

DEVELOPING INNOVATIVE SYNTHETIC TECHNOLOGIES OF INDUSTRIAL RELEVANCE BASED ON CARBON DIOXIDE AS RAW MATERIAL

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Abstract: The reduction of carbon dioxide emission requires the implementation of several convergent technologies in different production sectors. The chemical industry can contribute to the issue with innovative synthetic technologies, that implement the principles of atom-economy, dematerialisation, energy saving, and raw material diversification with carbon recycling. The innovative synthetic methodologies merge the issues of avoiding the production of CO₂ and carbon recycling, through carbon dioxide utilisation. In this paper, some options will be discussed, namely the synthesis of carboxylic acids, organic carbonates, and carbamates/isocyanates. The synthesis of methanol from CO₂ and CO will be compared.

Keywords: carbon dioxide, innovative syntheses

Introduction

The implementation of innovative synthetic technologies based on CO₂ can considerably contribute to the reduction of carbon dioxide emission. The avoided amount is not simply represented by the amount of CO₂ fixed. As we have already discussed, the assessment of the exact amount of avoided CO₂ requires an integrated approach which takes in consideration several parameters, as shown in Scheme 1.¹

Amount of CO₂ fixed per t reacted

$$1 - Y + Z$$

$$Y = \sum (e_r, e_{co}, e_{pi}, e_{wt}, \dots)$$

$$Z = \sum (e_{sc}, e_{vr}, e_{vpi}, e_{vwt}, \dots)$$

as CO₂ equivalent

*e_r = energy of reaction; e_{co} = energy of other reagents; e_{pi} = energy of purification; e_{wt} = energy of waste treatment; e_{sc} = energy of substituted reagents and solvents; e_{vr} = variation of the reaction energy with respect to the synthesis that does not use CO₂; e_{vwt} = variation of waste treatment energy; e_{vpi} = variation of energy of purification

Scheme 1.

The exact evaluation of each parameter can be only made by using a methodology like Life Cycle Analysis, LCA,² that demands an exhaustive basis of process-data, including emission, energy and mass data.²

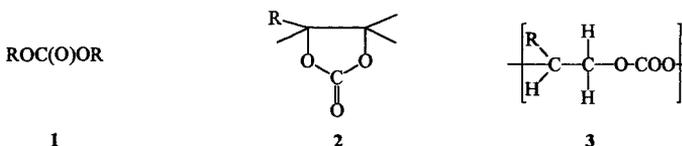
New synthetic methodologies that implement the principles of atom economy, solvent shift, waste minimisation at source, use of less noxious materials and carbon recycling, contribute to CO₂ reduction in many different ways, that cannot be discovered and quantified by simply looking at the stoichiometry of a reaction.

The target compounds considered in this paper are: organic carbonates, carboxylic acids (long-chain aliphatic, or mono- and di-carboxylic aromatic), carbamates and isocyanates. They are today prepared using quite energy- and material-intensive synthetic methodologies, while could be synthesised by using more eco-efficient and economic pathways, including those based on carbon dioxide.

The last section of the paper will be devoted to the analysis of methanol synthesis from CO₂ and CO.

Discussion

Monomeric (linear **1** and cyclic **2**) and polymeric organic carbonates **3** have a market of ca. 1.8



Mt/y, bisphenol-A-polycarbonate being by far the largest commercialised product.

However, the large majority of the production of non polymeric carbonates does not reach the market, as they have a captive use as solvents and internal commodities.

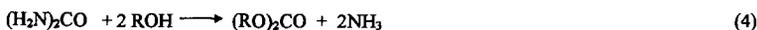
The large majority of the products is produced by the old phosgenation of alcohols, (Eq. 1)



a technology that has a positive aspect in the high reactivity of phosgene, and black spots in the high energy requirement for the synthesis of chlorine, the limitation to the transport of phosgene, the safety measures required for the use of phosgene, the chloride and halogenated solvents end-production. These aspects may be a barrier to further enlargement of the technology exploitation and to a many-purpose use. As a matter of facts, the limitation to the transport of phosgene, concentrates its use at its production site and has encouraged the building up of small-medium-units that can be mounted at the customer site. This is not the solution to problems.

Alternative syntheses are now on stream based on the oxidative-carbonylation of methanol (ENIChem and Ube processes).

The synthetic approaches proposed in this paper consider the reaction of alcohols (Eq. 2), ethers (Eq. 3), or urea with carbon dioxide (Eq. 4), the reaction of ketals with carbon dioxide and alcohols (Eq. 5), and the oxidative-carboxylation of olefins (Eq. 6).



All these syntheses are characterised by a high atom efficiency. The only by-product is water.

This is true also for reaction 5, in which the ketone and glycol can be reconverted into the ketal, that is used as promoter of the reaction of carbon dioxide with alcohol.

Reactions 3 and 5 avoid the water formation in the reaction medium, that can be crucial for equilibrium shift.

Processes based on reactions 2-6 are more eco-efficient than existing ones and are characterised by an atom economy close to 100%. The phosgene based technology (Eq. 1), quite attractive for the easy reaction conditions and high yield, as reported above, has weak points in the fact that it is energy intensive and produces undesired chloride ions and waste chlorinated solvents. These attributes may not guarantee that phosgenation will continue to be the leader technology in the future and will be able to cover the demand of carbonates that is expanding, especially for the production of speciality chemicals and DMC.

The use of carbon dioxide is a better option with respect to both phosgene and carbon monoxide. CO_2 can be recovered from industrial plants, responding, thus, to the principle of recovery and recycling, and to the international agreement of reducing greenhouse gases emission.

This goal is met not only for the recycled fraction of carbon dioxide, but also, and essentially, for the avoided use of natural resources, necessary for the synthesis of carbon monoxide or phosgene, and, the reduced production of waste.

A preliminary Life Cycle Assessment, LCA, study performed considering reactions 1, 2 and 4 has clearly shown that reaction 1 has an impact factor much higher than reactions 4 and 2, (Fig. 1) the key steps responsible for such high impact being the energy required for the synthesis of chlorine, and the production of chloride.

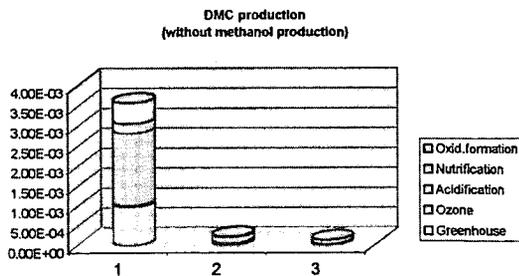


Figure 1. LCA of alternative synthetic pathways for the synthesis of DMC.

1: DMC from phosgene and methanol; 2: DMC from urea and methanol;

3: DMC from methanol and CO_2 .

Long chain mono- and di-carboxylic acids, **4** and **5** respectively, are high quality products with a major use in polymer chemistry.

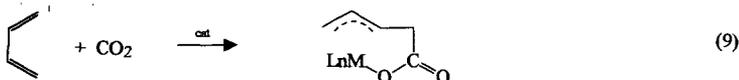


Presently, the latter are synthesised by oxidation of di-alcohols (Eq. 7) or cyclic alkanes/alkenes (Eq. 8) by oxidative ring cleavage with formation of the two carboxylic functionalities.

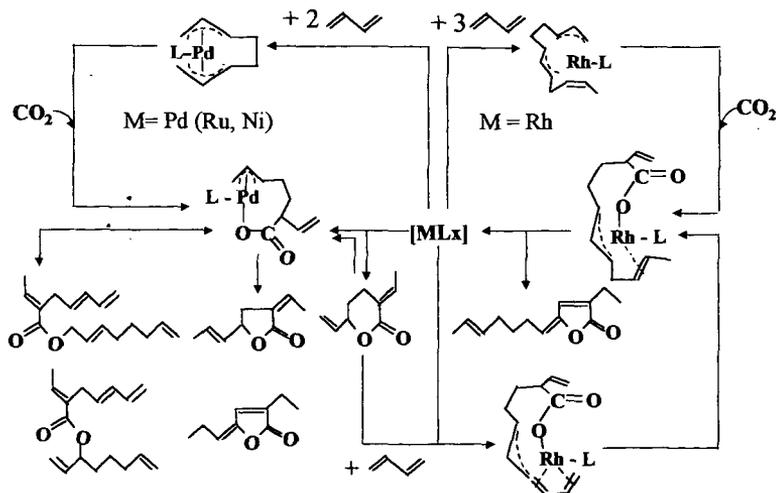


Such processes are neither atom-efficient nor selective. Such non-convergent and destructive synthetic approach, with high waste production, is a major draw-back that cancels-out the advantages of the use of heterogeneous catalysts. An analogous situation exists for long chain mono-carboxylic acids that find a wide application as additives, and in the production of surfactants.

The use of dienes and carbon dioxide as substrates (Eq. 9) brings in the great advantages of atom-economy and selectivity.⁴



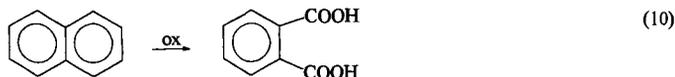
Such synthetic approaches are now known for lactones and can be also used for both the synthesis of either di- or mono-carboxylic acids, by changing the catalyst and controlling the reaction conditions. C-5 or C-9 mono-carboxylic or C-10 di-carboxylic acids can be prepared in mild conditions from butadiene and carbon dioxide. Longer chains can be also built up, according to the metal used. (Scheme 2)



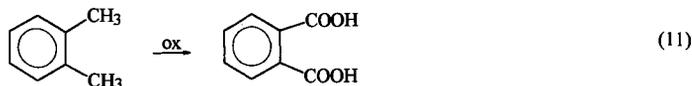
Scheme 2. Metal catalysis in butadiene-CO₂ chemistry.

The reaction is controlled through the use of specific ligands on the metal centre.

Aromatic mono- and di-carboxylic acids are prepared using drastic oxidation reactions (Eq. 10) with low atom efficiency.

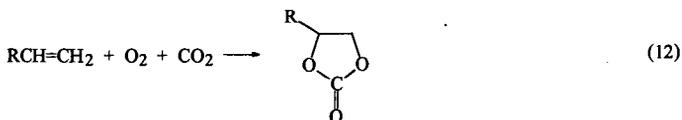


The side chain oxidation of alkyl-aromatic compounds (Eq. 11), which may yield different type of oxygenated organic chemicals, pertains to a large number of industrial intermediates addressed to the manufacture of plastics, fibres, pharmaceuticals, agrochemicals, etc.



At present, these oxidation reaction, namely to obtain the correspondent aromatic acids, are commercially carried out both in the gas and liquid phase. Gas phase processes adopt fixed or fluidised-bed, on V_2O_5 based catalysts, with air as oxidant, at temperatures ranging from 350 to 550 °C; liquid phase oxidation routes, usually with metal salt catalysts dissolved, adopt milder reaction conditions, 110-180 °C, pressure up to 2 MPa. Soluble acetates or naphthenates of Co, Mn, or Mo are generally used with bromine-based co-catalysts. Carboxylic acids, mainly acetic acid, are added as solvents. Benzoic and phthalic acids or anhydride production, accounting for more than 16 Mt/y, rely on these current technologies, by processes with relevant objections for what concerns the formation of polluting effluents, the use of corrosive conditions due to the aggressivity of the reaction medium employed, the low or moderate selectivity in the synthesis of partially oxygenated intermediates, such as ketones and aldehydes, the low or moderate conversions, due to the necessity to maintain the reaction system outside the explosion limits. In addition some of these processes are not continuous.

The oxidation of olefins with dioxygen is a process that has found a seldom exploitation like in the synthesis of ethylene oxide.³ In most other cases, peroxides are used as oxidants with high costs. The oxidation of olefins with dioxygen and CO_2 (Eq. 12) may bring in positive results.⁶



The use of sc- CO_2 may add some more benefits for what concerns critical aspects difficult to drive in solution, namely: the control of the reaction selectivity (one- or two-oxygen transfer to the substrate), yield, working conditions, eventual radical life-time control.

Moreover, the use of sc- CO_2 offers a unique opportunity of using carbon dioxide as solvent and reagent.

Another area of application for carbon dioxide is the use in the synthesis of methanol that is actually synthesised from CO/H_2 mixtures. (Eq. 13) Methanol may have a large market as fuel and chemical and its synthesis from carbon dioxide attracts the attention and interest of several research groups around the world in order to define the potential.



The use of carbon dioxide (Eq. 14) has as major draw-back the higher consumption of dihydrogen with respect to CO.



However, higher selectivity and better yields may counterbalance such apparent negative point. We have performed a LCA study of the possible synthetic methodologies of methanol⁷ and found that the most eco-efficient synthesis is based on the use of a mixture of $\text{CO}:\text{CO}_2=2:1$.

Conclusions

All the synthetic methodologies described above respond to the enviro-economics principles. They are characterised by a great level of innovation and promote the corporate image of the

chemical industry as they couple the reduction of carbon dioxide emission and waste minimisation at source with possible recycling of carbon. Their implementation is on a time scale short to medium, with great benefits for the chemical industry.

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