

Carboxylation reactions for integrating CO₂ capture with the production of renewable monomers

Laura Faba, Paula Rapado and Salvador Ordóñez , Catalysis, Reactors and Control Research Group (CRC), Department of Chemical and Environmental Engineering, University of Oviedo, Oviedo, Spain

Abstract: Research advances in carboxylation reactions using CO₂ and light organic molecules of renewable origin are reviewed in this work, especially considering chemical catalytic approaches. Carboxylation, one of the most promising carbon capture and utilization (CCU) technologies, has a double environmental benefit, reducing greenhouse gas emissions by developing sustainable processes for commodity synthesis. The industrial interest is based on its potential use in the synthesis of biopolymer precursors from bioplatfrom molecules such as ethanol or furfural. Acrylic acid is obtained from ethylene (after ethanol dehydration), by a liquid phase reaction activated by organometallic catalysts. Promising yields are reported for different ligands and solvents, but a practical and sustainable implementation of these reactions is still challenging. On the other hand, the furoic acid carboxylation (furoic acid obtained by oxidation of furfural) is a solid-gas reaction that produces 2,5furandicarboxylic acid in presence of alkaline carbonates. In this case, the economic feasibility is the main bottleneck to solve for scaling-up, and efforts should be focused on substituting the most active alkaline carbonate (Cs) by more available alternatives. © 2022 The Authors. *Greenhouse Gases: Science and Technology* published by Society of Chemical Industry and John Wiley & Sons Ltd.

Keywords: ethylene; acrylic acid; furoic acid; 2,5dicarboxylic acid; biomass

Introduction

Carbon dioxide emissions have exponentially increased in the last decades, with over 34 billion tons emitted each year quantified in 2020.¹ Considering the high relevance of this problem, controlling CO₂ concentration in the atmosphere is a worldwide issue that needs to be solved urgently. In the last two decades, the CO₂ capture and storage/sequestration (CCS) strategies have focused the

main research attention on developing a plethora of physical and chemical technologies.^{2–6} Nowadays, high efficiencies are obtained but their industrial implementation is hindered because of the high costs required for the transportation and stable storage of the recovered CO₂, as well as the technical limitations to guarantee the security and viability of these approaches.

With these perspectives, the ambitious targets of the European Union require the development of other

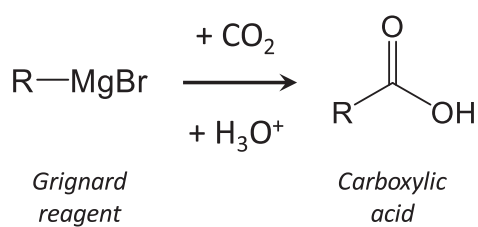
Correspondence to: Salvador Ordóñez, Catalysis, Reactors and Control Research Group (CRC), Department of Chemical and Environmental Engineering, University of Oviedo, Oviedo 33006, Spain.

Email: sordonez@uniovi.es

Received May 26, 2022; revised June 26, 2022; accepted July 18, 2022

Published online at Wiley Online Library (wileyonlinelibrary.com). DOI: 10.1002/ghg.2175

This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made.

Scheme 1. Reaction of Grignard with CO₂.

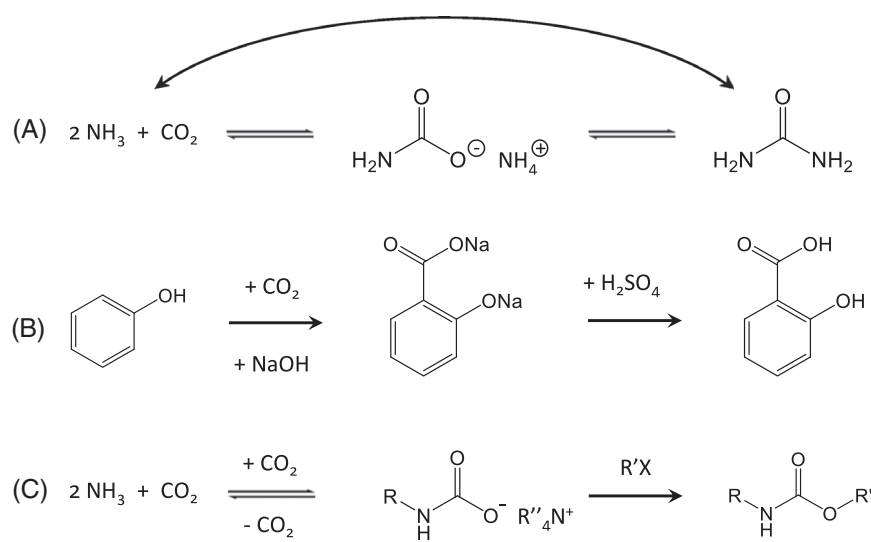
techniques, not only for CO₂ capture, but also its use as a chemical feedstock (CCU technologies). This strategy considers CO₂ as an activated molecule, a feedstock to synthesize value-added chemicals. From the process sustainability point of view, CO₂ is the most attractive C₁ carbon source (renewable and overly abundant), destined to be the substitute for common C₁ precursors, such as methane, formaldehyde, methyl halides, or carbon monoxide in coupling reactions. On the other hand, CO₂ insertion into organic molecules lead to formation of carboxylic functions, key functional groups in further chemical processing (active sites for polymerization reaction, tuning chemicals biocompatibility, etc.). The ideal approach must consider its upgrading reactions at mild temperatures and low pressures, according to the principles of the green chemistry. These conditions can be achieved by enzymatic, biochemical and chemical routes. In this review, only the chemical routes are considered, with a clear approach to highlight the main relevant aspects from a chemical engineering point of

view, issues that are relevant for a future scale-up to the industrial application.

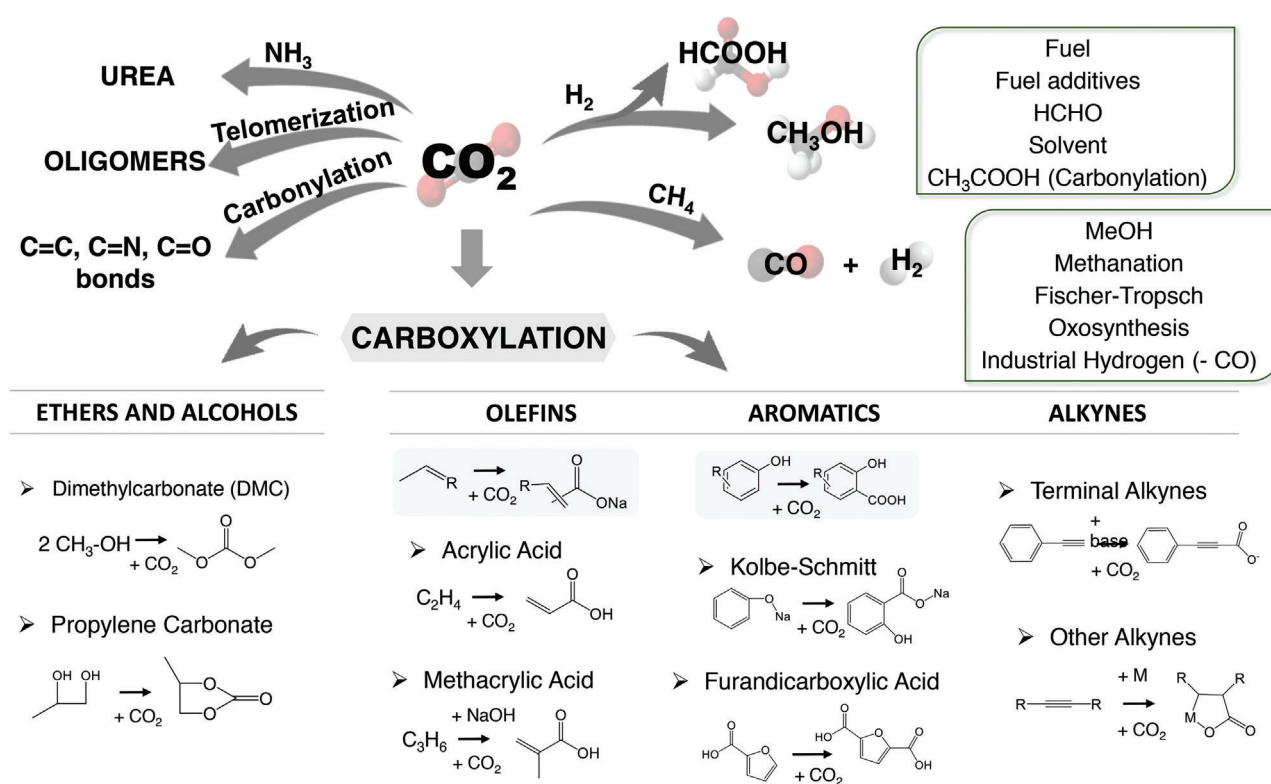
The incorporation of CO₂ into organic molecules was first proposed more than 100 years ago, as a particular application of the reaction of Grignard (see Scheme 1).⁷ However, the limited availability of the parent reagents, as well as their chemical reactivity and complex manipulation makes CO₂ fixation by this method unattractive for industrial implementation.

Currently, there are many organic reactions involving carbon dioxide. Nevertheless, the CO₂ thermodynamic stability and kinetic inertness (high oxidation state of carbon atom, linear geometry) restrict the industrial applicability to a very limited number of processes, highlighting the synthesis of urea and its derivatives,⁸ such as the Kolbe–Schmitt process to produce salicylic acid and other aromatic hydroxy acids⁹ and, in the last years, the production of organic carbonates, replacing phosgene as the C₁ building unit.^{10–15} These mechanisms are illustrated in Scheme 2.

Strong research efforts are devoted to developing alternative and effective processes to activate CO₂ and open the range of possibilities for its utilization. At present, several reaction systems have been proposed in the literature considering CO₂ as a reactant for synthesizing high-molecular polymers and fine chemicals, including carbonylations, cycloadditions, telomerizations, methylations, etc.^{16–21} The most promising ones are reviewed in Scheme 3. Except for the previously mentioned processes, most of these



Scheme 2. Schemes of CO₂ industrial processes: (A) urea production; (B) salicylic acid production by Kolbe–Schmitt process; (C) production of organic carbamates.



Scheme 3. Summary of the most promising chemical routes for the CO₂ valorization, highlighting carboxylation, the objective of this work.

alternatives are still at the lab scale, requiring stronger research efforts to make them attractive for a scale-up. In most of them, the development of active and selective catalysts is still the weakest point. Moreover, effective contact between CO₂ (gas) and the reactants (solids in many cases) and their chemical activation is also a relevant challenge, observing weak equilibria to overcome the thermodynamic barrier without compromising the stability of any of the reagents or intermediates involved.

A large part of the research efforts has focused on the development of technologies that allow a suitable and sustainable conversion of CO₂ to liquid fuels such as methanol, ethanol, dimethyl ether and other hydrocarbons. Relevant reviews analyze the state-of-art of these studies.²¹ The direct transformation of CO₂ into methanol (Eqn 1) has attracted much attention, mainly using Cu/ZnO/Al₂O₃ as the catalyst.^{22–28} The kinetics of the reaction significantly decrease in presence of CO/CO₂/H₂ mixtures, a situation for which theoretical calculations (using Density Functional Theory, DFT) demonstrate a high activity of materials based on molybdenum phosphides.²⁹ In any case, the direct CO₂ transformation into methanol

is technically hindered by the role of water as an inhibitor on the catalyst^{30,31} and economically limited nowadays by the availability and cost of hydrogen. The improvements of the manufacture of renewable hydrogen increases its availability and significantly reduces its cost. For the water inhibition, most of the approaches suggest the two-step process, with previous partial hydrogenation to obtain carbon monoxide by the reverse water-gas shift (RWGS) reaction (Eqn 2).



RWGS is an endothermic reversible reaction. Its main drawback is the development of active catalyst (usually based on copper or ceria oxides) at temperatures low enough to prevent the severe limitation by equilibrium. Since most of the catalysts studied require a temperature above 400°C,^{32–34} the equilibrium constant is low, requiring different methodologies to increase this conversion, such as working with high H₂ pressure, removing water vapor or using selective membranes.

Once the carbon monoxide is obtained, there is a huge of well-established process to produce not only methanol (by second hydrogenation) but also other interesting compounds and fuels, such as dimethyl ether, light alkanes, ethanol or formic acid, including catalytic, photochemical and electrochemical routes.^{35–38} These technologies are out of the scope of this work since, once the CH₄ is obtained, the subsequent steps are already implemented at an industrial scale.

Among the alternative routes, carboxylation deserves a special attention. It can be used to produce the precursors different kinds of polymers (mainly plastics). Nowadays these materials are produced from petroleum, with relevant drawbacks derived from this non-renewable origin and their slow biodegradation. The need to replace non-bio and nonrenewable plastics is clearly stated but, nowadays, bioplastics only represent 1% of the 368 million tons of plastic produced worldwide each year.³⁹ This percentage is expected to increase by 50% in the next 25 years,³⁹ a goal that requires strong efforts in development of efficient, sustainable and cheap industrial processes for manufacturing the appropriate monomers.

Biomass has become the most effective substitute of petroleum to obtain polymers precursors. This complex and renewable resource is composed of different extractives and natural polymers, which could be isolated and transformed (via chemical or enzymatic routes) into a plethora of platform molecules, some of them relevant in this context.⁴⁰ Among these compounds, bioethanol or cellulose-derived aldehydes (as furfural or hidroxymethylfurfural) play a key role as bioplatfrom molecules.

The production of bioethanol by sugar fermentation is a well-known process, already stablished at industrial scale. In addition to its use as fuel, ethanol is a promising precursor of many commodities, such as butanol and heavier alcohols.⁴¹ Moreover, its dehydration produces ethylene, a widely used hydrocarbon, one of the most typical monomer in the plastic industry, and also a promising reactant for CO₂ upgrading. On the other hand, the aqueous phase hydrolysis of hemicellulosic fractions produces cyclic aldehydes, highlighting 5hydroxymethylfurfural (5HMF) and furfural, from hexoses and pentoses, respectively.⁴² Their carboxylic functionalization is the starting point of the synthesis of polyethylene 2,5-furandicarboxylate (PEF), the renewable substitute of the most used plastic (PET).

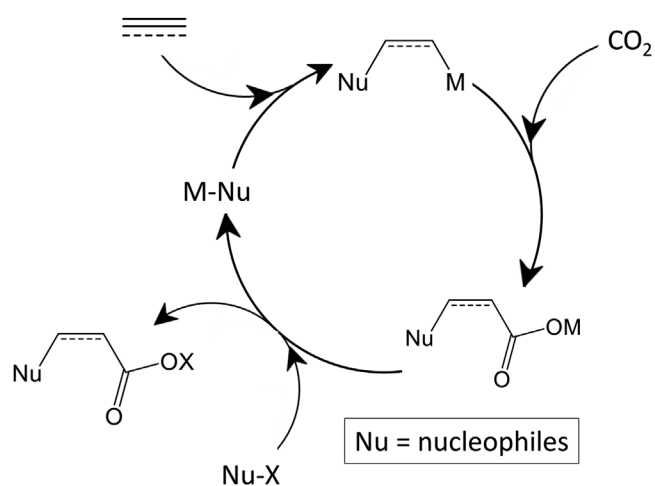
This brief review is intended to provide an overview of the research progress in chemical carboxylation, one of the most promising new routes to both functionalize and increase the carbon-chain length of different compounds by the insertion of a carbon dioxide molecule, directly preparing mono- and di-carboxylic acids and other derivatives.^{43,44} After an initial exposition of the main concepts and general mechanisms of carboxylation, the application of this approach to different platform molecules is considered, with special interest in molecules of renewable origin, analyzing the main systems proposed in the literature, the reaction conditions and the main drawbacks linked to each process.

Chemical carboxylation mechanisms

Carboxylic acids are important building blocks in the chemical industry for manufacturing rubbers, plastics, cosmetics, detergents, dyes, surfactants, among others.⁴⁵ Most of these chemicals are nowadays produced by different oxidation processes, reactions carried out at severe conditions (high temperature for gas phase reactions or strong acidity for liquid phase processes). On the other hand, these oxidation reactions are characterized by very low selectivities to the target carboxylic acid, an important fraction of the carbon atoms of the parent molecule being transformed into carbon oxides.^{46,47} The substitution of these routes by the direct carboxylation using CO₂ could also improve the sustainability and atom economy of these industrial processes.

Due to the thermodynamic stability of CO₂, its incorporation into an organic molecule requires demanding activation steps, resulting into different approaches: the biochemical, the electrocatalytic, the photocatalytic and the chemocatalytic one. The last one can take place by two different mechanisms: (1) in liquid phase, at soft temperatures using organometallic intermediates (homogeneous catalysis); (2) or at higher temperatures, with a solvent-free configuration, using inorganic salts as precursors.

According to the first one, the formation of a carboxylic acid by CO₂ carboxylation takes place through the nucleophilic addition of (transition) metal ligand species (label as M-Nu) to the unsaturated bond of a substrate molecule, followed by the insertion of CO₂ into the resulting organometallic intermediate (usually considered as the real homogeneous catalyst).



Scheme 4. Typical reaction patterns of transition metal promoted carboxylation of unsaturated substrates with CO₂ (adapted from Ref. 49).

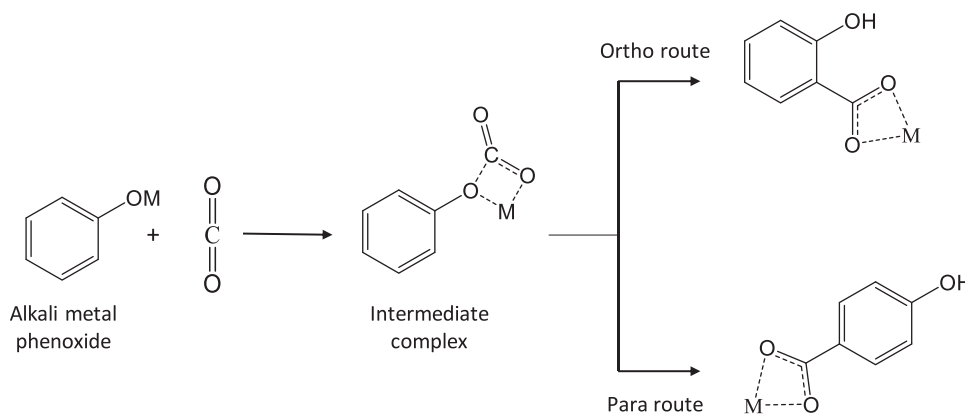
The general pathway is depicted in Scheme 4. This route has been proposed using several transition metals, such as Ni, Cu, Co, Ni, Pd, Au and Ru, and some noble metals, such as Rh, Pd.^{48–50} The reaction takes place in the liquid phase at low pressure (15 bar of CO₂) and low temperatures (from –70 to 60°C) using different solvents to dissolve the organics.

This mechanism can be applied to different unsaturated organic compounds, including alkynes, alkenes, allenes and aldehydes, both cyclic and acyclic compounds, resulting in a huge diversity of potential reactants. Despite the chemical potential, this route has significant drawbacks from the sustainability point of view, which hinders its applicability at industrial scale. The lack of heterogeneous catalysts reduces the

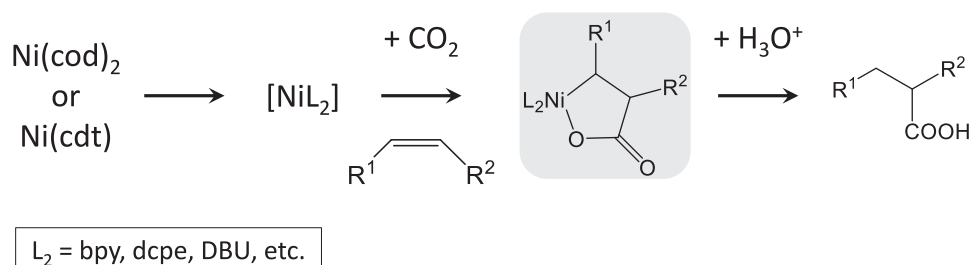
possibility of reusability and hamper the stream purification. Moreover, most of the organic solvents (THF, dioxane),^{51–54} ligands (trialkylboranes, metallactones),⁵⁵ and metal precursors ((IPr)CuCl, Ni(cod)₂, bis(amidine))^{51–53} used in the reaction are expensive and have a clear toxic character. Thus, their cost and stoichiometric consumption could reduce the economic feasibility and produce relevant environmental drawbacks in case of an incomplete stream purification.

An alternative carboxylation pathway (second mechanism, illustrated in Scheme 5) considers the direct coupling between aromatics and CO₂ without requiring the presence of an external organometallic nucleophile. This route was firstly proposed in 1860,⁵⁶ when salicylic acid was prepared by heating a mixture of phenol and sodium in the presence of carbon dioxide at atmospheric pressure. Further studies demonstrated that higher yields are obtained using phenolic salts and under enhanced pressure, developing the process currently known as the Kolbe–Schmitt reaction. This reaction is defined as a heterogeneous gas–solid reaction that enables synthesizing aromatic hydroxycarboxylic acids via carboxylation of a phenol salt of an alkali metal under severe reaction conditions at 125°C and 4–7 atm carbon dioxide pressure.^{5,57}

Nowadays, this mechanism is well established, for example, in the industry for the salicylic acid production. Its application to different aromatics opens a new route to obtain biopolymer precursors without the use of organic solvents and organometallic catalysts, preventing the previously mentioned environmental problems derived from the first mechanism. Most of the reported studies are



Scheme 5. Kolbe–Schmitt reaction pathway. In the scheme, “M” represents an alkali metal (adapted from Markovic *et al.*, 2007⁹).



Scheme 6. Carboxylation of olefins using Ni organometallic complexes as catalysts (adapted from Ref. 59).

performed in the absence of any solvent, the main requirement to establish a good contact between the salt and the CO_2 is to guarantee the melting state of the solid without its decomposition. This fact establishes different temperatures and metals as a function of the original aromatic to be transformed.

Liquid phase carboxylation of unsaturated molecules using organometallic complexes

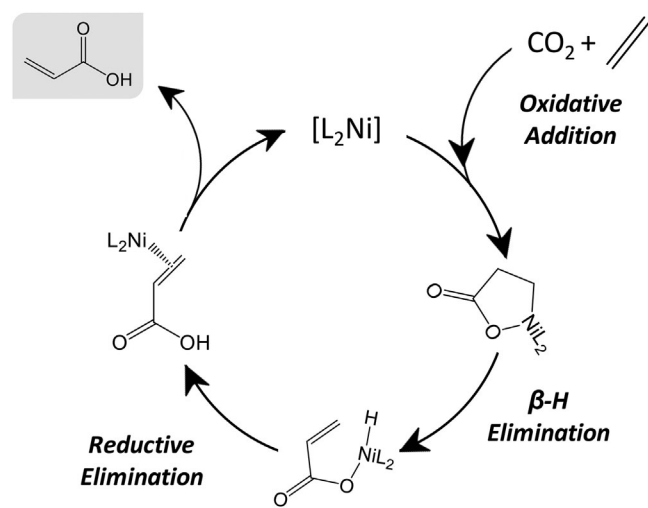
The reaction of alkenes with CO_2 was reported for the first time in the 1980s, using nickel complexes (lactones, homogeneous catalysis) to stabilize the reaction intermediates, Scheme 6.⁵⁸ Despite the plethora of alkenes that could be used as reactant, the most interesting studies are focused on the valorization of the lightest alkenes, ethylene and propylene, since they are the raw materials necessary to obtain industrial interesting carboxylic acids, such as malonic, succinic, acrylic and methacrylic acid.

In 1987, the first studies focused on the reactivity of ethylene proposed using homogeneous iron salts as metal catalyst. FeCl_2 was dissolved in THF at very low temperatures (-78°C), the solution was then saturated in ethylene, obtaining a complex (metal lactone) once the corresponding ligand is added. This complex stabilized the ethylene, allowing the carboxylation ($\text{C}=\text{C}$ bond) when treated the solution with a CO_2 stream at 1 bar.⁵⁹ This study suggests for the first time the strong influence of the ligand of the position of the new $\text{C}=\text{C}$ bond, obtaining succinic or methylmalonic acid as a function of if bidentate or monodentate ligands are used. In both cases, a double CO_2 addition is produced, obtaining C4 carboxylates that could be transformed into the corresponding acids by hydrolysis.

From ethylene to acrylic acid

The direct acrylic acid production from ethylene and CO_2 is a desired but challenging reaction due to relevant thermodynamic limitations ($\Delta G_0 = 42.7 \text{ kJ/mol}$). Acrylic acid has an essential value as monomer (50% of the total esters) and as an intermediate to produce paints and coatings, adhesives, construction chemicals and hygienic products, among other examples. Currently, this acid is industrially synthesized by the oxidation of propylene (non-renewable resource), a two-step reaction with acrolein as intermediate. This route has relevant drawbacks from the environmental point of view, highlighting the strong material requirements for the reactors (due to the high corrosive reaction conditions) and the low E-factor derived from the production of acetic acid and CO_2 as side-product. Despite the thermal optimization to reduce these undesired products, this process has a global warming potential of 2.3–2.5 kg CO_2/kg acrylic acid.⁶⁰ Thus, in the context of the circular economy and sustainability, there is a high interest in developing a sustainable and economical alternative process, with the ethylene carboxylation being one of the most promising alternatives.

The first studies date from the first decade of the 21st century, being based on the conclusions of the pioneer studies of Hobert et al. in 1987, that is, proposing the stabilization of ethylene taking part of a metal lactone complex.⁶¹ These preliminary works were partial studies that analyze the process step by step. The first one analyzes the coupling step, proposing a theoretical mechanism for the ethylene carboxylation (Scheme 7).⁶² According to this mechanism, corroborated by DFT studies, the oxidative coupling step of the substrate to form metallactones is possible but the distance between the transition metal and βH is so large that the βH elimination (step required to the



Scheme 7. Reaction mechanism for the synthesis from ethylene and CO₂ (adapted from Ref. 59).

release of the acrylate and to regenerate the metal species) is not possible without the cleavage of metal-C bond. This drawback is a common problem identified in the first studies, despite proposing catalysts based on Ni,^{58,61,63} Mo or W.^{64–66} The stabilization of this bond has been the crucial point in most of the further studies, suggesting different ligands that could form stable intermediates. Thus, Walther and co-workers propose the use of bis(dicyclohexyl-phosphino)methane using Ni as transition metal.⁶⁷ This ligand produces a binuclear complex in which the methane acts as hydride acceptor, and the high flexibility of this complex (exhibiting monodentate, chelating or bidentate behavior) favors the β hydride transfer. Although the release of acrylic acid or an acrylate cannot be achieved, this study marked the starting point of further improvements in this issue.

In a specific work of 2007 about this release, Aresta *et al.* demonstrated that the acrylic acid liberation is possible if carboxylation is combined with the esterification of the carboxylic moiety (ethyl acrylate), using Pd complexes, preventing the formation of M-H and M-O stable bonds (see Scheme 8).⁶⁸ In the same direction, in 2010, Bruckmeier *et al.*, propose the use of methyl iodide to improve the β hydride elimination and the liberation of the acrylate, reaching maximum yields of 33% when the reaction was carried out at 40°C, using dichloromethane as solvent.⁶⁹ Based in all these previous studies, in 2012, Limbach and co-workers published the first complete catalytic synthesis of acrylate from CO₂ and ethylene, using a

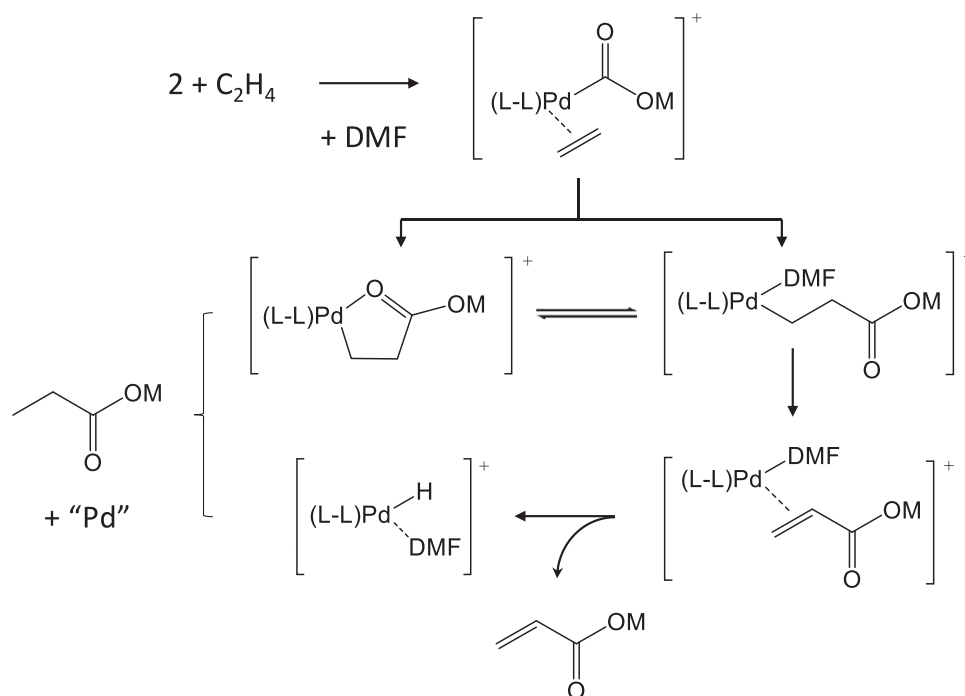
nickel complex as homogeneous catalyst, demonstrating a high dependence on the reaction conditions.⁷⁰ A temperature of 50°C allows the equilibrium that maximizes the kinetic of the process preventing the decomposition of any intermediate when using THF as solvent (54% yield after 6 h with 5 bar of ethylene and 40 bar of CO₂).

A significant increase in the reaction rate (91%) was observed by substituting the THF by PhCl, in this case at 60°C. Further studies deepen the influence of different reaction conditions, mainly analyzing the role of ligand, solvent and the reducing agent, typically working with high CO₂ pressure (20 bar) to guarantee the required solubility on the organic solvents used.^{71,72} In most of the cases, Ni is proposed as metal, but there are also relevant studies considering Mo, Ti, Pd, Pt, Fe and Ru complexes.⁷³ Mechanistic studies suggest similar pathways for all these materials, but with different limiting steps. The oxidative coupling of CO₂ and ethylene is easier with Group VI metals than with Ni systems, being possible at room temperature and pressures when using Mo/W complexes, requiring more severe conditions when using Ni. However, the strong oxophilicity of these metals is an impediment to the acrylate removal, requiring strong bases not needed when working with Ni complexes.

To sum up, the acrylic acid production by the direct carboxylation of ethylene with CO₂ has been successfully proposed as a synthesis route, using organometallic complexes. This approach has significant drawbacks hindering its scale-up, highlighting the low turnover numbers (<0.1 h⁻¹), the stoichiometric amount of reducing agent or base required and the use of solvents, which is contrary to the sustainability and the economy of the process.⁷⁴ These disadvantages justify the lack of references from an engineering point of view. A different approach, a gas-phase reaction using solid catalysts (following the model of Ziegler-Natta catalysts) could overcome these limitations but, so far, this route has not been proposed in the literature for the coupling between ethylene and CO₂.

From propylene to methacrylic acid

Methacrylic acid (MAA) is an important intermediate in the production of different polymers. The current industrial processes, such as acetone cyanohydrin or isobutylene oxidation and subsequent hydrolysis, the dehydrogenation of isobutyric acid, and the



Scheme 8. Reaction mechanism for methyl acrylate formation, according to Aresta *et al.*⁶⁸

decarboxylation of different organic acids, must be substituted by a renewable route that reduces the drawbacks in terms of environmental pollution, toxicity, low selectivity and high cost of the current ones.

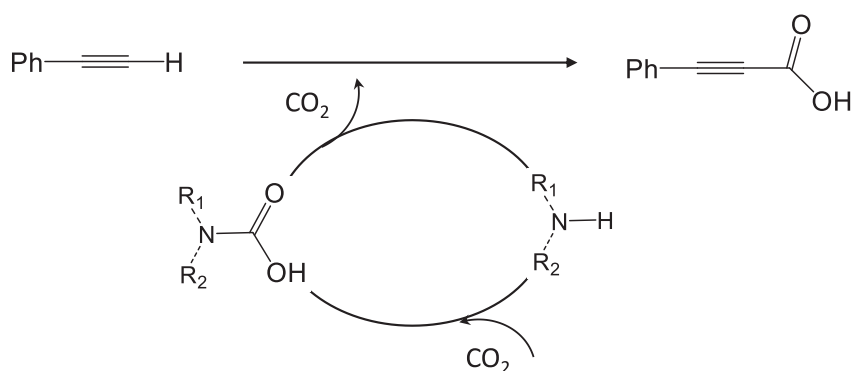
The propylene carboxylation using CO₂ was firstly proposed in 2003 by Zhong *et al.*, at 290°C and 1 MPa using Ni, P, Mo and W heteropolyacids as catalysts.⁷⁵ According to promising results, the research interest in this route was focused on the development of heterogeneous catalysts that increase the sustainability of the process. Thus, these heteropolyacids were supported on TiO₂. Despite the low propylene conversion obtained (4.2% at 1MPa, 290°C), a high selectivity is reported (96%), demonstrating the relevance of Lewis base and acid sites to promote the chemisorption of both reactants.⁷⁵ These tentative results have been improved by modifying the polymetallic oxygen salts, the best results being obtained with PW₁₁Ni/TiO₂, with 12.6% of propene conversion and a MMA selectivity of 95%.⁷⁶ Unfortunately, the veracity of these results has been questioned, since Bentrup and co-workers tried to reproduce them without obtaining any conversion.⁷⁷ According to their study, the *in situ* FTIR spectroscopy reveals the chemisorption of CO₂ as carbonate species on the surface of supported POM catalysts. However,

these carbonates do not react with propene. Moreover, the strong oxidizing character of these catalysts promote the propylene oxidation, obtaining different CO_x. No further studies have been published on this topic, despite the undoubted interest of a heterogeneous catalytic carboxylic route to obtain methacrylic acid.

Other carboxylation of alkenes and alkynes with CO₂

Other olefins have been also studied in coupling with CO₂ since carbon dioxide is an extremely attractive C1 feedstock in organic synthesis. Several studies deal with the carboxylation of styrene derivatives to obtain aryl carboxylic acids, proposing organometallic systems similar to those indicated for ethylene valorization.^{78–85} In general, promising results were obtained but with homogeneous organometallic and configuration systems that make these configurations difficult to implement at an industrial scale. Moreover, the selectivity of the reaction decreases in presence of more than one C=C unsaturation, such as in the case of butadiene^{86,87} or allene.^{88–90}

With the same strategy, different authors investigated the terminal carboxylation of alkynes as potential useful reactions to bear pyrones and, in the last years,



Scheme 9. Alkyne carboxylation using capture solutions (adapted from Yu *et al.*⁹⁷).

carboxylic acids or esters (see Scheme 9).^{91–96}

Experimental results demonstrate an easy reactivity of alkynes, obtaining molecules bearing the carboxylic functionality bonded to an olefin moiety.

As indicated before, these reactions are not relevant for the polymer industry, and they will not be explained in detail. However, there are some interesting works exploring these reactions in continuous configuration. These works have relevant information that could be the background of a future implementation of continuous carboxylation of more interesting platform molecules.

Liquid-phase carboxylation in continuous flow

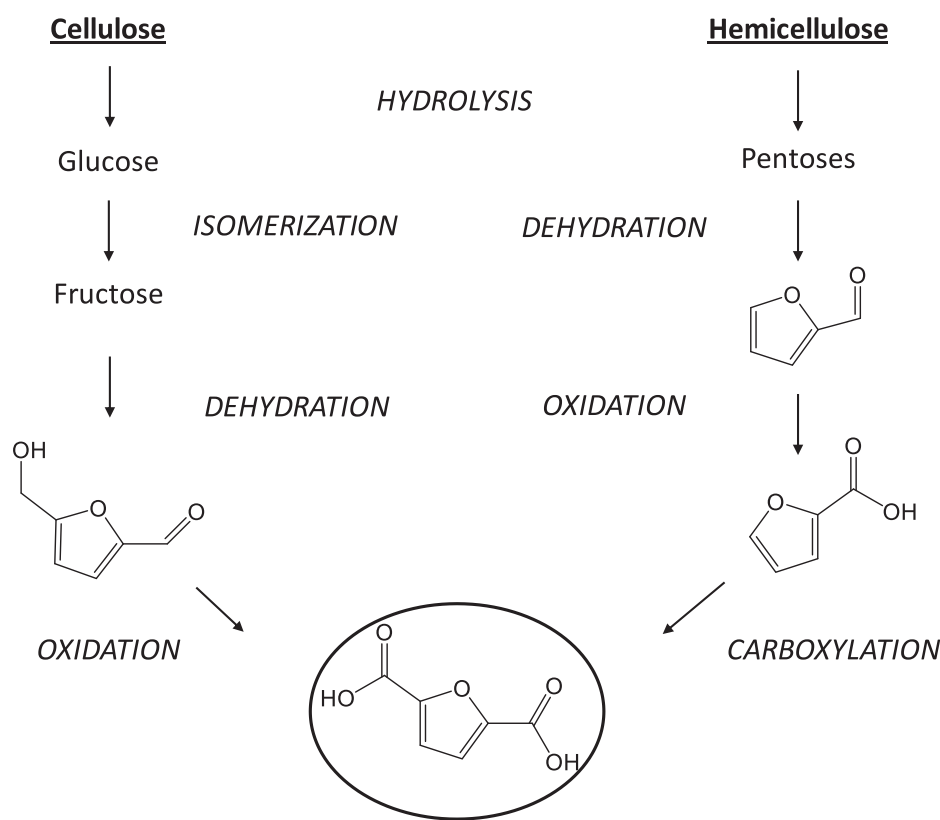
The first continuous flow carboxylation was carried out in 2011, obtaining promising results using a tube-in-tube gas–liquid biphasic reactor.⁹⁷ The Grignard reagents were pumped diluted in THF inside the inner tube. The space between the inner and the outer tubing was pressurized with 4 bar of CO₂, allowing the saturation of the liquid phase because the Teflon AF-2400 used for the inner tubing demonstrates a particularly effective gas permeability. Carboxylic acid was released after washing with a formic acid/THF solution the packed-bed columns used to trap the carboxylate intermediate. This procedure has been tested using aromatic, aliphatic, heteroatomic and alkynyl Grignard reagents with excellent yields (7 bar of CO₂, 1 mL·min⁻¹). In a further study, Broek and co-workers analyzed the influence of the mixing point, comparing the results obtained with a continuous CO₂ saturation of the THF and phenylmagnesium bromide solution with those reached when two THF streams (with CO₂ and the reactant) are independently

saturated. The first configuration demonstrates a higher conversion, but the second one presents a higher stability, being not significantly affected by differences in the temperature (up to 60°C, residence time (18–75 s) or CO₂ concentration (<2 M).⁹⁸ These studies were the basis of other works dealing with different aromatic alkenes,⁹⁹ and alkynes,¹⁰⁰ having a good background about reaction conditions as a function of the ligand used. Most of these studies are deeply analyzed in a review published in 2018.¹⁰¹

Though the development of catalytic systems for CO₂ carboxylation in continuous flow needs more studies to adapt these configurations to the sustainability requirements (heterogeneous catalysis, absence of solvents) and to make feasible the carboxylation of light alkenes (the most interesting ones from the industrial point of view), these works indicate relevant advantages of continuous flow to control this reaction.

Chemical carboxylation of aromatics and heterocyclic compounds

As mentioned in the introduction section, biomass has become the most effective substitute for petroleum to obtain polymers precursors. In this context, 2,5-furandicarboxylic acid (2,5-FDCA) is highlighted as one of the main pillars of the bioplastic industry. It is the ideal alternative to terephthalic acid (non-renewable monomer), allowing the substitution of polyethylene terephthalate (PET), one of the most used polymers, by a sustainable alternative, the polyethylene furoate (PEF), obtained by the 2,5FDCA polymerization with ethylene glycol. The chemical structures of both polymers are very comparable, which enables the almost direct substitution, obtaining a polymer with



Scheme 10. Routes to 2,5-FDCA synthesis from cellulose and hemicellulose.

45–55% lower greenhouse gas footprint, when calculated from cradle to grave,¹⁰² improved barriers and more attractive thermal properties with respect to its non-renewable predecessor (PEF's oxygen and CO₂ barriers are 10 and 6–10 times better, the glass transition temperature is 12°C higher, whereas the melting point decreases is 35°C).^{103,104} With a lower but also relevant market share, the production of 2,5FDCA is also relevant to obtain other polymers, as reviewed by Pandey *et al.* in 2021.¹⁰⁵

Currently, the production of 2,5-FDCA is studied from two different approaches (Scheme 10). The first one involves the oxidation of 5-hydroxymethylfurfural (5-HMF). This catalytic route allows obtaining high yields of 2,5FDCA with some problems in purity in the final mixtures.^{106–108} Moreover, most of the HMF is produced from edible biomass since its production from lignocellulose is characterized by its low purity and yield. To prevent conflicts with the food industry and to reduce the current cost of 2,5FDCA production, established in 2500 \$/kg,¹⁰⁹ the 2,5-FDCA production from lignocellulosic platform molecules that could be obtained from waste biomass, such as furfural,¹¹⁰ is essential.

The synthesis of 2,5-FDCA from furfural has been proposed in the literature by different catalytic routes, all of them considering furfural oxidation to obtain furoic acid (FA) as the first step. Once the carboxylic functional group is present, 2,5FDCA can be obtained by the disproportionation of FA (Henkel reaction), yielding furan as a co-product.^{111–116} By this route 2,4FDCA is also obtained, the 2,5FDCA is difficult to isolate due to the similar physical and chemical properties.^{111,117} Other alternative is the carbonylation pathway, include furoic acid bromination, esterification, carbonylation and hydrolysis steps.¹¹⁸ The restricted selectivity of the first approach, as well as the complexity and nonsustainable character of the second one, limit their future development, emphasizing the interest for the carboxylation routes.

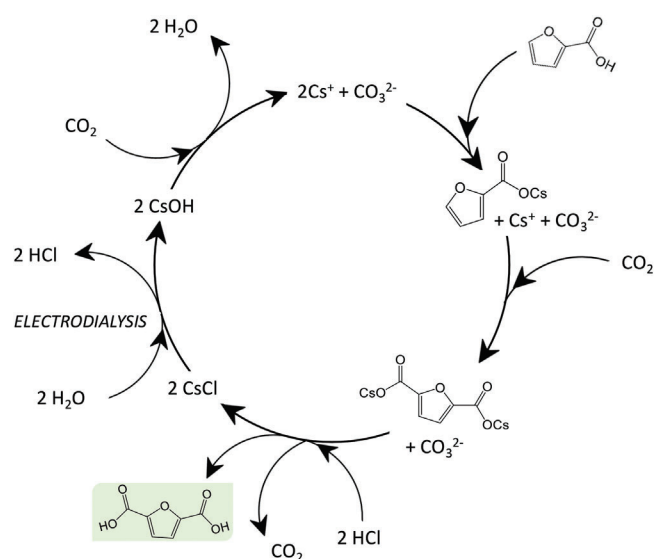
Furoic acid carboxylation in batch configuration

The carboxylation in acidic media requires a Lewis acid¹¹⁹ to activate via coordination of the CO₂, leading to a reaction with the furoic acid. Theoretically, this reaction occurs at relatively low temperatures but high

CO₂ pressure, making it impossible to take direct advantage of the CO₂ capture system (typically working at low pressure). Moreover, poor yield of the target product is reached due to the different parallel reactions yielding a large amount of undesired by-products. Due to these disadvantages, there are no further studies considering this approach.

The FA carboxylation using CO₂ and a base as reagent was proposed for the first time in 2016.¹²⁰ This reaction is a particular application of the Kolbe–Schmitt synthesis, possibly the oldest organic synthesis using CO₂, reported in 1860.¹²¹ The Kolbe–Schmitt reaction is a solidstate reaction usually carried out by contacting dry CO₂ with aromatic compounds activated by electron-donating substituents, such as alkaline cations. Although this reaction has been developed for hydrocarbon aromatics, its mechanism could be extended to other heterocyclic compounds with aromatic characteristics, such as pyridines or furans.¹²²

A pioneering work of Kanan and co-workers¹²⁰ establishes the pillars for future studies, obtaining very relevant conclusions about the mechanism and the reaction conditions. Previous researchers demonstrate that carbonates can deprotonate C-H bonds with pK_a values of up to 27 using organic solvents and high temperatures.^{123–125} Considering the high pK_a of the C-H at the five position of furan-2-carboxylate (≈35), the formation of 2,5-FDCA by carboxylation with CO₂ is thermodynamically unfavorable. This drawback is solved by the initial formation of metal furoate by the reaction of the furoic acid with an alkaline salt. Thus, the reaction involves two solids, and it is carried out in at solventless conditions. These solids must be melted to enable the ion mobility needed for the correct interaction of the different involved ions. Thus, the melting point of the carbonates is a critical aspect to prevent the decomposition of the organic compounds (furoic acid and reaction intermediates or side compounds). In this context, most of the alkaline salts are discarded (temperatures much higher than 200°C to melt), proposing Cs₂CO₃ as the best option. At working conditions, this carbonate deprotonates C-H bonds with pK_a > 40. This deprotonation leads to a strong nucleophilic carbon atom that could react with the weakly electrophilic CO₂. The reaction mechanisms proposed (Scheme 11) results in a net consumption of one equivalent of CO₂ per C-CO₂⁻ produced. Working with high concentration of carbonates guarantees the stabilization of the



Scheme 11. Reaction mechanism to selectively obtain 2,5-FDCA by the base carboxylation of furoic acid and CO₂.

conjugated base of 2,5-FDCA by ion pairing. The 2,5-FDCA is obtained by protonation with HCl, whereas the carbonate is recovered by electro dialysis.

The best results proposed in this work correspond to 76% yield of 2,5-FDCA²⁻ after 12 h when heated at 260°C under a CO₂ flow of 40 mL·min⁻¹, using 10% of excess of Cs₂CO₃. Acetate and malonate, among others, are identified as the main decomposition products, their production being limited when working in a pressurized batch reactor (89% of 2,5-FDCA²⁻ yield after 7 h at 200°C with 8 bar of CO₂).¹²⁰ The limited role of Cs⁺ only to reduce the melting point of the salt is corroborated by substituting this alkaline by potassium salts (potassium carbonate and carboxylate as a co-salt). Yields higher than 60% were reached (so Cs⁺ has not any specific role in the mechanism), but the temperatures are so high (320°C) that decomposition reactions cannot be prevented. As expected by the semi-molten state of the reactant, the reaction occurs at the gas–solid interface. Preliminary scale-up studies (from 1–10 to 100 mmol) result in lower yields because of the lower surface area to volume ratio obtained.¹²⁰ These results are justified by the hindered transport of CO₂ into the salt and removal of H₂O.

In a different approach, Nocito *et al.*, compare the activity of different cheaper carbonates, trying to obtain more evidences of the reaction pathway and the intermediates involved, concluding that inorganic carbonates, especially those with monovalent cations,

are the active species, observing an increasing activity as the charge density on the cations decreases.¹²⁶ This study also demonstrates the correlation activity-melting (decomposition) point of the carbonates and proposes the use of copper-difuroate ($\text{Cu}(\text{FC})_2$) as an alternative esterification of the furoic acid, reducing the amount of Cs involved in the reaction. A complete comparison between the carboxylation of $\text{Cu}(\text{FC})_2$ and FA demonstrate a higher yield when using the copper complex (selectivity of 89% versus 70%, after 6 h at 493 K, 6 MPa of CO_2). Moreover, the reaction involving $\text{Cu}(\text{FC})_2$ produces more than 50% of 2,5FDCA using K_2CO_3 , whereas only 13% is obtained when using the FA. Based on these results, the optimum configuration considers the use of $\text{Cu}(\text{FC})_2$ with $\text{CsCO}_3/\text{MgCO}_3$ (0.1:1 Cs/Mg), yielding 94% of 2,5FDCA after 20 h of carboxylation at 493 K with 6 MPa of CO_2 .

Only few authors propose the carboxylation of furan derivatives using homogeneous catalysis, such as Cu and Pd salts. However, this approach is mainly focused on the 2,5FDCA synthesis through a multistep process involving cascade reactions: bromination, esterification, carboxylation, and hydrolysis. The main advances in this topic are summarized in a review of Drault *et al.*¹²⁷

Furoic acid carboxylation in continuous flow

Trying to improve these results and guarantee the scale-up of the process, Dick and co-workers investigate the furoate carboxylation in a fixed-bed flow reactor using carbonate with different mixtures of cations. Very promising results at mole-scale were obtained using a 2:1 K^+/Cs^+ blend, reaching 89% of 2,5FDCA after 24 h at 260–285°C with 8 bar of CO_2 .¹²⁸ These results are also relevant to improve the profitability of the process, comparing the prizes of Cs^+ and K^+ , despite the theoretical recovery proposed by electrodialysis. The similar reaction under static pressure was not efficient, producing a mixture enriched in decomposition products. It is concluded that the removal of H_2O suppresses decomposition and improves the yield of FDCA.

Based on these results, Zhou and coworkers proposed in 2019 the direct production of 2,5FDCA from HMF and furfural.¹²⁹ They developed a supported metal catalyst (Co/Zn-lignin complex to N-doped carbon supported Co single-atom catalyst, Co SAs/N@C) that,

in presence of Cs_2CO_3 produces the simultaneous oxidation of HMF and furfural, obtaining 2,5FDCA and furoic acid, respectively. Since the cesium carbonated acts as a base that facilitates the oxidative dehydrogenation of furfural (no reaction is observed in absence of this carbonate), the same system is used directly to transform the FA into 2,5FDCA, substituting the O_2 by CO_2 . After 36 h at 260°C, 71.1% of 2,5FDCA is obtained from furfural oxidation derived product with a selectivity close to 83%. These results demonstrate a high similarity with those optimized when using pure FA,¹²⁰ the longer times required being justified by the low CO_2 pressure (1 bar).

Wang *et al.* carried out a complete study about the reaction conditions in fixed-bed flow reactors, analyzing the effect of Cs_2CO_3 and FA-Cs ratio, the temperature, reaction time and CO_2 pressure on the 2,5FDCA yield,¹³⁰ obtaining interesting results in agreement with values reported by other authors. Even more, these results were theoretically explained based on DFT studies, being very helpful to establish the optimum conditions to maximize the production of 2,5FDCA. Thus, the positive effect of an excess of Cs_2CO_3 reaches a maximum with a molar ratio 3:5 (50.6% of yield at 270°C after 3 h), whereas higher excesses reduce the activity. It is suggested that this excess negatively affects the effective collision between reaction intermediates and CO_2 . A maximum yield of 2,5FDCA (54%) is also observed when analyzing the effect of the temperature since results over 270°C demonstrate a FA-Cs decomposition into acetate, malonate and other compounds. The reaction time is also relevant since prolonged times generate so much water in the reaction system that the dissociation of the reactants is affected at the same time as part of the CsCO_3 suffers solubilization. Both phenomena hinder the reaction, defining a well-marked maximum (3 h when the reaction takes place at 280°C with 8 bar of CO_2). As for the CO_2 pressure, an optimum value is defined for each reaction temperature since larger CO_2 pressures promotes the transformation of carbonates into bicarbonates, reducing their promoting activity.

To sum up, different studies demonstrate that the furoic acid heterogeneous carboxylation is feasible in absence of solvent. Furoic acid is readily synthesized from furfural, and inexpensive compound that can be produced from non-edible biomass.⁷⁴ In addition to the previously mentioned advantages, this solid-gas phase reaction is recommended over the liquid phase one since the use of alkali metal salts instead of

transition metal catalysts allows performing the reaction using relative low purity CO₂ (industrial grade) because the alkali metal salts are much more tolerant of impurities in the CO₂ stream than transition metals. However, according to the current state-of-art, the process must be improved before its scale-up, paying more attention to the substitution of Cs by a cheaper element, or to the complete regeneration of the carbon salt to guarantee its total reusability. Moreover, for larger industrial-scale production, the kinetics must be improved, as well as the control on some parameters, such as the mass transport effects.

Furoic acid enzymatic carboxylation

In parallel to these chemical approaches to carboxylation, biocatalytic routes have also gained relevance in recent years for 2,5FDCA production. Thus, the carboxylative activity of some enzymes of the family decarboxylases was identified as a side conclusion of biodegradation studies.^{131–133} These results were the starting point for the Payne and co-worker study, demonstrating the carboxylation ability of HmF enzymes to produce 2,5FDCA.¹³⁴ The results are not very high (0.3% of yield after 12 h) and the reaction requires a severe control on the reaction conditions since it is very sensitivity to temperature (50°C being the optimum one), pH (almost null activity out of the neutral range), and CO₂ pressure (32 bar required to observe results). However, the inherent sustainability of enzymatic reactions as well as the possibilities of DNA recombination and engineering define this biocatalytic route as a promising field for future studies.

Kawanabe *et al.* propose a biocatalytic route to produce 2,5FDCA directly from furfural using bicarbonate as the carbon source and recombinant *Escherichia coli* cells co-expressing different enzymes. The hydrogen peroxide obtained during the furfural oxidation is identified as an inhibitor of the carboxylation activity, proposing the reduction of H₂O₂ levels as the future work to improve this one-pot configuration.¹³⁵

Conclusion

In conclusion, carbon dioxide has a promising future as a renewable and environmentally friendly source of carbon to synthesize monomers, such as acrylic acid and 2,5-furandicarboxylic acid. This review has shortly analyzed the state of the art on the two main

carboxylation chemical routes, the direct solid-gas phase contact using a metal salt of the aromatic precursor, and the carboxylation using an organometallic intermediate as ligand to promote the reaction. Both routes are demonstrated to be feasible, but their industrial implementation still requires further studies to overcome the relevant current difficulties.

The ethylene carboxylation to produce acrylic acid using the current pathway is very difficult to scale-up. The difficult recovery of the organometallic ligands and the use of organic solvents hinder the sustainability of this route, the development of effective heterogeneous catalyst and the optimization of the reaction conditions are the biggest challenges in this topic.

In the case of the 2,5-furandicarboxylic acid, an effective solid-gas configuration is already proposed in the literature. However, the narrow range of reaction conditions to produce the salt melting without jeopardizing the thermal stability of the compounds requires the use of caesium salts. The high cost of this metal compromises the economic feasibility of this process. The recovery of this metal to guarantee the close cycle and the reutilization of this precursor is then compulsory to evaluate this approach at a bigger scale. The use of environmentally friendly solvents could be a good approach to obtain soluble salts without needing the use of caesium, increasing also the temperature range of the reaction, minimizing the undesired compounds.

Acknowledgements

This study has been financial supported by the Spanish Ministry of Economy and Competitiveness (PID2020-112587RB-I00). Paula Rapado acknowledges to University of Oviedo the financial support of her PhD (PAPI-21-PF-19).

REFERENCES

1. Ritchie H, Roser M, Rosado P. CO₂ and greenhouse gas emissions. <https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions>. Accessed 11 May 2022.
2. Anwar MN, Fayyaz A, Sohail NF, Khokhar MF, Baqar M, Khan WD, *et al.* CO₂ capture and storage: a way forward for sustainable environment. *J Environ Manage.* 2018;226:131–44.
3. Zhang T, Zhang W, Yang R, Liu Y, Jafari M. CO₂ capture and storage monitoring based on remote sensing techniques: a review. *J Clean Prod.* 2021;281:124409.
4. Rubin ES. Understanding the pitfalls of CCS cost estimates. *Int J Greenh Gas Control.* 2012;10:181–90.

5. Li B, Duan Y, Luebke D, Morreale B. Advances in CO₂ capture technology: a patent review. *Appl Energy*. 2013;102:1439–47.
6. Steeneveldt R, Berger B, Torp T A. CO₂ Capture and storage: closing the knowing–doing gap. *Chem Eng Res Des*. 2006;84(9):739–63.
7. Dalton DM, Rovis T. C–H carboxylation takes gold. *Nat Chem*. 2010;2(9):710–1.
8. Shi F, Deng Y, SiMa T, Peng J, Gu Y, Qiao B. Alternatives to phosgene and carbon monoxide: synthesis of symmetric urea derivatives with carbon dioxide in ionic liquids. *Angew Chem-Int Edit*. 2003;42(28):3257–60.
9. Marković S, Marković Z, Begović N, Manojlović N. Mechanism of the Kolbe–Schmitt reaction with lithium and sodium phenoxides. *Russ J Phys Chem A*. 2007;81(9):1392–7.
10. Lu X-B, Darensbourg DJ. Cobalt catalysts for the coupling of CO₂ and epoxides to provide polycarbonates and cyclic carbonates. *Chem Soc Rev*. 2012;41(4):1462–84.
11. Sujith S, Min JK, Seong JE, Na SJ, Lee BY. A highly active and recyclable catalytic system for CO₂/propylene oxide copolymerization. *Angew Chem-Int Edit*. 2008;47(38):7306–9.
12. Darensbourg DJ. Making plastics from carbon dioxide: salen metal complexes as catalysts for the production of polycarbonates from epoxides and CO₂. *Chem Rev* 2007;107(6):2388–410.
13. Nakano K, Kamada T, Nozaki K. Selective formation of polycarbonate over cyclic carbonate: copolymerization of epoxides with carbon dioxide catalyzed by a cobalt(III) complex with a piperidinium end-capping arm. *Angew Chem-Int Edit*. 2006;45(43):7274–7.
14. North M, Pasquale R, Young C. Synthesis of cyclic carbonates from epoxides and CO₂. *Green Chem*. 2010;12(9):1514–39.
15. Decortes A, Castilla AM, Kleij AW. Salen-complex-mediated formation of cyclic carbonates by cycloaddition of CO₂ to epoxides. *Angew Chem-Int Edit*. 2010;49(51):9822–37.
16. Luo J and Larrosa I. C–H carboxylation of aromatic compounds through CO₂ fixation. *ChemSusChem*. 2017;10(17):3317–32.
17. Kudo K, Shima M, Kume Y, Ikoma F, Mori S, Sugita N. Carboxylation of cesium 2-naphthoate in the alkali metal molten salts of carbonate and formate with CO₂ under high pressure. *J Jpn Pet Inst*. 1995;38(1):40–47.
18. Zhang Y, Cen J, Xiong W, Qi C, Jiang H. CO₂: C1 synthon in carboxylation reactions. *Prog Chem*. 2018;30(5):547–63.
19. Dabral S and Schaub T. The use of carbon dioxide (CO₂) as a building block in organic synthesis from an industrial perspective. *Adv Synth Catal*. 2019;361(2):223–46.
20. Ma J, Sun N, Zhang X, Zhao N, Xiao F, Wei W, et al. A short review of catalysis for CO₂ conversion. *Catal Today*. 2009;148(3):221–31.
21. Centi G, Perathoner S. Opportunities and prospects in the chemical recycling of carbon dioxide to fuels. *Catal Today*. 2009;148(3):191–205.
22. Olah GA. Towards oil independence through renewable methanol chemistry. *Angew Chem-Int Edit*. 2013;52(1):104–7.
23. Behrens M, Studt F, Kasatkin I, Kühl S, Hävecker M, Abild-Pedersen F, et al. The active site of methanol synthesis over Cu/ZnO/Al₂O₃ industrial catalysts. *Science*. 2012;336(6083):893–7.
24. Kuld S, Thorhaug M, Falsig H, Elkjær Christian F, Helveg S, Chorkendorff I, et al. Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. *Science*. 2016;352(6288):969–74.
25. Studt F, Behrens M, Kunkes EL, Thomas N, Zander S, Tarasov A, et al. The mechanism of CO and CO₂ hydrogenation to methanol over Cu-based catalysts. *ChemCatChem*. 2015;7(7):1105–11.
26. Rodriguez JA, Liu P, Stacchiola DJ, Senanayake SD, White MG, Chen JGG. Hydrogenation of CO₂ to methanol: importance of metal-oxide and metal-carbide interfaces in the activation of CO₂. *ACS Catal*. 2015;5(11):6696–706.
27. Behrens M, Studt F, Kasatkin I, Kühl S, Havecker M, Abild-Pedersen F, et al. The active site of methanol synthesis over Cu/ZnO/Al₂O₃ industrial catalysts. *Science*. 2012;336(6083):893–7.
28. Kuld S, Thorhaug M, Falsig H, Elkjaer CF, Helveg S, Chorkendorff I, et al. Quantifying the promotion of Cu catalysts by ZnO for methanol synthesis. *Science*. 2016;352(6288):969–74.
29. Duyar MS, Tsai C, Snider JL, Singh JA, Gallo A, Yoo JS, et al. Highly active molybdenum phosphide catalyst for methanol synthesis from CO and CO₂. *Angew Chem-Int Edit*. 2018;57(46):15045–50.
30. Lachowska M, Skrzypek J, Ga, Mn and Mg promoted copper/zinc/zirconia—catalysts for hydrogenation of carbon dioxide to methanol. *Stud Surf Sci Catal*. 2004;153:173–6.
31. Yang C, Ma Z, Zhao N, Wei W, Hu T, Sun Y. Methanol synthesis from CO₂-rich syngas over a ZrO₂ doped CuZnO catalyst. *Catal Today*. 2006;115(1-4):222–7.
32. Ghenciu AF. Review of fuel processing catalysts for hydrogen production in PEM fuel cell systems. *Curr Opin Solid State Mat Sci*. 2002;6(5):389–99.
33. Tanaka Y, Utaka T, Kikuchi R, Sasaki K, Eguchi K. CO removal from reformed fuel over Cu/ZnO/Al₂O₃ catalysts prepared by impregnation and coprecipitation methods. *Appl Catal A-Gen*. 2003;238(1):11–8.
34. Mignard D and Pritchard C. Processes for the synthesis of liquid fuels from CO₂ and marine energy. *Chem Eng Res Des*. 2006;84(9A):828–36.
35. Du C, Lu P, Tsubaki N. Efficient and new production methods of chemicals and liquid fuels by carbon monoxide hydrogenation. *ACS Omega*. 2020;5(1):49–56.
36. Stelmachowski M, Nowicki L. Fuel from the synthesis gas—the role of process engineering. *Appl Energy*. 2003;74(1):85–93.
37. Mohammadi M, Najafpour GD, Younesi H, Lahijani P, Uzir M H, Mohamed A R. Bioconversion of synthesis gas to second generation biofuels: A review. *Renew Sust Energ Rev*. 2011;15(9):4255–73.
38. van de Loosdrecht J, Niemantsverdriet J. In R. Schlogl editor. Synthesis gas to hydrogen, methanol, and synthetic fuels, Chemical energy storage. Walter de Gruyter, Duitsland; 2012. p. 443–58.
39. Fabien D, Snoussi Y, Itabaiana I, Wojcieszak R. The use of CO₂ in the production of bioplastics for an even greener chemistry. *Sustainability*. 2021;13(20). <https://doi.org/10.3390/su132011278>
40. Maity SK. Opportunities, recent trends and challenges of integrated biorefinery: part I. *Renew Sust Energ Rev*. 2015;43:1427–45.

41. Quesada J, Arreola-Sánchez R, Faba L, Díaz E, Rentería-Tapia VM, Ordóñez S. Effect of Au nanoparticles on the activity of TiO₂ for ethanol upgrading reactions. *Appl Catal A-Gen.* 2018;551:23–33.
42. Steinbach D, Kruse A, Sauer J. Pretreatment technologies of lignocellulosic biomass in water in view of furfural and 5-hydroxymethylfurfural production—a review. *Biomass Convers Biorefinery.* 2017;7(2):247–74.
43. Wei W, Sun YH, Wen X, Sun NN. Opportunities and challenges of carbon dioxide utilization as a resource. *Chem Ind Eng Prog.* 2011;30(1):216–24.
44. Zhang Z, Zhou M, Sun J, Fang X. Carboxylative utilization of carbon dioxide. *Chem Ind Eng Prog.* 2019;38(1):236–50.
45. Correa Aand Martin R. Metal-catalyzed carboxylation of organometallic reagents with carbon dioxide. *Angew Chem-Int Edit.* 2009;48(34):6201–4.
46. Cassar L, Chiusoli G, Guerrieri F. Synthesis of carboxylic acids and esters by carbonylation reactions at atmospheric pressure using transition metal catalysts. *Synthesis.* 1973;1973(09):509–23.
47. Souma Y, Tsumori N, Willner H, Xu Q, Mori H, Morisaki Y. Carbonylation of hydrocarbons and alcohols by cationic metal carbonyl catalysts. *J Mol Catal A-Chem.* 2002;189(1):67–77.
48. Yan S-S, Fu Q, Liao L-L, Sun G-Q, Ye J-H, Gong L, *et al.* Transition metal-catalyzed carboxylation of unsaturated substrates with CO₂. *Coord Chem Rev.* 2018;374:439–63.
49. Zhang Land Hou Z. Transition metal promoted carboxylation of unsaturated substrates with carbon dioxide. *Curr Opin Green Sustain Chem.* 2017;3:17–21.
50. Saini S, Prajapati PK, Jain SL. Transition metal-catalyzed carboxylation of olefins with carbon dioxide: a comprehensive review. *Catal Rev-Sci Eng.* 2020;64(3):631–637. <https://doi.org/10.1080/01614940.2020.1831757>.
51. Ohishi T, Nishiura M, Hou Z. Carboxylation of organoboronic esters catalyzed by N-heterocyclic carbene copper(I) complexes. *Angew Chem Int Edit.* 2008;47(31):5792–5.
52. Saito S, Nakagawa S, Koizumi T, Hirayama K, Yamamoto Y. Nickel-mediated regio- and chemoselective carboxylation of alkynes in the presence of carbon dioxide. *J Org Chem* 1999;64(11):3975–8.
53. Aoki M, Kaneko M, Izumi S, Ukai K, Iwasawa N. Bidentate amidine ligands for nickel(0)-mediated coupling of carbon dioxide with unsaturated hydrocarbons. *Chem Commun* 2004;(22):2568–9. <https://doi.org/10.1039/B411802B>
54. Zhang X, Zhang WZ, Shi LL, Guo CX, Zhang LL, Lu XB. Silver(I)-catalyzed carboxylation of arylboronic esters with CO₂. *Chem Commun* 2012;48(50):6292–4.
55. Kuge K, Luo Y, Fujita Y, Mori Y, Onodera G, Kimura M. Copper-catalyzed stereodefined construction of acrylic acid derivatives from terminal alkynes via CO₂ insertion. *Org Lett.* 2017;19(4):854–7.
56. Kolbe H. Ueber synthese der salicylsäure. *Ann Chem Pharm.* 1860;113(1):125–7.
57. Schmitt R. Beitrag zur kenntniss der kolbe'schen salicylsäure synthese. *J für Praktische Chemie.* 1885;31(1):397–411.
58. Hoberg H, Schaefer D. Nickel(0)-induzierte c-c-verknüpfung zwischen alkenen und kohlendioxid. *J Organomet Chem* 1982;236(1):C28–30.
59. Yu B, Diao Z-F, Guo C-X, He L-N. Carboxylation of olefins/alkynes with CO₂ to industrially relevant acrylic acid derivatives. *J CO₂ Util.* 2013;1:60–68.
60. Lari GM, Pastore G, Haus M, Ding Y, Papadokonstantakis S, Mondelli C, *et al.* Environmental and economical perspectives of a glycerol biorefinery. *Energy Environ Sci.* 2018;11(5):1012–29.
61. Hoberg H, Jenni K, Angermund K, Krüger C. CC-Linkages of ethene with CO₂ on an iron(0) complex—synthesis and crystal structure analysis of [(PEt₃)₂Fe(C₂H₄)₂]. *Angew Chem-Int Edit.* 1987;26(2):153–5.
62. Graham DC, Mitchell C, Bruce MI, Metha GF, Bowie JH, Buntine M A. Production of acrylic acid through nickel-mediated coupling of ethylene and carbon dioxide—a DFT study. *Organometallics.* 2007;26(27):6784–92.
63. Hoberg H, Schaefer D. Sorbinsäure aus piperylen und CO₂ durch cC-Verknüpfung an nickel(0). *J Organomet Chem.* 1983;255(1):C15–7.
64. Alvarez R, Carmona E, Cole-Hamilton DJ, Galindo A, Gutierrez-Puebla E, Monge A, *et al.* Formation of acrylic acid derivatives from the reaction of carbon dioxide with ethylene complexes of molybdenum and tungsten. *J Am Chem Soc.* 1985;107(19):5529–31.
65. Alvarez R, Carmona E, Galindo A, Gutierrez E, Marin JM, Monge A, *et al.* Formation of carboxylate complexes from the reactions of carbon dioxide with ethylene complexes of molybdenum and tungsten. X-ray and neutron diffraction studies. *Organometallics.* 1989;8(10):2430–9.
66. Galindo A, Pastor A, Perez PJ, Carmona E. Bis (ethylene) complexes of molybdenum and tungsten and their reactivity toward carbon dioxide. New examples of acrylate formation by coupling of ethylene and carbon dioxide. *Organometallics.* 1993;12(11):4443–51.
67. Fischer R, Langer J, Malassa A, Walther D, Görls H, Vaughan G. A key step in the formation of acrylic acid from CO₂ and ethylene: the transformation of a nickelalactone into a nickel-acrylate complex. *Chem Commun* 2006;23:2510–2. <https://doi.org/10.1039/B603540J>
68. Aresta M, Pastore C, Giannoccaro P, Kovács G, Dibenedetto A, Pápai I. Evidence for spontaneous release of acrylates from a transition-metal complex upon coupling ethene or propene with a carboxylic moiety or CO₂. *Chem-Eur J.* 2007;13(32):9028–34.
69. Bruckmeier C, Lehenmeier M W, Reichardt R, Vagin S, Rieger B. Formation of methyl acrylate from CO₂ and ethylene via methylation of nickelalactones. *Organometallics.* 2010;29(10):2199–202.
70. Lejkowski ML, Lindner R, Kageyama T, Bódizs GÉ, Plessow PN, Müller IB, *et al.* The first catalytic synthesis of an acrylate from CO₂ and an alkene—a rational approach. *Chem-Eur J.* 2012;18(44):14017–25.
71. Huguet N, Jevtovikj I, Gordillo A, Lejkowski ML, Lindner R, Bru M, *et al.* Nickel-catalyzed direct carboxylation of olefins with CO₂: one-pot synthesis of α,β -unsaturated carboxylic acid salts. *Chem-Eur J.* 2014;20(51):16858–62.
72. Hendriksen C, Pidko EA, Yang G, Schäffner B, Vogt D. Catalytic formation of acrylate from carbon dioxide and ethene. *Chem-Eur J.* 2014;20(38):12037–40.
73. Hollering M, Dutta B, Kühn FE. Transition metal mediated coupling of carbon dioxide and ethene to acrylic acid/acrylates. *Coord Chem Rev.* 2016;309:51–67.

74. Burkart MD, Hazari N, Tway CL, Zeitler EL. Opportunities and challenges for catalysis in carbon dioxide utilization. *ACS Catal.* 2019;9(9):7937–56.
75. Wang D, Zhong S. Study on CuPMo/TiO₂ catalyst for direct synthesis of methacrylic acid from propylene and carbon dioxide. *Chin J Catal.* 2003;24(9):705–10.
76. Wang R, Yang F. A catalytic and application for carbon dioxide into methylacrylic acid. China patent 200910255801. 2009.
77. Rajagopalan P, Kühnle M, Polyakov M, Müller K, Arlt W, Kruse D, et al. Methacrylic acid by carboxylation of propene with CO₂ over POM catalysts — reality or wishful thinking? *Catal Commun.* 2014;48:19–23.
78. Ren Q, Wu N, Cai Y, Fang J. DFT study of the mechanisms of iron-catalyzed regioselective synthesis of α -aryl carboxylic acids from styrene derivatives and CO₂. *Organometallics.* 2016;35(23):3932–8.
79. Shao P, Wang S, Chen C, Xi C. Cp₂TiCl₂-Catalyzed regioselective hydrocarboxylation of alkenes with CO₂. *Org Lett.* 2016;18(9):2050–3.
80. Correa A, Martín R. Palladium-catalyzed direct carboxylation of aryl bromides with carbon dioxide. *J Am Chem Soc.* 2009;131(44):15974–5.
81. Tran-Vu H, Daugulis O. Copper-catalyzed carboxylation of aryl iodides with carbon dioxide. *ACS Catal.* 2013;3(10):2417–20.
82. Fujihara T, Nogi K, Xu T, Terao J, Tsuji Y. Nickel-catalyzed carboxylation of aryl and vinyl chlorides employing carbon dioxide. *J Am Chem Soc.* 2012;134(22):9106–9.
83. Tanaka S, Watanabe K, Tanaka Y, Hattori T. EtAlCl₂/2,6-disubstituted pyridine-mediated carboxylation of alkenes with carbon dioxide. *Org Lett.* 2016;18(11):2576–9.
84. Engel RV, Alsaiani R, Nowicka E, Pattisson S, Miedziak PJ, Kondrat SA, et al. Oxidative carboxylation of 1-decene to 1,2-decylene carbonate. *Top Catal.* 2018;61(5):509–18.
85. Williams CM, Johnson JB, Rovis T. Nickel-catalyzed reductive carboxylation of styrenes using CO₂. *J Am Chem Soc.* 2008;130(45):14936–7.
86. Aresta M, Quaranta E, Tommasi I. The role of metal centres in reduction and carboxylation reactions utilizing carbon dioxide. *New J Chem.* 1994;18(1):133–142.
87. Mason MG. A study of the interaction of carbon dioxide and carbon disulfide with low valent transition metal complexes. Northwestern University; 1982.
88. Takaya J, Iwasawa N. Hydrocarboxylation of allenes with CO₂ catalyzed by silyl pincer-type palladium complex. *J Am Chem Soc.* 2008;130(46):15254–5.
89. Albano P, Aresta M. Some catalytic properties of Rh(diphos)_(η -BPh₄). *J Organomet Chem.* 1980;190(3):243–6.
90. Döhring A, Jolly PW. The palladium catalyzed reaction of carbon dioxide with allene. *Tetrahedron Lett.* 1980;21(32):3021–4.
91. Tsuda T, Morikawa S, Sumiya R, Saegusa T. Nickel(0)-catalyzed cycloaddition of diynes and carbon dioxide to give bicyclic α -pyrones. *J Org Chem.* 1988;53(14):3140–5.
92. Hoberg H. Carbon dioxide as a source of carbon. *NATO ASI Series C.* 1987;206:275.
93. Hoberg H, Schaefer D, Burkhart G, Krüger C, Romão MJ. Nickel(0)-induzierte C-C-verknüpfung zwischen kohlendioxid und alkinen sowie alkenen. *J Organomet Chem.* 1984;266(2):203–24.
94. Burkhart G, Hoberg H. Oxanickelacyclopentene derivatives from nickel(0), carbon dioxide, and alkynes. *Angew Chem-Int Edit.* 1982;21(1):76–76.
95. Hoberg H, Schaefer D. Modellkomplexe des nickels für die [2+2+2]-cycloaddition von alkinen mit kohlendioxid. *J Organomet Chem.* 1982;238(4):383–7.
96. Albano P, Aresta M. Some catalytic properties of Rh(diphos)_(η -BPh₄). *J Organomet Chem.* 1980;190:243–6.
97. Polyzos A, O'Brien M, Petersen TP, Baxendale IR, Ley S V. The continuous-flow synthesis of carboxylic acids using CO₂ in a tube-in-tube gas permeable membrane reactor. *Angew Chem-Int Edit.* 2011;50(5):1190–3.
98. van Gool J J F, van den Broek S A M W, Ripken RM, Nieuwland PJ, Koch K, Rutjes FPJT. Highly controlled gas/liquid processes in a continuous lab-scale device. *Chem Eng Technol.* 2013;36(6):1042–6.
99. Nagaki A, Takahashi Y, Yoshida J-i. Extremely fast gas/liquid reactions in flow microreactors: carboxylation of short-lived organolithiums. *Chem-Eur J.* 2014;20(26):7931–4.
100. Pieber B, Glasnov T, Kappe CO. Flash carboxylation: fast lithiation-carboxylation sequence at room temperature in continuous flow. *RSC Adv.* 2014;4(26):13430–3.
101. Seo H, Nguyen LV, Jamison TF. Using carbon dioxide as a building block in continuous flow synthesis. *Adv Synth Catal.* 2019;361(2):247–64.
102. Eerhart AJJE, Faaij APC, Patel MK. Replacing fossil based PET with biobased PEF; process analysis, energy and GHG balance. *Energy Environ Sci.* 2012;5(4):6407–22.
103. Araujo CF, Nolasco MM, Ribeiro-Claro PJA, Rudić S, Silvestre AJD, Vaz PD, et al. Inside PEF: chain conformation and dynamics in crystalline and amorphous domains. *Macromolecules.* 2018;51(9):3515–26.
104. Avantium, Avantium annual report. <https://www.avantium.com>. Accessed 23 May 2022.
105. Pandey S, Dumont M-J, Orsat V, Rodrigue D. Biobased 2,5-furandicarboxylic acid (FDCA) and its emerging copolyesters' properties for packaging applications. *Eur Polym J.* 2021;160:110778.
106. Casanova O, Iborra S, Corma A. Biomass into chemicals: aerobic oxidation of 5-hydroxymethyl-2-furfural into 2,5-furandicarboxylic acid with gold nanoparticle catalysts. *ChemSusChem.* 2009;2(12):1138–44.
107. Miao Z, Zhang Y, Pan X, Wu T, Zhang B, Li J, et al. Superior catalytic performance of Ce_{1-x}BixO_{2- δ} solid solution and Au/Ce_{1-x}BixO_{2- δ} for 5-hydroxymethylfurfural conversion in alkaline aqueous solution. *Catal Sci Technol.* 2015;5(2):1314–22.
108. Davis SE, Houk LR, Tamargo EC, Datsy AK, Davis RJ. Oxidation of 5-hydroxymethylfurfural over supported Pt, Pd and Au catalysts. *Catal Today.* 2011;160(1):55–60.
109. Wojcieszak R, Itabaiana I. Engineering the future: perspectives in the 2,5-furandicarboxylic acid synthesis. *Catal Today.* 2020;354:211–7.
110. Faba L, Díaz E, Ordóñez S. From biomass to second generation biofuels. *Madera Bosques.* 2014;20(3):11–24.
111. Pan T, Deng J, Xu Q, Zuo Y, Guo Q-X, Fu Y. Catalytic conversion of furfural into a 2,5-furandicarboxylic acid-based polyester with total carbon utilization. *ChemSusChem.* 2013;6(1):47–50.

112. Patton J W, Son M O. The synthesis of naphthalene-2, 3-dicarboxylic acid by the henkel process. *J Org Chem* 1965;30(8):2869–70.
113. Furuyama S. An investigation of the mechanism of the henkel reaction by deuterium and carbon-14 isotope techniques. *Bull Chem Soc Jpn.* 1967;40(5):1212–7.
114. Ogata Y, Nakajima K. Kinetics and mechanism of the rearrangement of potassium phthalate. *Tetrahedron.* 1965;21(9):2393–400.
115. Ratusky J. Transcarboxylation reactions of salts of organic acids. 14. Reactions of salts of deuterated benzene-carboxylic acids. *J Label Compd Radiopharm.* 1970;6(2):124.
116. Fujishiro K, Mitamura S. The zinc(II)-catalyzed henkel reaction of dipotassium 1,8-naphthalenedicarboxylate in a dispersion medium. *Bull Chem Soc Jpn.* 1989;62(3):786–90.
117. Thiyagarajan S, Pukin A, Van Haveren J, Lutz M, Van Es D S. Concurrent formation of furan-2,5- and furan-2,4-dicarboxylic acid: unexpected aspects of the Henkel reaction. *RSC Adv.* 2013;3(36):15678–86.
118. Zhang S, Lan J, Chen Z, Yin G, Li G. Catalytic synthesis of 2,5-furandicarboxylic acid from furoic acid: transformation from C5 Platform to C6 derivatives in biomass utilizations. *ACS Sustain Chem Eng.* 2017;5(10):9360–9.
119. Olah GA, Török B, Joschek JP, Bucsi I, Esteves PM, Rasul G, *et al.* Efficient chemoselective carboxylation of aromatics to arylcarboxylic acids with a superelectrophilically activated carbon dioxide–Al₂Cl₆/Al system. *J Am Chem Soc.* 2002;124(38):11379–91.
120. Banerjee A, Dick GR, Yoshino T, Kanan MW. Carbon dioxide utilization via carbonate-promoted C–H carboxylation. *Nature.* 2016;531(7593):215–9.
121. Kolbe H, Lautemann E. Ueber die constitution und basicität der salicylsäure. *Ann Chem Pharm.* 1860;115(2):157–206.
122. Gibson JA, Kynaston W, Lindsey AS. The infrared spectra of some pyridones and quinolones and their behaviour in the Kolbe–Schmitt reaction. *J Chem Soc.* 1955;(0):4340–4. <https://doi.org/10.1039/JR9550004340>
123. Dingyi Y, Yugen Z. The direct carboxylation of terminal alkynes with carbon dioxide. *Green Chem.* 2011;13(5):1275–9.
124. Kudo K, Ikoma F, Mori S, Sugita N. Synthesis of glutaconic acid salt from cesium 3-butenolate with carbon dioxide. *J Jpn Pet Inst.* 1995;38(1):48–51.
125. Vechorkin O, Hirt N, Hu X. Carbon dioxide as the C1 source for direct C–H functionalization of aromatic heterocycles. *Org Lett.* 2010;12(15):3567–9.
126. Nocito F, Ditaranto N, Dibenedetto A. Valorization of C5 polyols by direct carboxylation to FDCA: synthesis and characterization of a key intermediate and role of carbon dioxide. *J CO₂ Util.* 2019;32:170–7.
127. Drault F, Snoussi Y, Paul S, Itabaiana I Jr, Wojcieszak R. Recent advances in carboxylation of furoic acid into 2,5-furandicarboxylic acid: pathways towards bio-based polymers. *ChemSusChem.* 2020;13(19): 5164–72.
128. Dick GR, Frankhouser AD, Banerjee A, Kanan MW. A scalable carboxylation route to furan-2,5-dicarboxylic acid. *Green Chem.* 2017;19(13):2966–72.
129. Zhou H, Xu H, Wang X, Liu Y. Convergent production of 2,5-furandicarboxylic acid from biomass and CO₂. *Green Chem.* 2019;21(11):2923–7.
130. Wang Y-G, Guo C-Y, Shen J, Sun Y-Q, Niu Y-X, Li P, *et al.* A sustainable and green route to furan-2,5-dicarboxylic acid by direct carboxylation of 2-furoic acid and CO₂. *J CO₂ Util.* 2021;48:101524.
131. Cajnko MM, Novak U, Grilc M, Likozar B. Enzymatic conversion reactions of 5-hydroxymethylfurfural (HMF) to bio-based 2,5-diformylfuran (DFF) and 2,5-furandicarboxylic acid (FDCA) with air: mechanisms, pathways and synthesis selectivity. *Biotechnol Biofuels.* 2020;13(1):66.
132. Lupa B, Lyon D, Gibbs MD, Reeves RA, Wiegel J. Distribution of genes encoding the microbial non-oxidative reversible hydroxyarylic acid decarboxylases/phenol carboxylases. *Genomics.* 2005;86(3):342–51.
133. Wierckx N, Koopman F, Bandounas L, De Winde JH, Ruijsenaars HJ. Isolation and characterization of *Cupriavidus basilensis* HMF14 for biological removal of inhibitors from lignocellulosic hydrolysate. *Microb Biotechnol.* 2010;3(3):336–43.
134. Payne KAP, Marshall SA, Fisher K, Cliff MJ, Cannas DM, Yan C, *et al.* Enzymatic carboxylation of 2-furoic acid yields 2,5-furandicarboxylic acid (FDCA). *ACS Catal.* 2019;9(4):2854–65.
135. Kawanabe K, Aono R, Kino K. 2,5-Furandicarboxylic acid production from furfural by sequential biocatalytic reactions. *J Biosci Bioeng.* 2021;132(1):18–24.



Laura Faba

Laura Faba received her PhD in Chemical Engineering in January 2013. She is an Associate Professor at the Department of Chemical and Environmental Engineering of the University of Oviedo. Her research interests focus on the development of sustainable catalytic processes to valorise waste biomass.



Salvador Ordóñez

Salvador Ordóñez is Full Professor (Chem. & Environ. Engineering) at the University of Oviedo, and Group Leader of the Catalysis, Reactors and Control Research Group. His research interests are focused in the field of heterogeneous catalysis, advanced chemical reactors, hydrogen storage and biomass upgrading.



Paula Rapado

Paula Rapado is Chemical Engineer (M.Sc.) and PhD student at University of Oviedo (Chemical Engineering), belonging to the Catalysis, Reactors and Control Research group. Her research interests are focused on the bioplatfrom molecules synthesis and upgrading via partial oxidation and carboxylation reactions.