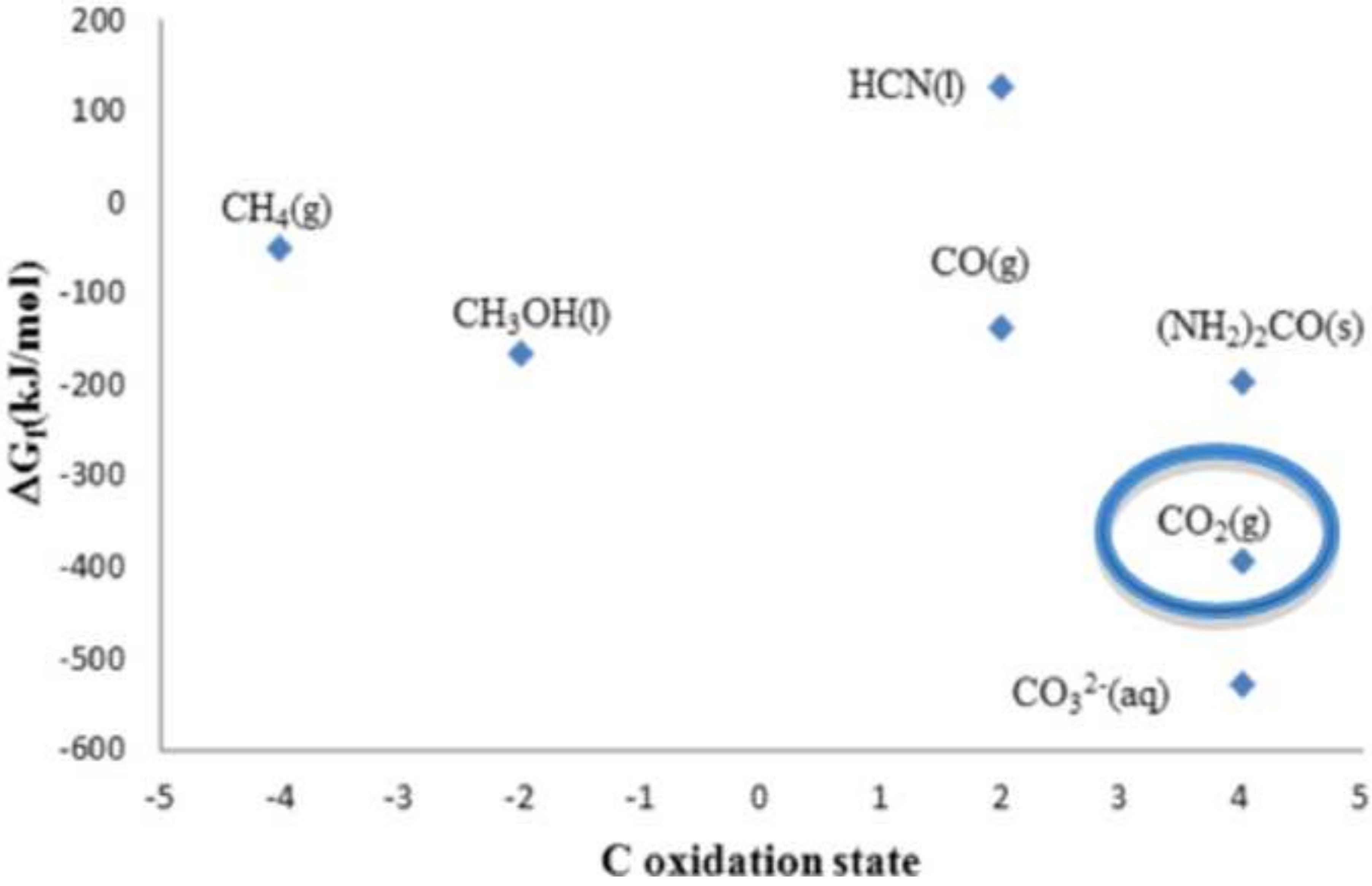
Table 6. Useful substances contained in algal biomass

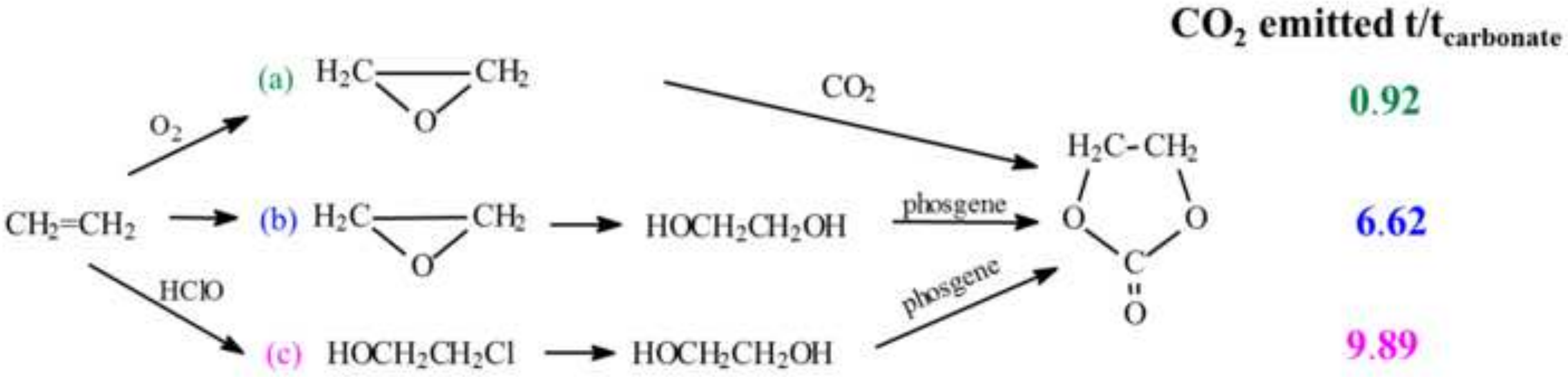
Pigments/ carotenoids	ε-carotene, lycopene, γ-carotene and β-carotene, xanthophylls astaxanthin, canthaxanthin, β-cryptoxanthin, echinenone, myxoxanthophyll and oscillaxanthin
Poly-unsaturated fatty acids (PUFAs)	γ-linolenic acid (GLA-C18:3), arachidonic acid (AA-C20:4), eicosapentaenoic acid (EPA-C20:5) and docosahexaenoic acid (DHA-C22:6)
Antioxidants	Catalases, polyphenols, superoxide, dismutase, tocopherols
Vitamins	A, B1, B6, B12, C, E, Biotin, riboflavin, nicotinic acid, pantothenate, folic acid
Others	Antifungal, antimicrobial and antiviral agents, toxins, aminoacids, proteins, sterols

Table 7. Producers of microalgae and products

Microalgae species	Application/products	Company	Country
Nannochloropsis *Tetraselmis* *Pheodactrylum*	Cosmetics and aquaculture	Astaxa	Germany
Nannochloropsis *Haematococcus pluvialis* *Spirulina* *Chlorella*	PUFA, omega 3, EPA astaxanthin	Bluebiotech	Germany
Haematococcus pluvialis	Astaxanthin/human, fish and animal consumption	Alga Technologies	Israel
Nannochloropsis sp *Pheodactrylum tricornutum* *Amphora sp* *Navicular sp* *Dunaliella sp* *Chlorococcum sp* *Tetraselmis sp* *Nannochloris sp*	Food additives, animal and fish feed, biofuel	Seambiotic	Israel
Haematococcus pluvialis	Astaxanthin	Biogenic Co., Ltd.	Japan
Haematococcus pluvialis *Spirulina*	Astaxanthin	Cyanotech	USA
Chlorella	Biofuels, nutritional, health sciences, chemicals	Solazyme	USA
Spirulina *Chlorella* *Crypthecodinium Cohnii*	DHA/dietary supplements, aquaculture feeds, cosmetics	Femico	Taiwan

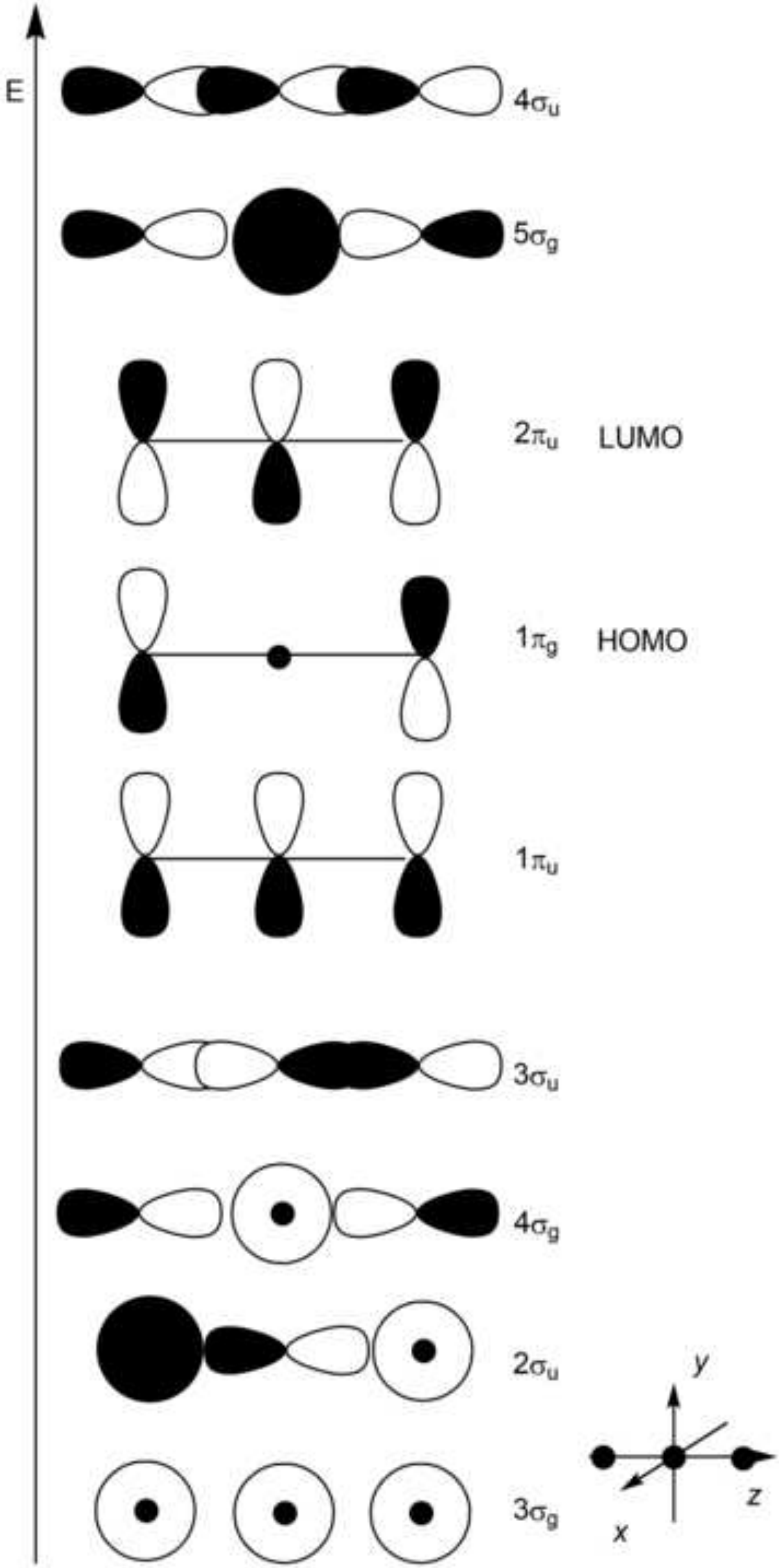
Figure


200
100
0
-100
-200
-300
-400
-500
-600
ΔGf(kJ/mol)
HCN(l)
CH4(g)
CO(g)
CH3OH(l)
(NH2)2CO(s)
CO2(g)
CO3 2-(aq)
-5
-4
-3
-2
-1
0
1
2
3
4
5
C oxidation state


CO2 emitted t/tcarbonate
(a)
H2C
CH2
O
O2
CO2
0.92
CH2=CH2
(b)
H2C
CH2
O
HOCH2CH2OH
phosgene
H2C-CH2
O
O
C
O
6.62
HClO
phosgene
(c)
HOCH2CH2Cl
HOCH2CH2OH
9.89

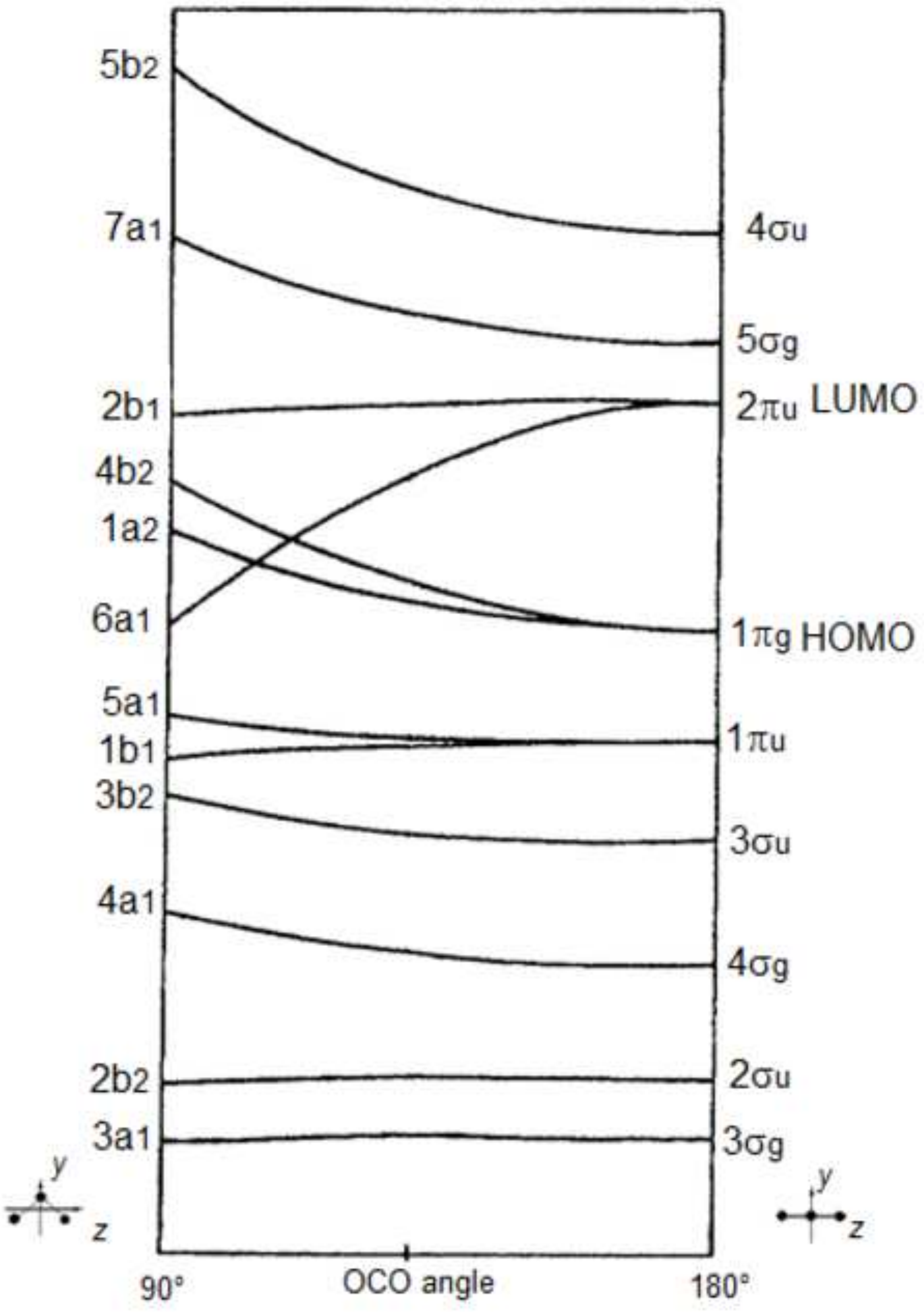
Figure

Click here to download high resolution image



Figure

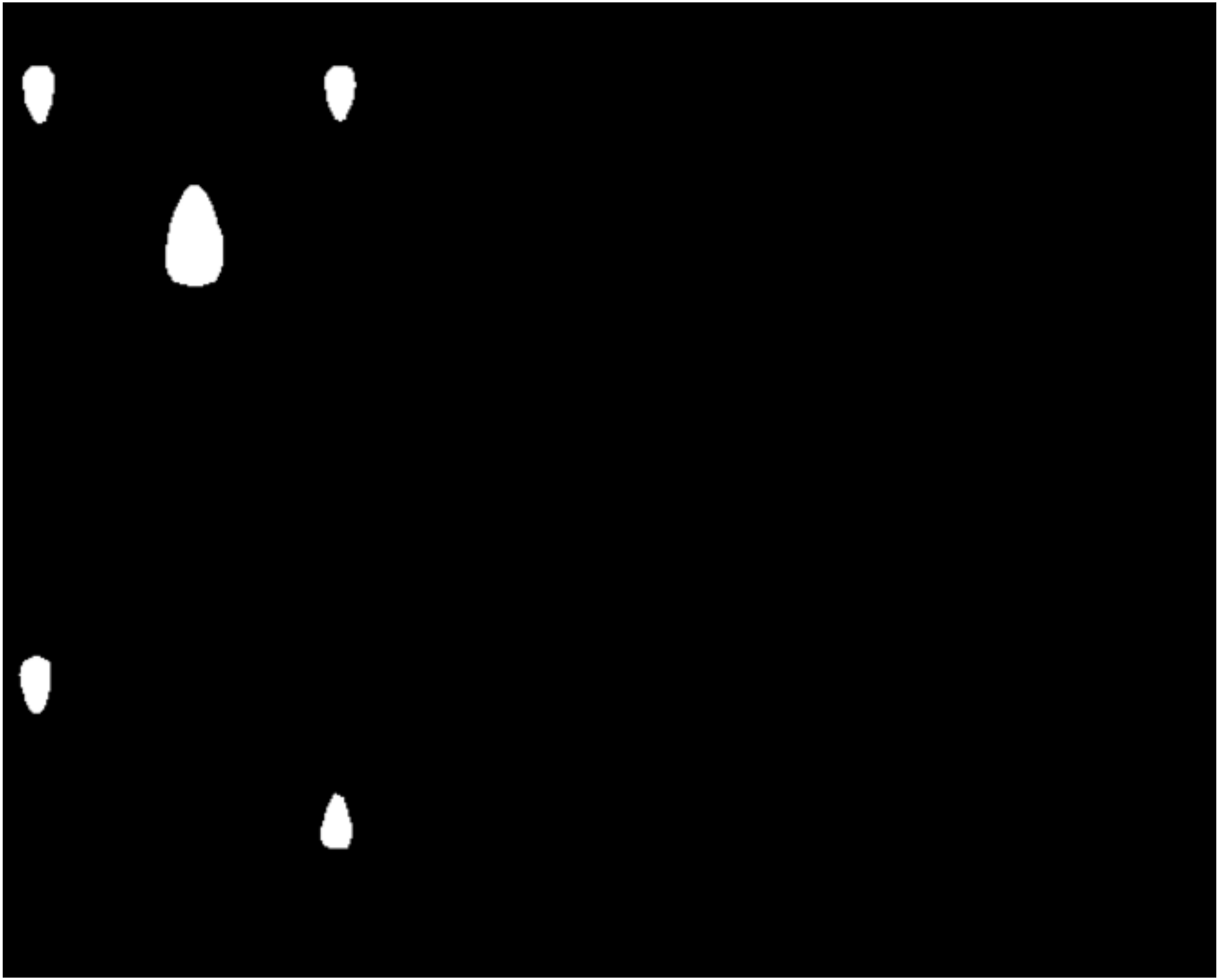
Click here to download high resolution image

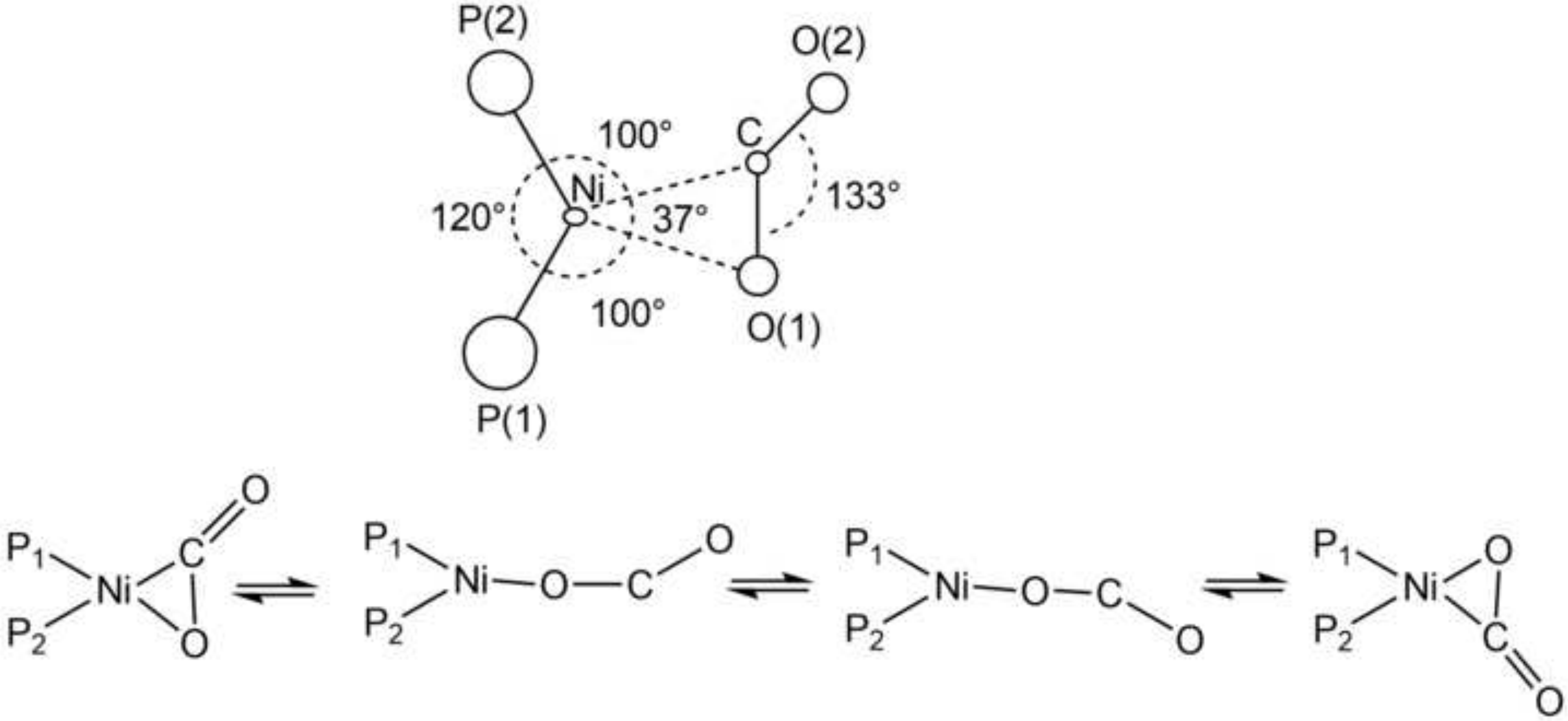


Figure

Figure

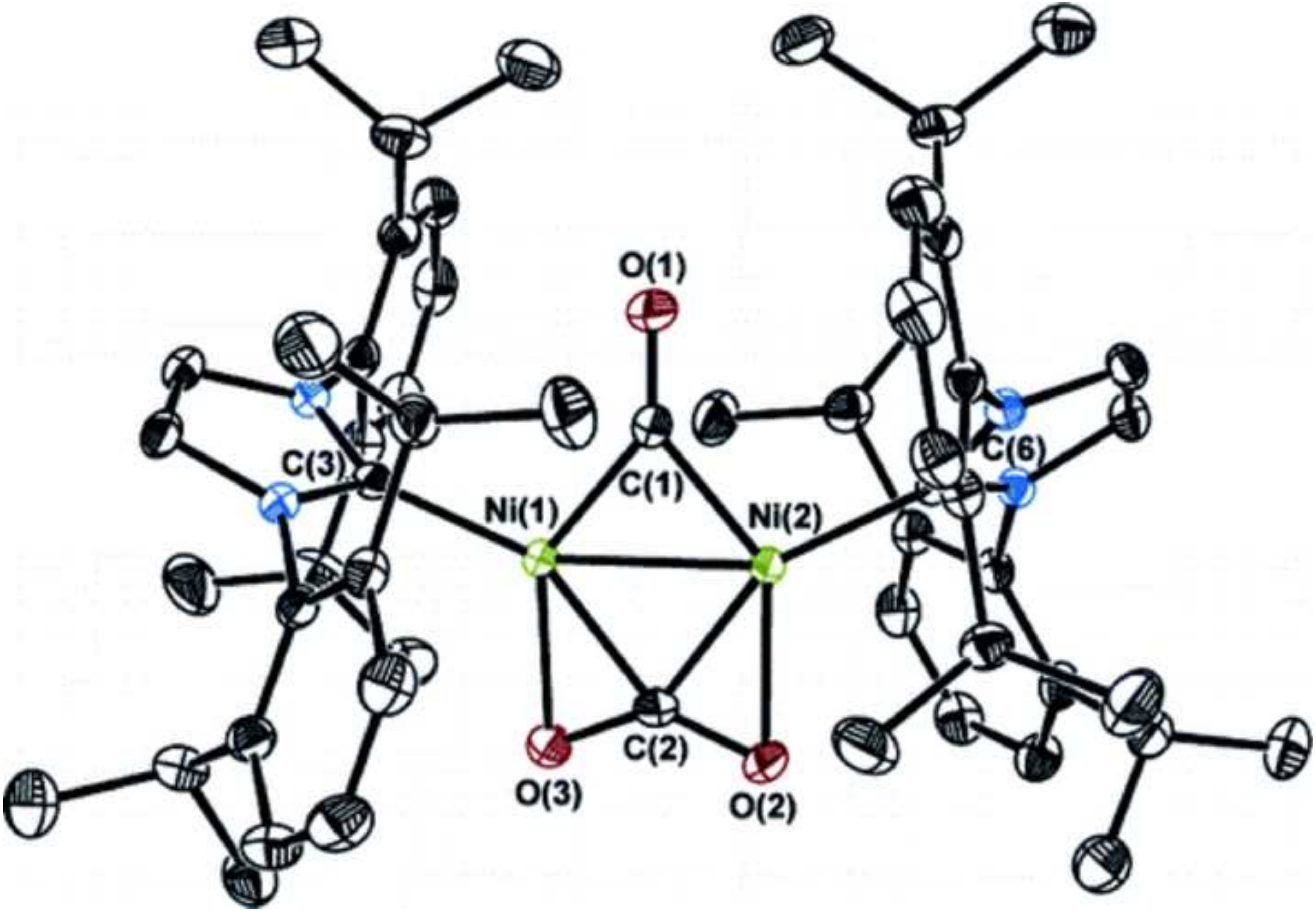
Click here to download high resolution image

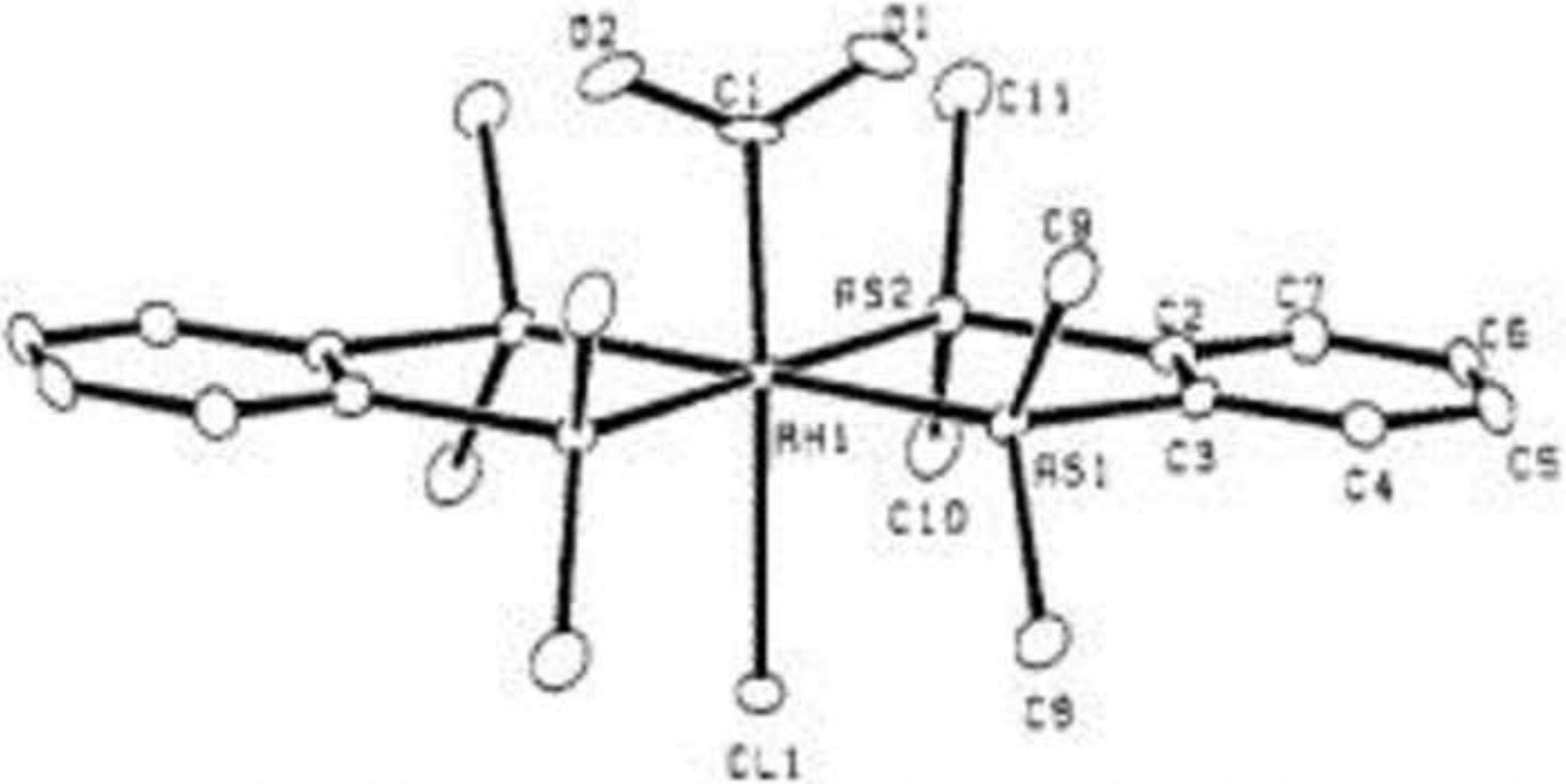


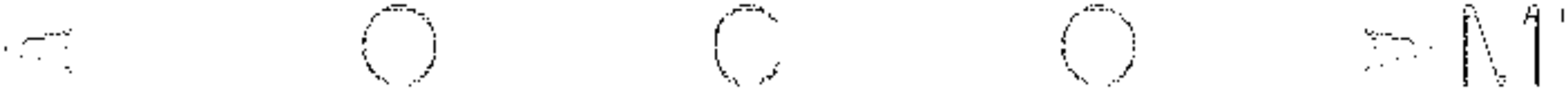

P(2)
O(2)
100°
C
Ni
120°
37°
133°
100°
O(1)
P(1)
P1
P2
Ni
C
O
O

Figure

Click here to download high resolution image

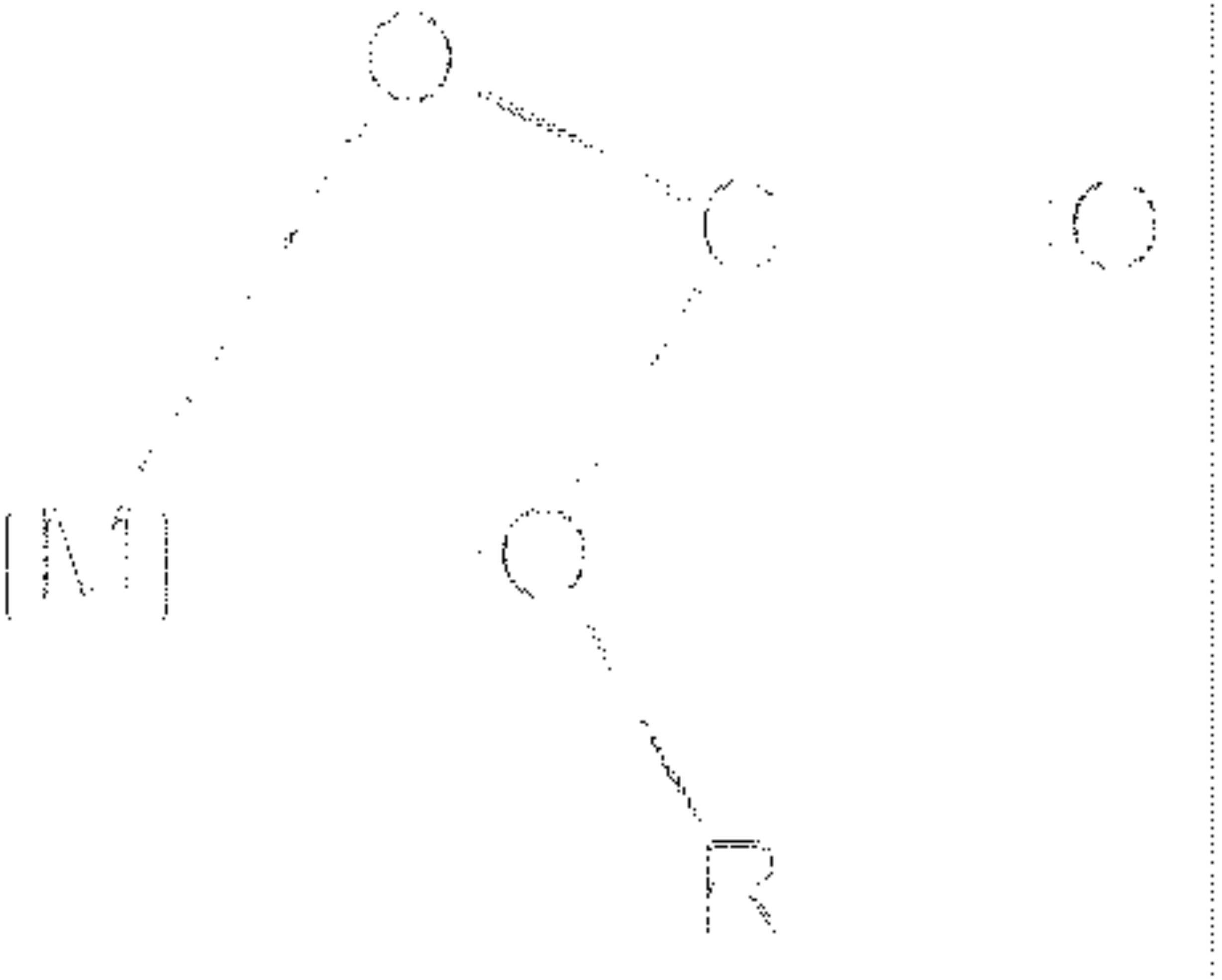



O2
C1
O1
C11
C9
AS2
C7
C2
C6
RH1
C10
AS1
C3
C4
C5
C8
CL1



Figure

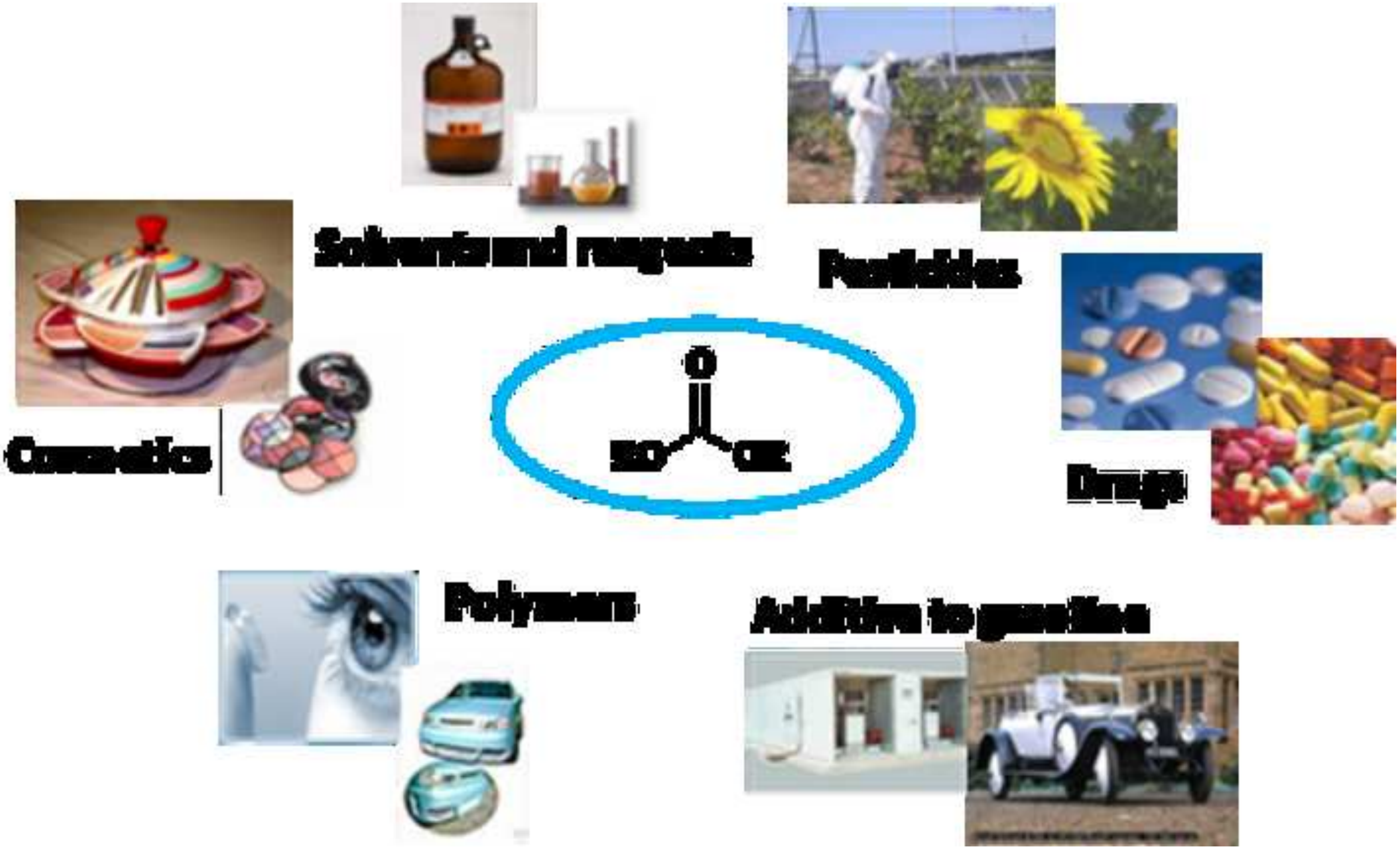
Figure



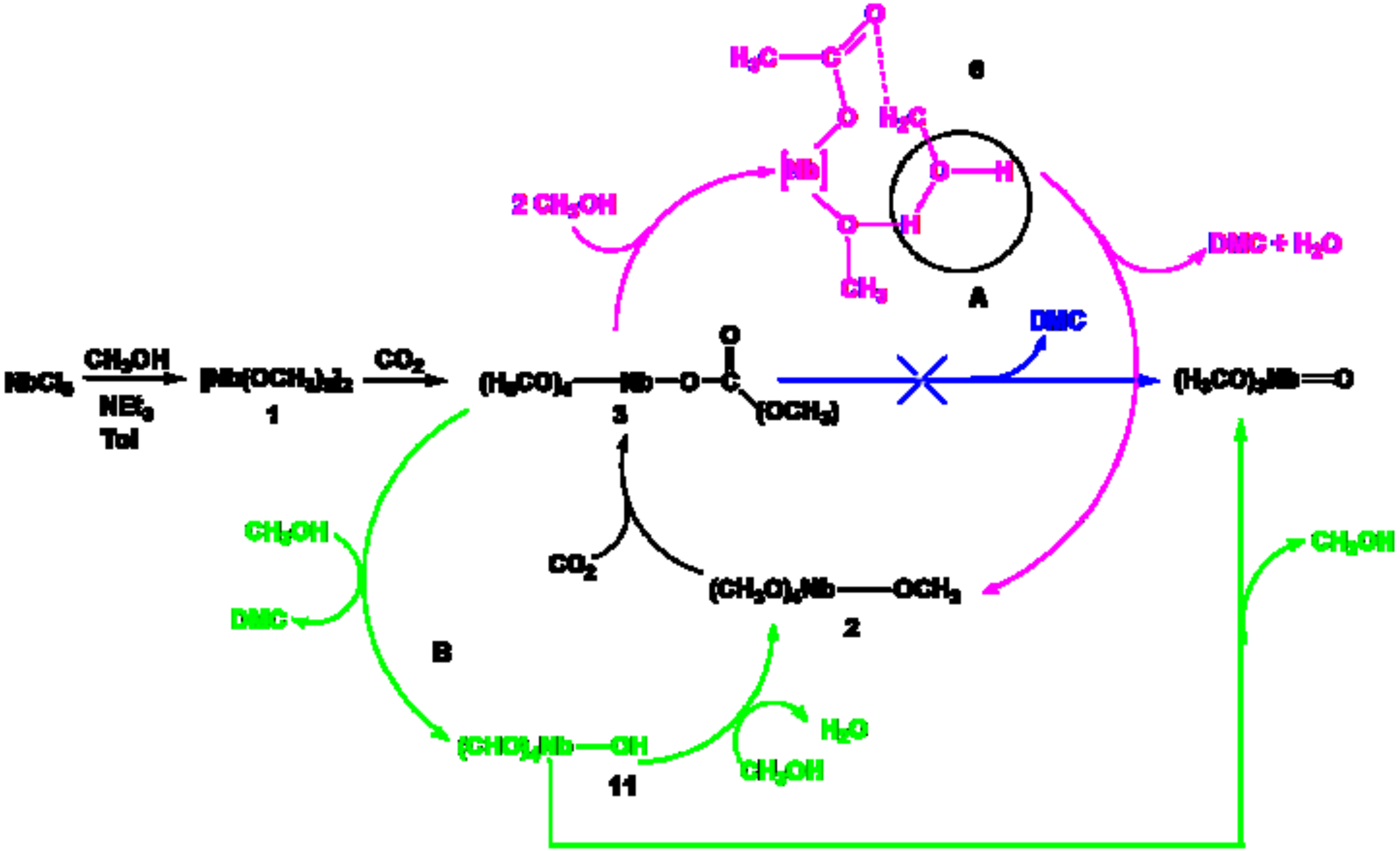
(a)

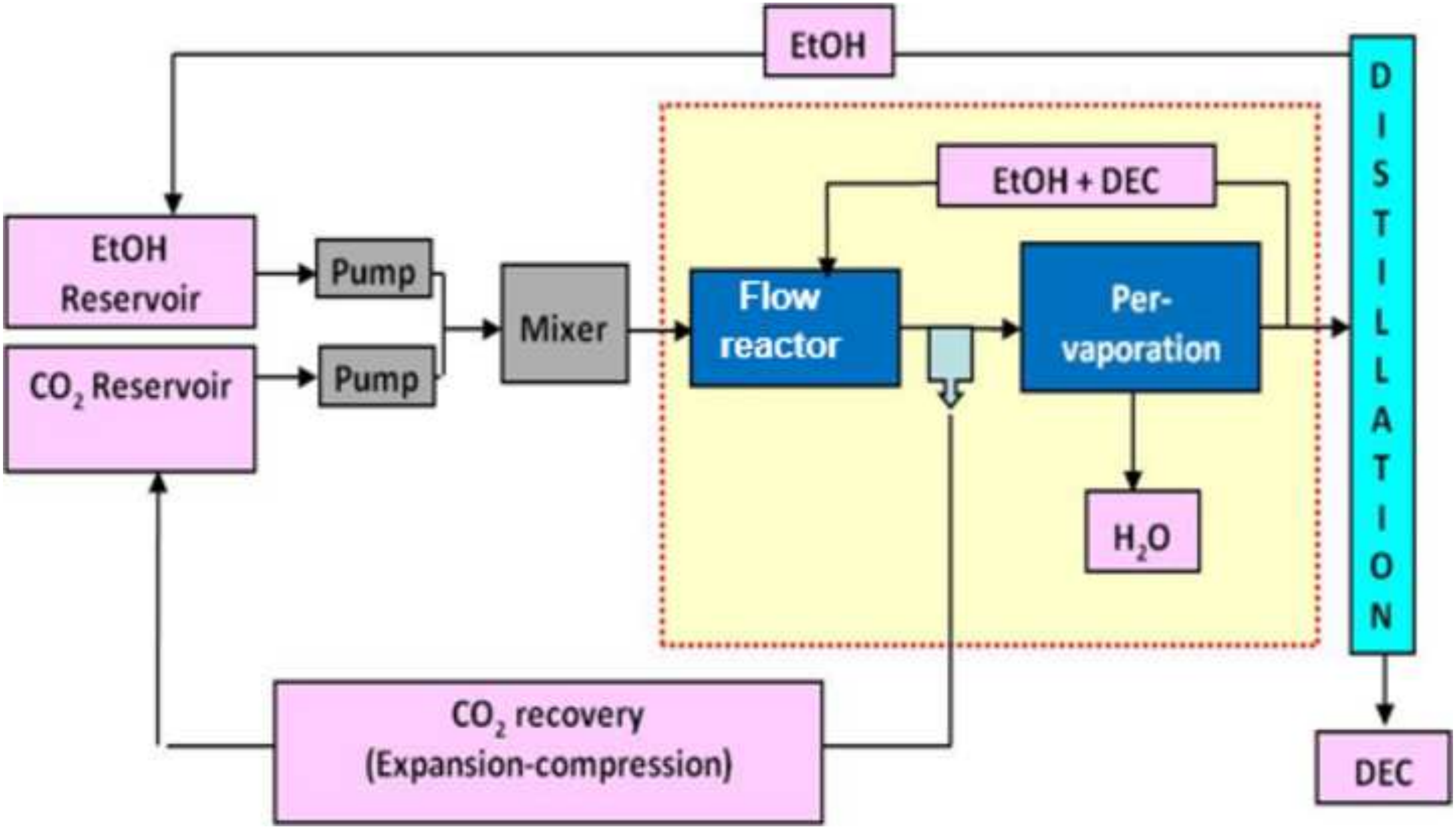
(b)

Figure


Solvents and reagents
Pesticides
Cosmetics
O
RO
OR
Drugs
Polymers
Additive to gasoline

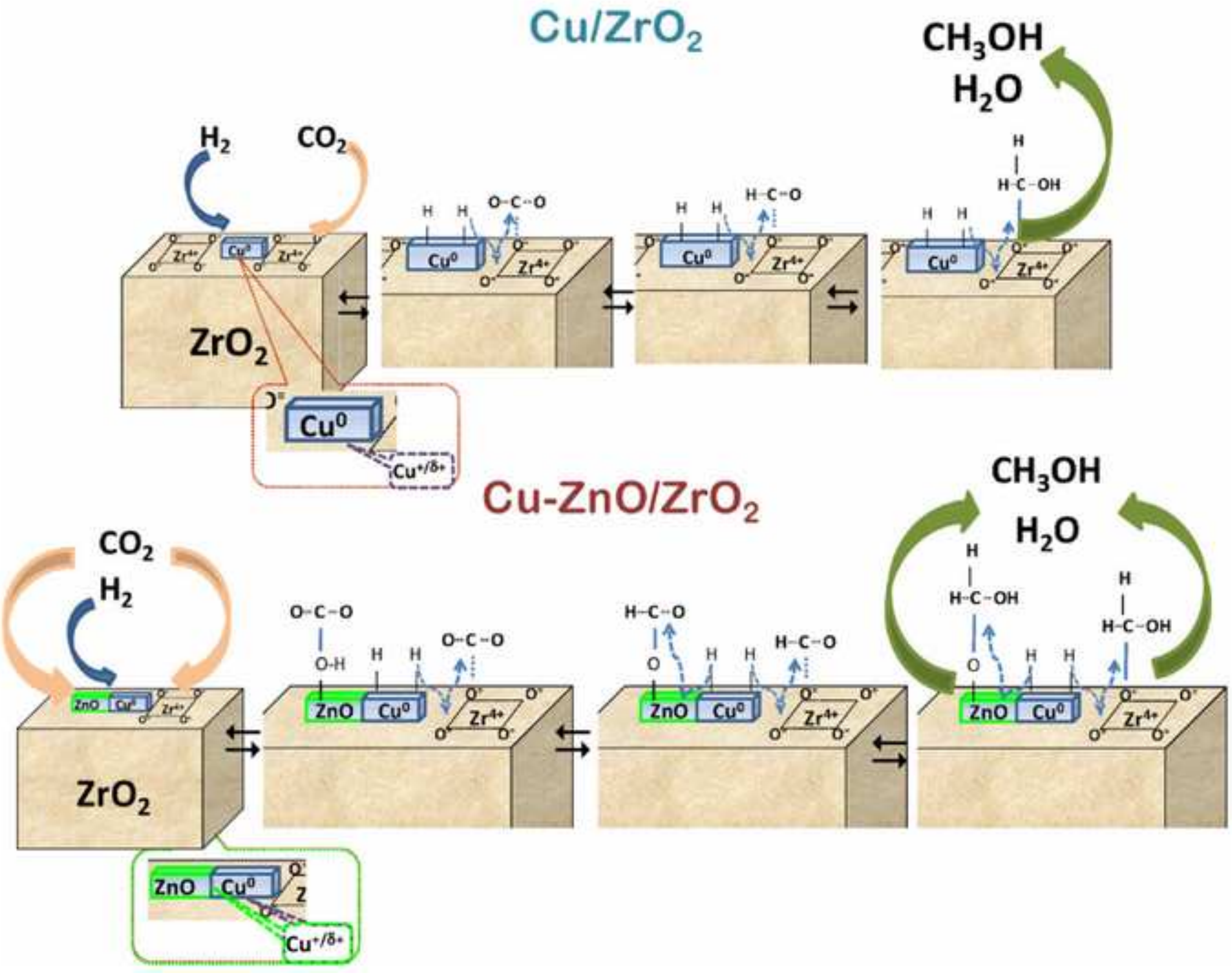

Drugs
Li-ion batteries
Paint-stripper
Chemicals
Degreasing solvents
O
O
O
n
Diluent for resins
Cosmetics
Polycarbonates


NbCl5
CH3OH
NEt3
Tol
[Nb(OCH3)5]2
1
CO2
(H3CO)4
Nb
O
C
O
(OCH3)
3
DMC
(H3CO)3Nb=O
2 CH3OH
H3C
C
O
O
[Nb]
H3C
O
H
O
H
CH3
6
A
DMC + H2O
CH3OH
DMC
B
CO2
(CH3O)4Nb—OCH3
2
(CHO)4Nb—OH
11
H2O
CH3OH
CH3OH


EtOH
EtOH Reservoir
CO_2 Reservoir
Pump
Pump
Mixer
EtOH + DEC
Flow reactor
Per-vaporation
H_2O
DISTILLATION
DEC
CO_2 recovery (Expansion-compression)

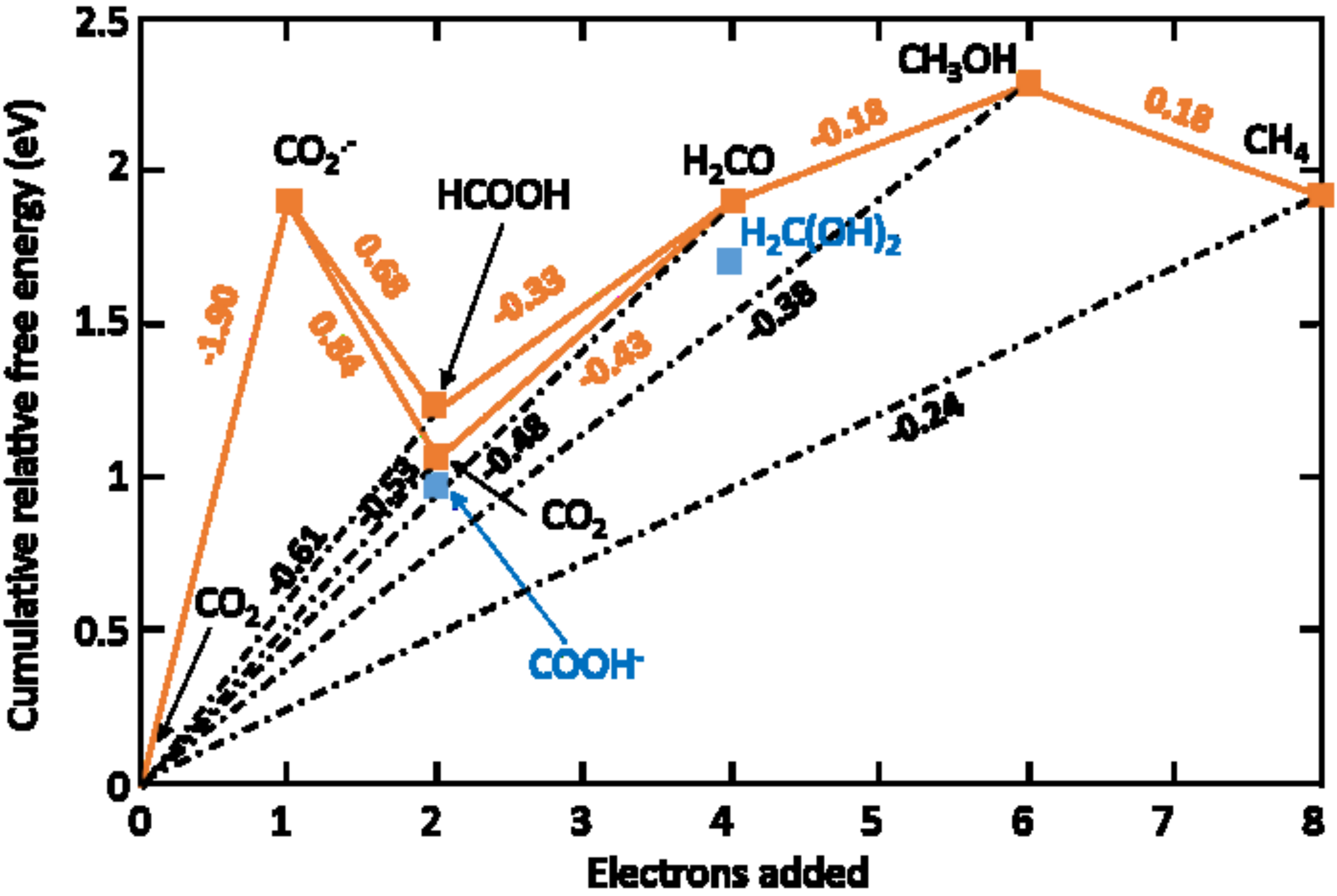
Figure

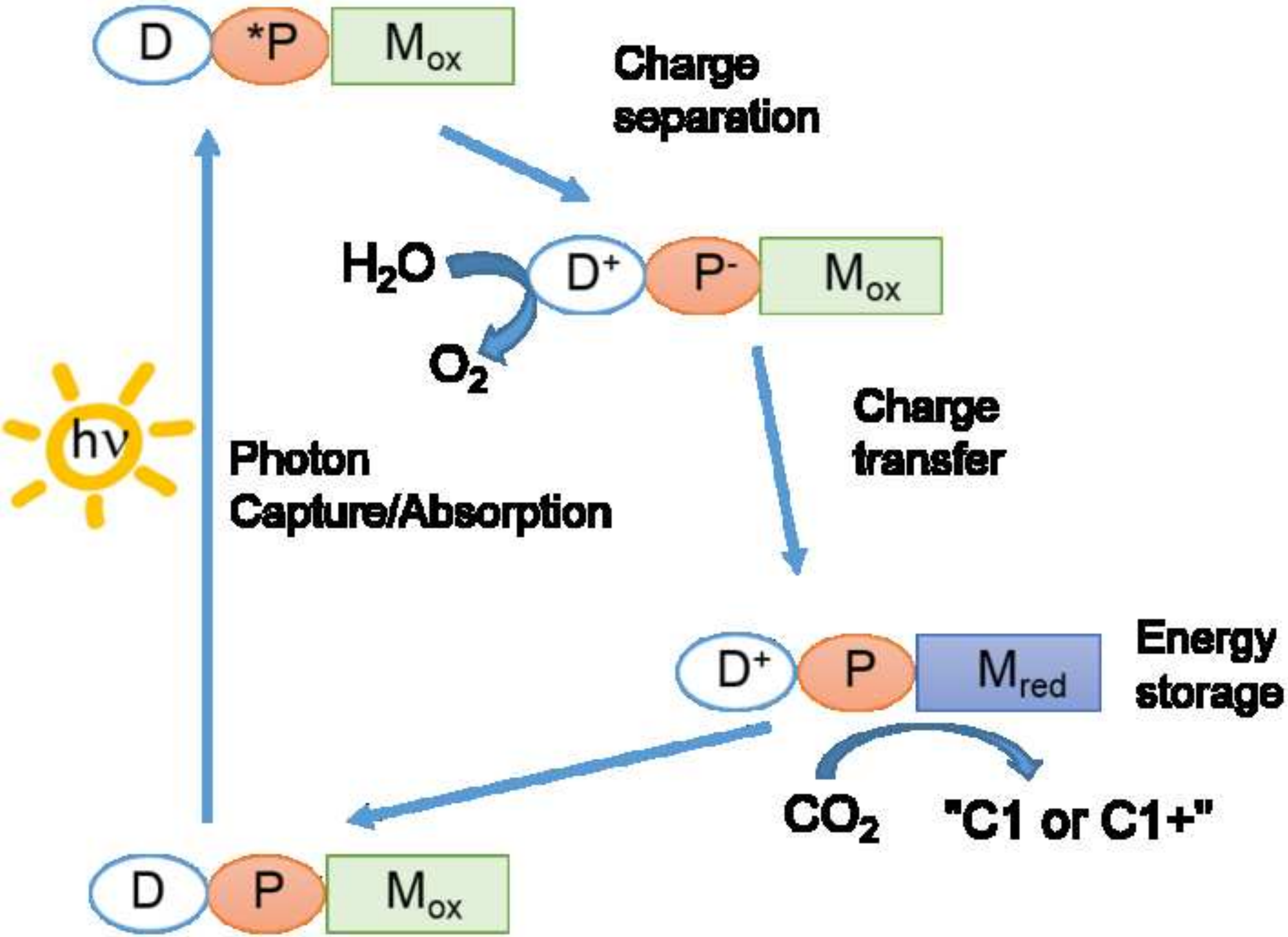
Click here to download high resolution image



Figure

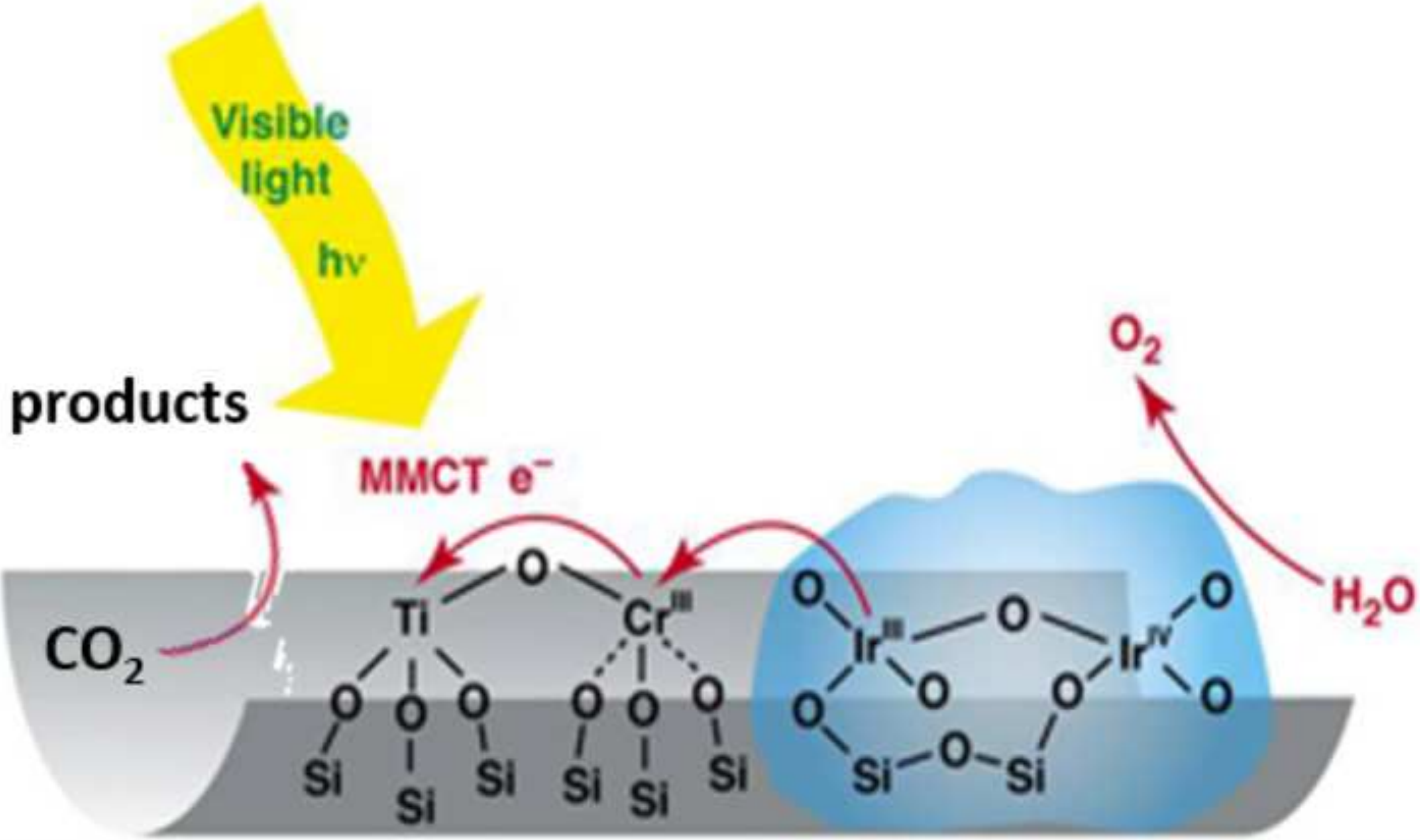
Click here to download high resolution image

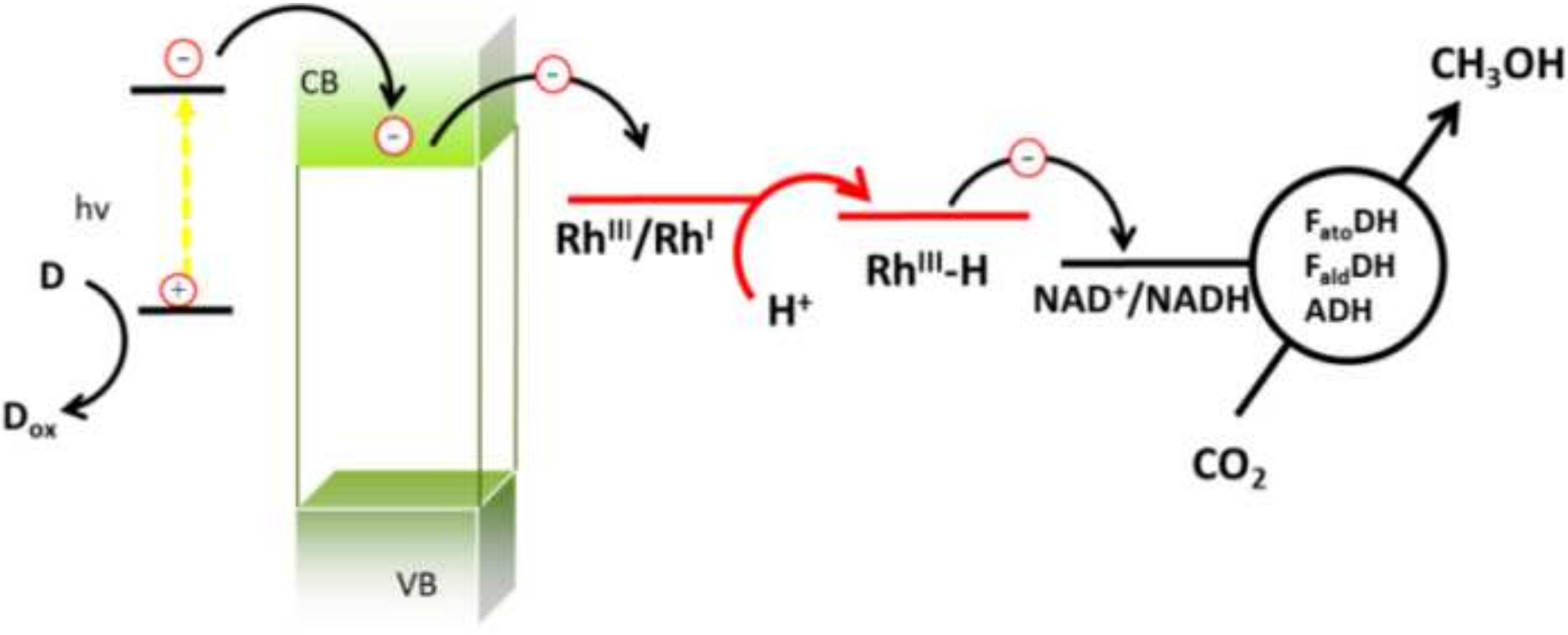



D
*P
M$_{ox}$
Charge separation
H$_2$O
O$_2$
D$^+$
P$^-$
M$_{ox}$
hν
Photon Capture/Absorption
Charge transfer
D$^+$
P
M$_{red}$
Energy storage
CO$_2$
"C1 or C1+"
D
P
M$_{ox}$

Figure

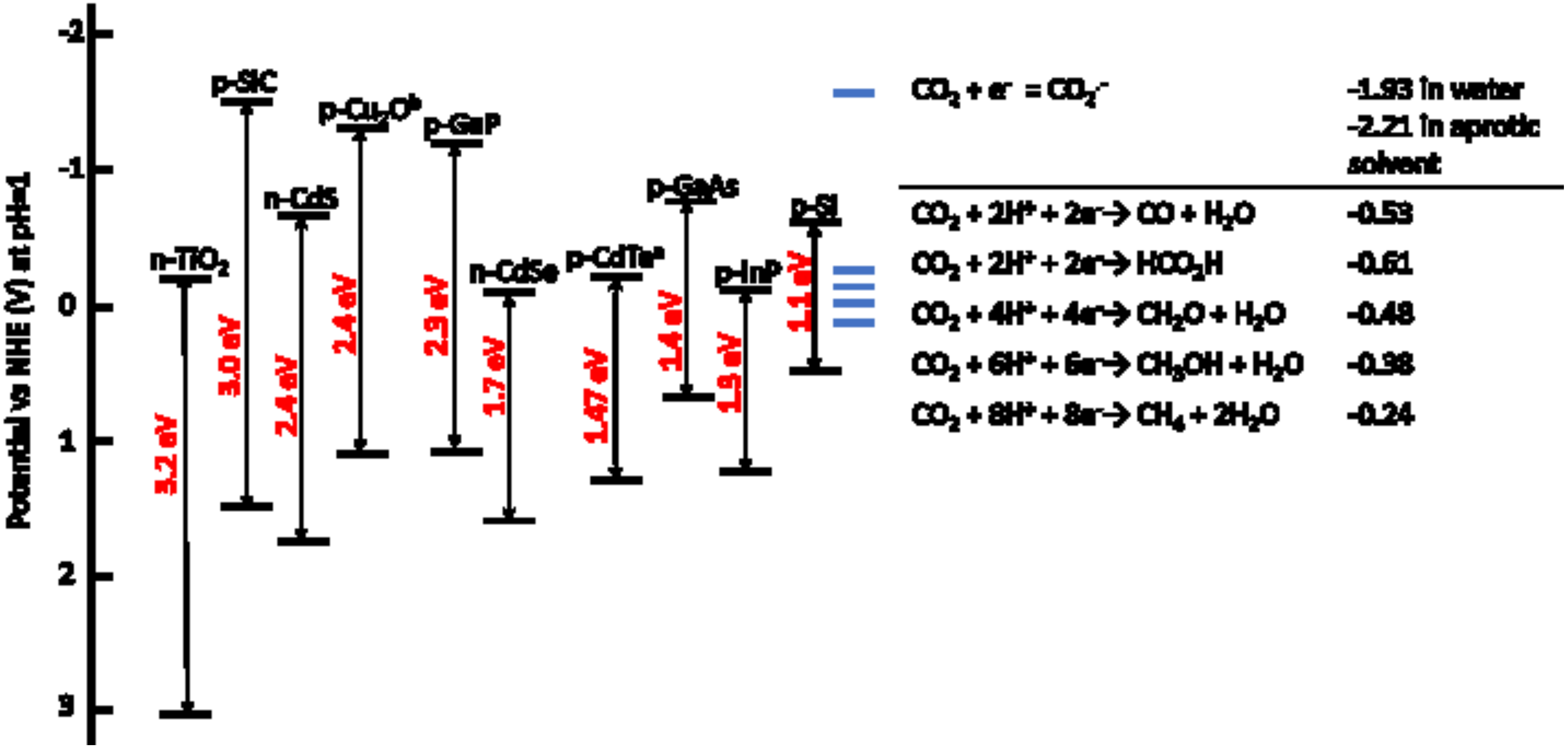
Click here to download high resolution image




CB
hv
D
D_{ox}
VB
Rh^{III}/Rh^{I}
H^+
Rh^{III}-H
$NAD^+/NADH$
$F_{ato}DH$
$F_{ald}DH$
ADH
CH_3OH
CO_2

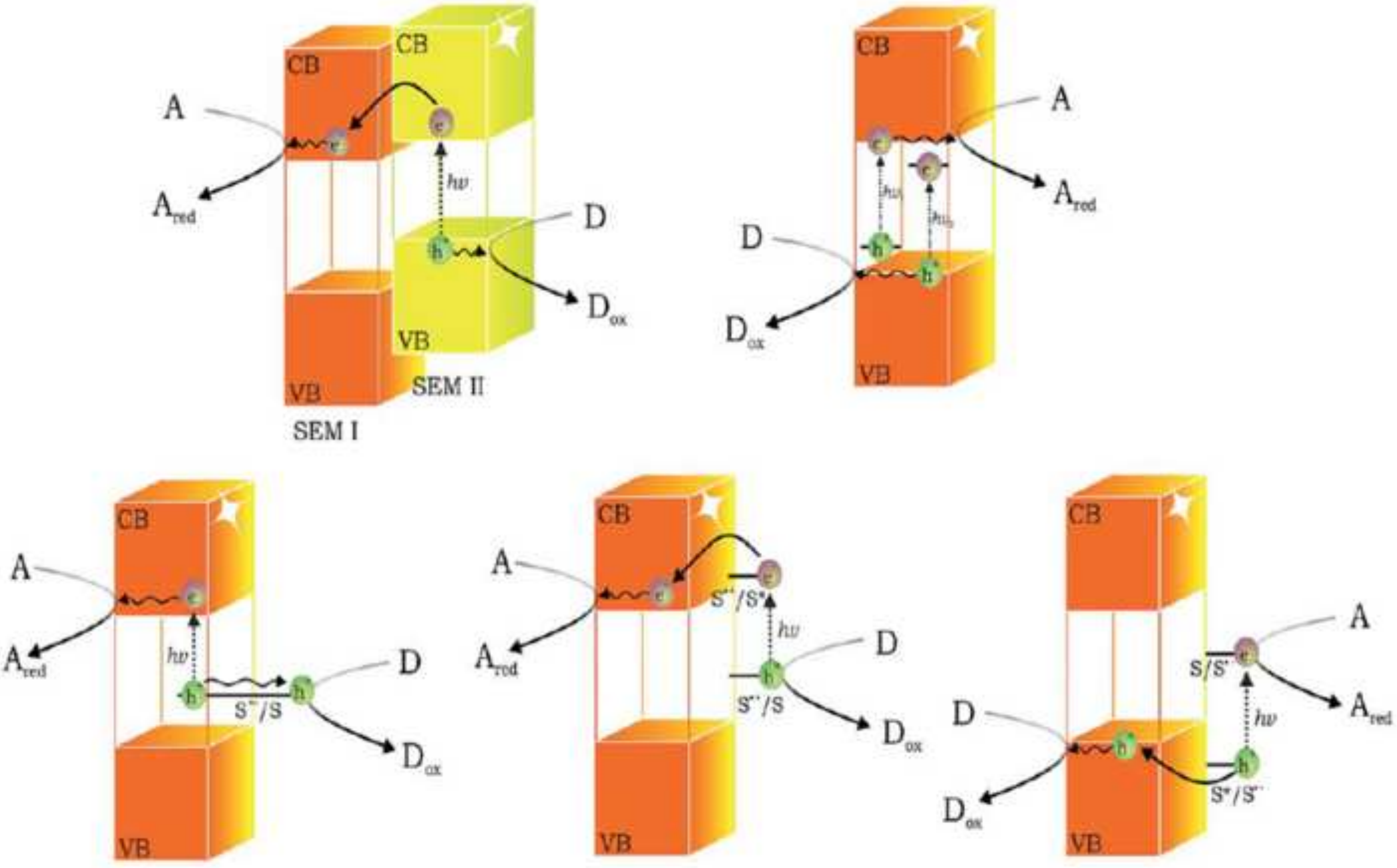
Figure

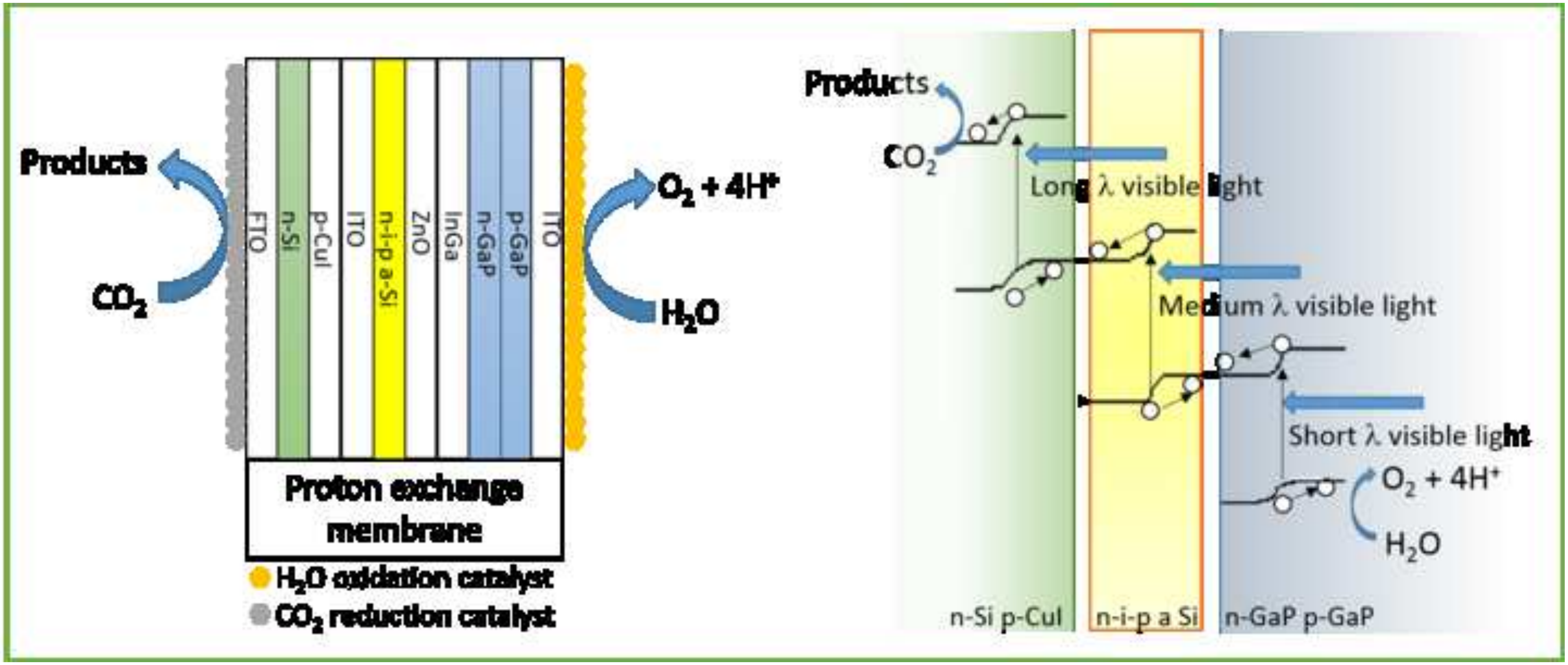
Click here to download high resolution image



🟦	$CO_2 + e^- = CO_2^{\cdot -}$	–1.93 in water –2.21 in aprotic solvent
🟦	$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O$	–0.53
🟦	$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$	–0.61
🟦	$CO_2 + 4H^+ + 4e^- \rightarrow CH_2O + H_2O$	–0.48
🟦	$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O$	–0.38
	$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O$	–0.24

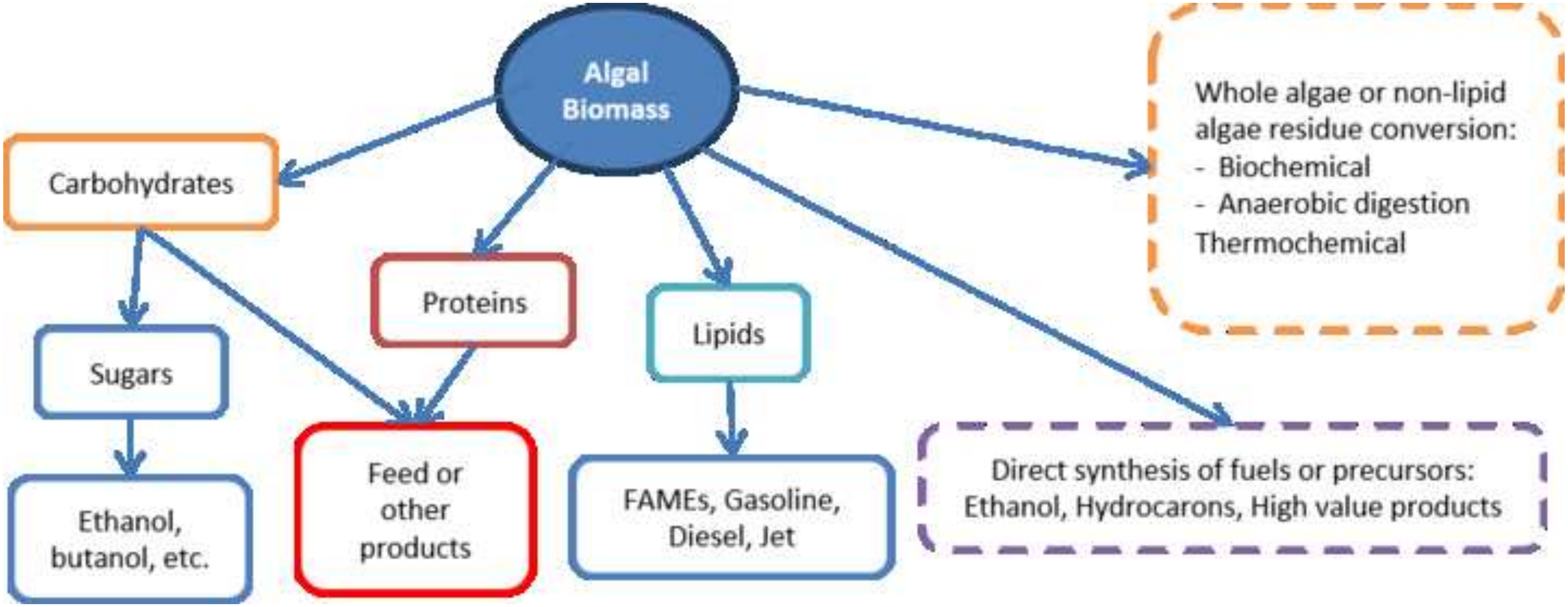
Figure

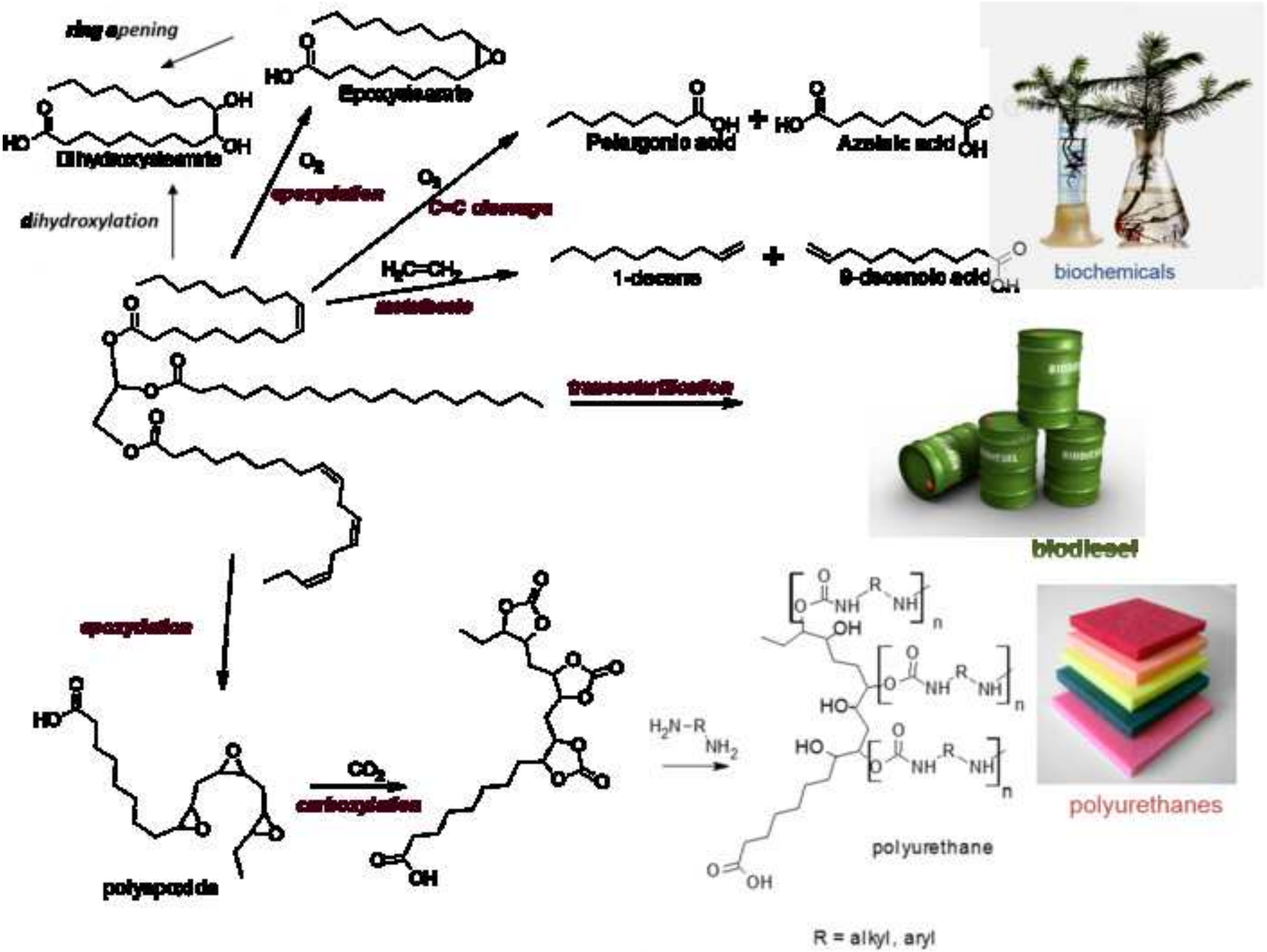

CB
CB
A
e⁻
e⁻
A_red
hν
h⁺
D
D_ox
VB
VB
SEM II
SEM I
CB
A
e⁻
e⁻
A_red
hν
hν
D
h⁺
h⁺
D_ox
VB
CB
A
e⁻
A_red
hν
h⁺
h⁺
S⁺/S
D
D_ox
VB
CB
A
e⁻
e⁻
A_red
S⁺/S*
hν
D
h⁺
S⁺/S
D_ox
VB
CB
A
S/S⁻
e⁻
hν
A_red
D
h⁺
h⁺
S*/S⁻
D_ox
VB


Products
CO2
FTO
n-Si
p-CuI
ITO
n-i-p a-Si
ZnO
InGa
n-GaP
p-GaP
ITO
O2 + 4H+
H2O
Proton exchange membrane
H2O oxidation catalyst
CO2 reduction catalyst
Products
CO2
Long λ visible light
Medium λ visible light
Short λ visible light
O2 + 4H+
H2O
n-Si p-CuI
n-i-p a Si
n-GaP p-GaP

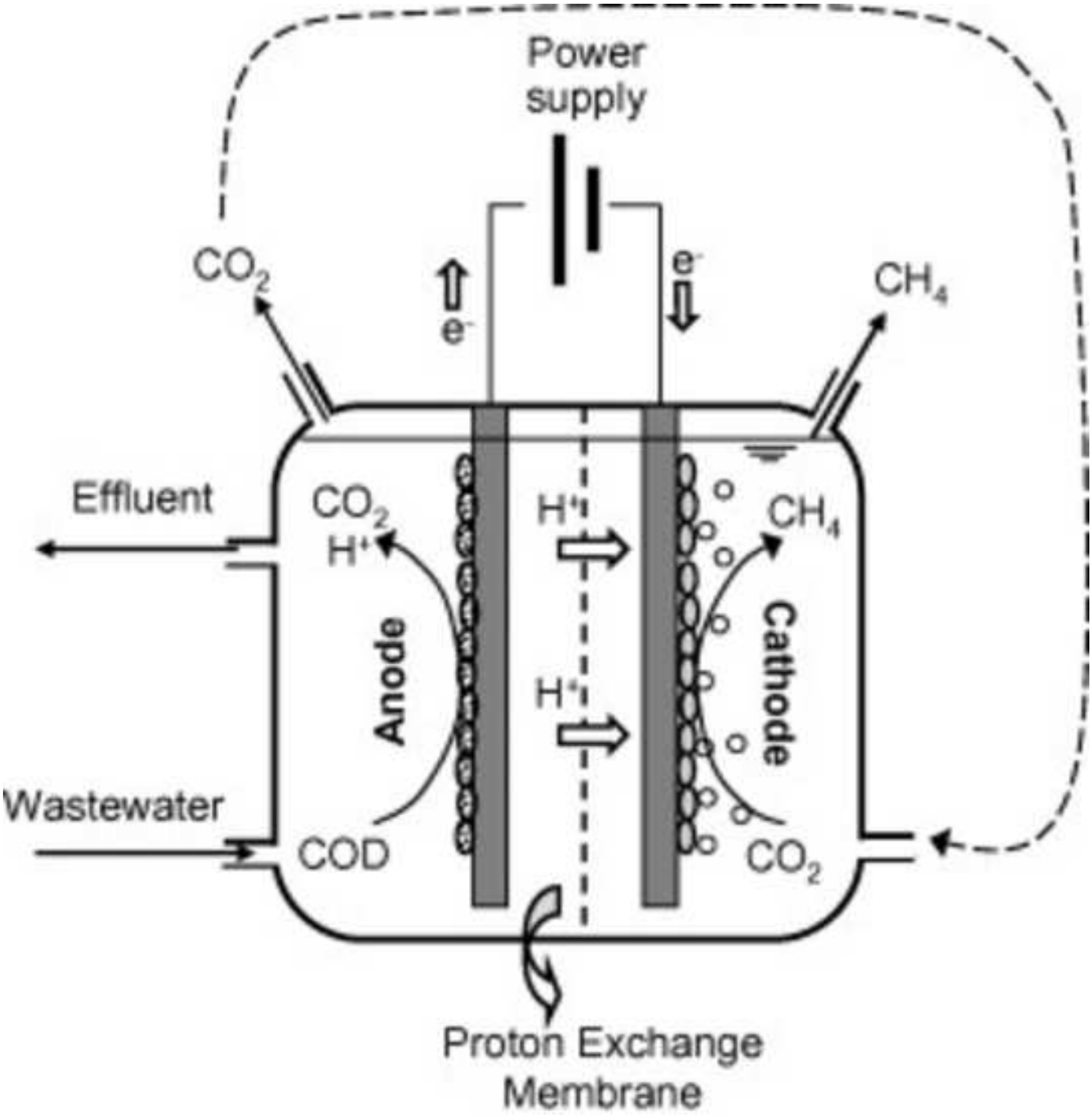
Figure

Click here to download high resolution image



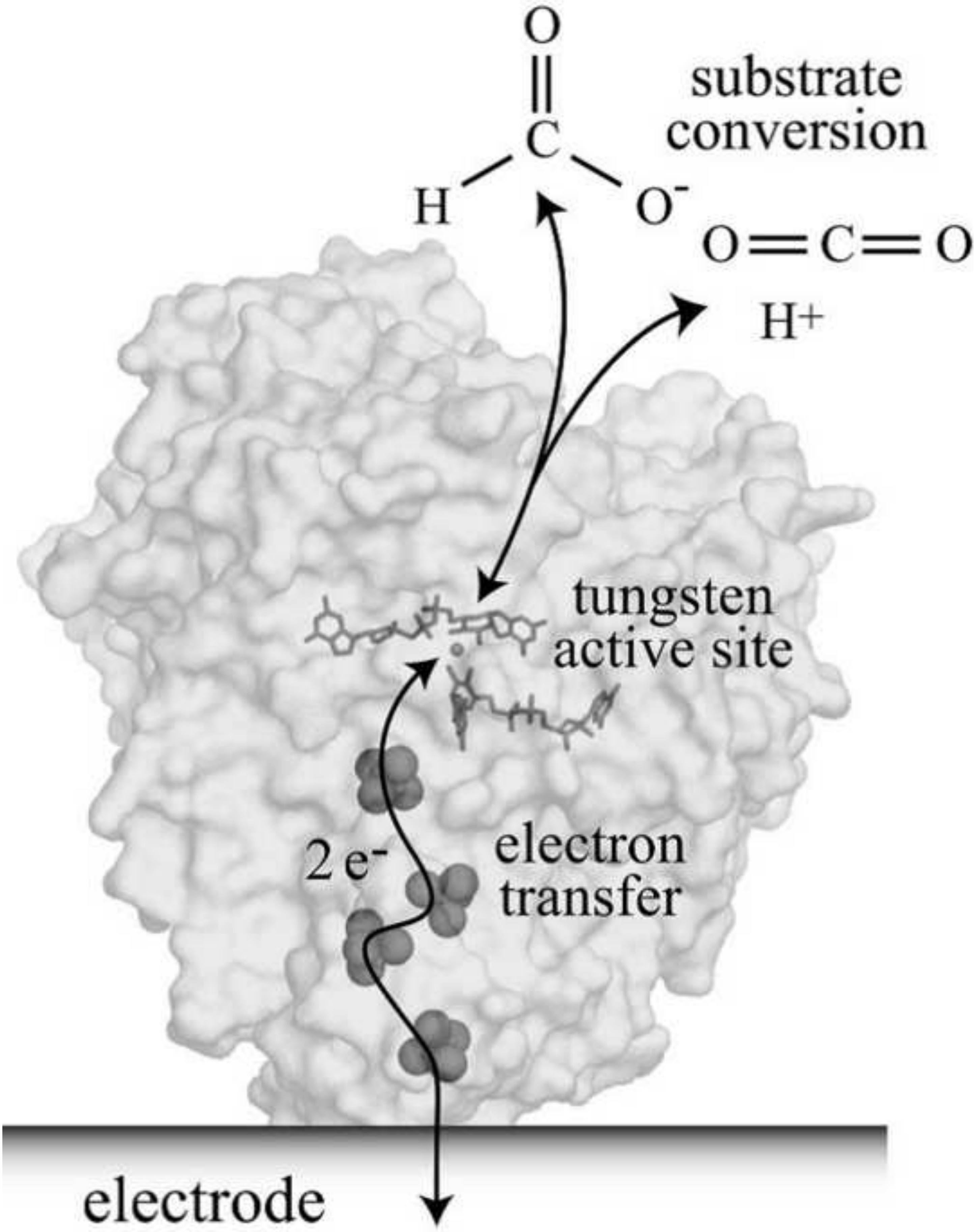

ring opening
Epoxystearate
Dihydroxystearate
dihydroxylation
O_2
epoxydation
O_3
C=C cleavage
Pelargonic acid
Azelaic acid
$H_2C=CH_2$
metathesis
1-decene
9-decenoic acid
biochemicals
transesterification
biodiesel
epoxydation
polyepoxide
CO_2
carboxylation
$H_2N-R-NH_2$
polyurethane
R = alkyl, aryl
polyurethanes

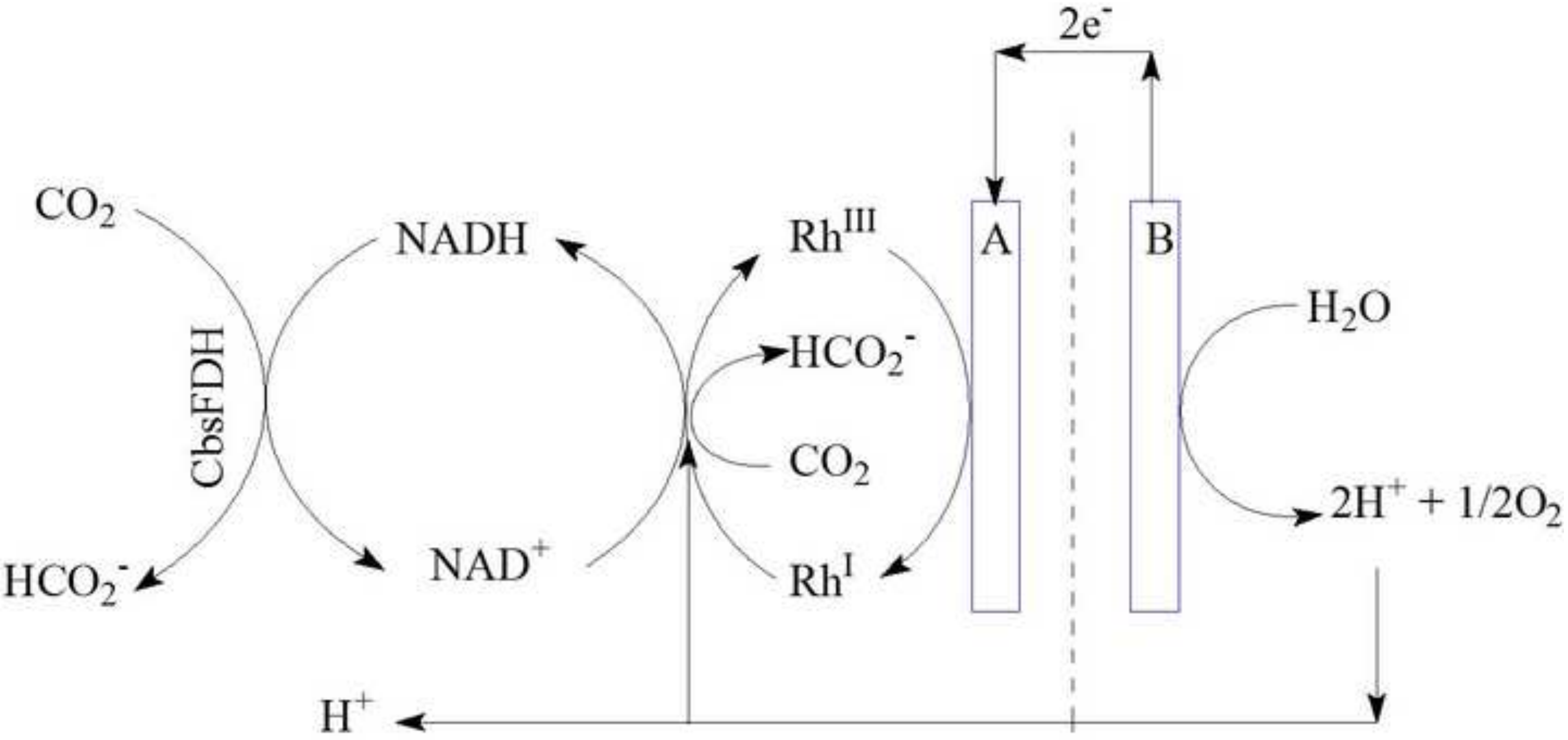
Figure


Power supply
CO_2
e^-
e^-
CH_4
Effluent
CO_2
H^+
H^+
CH_4
Anode
H^+
Cathode
Wastewater
COD
CO_2
Proton Exchange Membrane

Figure

Click here to download high resolution image

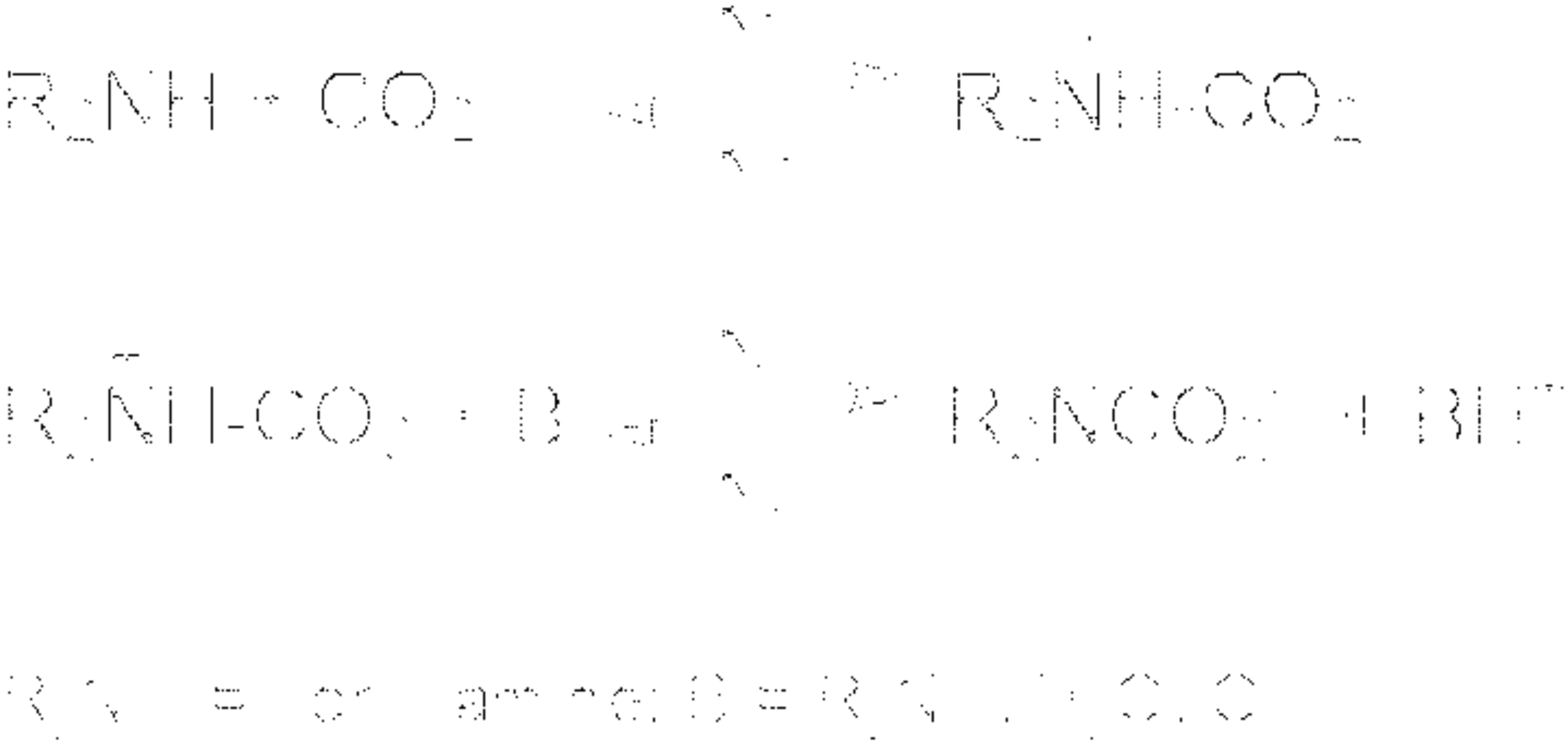




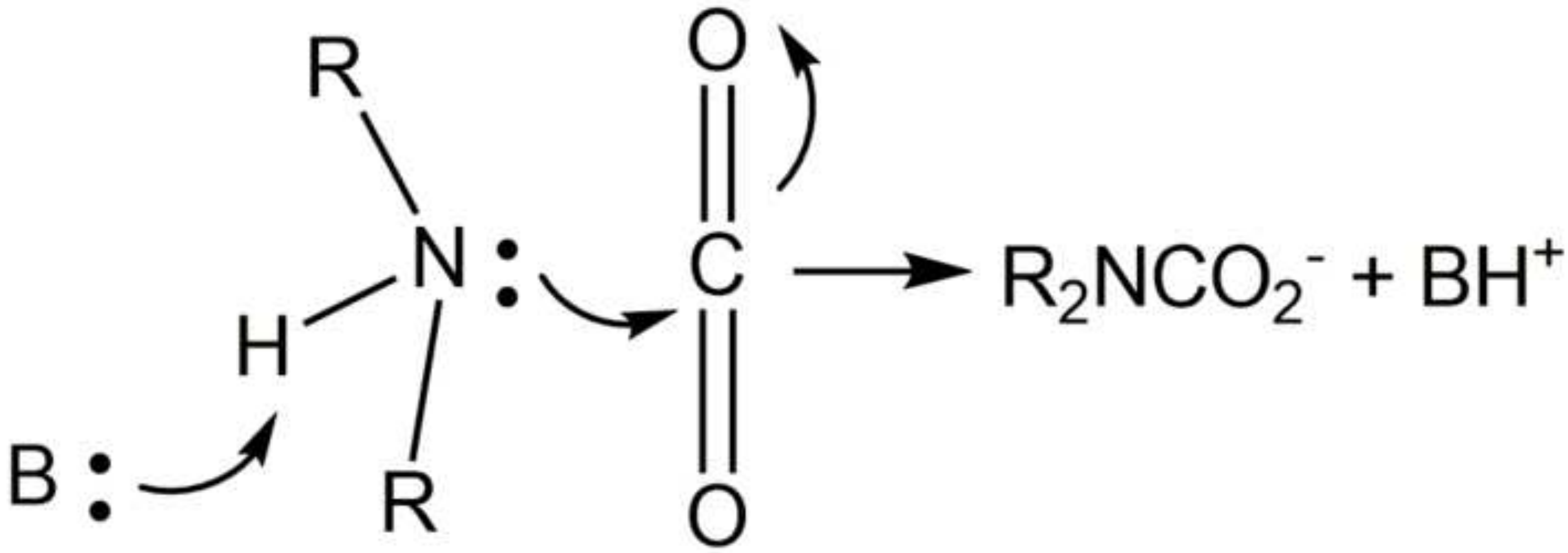
A= Cu electrode
B = Pt electrode

Scheme

Click here to download high resolution image

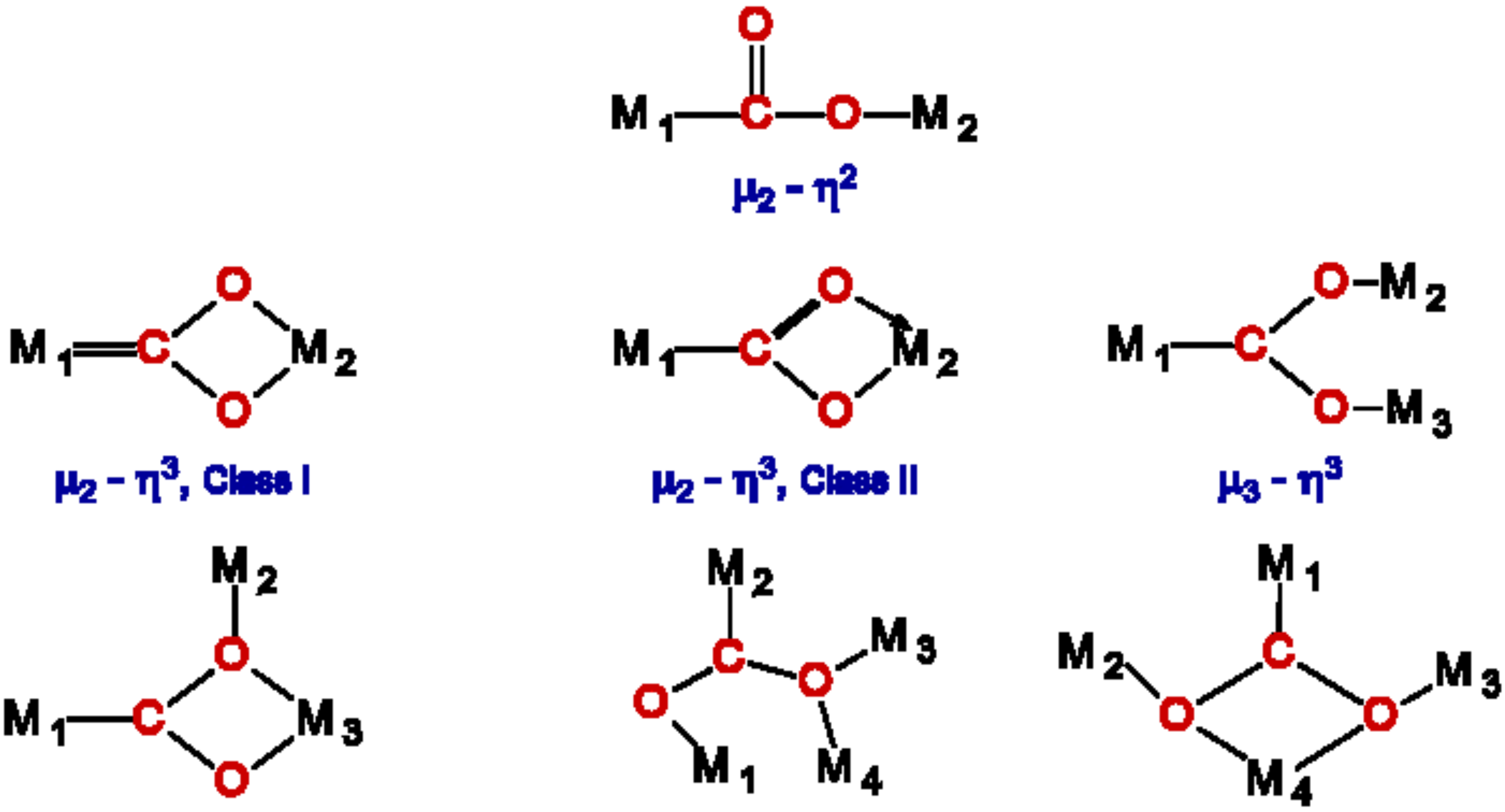


Scheme



Scheme

Scheme



$\mu_2 - \eta^2$

$\mu_2 - \eta^3$, Class I

$\mu_2 - \eta^3$, Class II

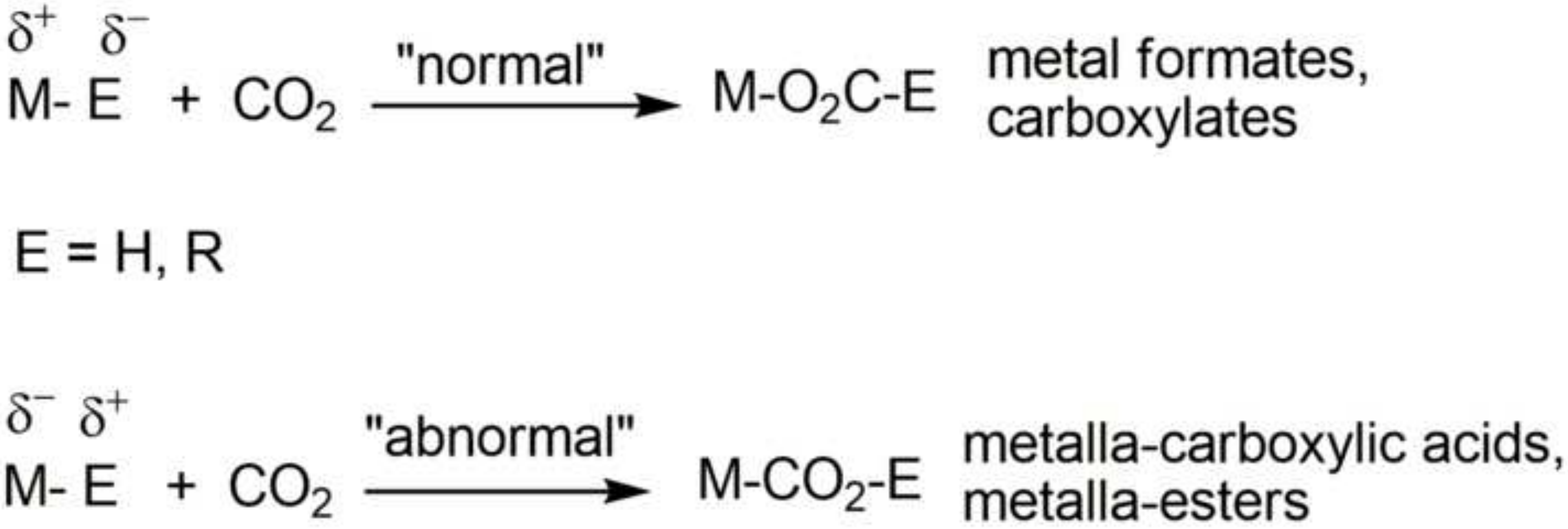
$\mu_3 - \eta^3$

$\mu_3 - \eta^4$

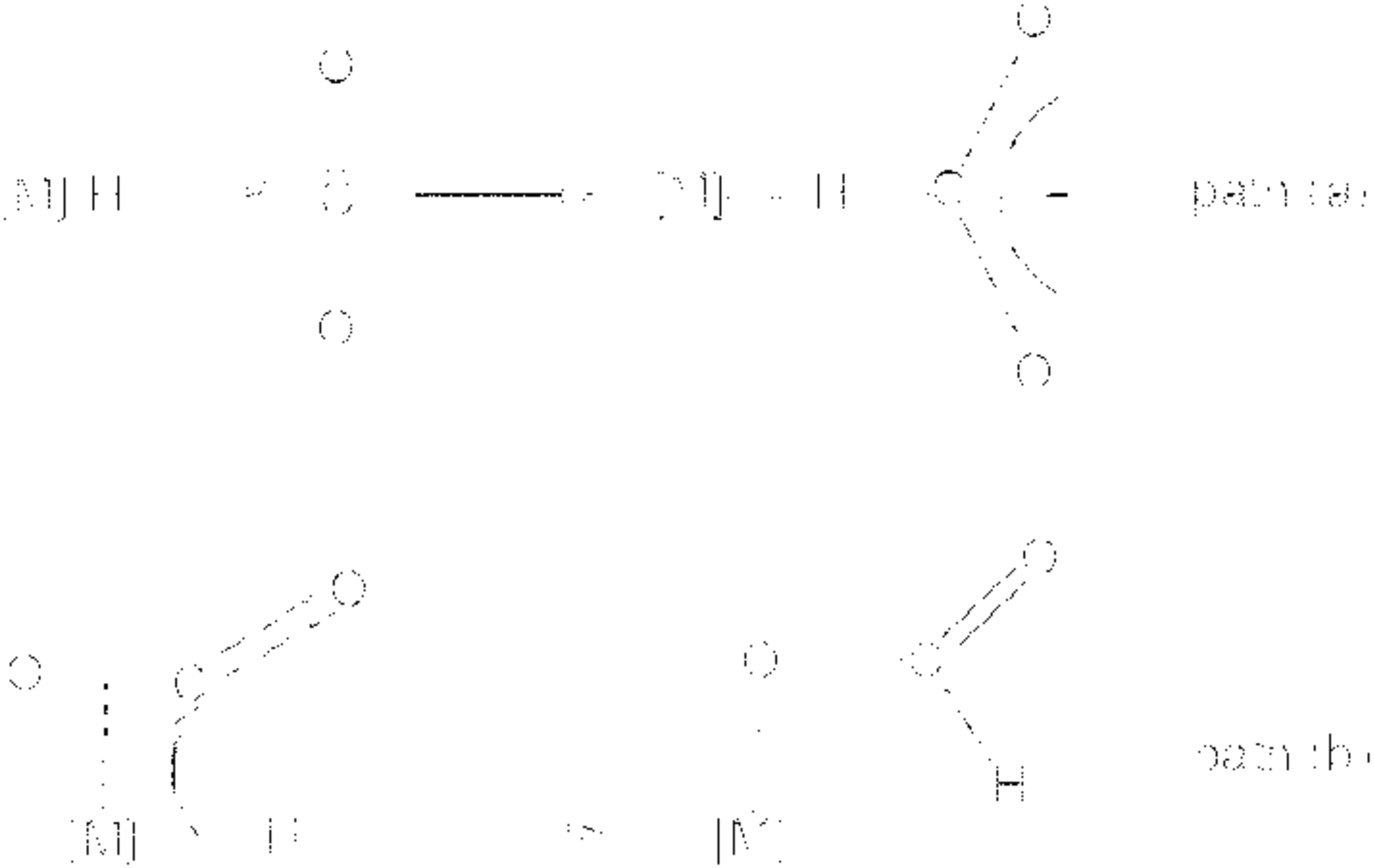
$\mu_4 - \eta^4$

$\mu_4 - \eta^5$

Scheme


δ+ δ−
M- E + CO2
"normal"
M-O2C-E
metal formates, carboxylates
E = H, R
δ− δ+
M- E + CO2
"abnormal"
M-CO2-E
metalla-carboxylic acids, metalla-esters

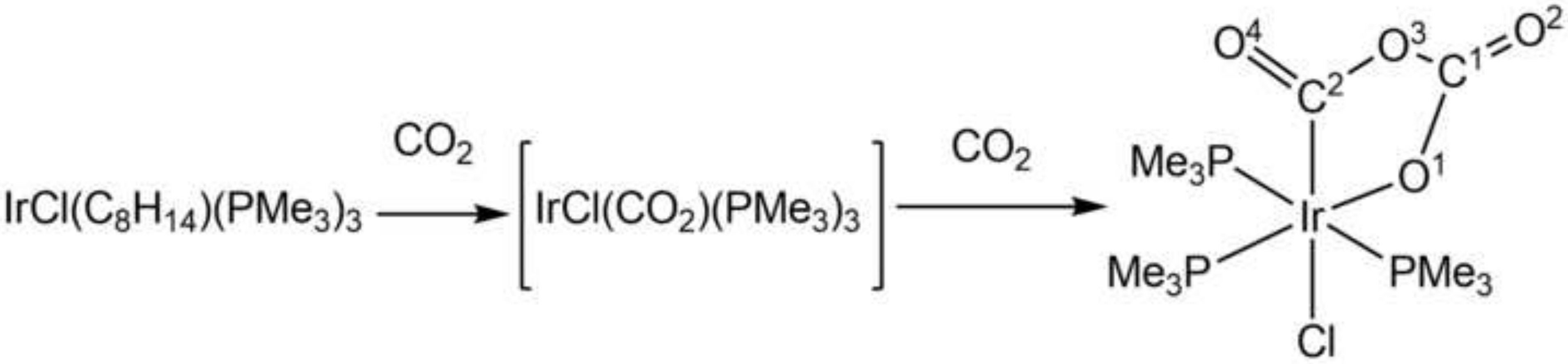
Scheme



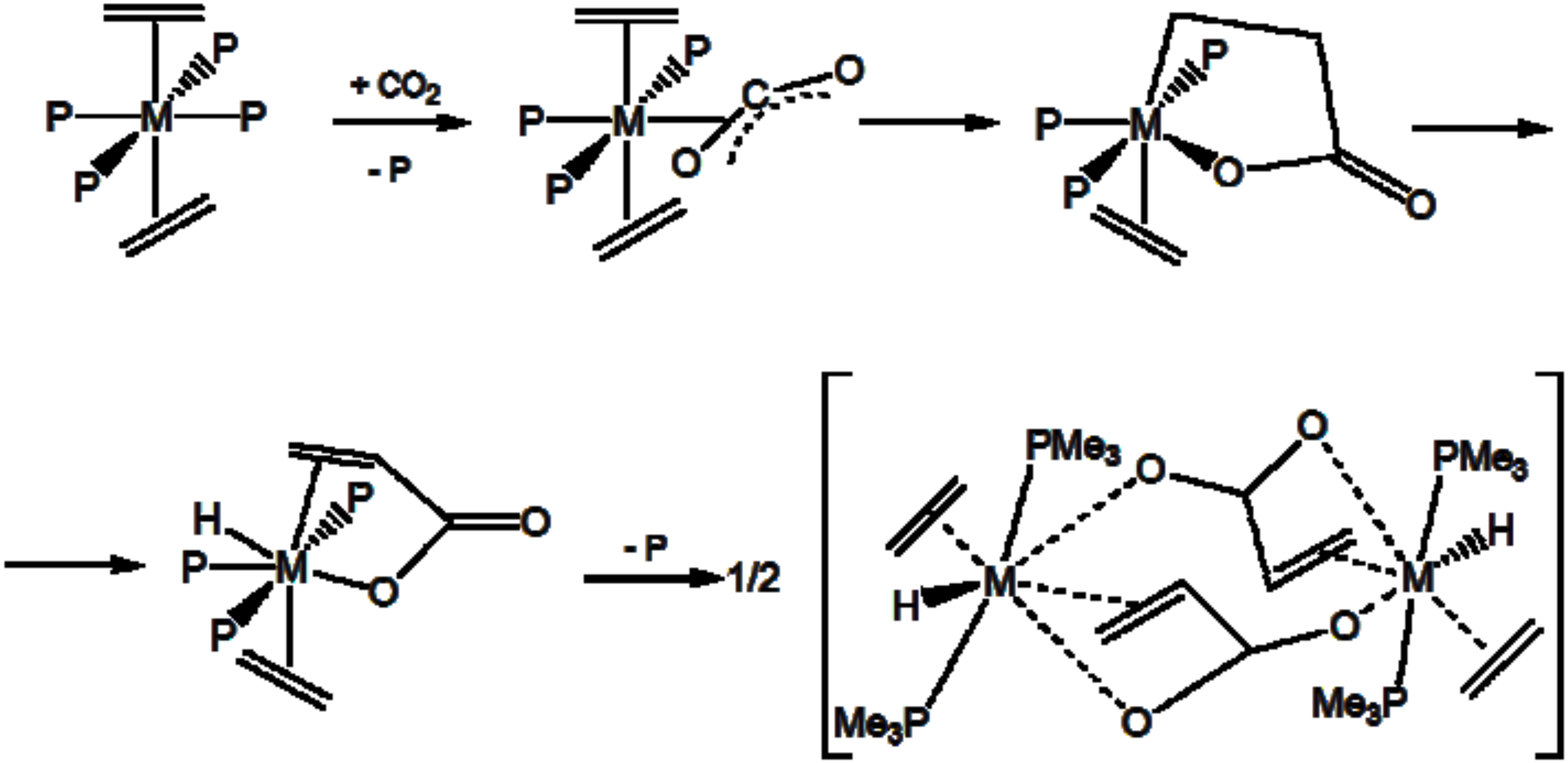
Scheme

Click here to download high resolution image

Scheme


IrCl(C8H14)(PMe3)3
CO2
IrCl(CO2)(PMe3)3
CO2
O4
O3
C1
O2
C2
Me3P
O1
Ir
Me3P
PMe3
Cl

Scheme

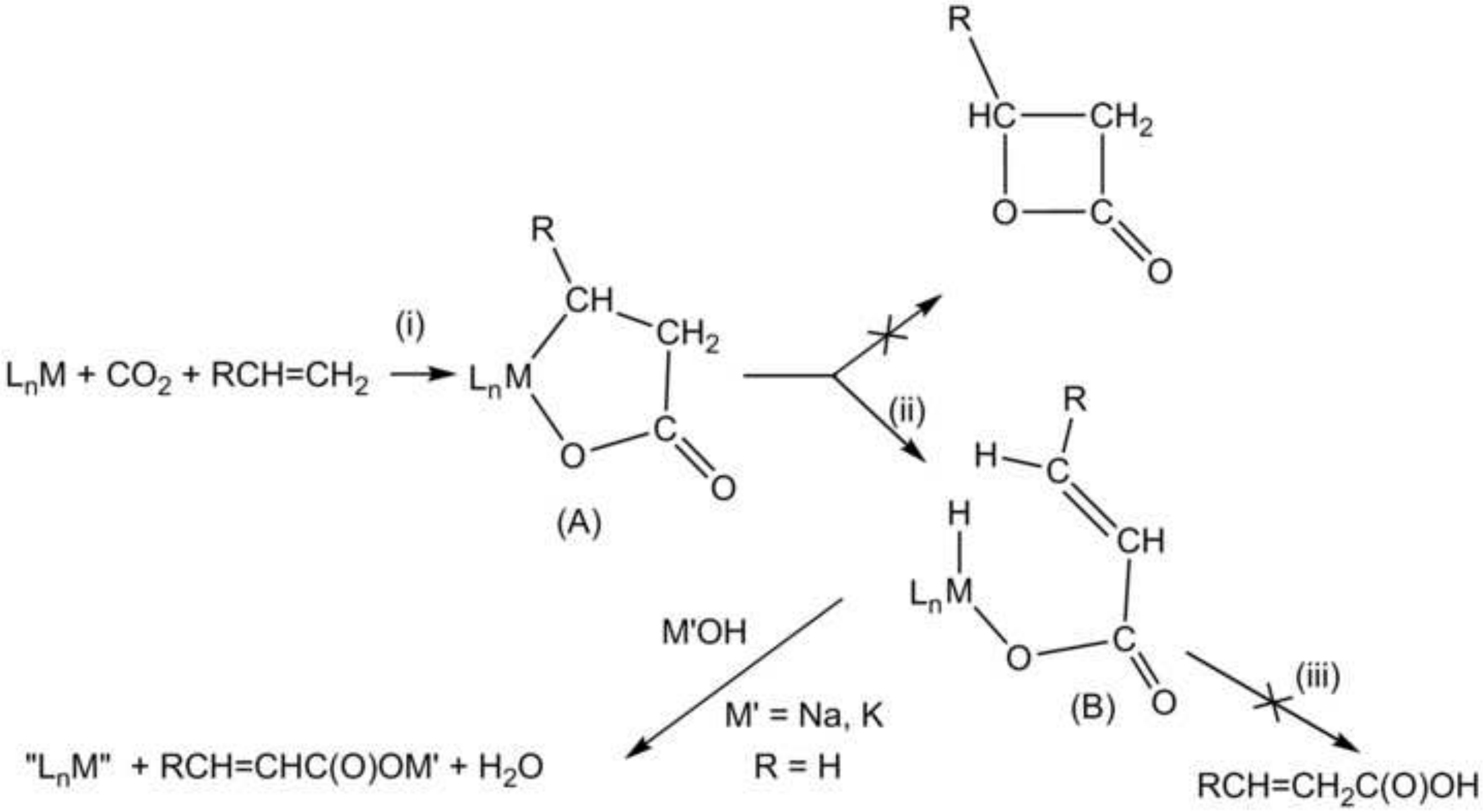


P= PMe$_3$

Scheme

Scheme

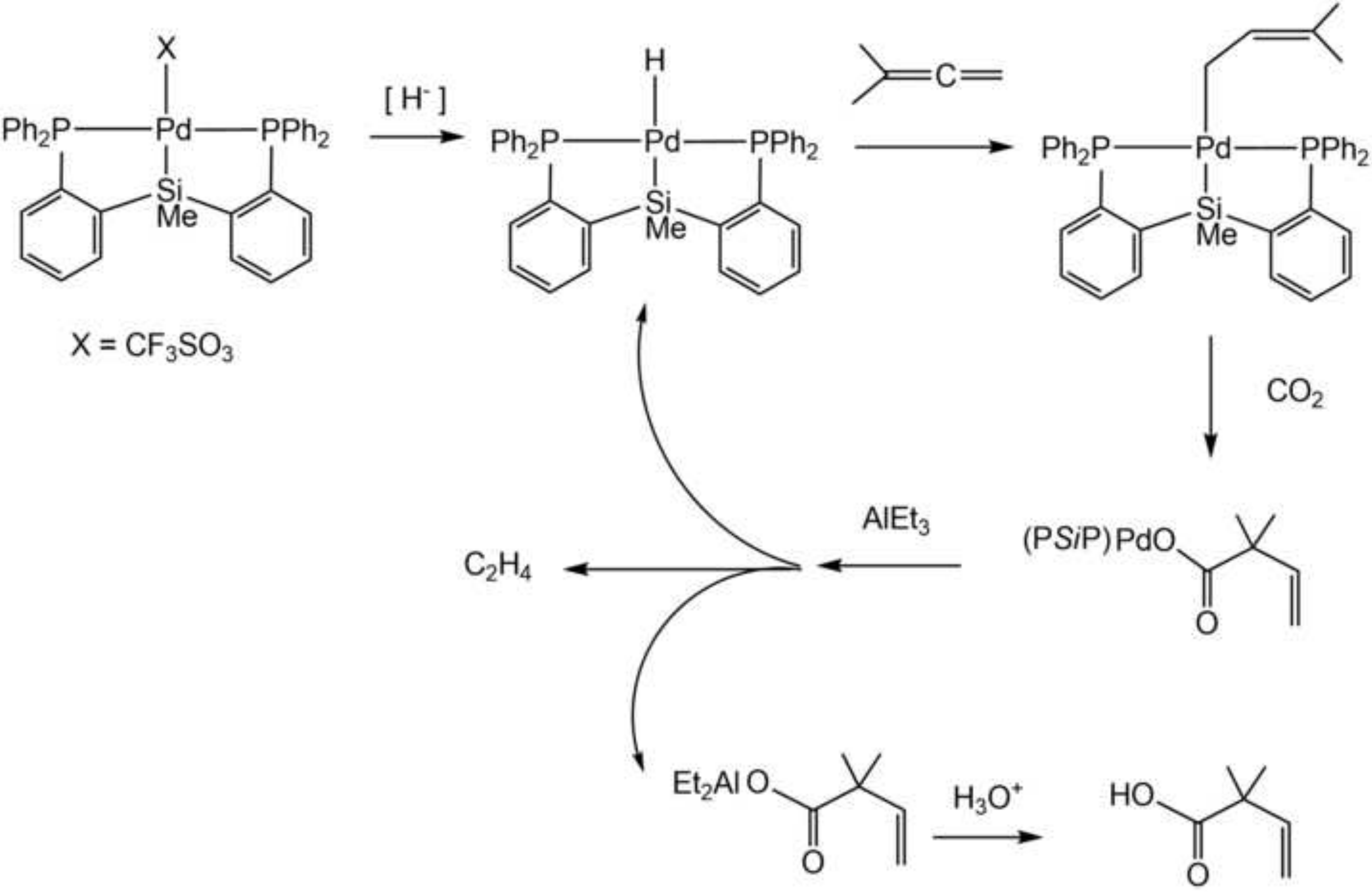
Click here to download high resolution image



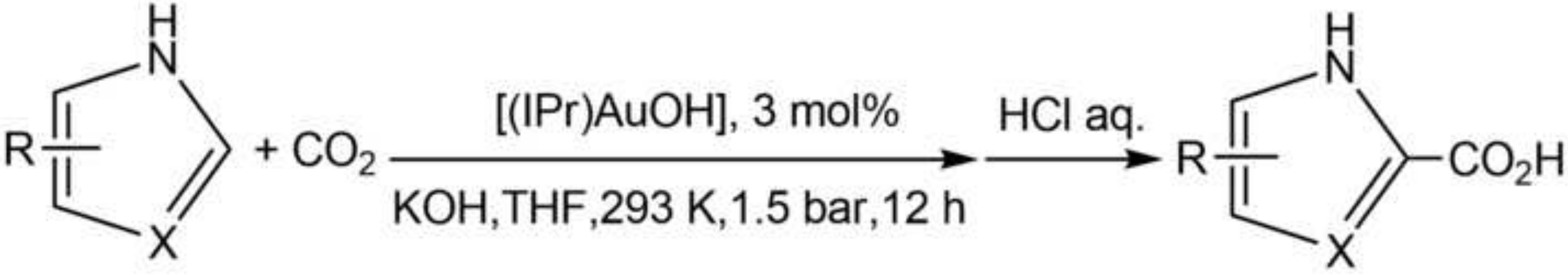
Scheme

Scheme

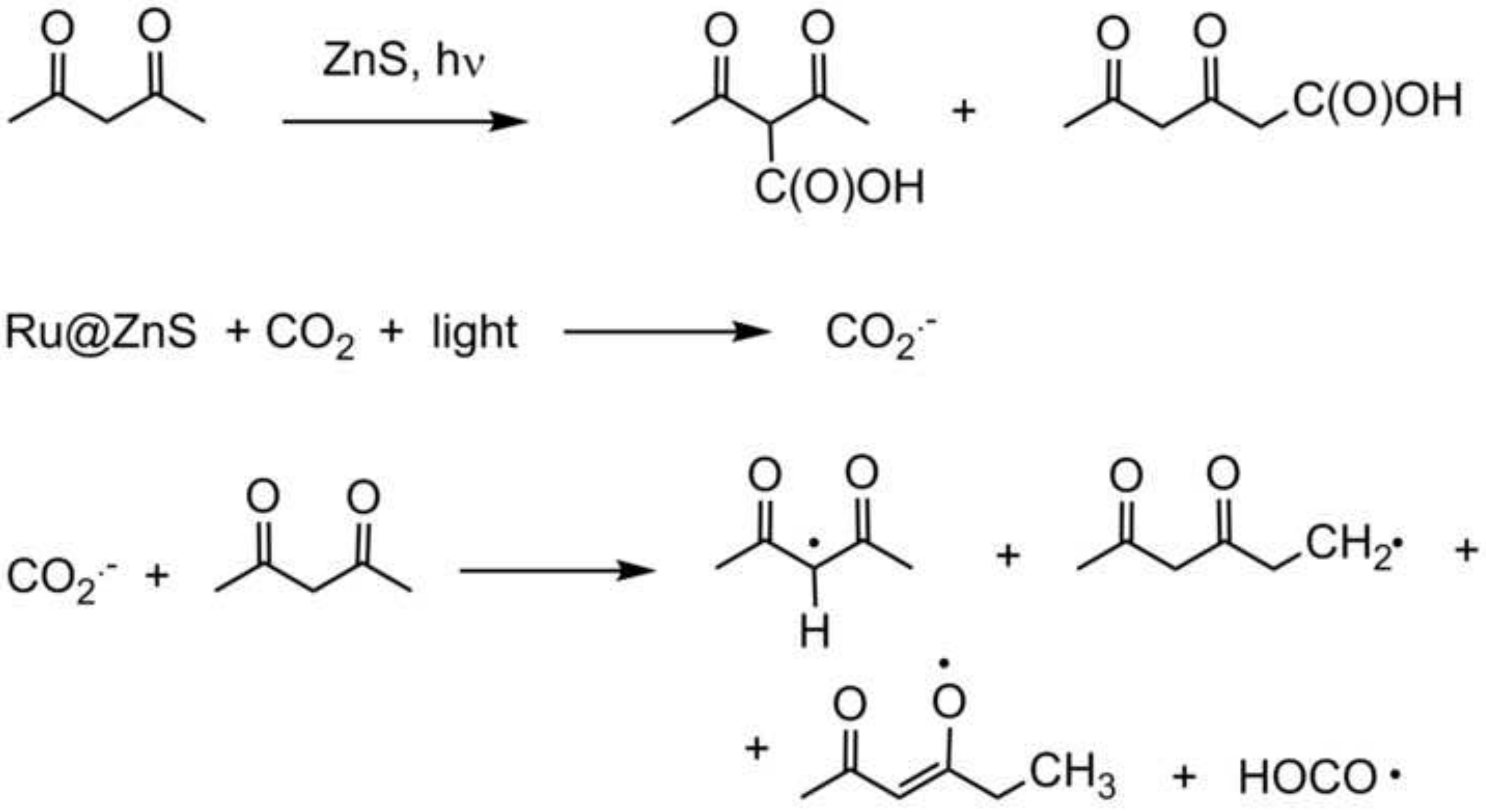
Scheme


X
Ph2P
Pd
PPh2
Si
Me
X = CF3SO3
[H-]
H
C
CO2
AlEt3
(PSiP)PdO
O
C2H4
Et2Al O
H3O+
HO

Scheme

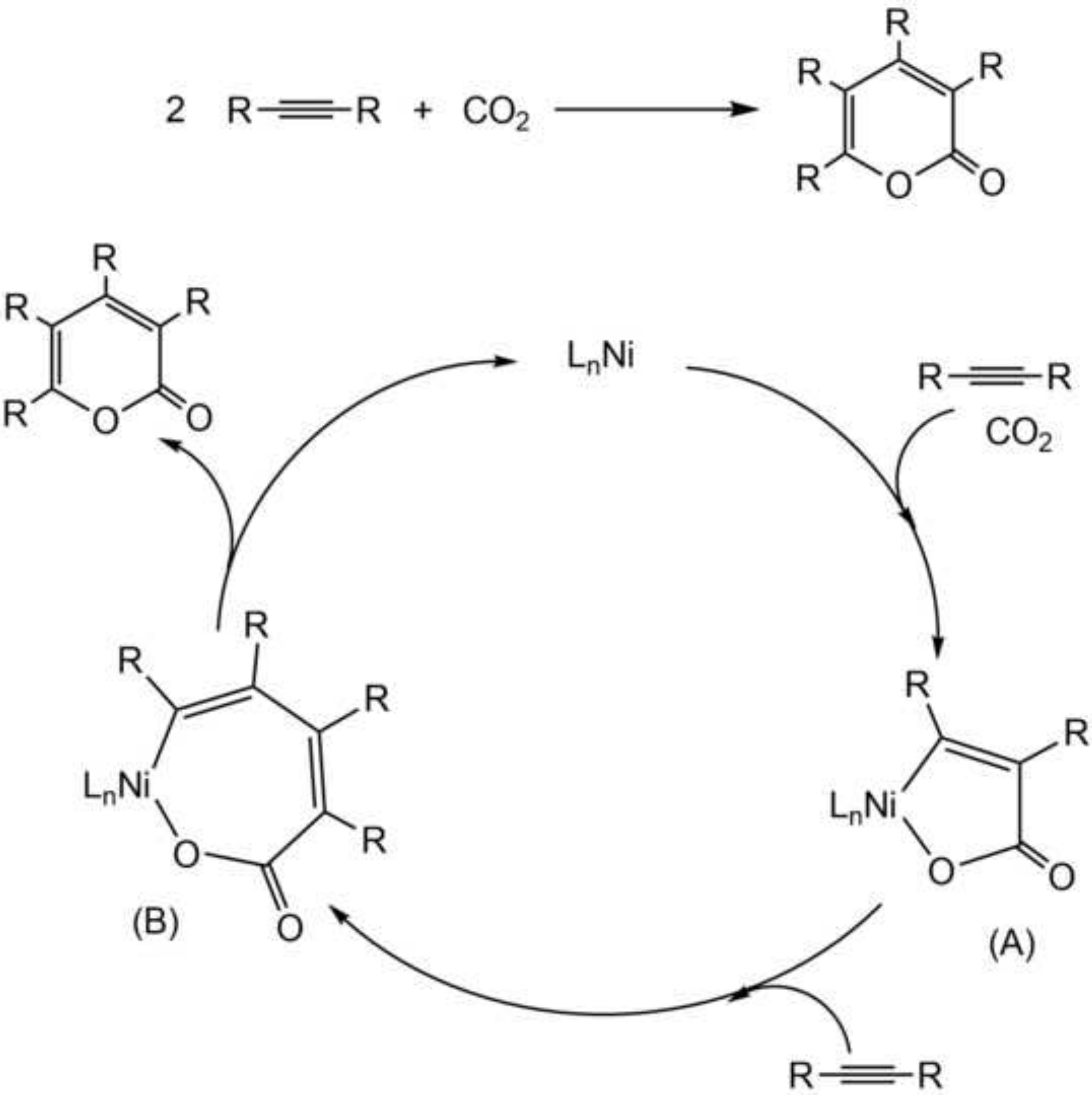


Scheme



Scheme

Click here to download high resolution image



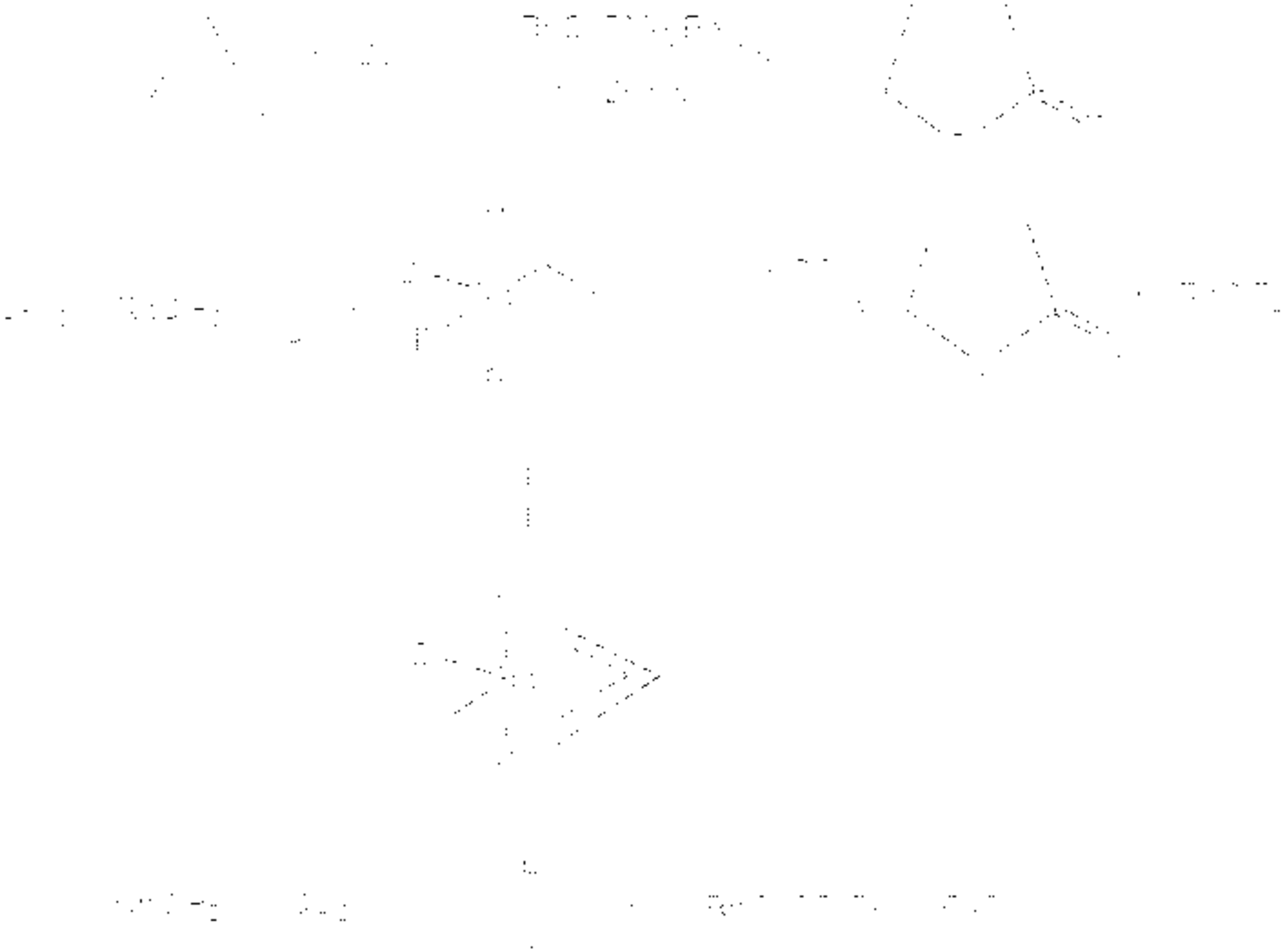
Scheme

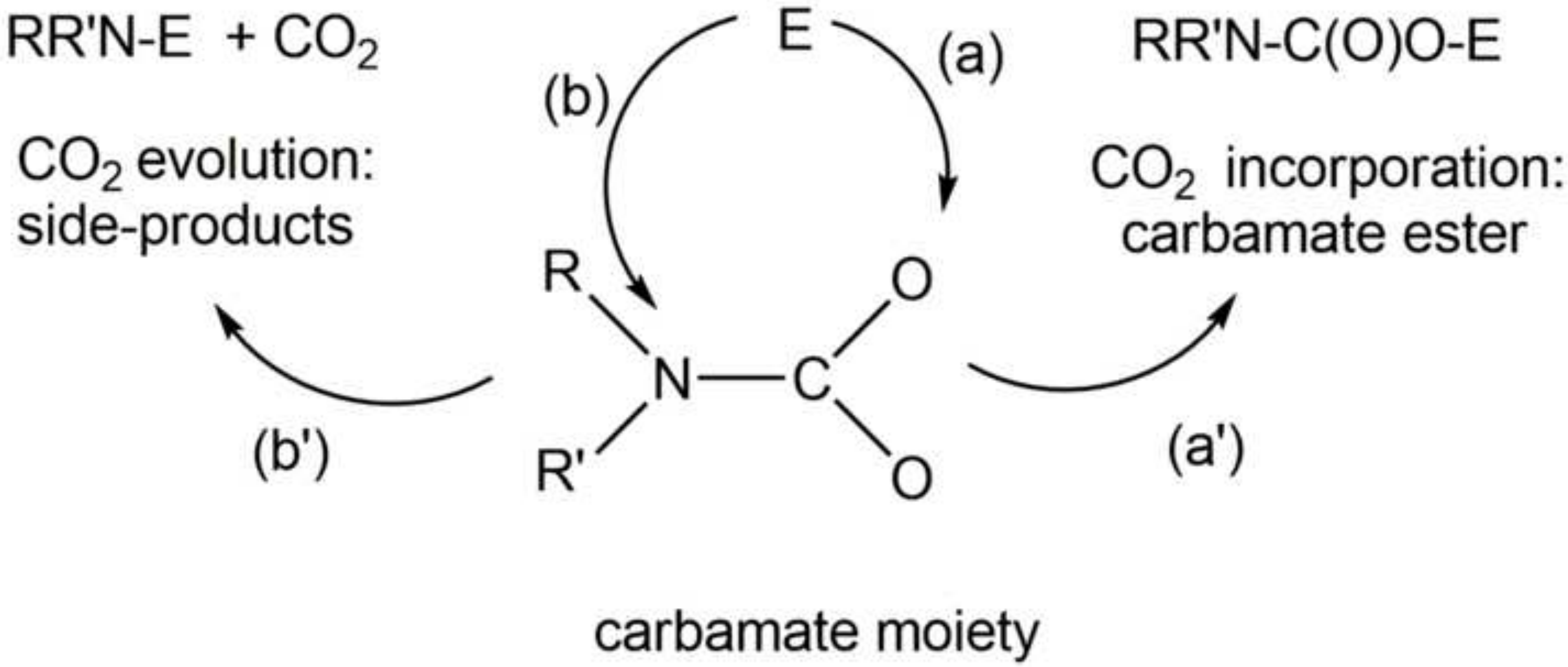
Scheme

Scheme

Scheme

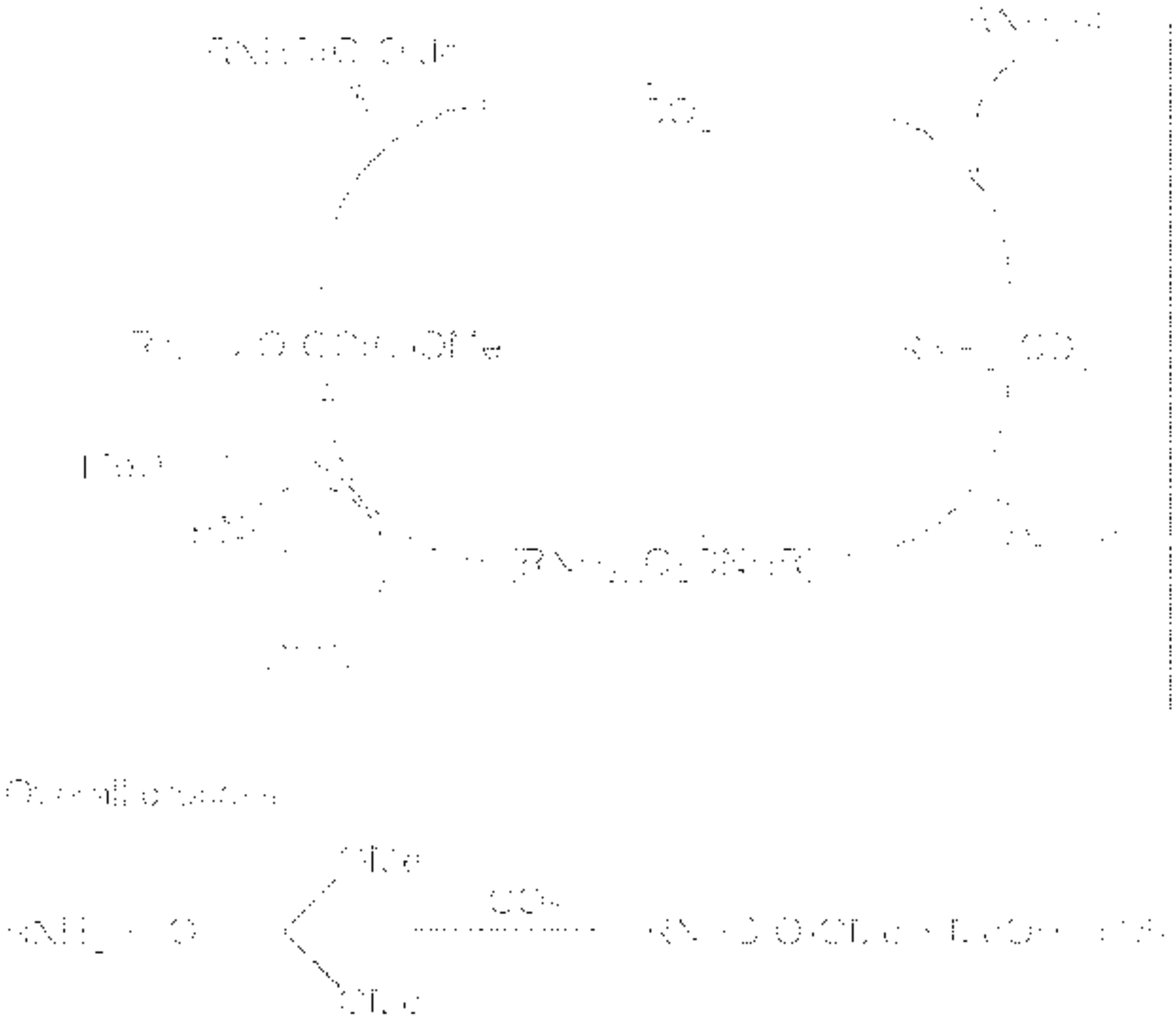
Click here to download high resolution image




RR'N-E + CO_2
CO_2 evolution:
side-products
(b)
E
(a)
RR'N-C(O)O-E
CO_2 incorporation:
carbamate ester
R
R'
N
C
O
O
(b')
(a')
carbamate moiety

Scheme

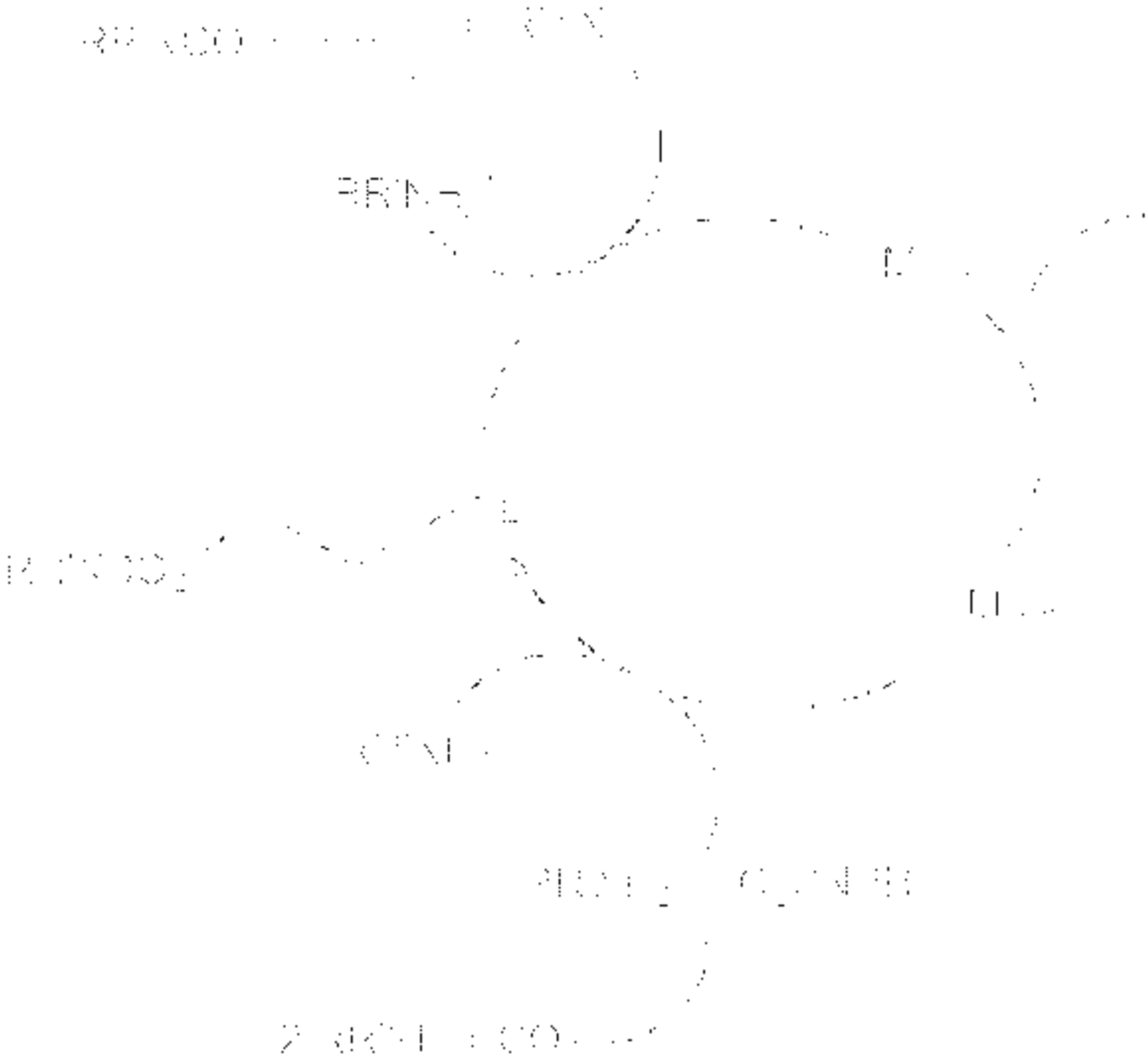
Click here to download high resolution image



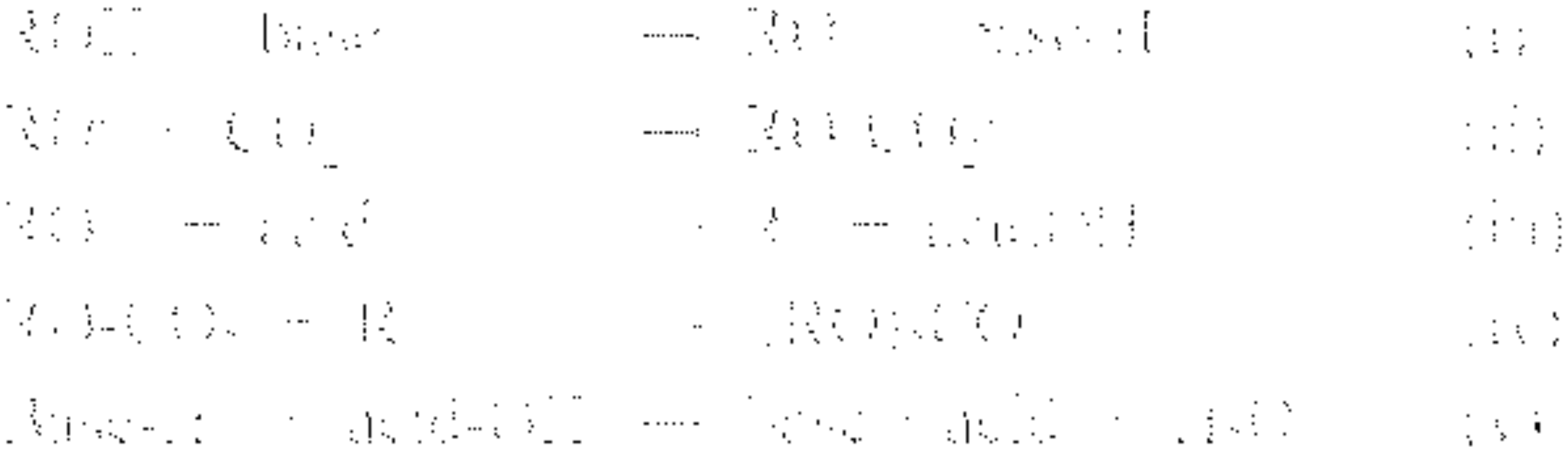
Scheme

Scheme

Click here to download high resolution image

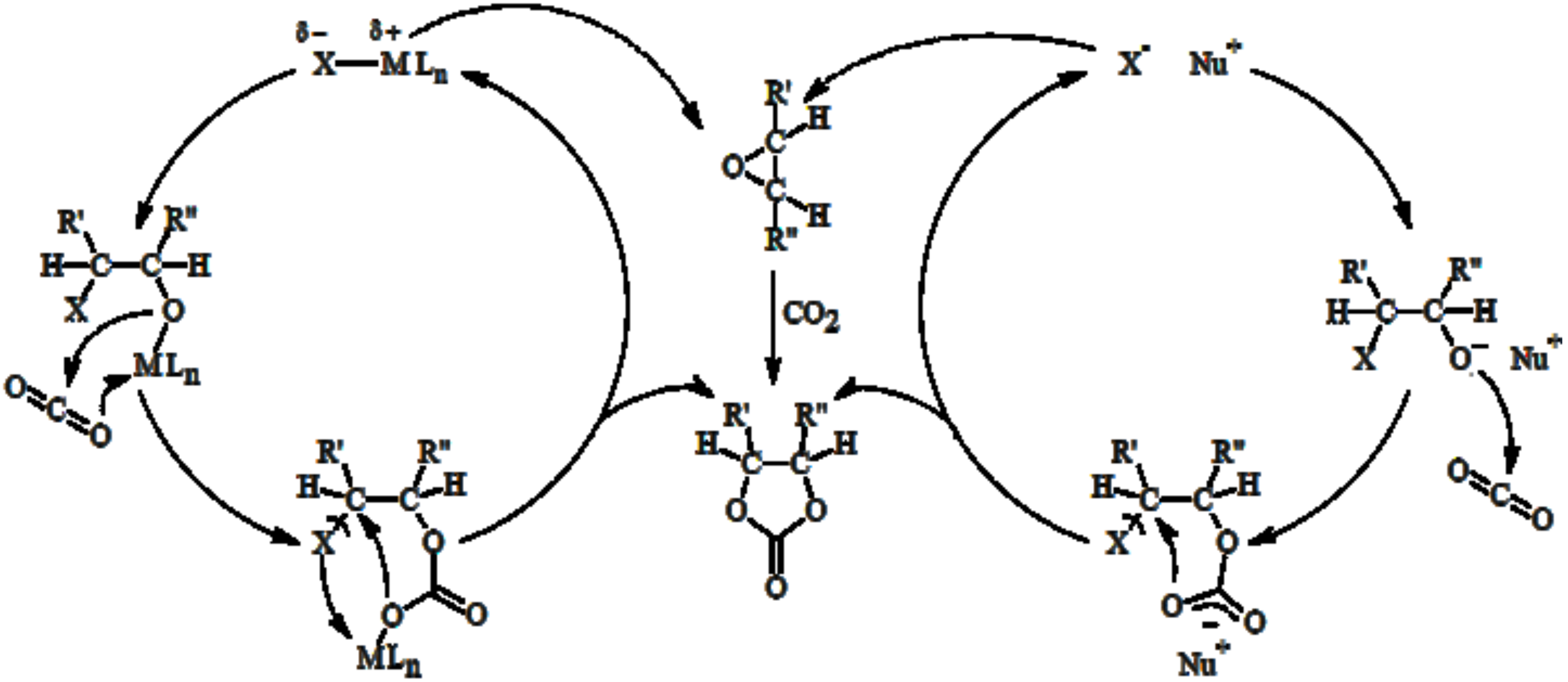


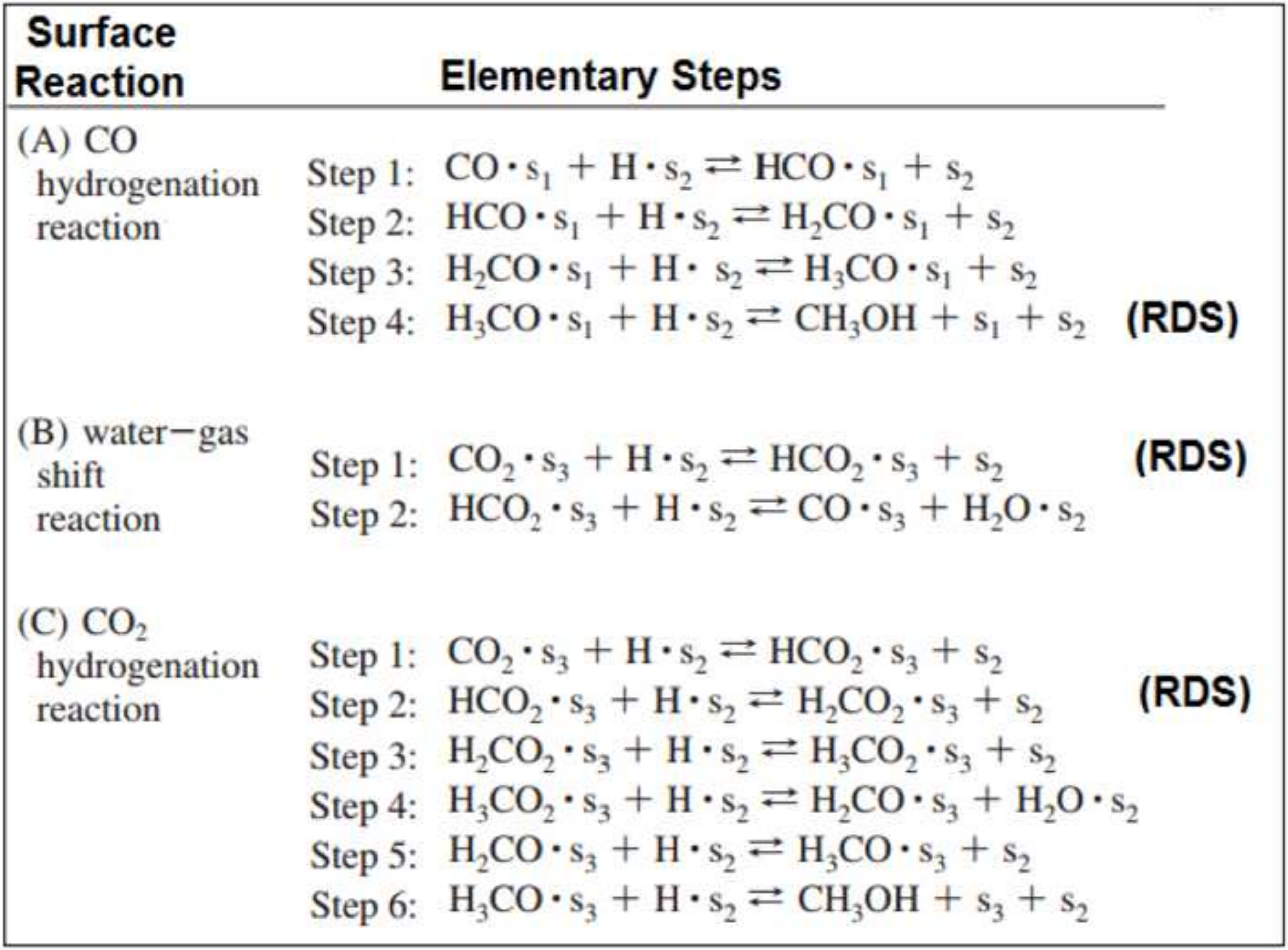
Scheme



Scheme

Scheme



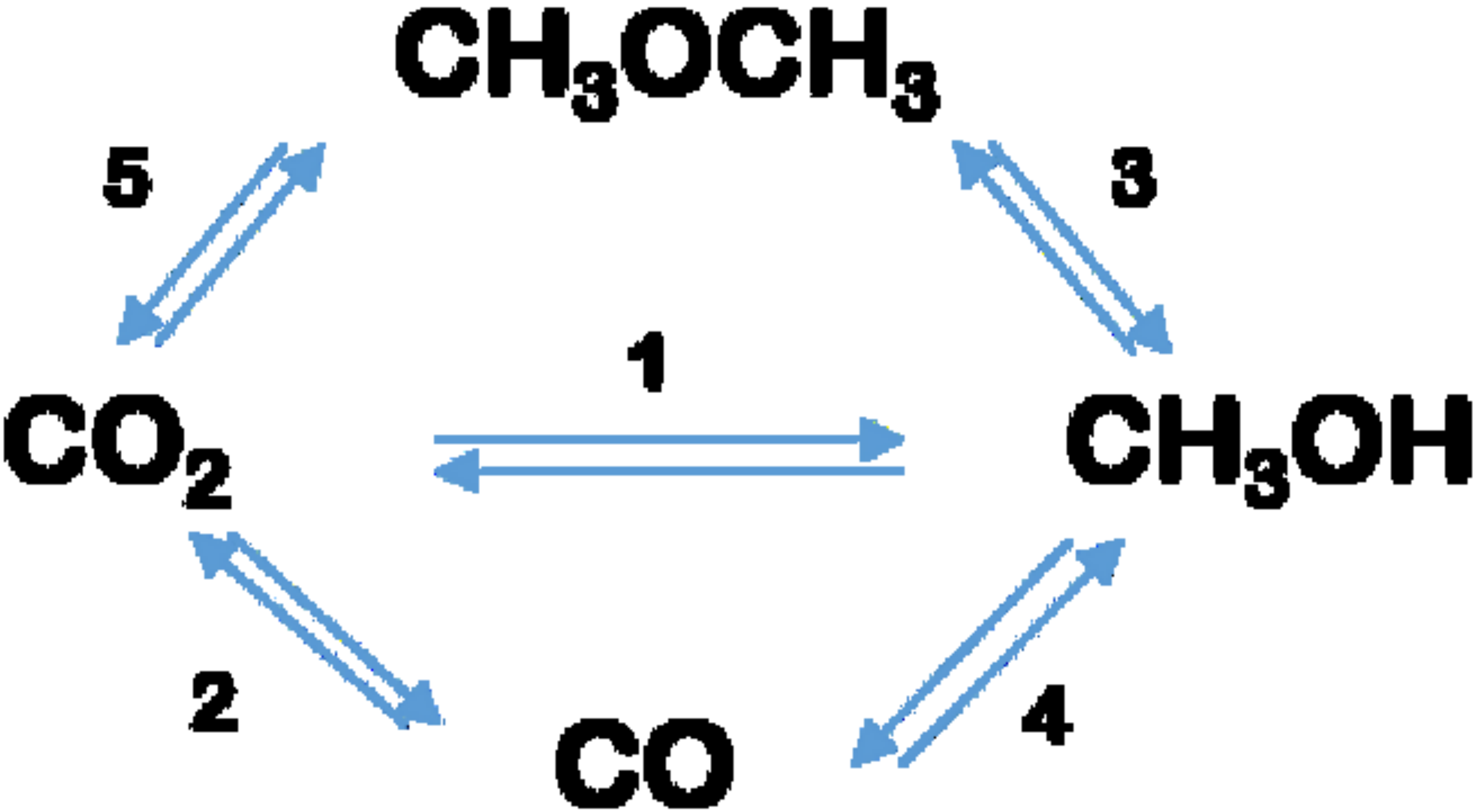


Surface Reaction		Elementary Steps	
(A) CO hydrogenation reaction	Step 1:	$CO \cdot s_1 + H \cdot s_2 \rightleftarrows HCO \cdot s_1 + s_2$	
	Step 2:	$HCO \cdot s_1 + H \cdot s_2 \rightleftarrows H_2CO \cdot s_1 + s_2$	
	Step 3:	$H_2CO \cdot s_1 + H \cdot s_2 \rightleftarrows H_3CO \cdot s_1 + s_2$	
	Step 4:	$H_3CO \cdot s_1 + H \cdot s_2 \rightleftarrows CH_3OH + s_1 + s_2$	**(RDS)**
(B) water−gas shift reaction	Step 1:	$CO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows HCO_2 \cdot s_3 + s_2$	**(RDS)**
	Step 2:	$HCO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows CO \cdot s_3 + H_2O \cdot s_2$	
(C) CO_2 hydrogenation reaction	Step 1:	$CO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows HCO_2 \cdot s_3 + s_2$	
	Step 2:	$HCO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows H_2CO_2 \cdot s_3 + s_2$	**(RDS)**
	Step 3:	$H_2CO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows H_3CO_2 \cdot s_3 + s_2$	
	Step 4:	$H_3CO_2 \cdot s_3 + H \cdot s_2 \rightleftarrows H_2CO \cdot s_3 + H_2O \cdot s_2$	
	Step 5:	$H_2CO \cdot s_3 + H \cdot s_2 \rightleftarrows H_3CO \cdot s_3 + s_2$	
	Step 6:	$H_3CO \cdot s_3 + H \cdot s_2 \rightleftarrows CH_3OH + s_3 + s_2$	

Scheme

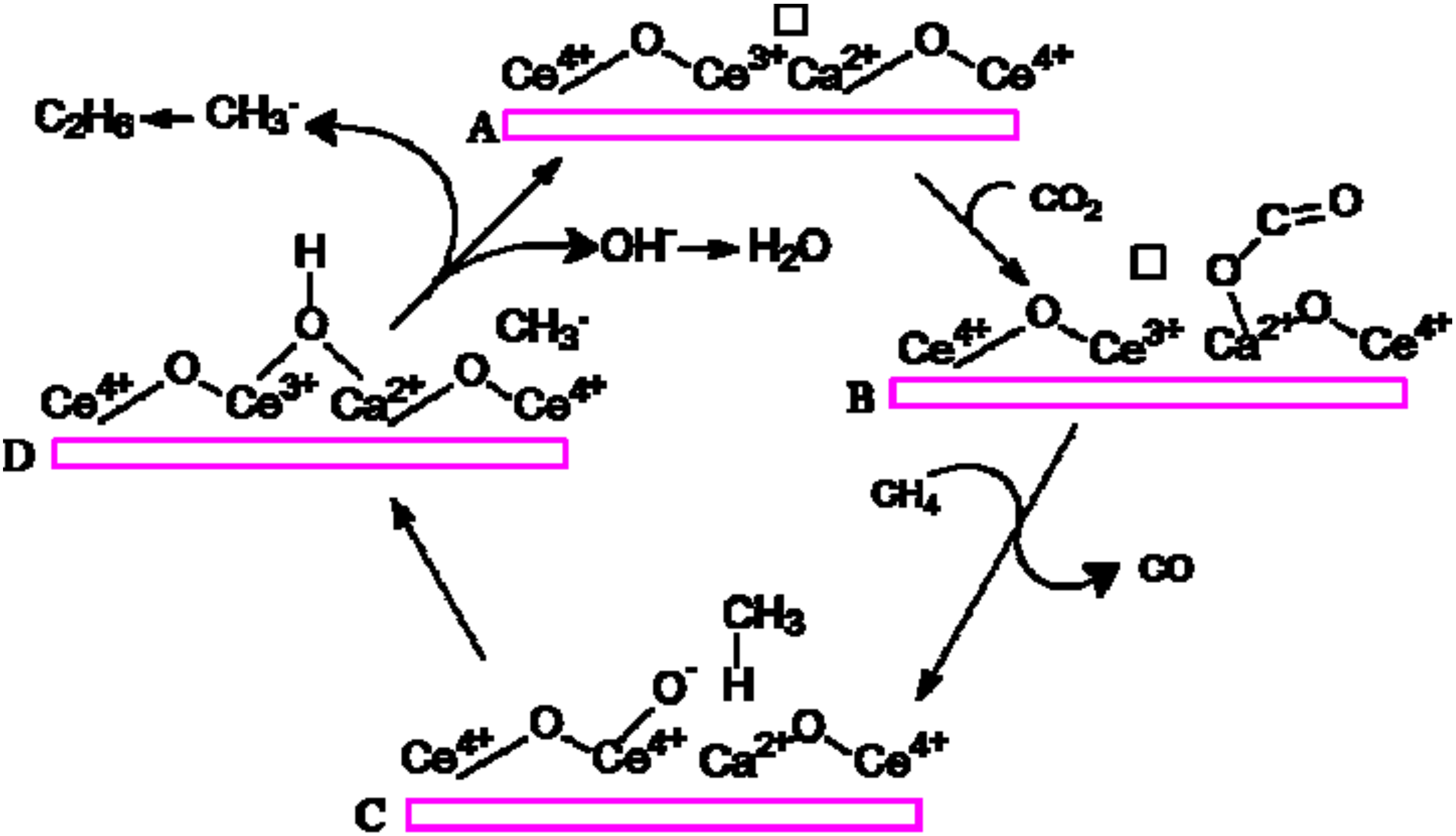
Click here to download high resolution image

Scheme

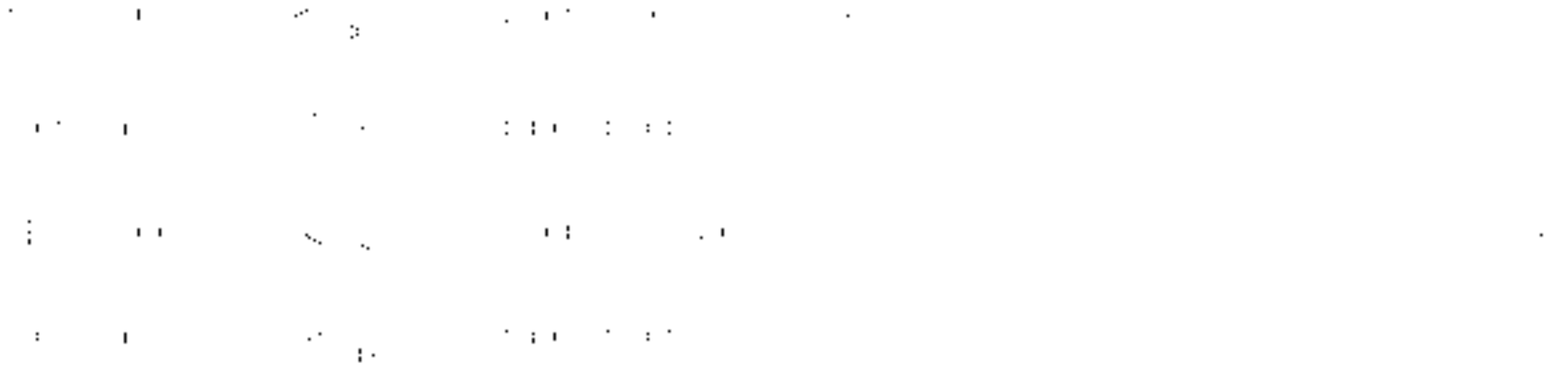


Scheme

Click here to download high resolution image

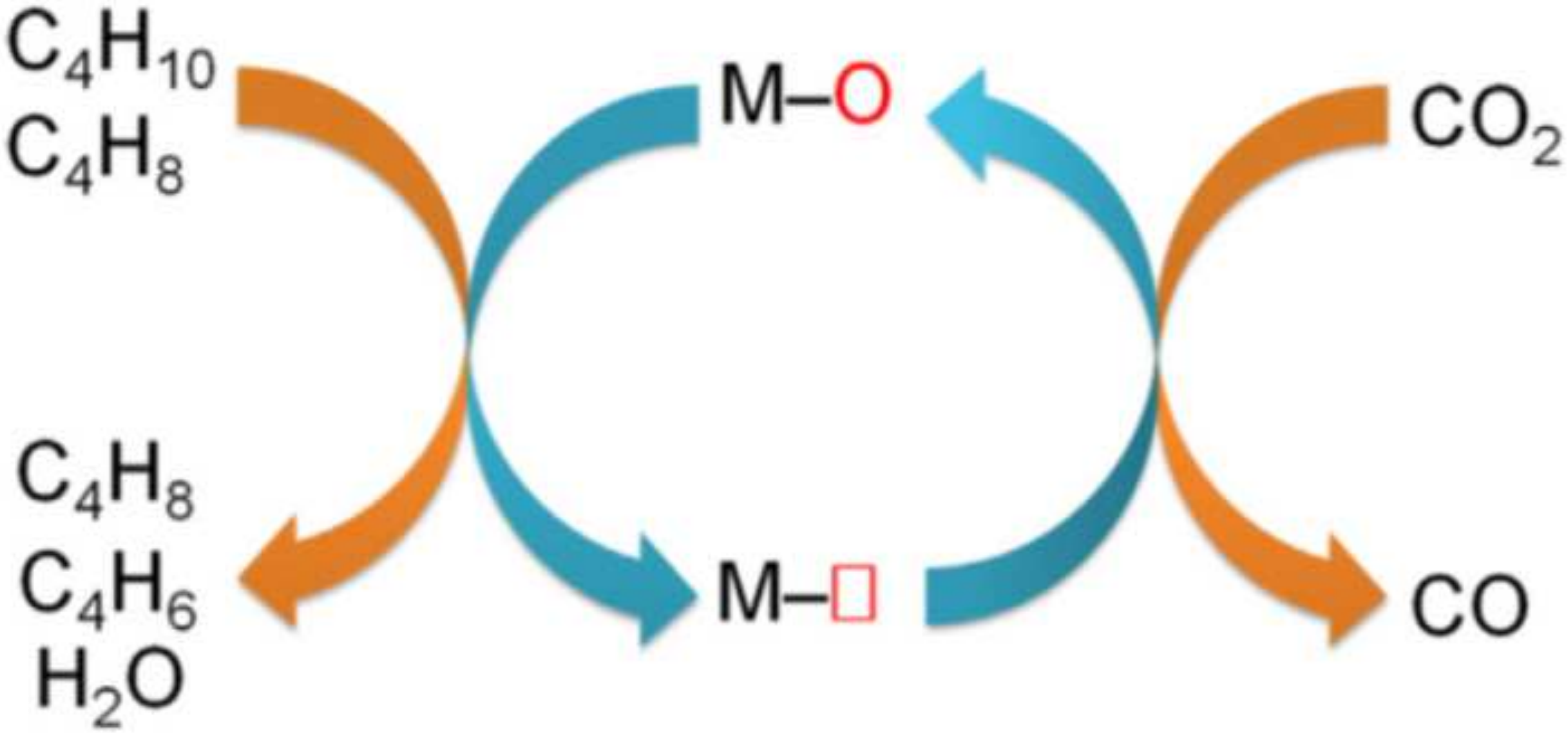


Scheme

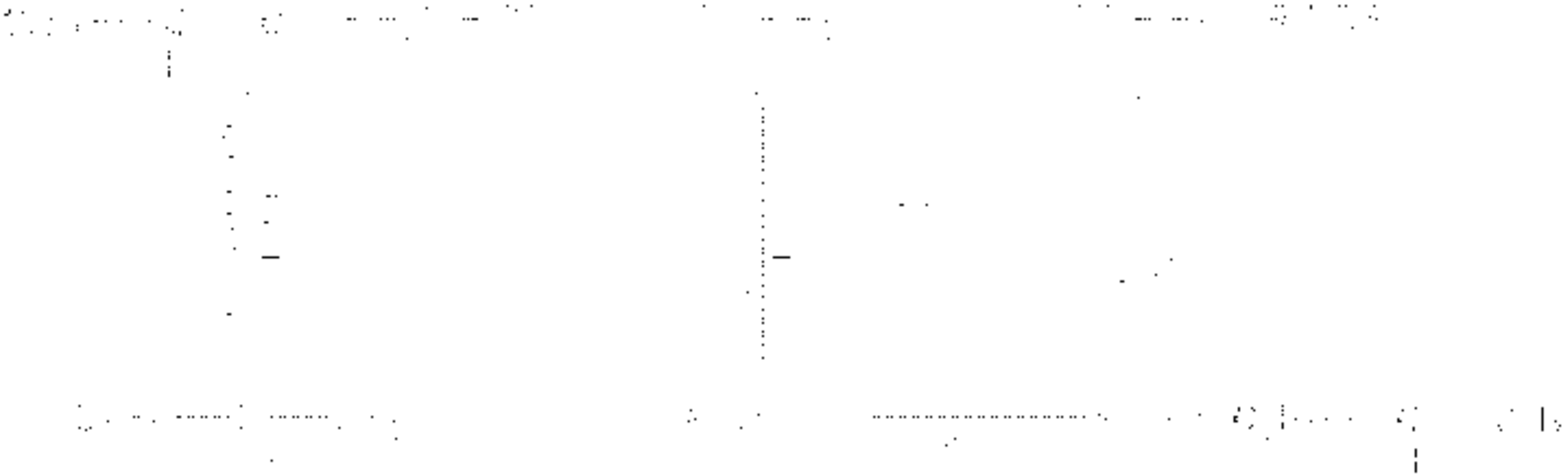


Scheme

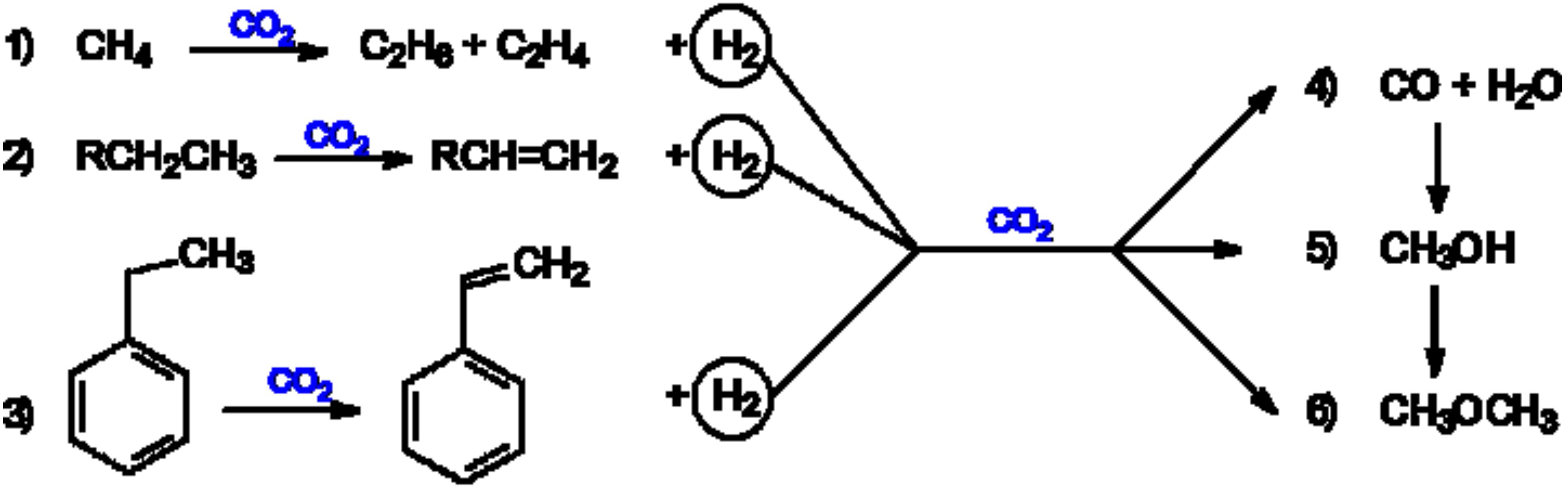
Click here to download high resolution image



Scheme



Scheme



1) CO_2-OCM; 2) CO_2-ODH; 3) CO_2-ODE; 4) RWGS; 5) CO_2 to Methanol; 6) CO_2 to DME

Scheme

(A)

$$\text{Surface} + CO_2 + ne^- \longrightarrow \text{Surface-}CO_2(^{n-}) \longrightarrow \text{Surface} + CO_2\text{-reduction products} + \ldots.$$

(B)

$$\text{Surface} + \text{Catalyst} + ne^- \longrightarrow \text{Surface} + \text{Catalyst}(^{ne-})$$

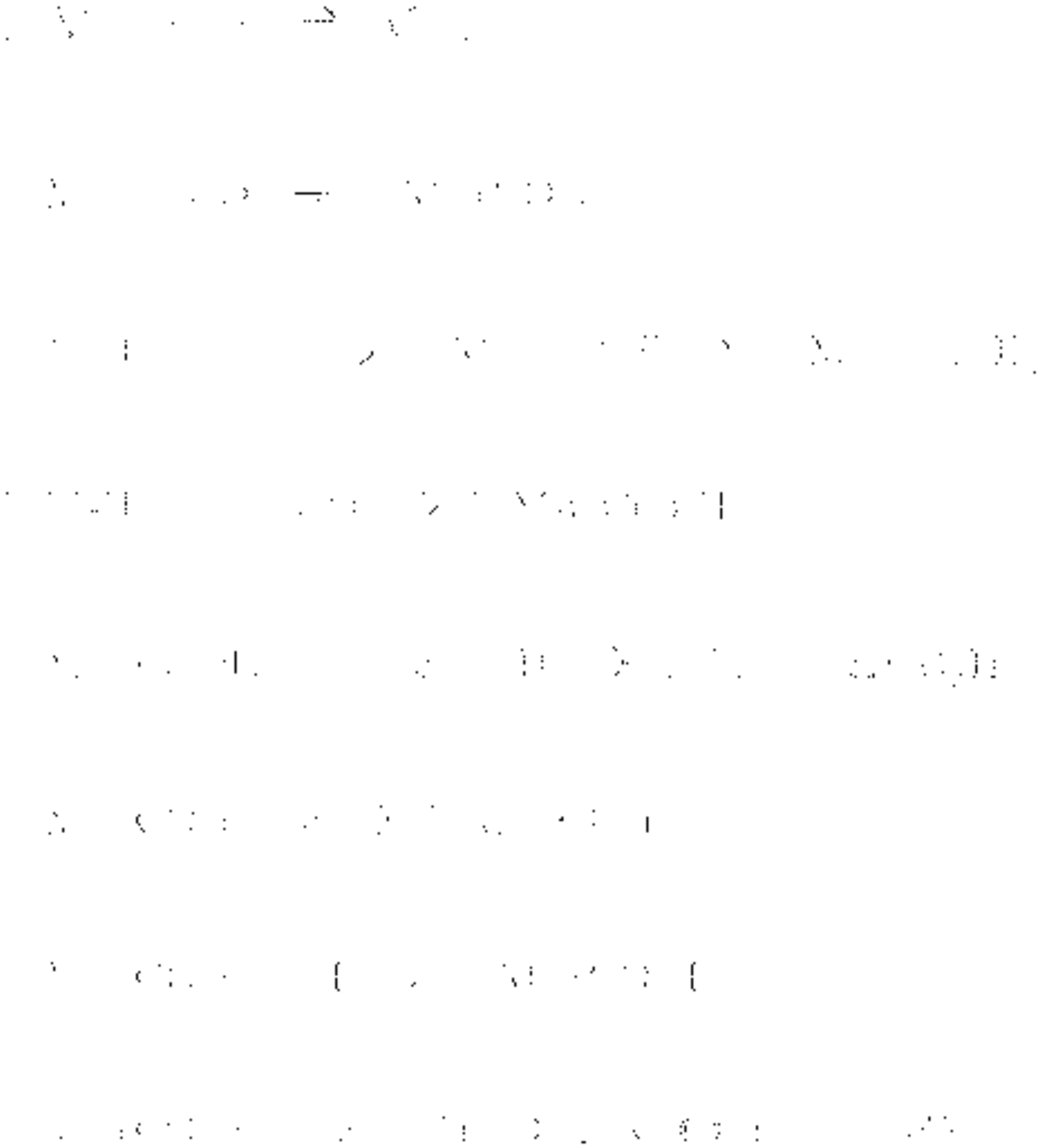
$$\text{Catalyst}\ (^{ne-}) + CO_2 \rightarrow \text{Catalyst-}CO_2(^{ne-}) \xrightarrow{\text{substrate}} \text{Catalyst} + CO_2\text{-reduction products} + \ldots$$

$$\text{Catalyst}\ (^{ne-}) + \text{substrate} \rightarrow \text{Catalyst-substrate}(^{ne-}) \xrightarrow{CO_2} \text{Catalyst} + CO_2\text{-reduction products} + \ldots$$

Scheme

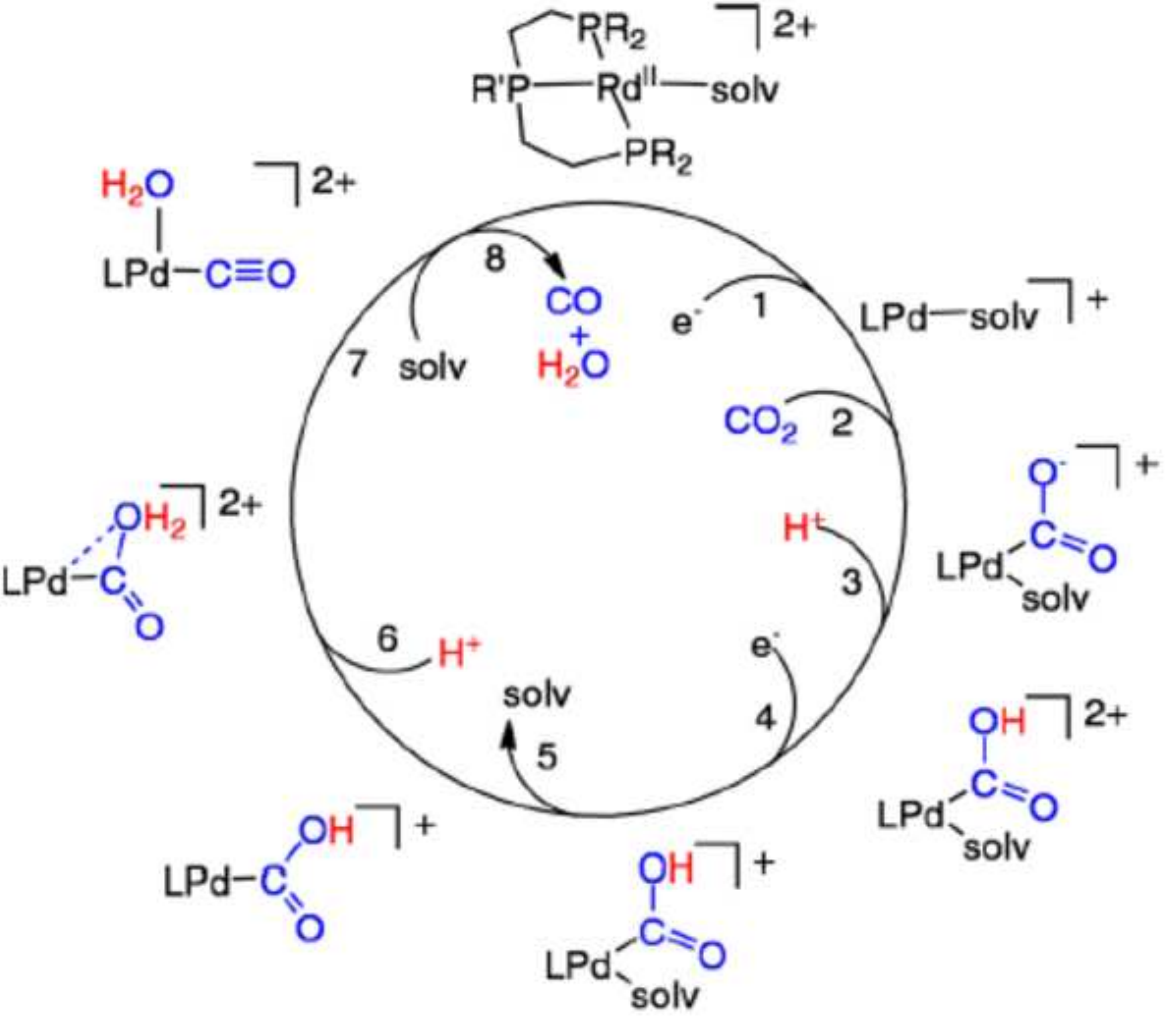
Scheme

Click here to download high resolution image



Scheme

Click here to download high resolution image



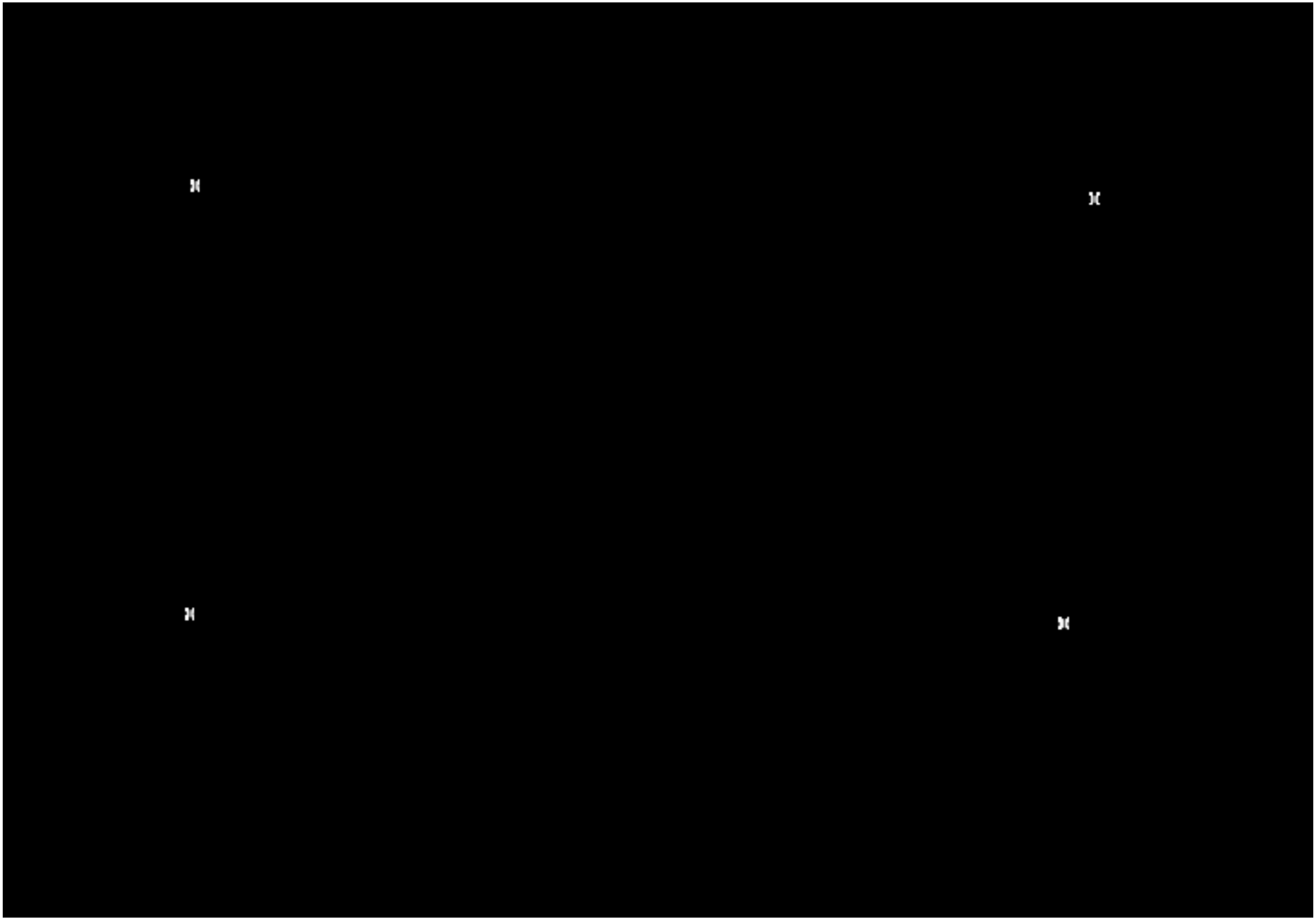
Scheme

Click here to download high resolution image

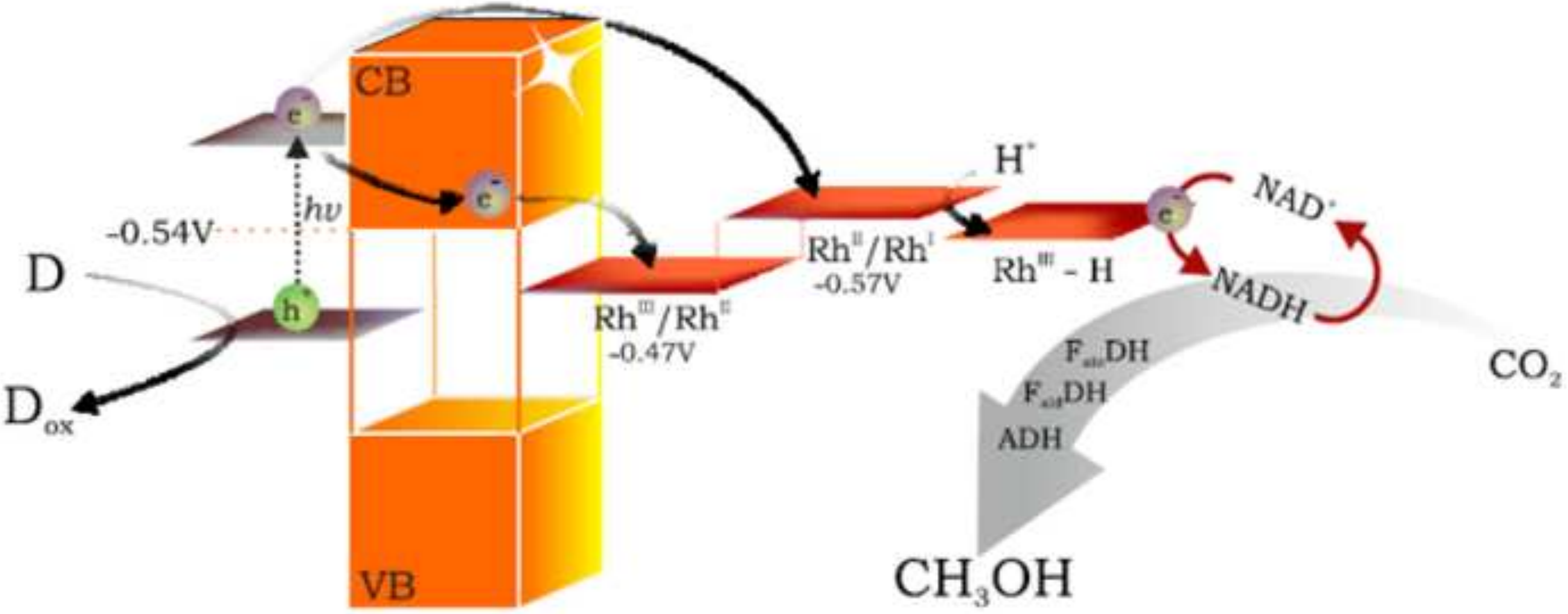
Scheme

Scheme

Scheme



Scheme


CB
VB
e^-
e^-
e^-
h^+
hν
-0.54V
D
D_{ox}
Rh^{III}/Rh^{II}
-0.47V
Rh^{II}/Rh^{I}
-0.57V
H^+
Rh^{III} - H
NAD^+
NADH
CO_2
$F_{ate}DH$
$F_{ald}DH$
ADH
CH_3OH

Scheme

Click here to download high resolution image