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CATALYST DEVELOPMENT FOR THE UTILIZATION OF CO_2 AS BUILDING BLOCK FOR CHEMICALS

The utilisation of carbon dioxide as a source of carbon in synthetic chemistry appears very attractive in view of the fact that, if recovery of carbon dioxide will be adopted as a technology for controlling its emission into the atmosphere, large amounts will be easily available. Supposed that it has the correct purity, CO_2 can be used as building block for chemicals, an approach that also meets the need of developing new clean processes.

The development of a "carbon dioxide-based industry" requires the discovery of new transition metal-assisted reactions. Therefore, the knowledge of the behaviour of carbon dioxide and organic substrates towards metal centres plays a fundamental role for the exploitation of the chemical utilisation option, and needs further development as the modern carbon dioxide chemistry is very young, as it has taken important steps only after the first structural evidence of a "carbon dioxide molecule coordinated to a metal centre" was provided in 1975. In this paper, we discuss the use of CO_2 as building block for organic compounds, while the use of CO_2 as carbon source for fuels is not considered.

Energetics of carbon dioxide utilising reactions

The carbon dioxide-utilizing reactions can be divided into two main classes from the energetic point of view, as categorized below.

Reactions of *Class 1* in which the whole carbon dioxide molecule is used. The substrate (amines, unsaturated hydrocarbons) is the energy vector and the amount of extra energy, if required, is usually very low. These reactions include the carboxylation reactions with the formation of a C-C or C-heteroatom bond (C-E; E=O, N, P, other element).

Reactions of *Class 2*, or reduction reactions to C1 or C_n species, using dihydrogen, electrons, or heat as energy source.

Both the above types of reactions are common to, and very important in biological systems (plants and bacteria), in which several enzymes involved in carbon dioxide utilisation are metal enzymes with the metal acting as the active site [1].

Interaction of carbon dioxide with metal centres

Metal systems are good candidates for driving new reactions based on CO_2. After the discovery of the first transition metal complex bearing CO_2 η^2-C,O bonded to Ni, [2] the co-ordination of CO_2 to metal-systems and the insertion of CO_2 into M-E bonds have been intensively investigated with the aim of discovering new catalysts for CO_2 conversion. Several modes of bonding of CO_2 to a metal centre, from the η^1 to the μ_4-η^5 [1b, 3], have been documented in which the carbon-oxygen bond order decreases and the length of the C-O bond increases. Nevertheless, such complexes do not show any significant activity as promoters of coupling reactions of CO_2 to organic substrates, most probably because the high energy of the M-O bonds makes the CO_2 complexes kinds of "stabilized forms of activated CO_2", or because the C-atom is engaged in a bond with a metal that prevents the further C-C bond coupling to an incoming substrate.

FTIR spectroscopy, [4] more recently coupled to density functional theory-DFT, [5] has been used for the investigation of matrix interaction of CO_2 with metal atoms: the co-ordination of CO_2 and the stability of the adduct are influenced by the metal and the gas matrix. Late-transition metals [Fe, Co, Ni, Ag and Cu] form one-to-one $M(CO_2)$ complexes, while left-hand elements [Ti, V, and Cr] easily insert into one of the C=O bonds yielding oxo-carbonyl species as does U(III) [3b-5].

Carbon dioxide as a building block for organic products

The incorporation of carbon dioxide into an organic substrate with formation of compounds containing the entire COO moiety (carboxylates), is a good example of a "sustainable process". In fact, compared to processes on stream, the direct carboxylation of organic substrates may reduce the production of waste at source making use of diversified starting materials, and recycling carbon. One can also expect that, under the appropriate reaction conditions, such direct carboxylations may cause a reduction of energy consumption with respect to processes on stream.

Synthesis of monomeric carboxylated products

The incorporation of CO_2 into an organic substrate to afford C-COOH, C-COOC, E-COO-C (E=N,O), or C-OC(O)O-C moieties is a process of great importance from the industrial point of view. Nevertheless, to date there are still severe barriers to its exploitation. The formation of a terminal "carboxylic moiety" C-COO, is industrially achieved through multi-step syntheses (such as oxidation of aliphatic or aromatic moieties, hydration of cyanides, use of Grignard reagents), that lack of selectivity [1c], but are thermodynamically and kinetically possible. Cyclic compounds containing a "COO" moiety actually require even more complex synthetic procedures. The moieties reported above can be considered as the result of the insertion of CO_2 into C-H, C-C, E-C, C-O-C bonds, respectively. Such reactions are expected to have a favourable thermodynamics eventually associated to an adverse kinetics. An appropriate catalyst may help to overcome such energetic barrier, once the appropriate synthetic strategy has been developed.

C-C bond formation to afford acids, esters, lactones, pyrones

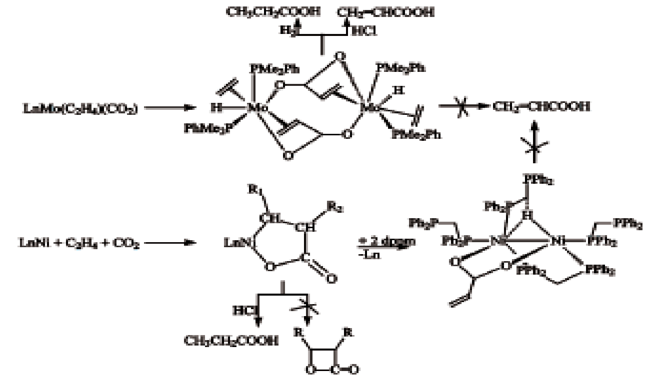
The direct synthesis of formic acid, HCOOH, the simplest carboxylic acid, from H_2 and CO_2 has attracted the interest of several research groups [6] as it would represent a real improvement with respect to the actual technologies on stream [1c]. New catalysts have been developed that open a new perspective to the exploitation of this reaction that is environmentally and energetically beneficial.

The carboxylation of an organic aliphatic or aromatic hydrocarbon can be considered as a formal insertion of CO_2 into a C-H bond. The reaction requires a preliminary C-H splitting that presents a high kinetic barrier and may occur in a homolytic ($R^\cdot + H^\cdot$) or heterolytic mode ($R^- + H^+$). In Nature, carboxylations occur *via* carbanions (Eq. 1) that easily react with CO_2 to afford the corresponding carboxylate.

$$R\text{-}H + B \rightarrow R^- + BH^+ \xrightarrow{CO_2} RCOO^- + BH^+ \rightarrow RCOOH + B \qquad (1)$$

Despite the direct carboxylation of organic substrates represents a synthetic opportunity that would greatly improve the environmental quality of existing processes, [7] only very few attempts have been made for its implementation. The synthesis of salicylic acid [8] (Kolbe-Schmidt reaction) is one of the processes that is known and used since the 19th century, but it uses one mol of Group 1 metal per mol of fixed CO_2.

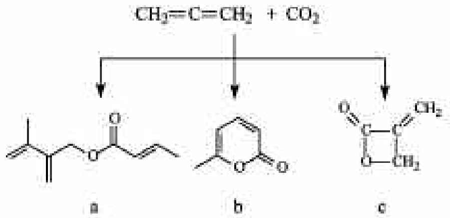
The direct carboxylation of hydrocarbons containing active-hydrogens can be carried out using the phenolate anion (PhO^-) as CO_2-transfer agent [9] or the 2-carboxylated form of imidazolium salts [10] (Eq. 2). Such processes are not catalytic and are very similar



Scheme 1 - Modes of carboxylation of an olefin: the carboxylate is released only upon protonation to the Kolbe synthesis reported above. Making such reactions catalytic would represent a great innovation.

$$R^1R^2Im\text{-}2\text{-}CO_2 + \text{substrate-H} + MX \rightarrow R^1R^2ImX + \text{substrate-COOM} \qquad (2)$$

where $R^1R^2Im\text{-}2\text{-}CO_2$ = 1,3-dialkylimidazolium-2-carboxylate; substrate = $PhC(O)CH_3$, CH_3OH; MX = $NaBF_4$, $NaBPh_4$, KPF_6.
Olefins, that are rich in energy, easily react with CO_2 in presence of transition-metal systems in a low oxidation state, such as Ni(0) [11], Ti [12], Fe(0) [13], Mo(0) [14], Rh(I) [15]. The reaction of ethene and CO_2 is of great industrial interest as it may represent a direct route to acrylic acid, a monomer used at a Mt/y scale. Until recently, only the "oxidative addition" to afford either a metallacycle or a metal-hydride was documented (Scheme 1). In both cases the elimination of the product (four membered lactone or acrylic acid) does not occur spontaneously, despite the fact that the formation of either product from ethene and CO_2 is thermodynamically permitted.
An organic carboxylate (propanoic acid or acrylic acid) can be released upon reaction of the metalla-carboxylate with a strong acid such as HCl that leaves the metal in an oxidation state higher by two units with respect to the starting one: such metal-species is not able to act as catalyst. Recently [16], the mechanism of metal assisted CO_2-C_2H_4 coupling reactions has been examined by means of DFT calculations and some of the above findings have been rationalized. It has also been shown that the activation barrier of the rate-determining step (the C-C coupling) and the stability of related intermediates are rather sensitive to the nature of the chelating ancillary ligand.
More recently a preformed "Pd-COOMe" moiety has been used as a model system for the insertion of olefins (ethene and propene) into the Pd-C bond and the subsequent acrylate elimination [17]. The formation of ethyl acrylate from ethene and CO_2 has also been documented. This promising area requires the development of new catalysts that may efficiently favour the acrylic acid or acrylate release.
Cumulated and conjugated dienes are converted with high yield and good TONs into products such as: five and six membered lactones, linear esters and acids. Such reactions may lack in selectivity also if they are characterized by a good yield of conversion of the diene (>90%). Pd and Rh catalysts have been shown to promote the coupling of a different number of molecules of butadiene before carboxylation occurs, bringing to products with chains of different length. Selective catalysts have been developed by changing the ancillary phosphine ligands. For example, the carboxylation of butadiene to six-membered lactones has been achieved with high selectivity and yield by using $(i\text{-}C_3H_7)_2P(CH_2)_nCN$ (n=2-5) phosphane-ligands in various solvents, including pyridine [18-19]. The reaction has a good selectivity under electrochemical catalysis [18b]. In $scCO_2$, using $Pd(dba)_3$ [18c] as catalyst, interesting results have also been obtained. The synthesis of six membered lactones following this reactive route has been developed to the pilot-plant scale [20]. The reaction can have an interesting exploitation for the synthesis of fragrances or long chain carboxylic acids: the latter may find application in the synthesis of biodegradable surfactants. This chemistry represents a good example of how yield and selectivity can be driven and improved by catalyst design. Further improvement can be foreseeable in this area.
Allene may be reacted with CO_2 to afford not only pyrones or linear esters [21], with Ni or Rh as catalysts (Scheme 2, a-b), but also, although with lower yields, a four-membered lactone that is the result of a formal unprecedented "2+2" addition of the two cumulenes [22] (Scheme 2c). This area requires more investigation for its full exploitation.

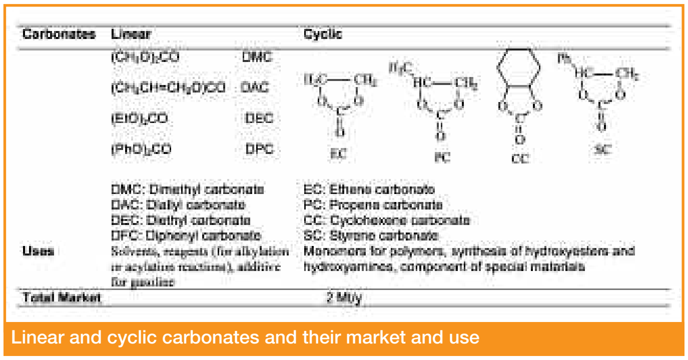


Scheme 2 - Conversion of allene into linear carboxylated products

The carboxylation of strained rings promoted by transition metal catalysts [23] originates different products, including products of formal insertion of CO_2 into a C-C bond. Such reactions are still a "curiosity" as the TON rarely exceeds the unit. The development of new catalysts that may promote both the C-H bond splitting and C-C bond formation is necessary for a practical application of such reaction of great industrial importance.

C-O bond formation for the production of cyclic carbonates and poly-carbonates

The O-C bond formation is relevant to the synthesis of organic carbonates characterized by the O-C(O)O- moiety. Both linear and cyclic carbonates have an industrial interest and are today produced mainly from phosgene (Table).
The reaction of epoxides with CO_2 has been studied for long time. It affords either molecular cyclic carbonates or polymers [24]. Main group metal-halides [25] and metal-complexes [26], ammonium salts (both free [27] and supported [28]), phosphines [28], transition metal complexes [30], metal-oxides [31, 36], and ionic liquids [32] afford monomeric carbonates. Heterogeneous catalysts such



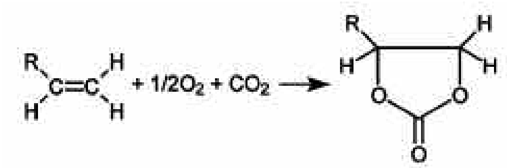
Carbonates	Linear		Cyclic
	$(CH_3O)_2CO$	DMC	EC PC CC SC
	$(CH_2CH=CH_2O)CO$	DAC	
	$(EtO)_2CO$	DEC	
	$(PhO)_2CO$	DPC	
	DMC: Dimethyl carbonate DAC: Diallyl carbonate DEC: Diethyl carbonate DFC: Diphenyl carbonate		EC: Ethene carbonate PC: Propene carbonate CC: Cyclohexene carbonate SC: Styrene carbonate
Uses	Solvents, reagents (for alkylation or acylation reactions), additive for gasoline		Monomers for polymers, synthesis of hydroxyesters and hydroxyamines, component of special materials
Total Market	2 Mt/y		

Linear and cyclic carbonates and their market and use

as oxides [31, 36] and supported ammonium salts [28] or metal complexes [30] are more long-lived than homogeneous catalysts. Instead, Al- [33] and Zn-catalysts [34] promote the formation of polymers. Sc-CO_2 also favours [35] the formation of cyclic carbonates. Amides such as dimethylformamides (DMF) or dialkylacetamides (DAA) are often used as solvents in such reactions and can themselves promote the carboxylation of epoxides, also if with low TON [36].

Optically active carbonates [37] have been prepared from pure enantiomers of the parent epoxide with total retention of configuration. When a racemic mixture of the epoxide was used, an *ee* of the order of 22% was obtained using Nb(IV) complexes with optically active (N, O, P as donor atoms) ligands: the low *ee* is due to the de-anchoring of the ligand from the metal centre, as shown by an NMR study [37].

The limitation to the carboxylation of epoxides is the available amount and cost of H_2O_2 used for the synthesis of the epoxide. A good alternative is the "oxidative carboxylation" of olefins that converts cheap products such as olefins and a waste as CO_2 into valuable compounds. (Eq. 3):



(3)

Such reaction has been tested on a few olefins such as ethene, propene and styrene. An early process reported in the patent literature used a complex catalytic mixture [38]. Recent studies have elucidated the reaction mechanism for both homogeneous [39] and heterogeneous [40] catalysts showing two concurrent processes, i.e. the "one oxygen" addition to the double bond that affords the epoxide and carbonate and the "two-oxygen" addition that causes the splitting of the olefin to afford aldehydes, acids and their derivative.

Using $RhCl(PEt_2Ph)_3$ [39] as homogeneous catalyst, a detailed study has allowed to show that O_2 and CO_2 originate a peroxocarbonate of Rh(III) that is the real oxidant. The carbonate resulting after O-transfer to an oxophile can be converted back into a Rh(I) complex via de-oxygenation of the carbonate moiety by a free phosphine, either added or released by the complex. In the latter case the original Rh(I) catalyst after a limited number of cycles (2-4) is not able anymore to promote the epoxidation of the olefin. Using Co, Cr, Mn analogues does not give a real improvement of the TON.

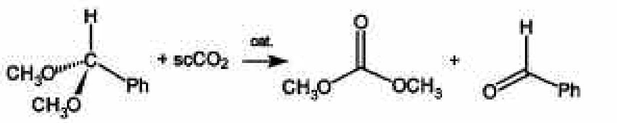
Group 1 or 2 metal oxides [40] or transition metal oxides are effective but do not prevent radical reactions with loss of the olefin, a process that must be limited for a practical application of the synthetic methodology. This area needs further investigation as finding a catalyst that may efficiently convert olefin, CO_2 and O_2 into carbonate has a high value. Moreover, the reaction is inherently safe as the presence of CO_2 prevents any explosion risk possibility linked to the use of O_2 and olefins.

C-O bond formation for the synthesis of linear carbonates

A most interesting route to linear carbonates is the direct carboxylation of alcohols, (Eq. 4):

$$2ROH + CO_2 \rightarrow (RO)_2CO + H_2O \qquad (4)$$

that is very clean and has a high atom-efficiency. Unfortunately, such reactions are almost neutral for the free energy change [41] [ΔH for $(MeO)_2CO = -16.74$; $(EtO)_2CO = -15.90$; $(allyl\text{-}O)_2CO = -16.37$; $(PhO)_2CO = +50.49$ kJ mol^{-1}] that causes a low yield [1-2%] at the equilibrium [42]. Trapping water may displace the equilibrium to the right, but molecular sieves cannot be used at the reaction temperature as the formed surface -OH groups are enough acid to protonate the carbonate, reversing the reaction. Organic water traps are better suited: aldols (Eq. 5) [43], ketals (Eq. 6) [44], and dicyclohexylcarbodiimide-DCC [45] have been used as such.



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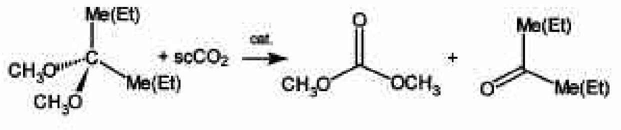
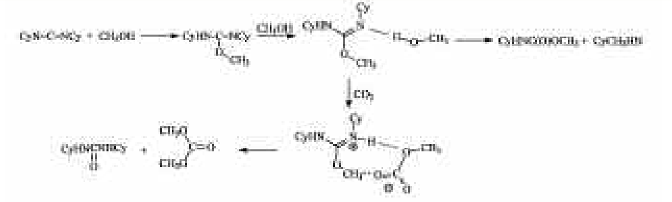


(6)

A detailed study has shown that DCC is a promoter of the carboxylation more than a simple dewatering agent. Combining experimental studies and DFT calculations, the reaction mechanism has fully been elucidated, as shown in Scheme 3 [45]. Several carbonates have been produced using different alcohols with yields between 35 and 90% and selectivity always higher than 95%, that is influenced by the temperature. Above 335 K the favoured reaction is the formation of carbamate (Scheme 3, right upper part).



Scheme 3 - Reaction mechanism of carboxylation of alcohols promoted by DCC

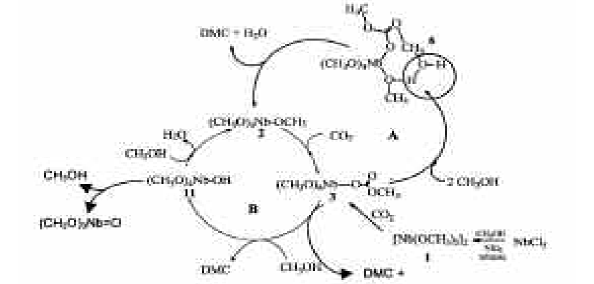
This reaction represents an interesting route to carbonates, that occurs in mild reaction conditions, but is limited by the fact that one mol of DCC is used per mol of carbonate. Should the formed urea be quantitatively be converted back to DCC the method could have a practical application at least for small scale carbonates.

Transition metal alkoxides have been used as homogeneous catalysts. The reaction mechanism has been investigated for the Sn and Nb systems. The intramolecular mechanism that operates with Sn (Scheme 4) is based on a double "base-activation" of methanol that produces two MeO$^-$ units. The subsequent elimination of DMC causes the formation of a E=O double bond (E=C in Scheme 3 or Sn in Scheme 4) that strongly reduces the activity of the catalyst (or makes it inert).

Scheme 4 - Intramolecular mechanism of formation of linear carbonates based on the "double base-activation" of methanol

The intermolecular mechanism, that seems to be operative with Nb-systems (Scheme 5), can follow two different routes: with the intermediacy of one or two alcohol molecules. In the latter case (part A of Scheme 5), the reaction mechanism is based on a "acid-plus-base" activation of methanol: the catalyst can perform much better and does not loose its activity over several cycles [46].

In order to eliminate water, new concept reactors should be used (membrane reactors for water separation, or pervaporation processes) or new techniques for equilibrium shifting, together with new-robust catalysts.



Scheme 5 - Intermolecular mechanism based on the "acid-plus-base" activation of methanol. Scheme A is operative

Heterogeneous catalyst may be better suited than homogeneous one, as they can be easily separated. The key issue here is to have catalysts that preserve their surface activity for long time and several cycles. This has not yet been achieved [47].

Conclusions

The utilization of CO_2 as a "building block" for chemicals may find an application in some selected areas, provided that new active catalysts are developed. Innovative syntheses based on CO_2 may represent a push towards the implementation of the principle of the "sustainable chemical industry". More knowledge needs to be developed for a better exploitation of the opportunities offered by the CO_2-based chemistry. New catalysts must be synthesized that are active, selective and stable for promoting several of the reactions described above.

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