Chinese Chemical Letters 35 (2024) 109394

Contents lists available at ScienceDirect

Chinese Chemical Letters

journal homepage: www.elsevier.com/locate/cclet

Valorization of carbon dioxide with alcohols

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ARTICLE INFO

Article history:
Received 12 October 2023
Revised 30 November 2023
Accepted 6 December 2023
Available online 11 December 2023

Keywords:
Carboxylation
Carbon dioxide
Alcohol
Carboxylic acid
Transition metal catalysis

ABSTRACT

Utilizing CO_2 for the production of bulky and valuable chemicals presents an attractive solution to address environmental and fossil energy crises. Among the various approaches, direct carboxylation of alcohols with CO_2 stands out as an eco-friendly process capable of efficiently producing carboxylic acids in a sustainable manner. However, the high dissociation energy of the C–O bond poses a significant challenge in this process. Over the past few decades, several strategies have been developed to activate alcohols and establish efficient catalytic systems for carboxylation with CO_2. Nevertheless, the sporadic nature of reported approaches makes it difficult to determine the most effective one. This perspective aims to provide an overview of the current state-of-the-art catalytic protocols for carboxylating alcohols with CO_2, encompassing esterification, halogenation, and photocatalysis, while considering their respective advantages and limitations. We aim to discern the most promising avenues for future development in this field. The insights presented in this perspective will contribute to the advancement of efficient and sustainable carboxylation methods using CO_2, leading to the production of valuable chemicals in future.

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1. Introduction

Carbon dioxide (CO_2) is a widely recognized greenhouse gas that has significant implications for global climate change and the environment due to its continuous release from the extensive use of fossil fuels. To address this issue, the capture and utilization of excessive CO_2, as a cheap, abundant, and renewable C1 source has gained considerable attention in recent years. This emerging strategy to convert CO_2 into valuable fine and bulky chemicals, including methanol, formic acid, methane, carbonates, amides, and carboxylic acids [1–5]. Despite its potential, the current utilization of CO_2 remains limited. Given the approximate global emission of 30Gt CO_2 per year, only a small amount of it is currently utilized and transformed into urea (200 Mt/year) [6]. Hence, there is a pressing need to develop efficient and novel approaches for its valorization, possessing significant challenges in the current stage.

Carboxylic acids play a vital role in various industries such as cosmetics, plastics, dyes, pesticides, and pharmaceuticals due to their diverse applications [7–9]. Conventional methods for their synthesis, as shown in Fig. 1a, typically involve oxidation reactions. In contrast, the transition metal-catalyzed carboxylation of nucleophilic reagents with CO_2 offers an alternative approach to obtain C1-elongated carboxylic acids. This method offers several advantages, including the avoidance of excessive use of oxidizing agents and the consequent generation of pollutants. Moreover, it enables the convenient synthesis of a diverse library of products [10].

In contrast to the extensively studied transition metal-catalyzed carboxylation of active olefins [11–14], organic halides [15], and esters [16,17], which are typically derived from alcohols (Fig. 1b), the direct carboxylation of alcohols with CO_2 represents a straightforward and more sustainable approach. This method constitutes particularly attractive when utilizing abundant and cost-effective bioalcohols. For instance, propylene, which costs approximately 2.48 \$/kg, and glycerin, which costs only 0.435 \$/kg, can serve as readily available starting materials [18–20].

However, the exploration of direct carboxylation of alcohols with CO_2 is still in its early stage, primarily due to several challenges. Firstly, the activation energy of CO_2 is relatively high, with strong O=C=O bonds (C=O bond strength of 532 kJ/mol) [21]. This poses a significant hurdle for efficient CO_2 activation. Secondly, the dissociation energy of the C–O bond in alcohols is also high, and hydroxide (–OH) functions as a poor leaving group [22,23]. Additionally, the presence of unprotected –OH groups in alcohols makes them highly reactive [24], leading to the formation of various side products through etherification, elimination, or

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https://doi.org/10.1016/j.cclet.2023.109394
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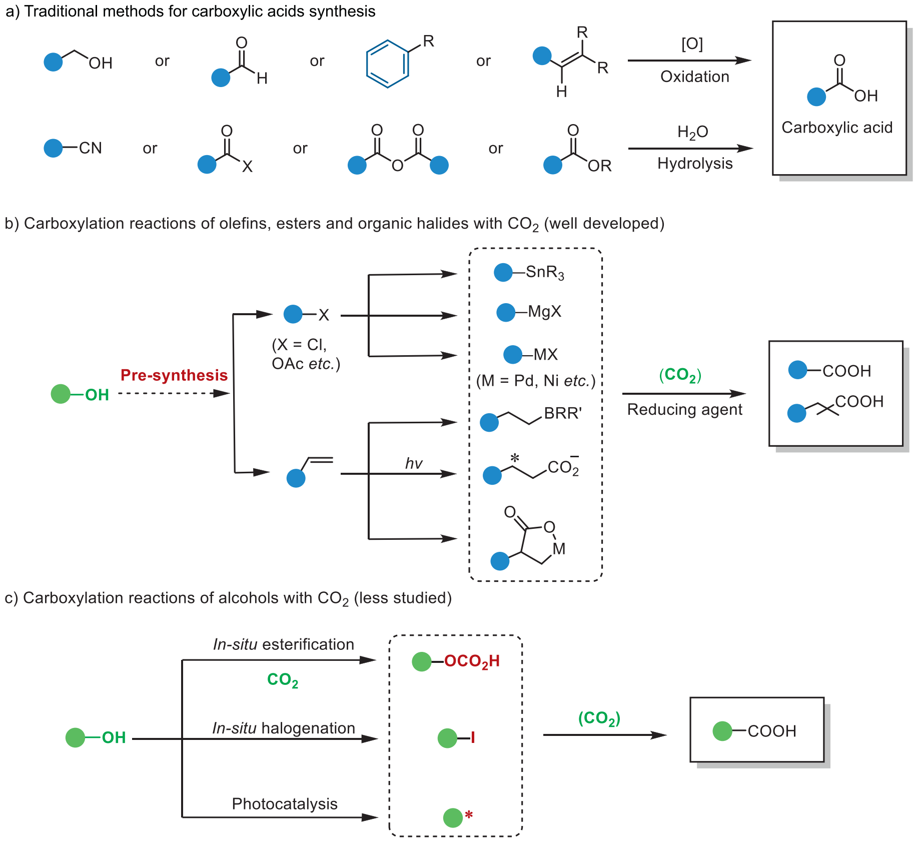


Fig. 1. Carboxylic acids synthesis. (a) Traditional methods for carboxylic acids synthesis. (b) Carboxylation reactions of olefins, esters and organic halides with CO_2. (c) Carboxylation reactions of alcohols with CO_2.

substitution reactions. Therefore, the development of suitable strategies that can selectively activate the C–O bond and enable efficient carbonyl insertion is essential for the direct synthesis of carboxylic acids from alcohols.

Currently, three main strategies have been identified to address the challenges associated with the carboxylation of alcohols with CO_2, taking into account the unique activation requirements of different alcohols. These strategies include: (a) *in-situ* esterification, (b) *in-situ* halogenation, and (c) photocatalysis (Fig. 1c). In this perspective, we discuss recent advancements in the carboxylation of alcohols with CO_2 mainly based on these activation strategies. Furthermore, we provide an outlook on potential future trends in this field.

2. *In-situ* esterification strategy

Esters are widely recognized as one kind of good leaving groups compared to hydroxyl (–OH) groups, and they have been extensively used in organic synthesis [25]. Martin and coworkers have developed several methods for the carboxylation of alcohol esters with CO_2 using Ni or Co catalysts in the presence of appropriate reductants [16,17]. Both acetates and pivalates were successfully converted into the desired carboxylic acids (Fig. 1b). Furthermore, Martin and Mei achieved the direct synthesis of carboxylic acids from allylic alcohols *via* regioselective catalytic carboxylation without the need to pre-synthesize alcohol esters (Fig. 2) [26–29]. In this process, CO_2 not only acts as the C1 source, but also activates the –OH group through the formation of a hydrogen carbonate intermediate [28]. This activation occurs through a "proton-relay" process facilitated by hydrogen bonding interactions between the alcohols and residual moisture. These interactions promote Ni-catalyzed C–O bond cleavage, which is the rate-determining step [29]. The use of specific ligands allows for precise modulation of the regiodivergence of the reactions, leading to the selective production of α-branched or linear carboxylic acids. However, it should be noted that these newly developed protocols are only applicable to allylic and propargylic alcohols and require a large excess of metallic (Zn, Mn) reductants.

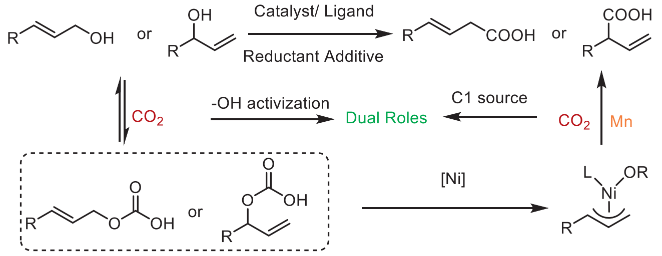


Fig. 2. Carboxylation of allylic and propargylic alcohols with CO_2 using the *in-situ* esterification strategy.

3. *In-situ* halogenation strategy

The carboxylation of simple small-molecule alcohols, such as methanol and cyclohexanol, poses a significant challenge and has been identified as one of bottlenecks in expanding the industrial application of CO_2 utilization. To address this challenge, Han and colleagues developed an *in-situ* halogenation strategy that effectively activates alcohols, resulting in the successful synthesis of valuable carboxylic acids [4]. This transformation involves the use of lithium halides to facilitate the *in-situ* halogenation process, known as hydrocarboxylation, which can be applied not only to methanol but also to other higher alcohols.

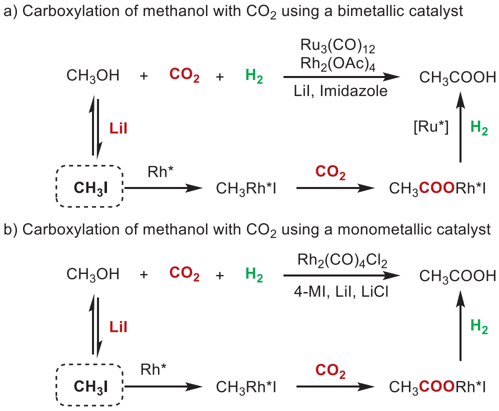


Fig. 3. Carboxylation reactions of methanol with CO_2 and H_2 using the *in-situ* halogenation strategy.

In 2016, Han's group achieved a significant milestone by successfully conducting the hydrocarboxylation of methanol with CO_2 and H_2 using a Ru-Rh bimetallic catalyst, which selectively produced acetic acid (Fig. 3a) [30]. The process involved several key steps. Initially, methanol underwent *in-situ* conversion into CH_3I in the presence of LiI. The resulting CH_3I then underwent oxidative addition with an active Rh species (RhL), forming CH_3-RhL-I. Subsequent insertion of CO_2 into the CH_3-Rh bond yielded the intermediate CH_3COO-RhL-I. Through reductive elimination in the presence of H_2, the active Ru-L species facilitated the production of acetic acid. LiI was identified as the optimal promoter for this transformation due to its strong Lewis acidity, appropriate Li-ion size, and the high nucleophilicity of the iodide anion. Additionally, imidazole was found to influence the selectivity by facilitating CO_2 insertion while inhibiting CO formation.

Subsequently, the same group discovered a more efficient catalytic system by utilizing a monometallic catalyst $Rh_2(CO)_4Cl_2$ in the presence of 4-methylimidazole (4-MI), LiCl, and LiI (Fig. 3b) [31]. This new catalytic system exhibited significantly improved turnover frequency (TOF) and yield compared to the previous one (26.2 h^{-1} and 81.8% *vs.* 10.1 h^{-1} and 23.2%) at 180 °C. Control experiments confirmed that the reaction proceeded *via* direct CO_2 insertion rather than the CO pathway. The addition of LiCl not only enhanced the catalytic activity and stability of the catalyst but also reduced the amount of corrosive LiI, making it more suitable for potential industrial applications.

Besides the synthesis of acetic acid, Han, Qian, and other colleagues have recently introduced two additional catalytic protocols for the hydrocarboxylation of alcohols with CO_2 and H_2 to produce higher carboxylic acids (Fig. 4). Building upon their previous monometallic system [32], they combined a Rh catalyst with I_2 in an ionic liquid-water mixture (1-butyl-3-methylimidazolium iodide, Fig. 4a) [33]. At 170 °C, they successfully converted various polyols including glycerol, erythritol, xylitol, and mannitol into C1-elongated carboxylic acids with reasonable yields. Even crude glycerol, a major by-product of the biodiesel industry [34], was compatible with the system, although the yield was slightly lower compared to pure glycerol (76.5% *vs.* 86.4%).

The second protocol involved the use of iridium(III)acetate with LiI as the promoter in acetic acid (Fig. 4b) [35]. Under the optimized reaction conditions, primary, secondary, and tertiary alcohols as well as polyols were well compatible, leading to the formation of various higher carboxylic acids with yields ranging from 7.7% to 59.6%. Very recently, they further successfully extended this strategy to saccharides, including glucose, xylose, fructose, and other analogues [36]. Moderate to good yields of desired carboxylic acids were attained (up to 72%, Fig. 4c). Intermediates including CO, 2,5-dimethyltetrahydrofuran, ketones, olefins, alco-

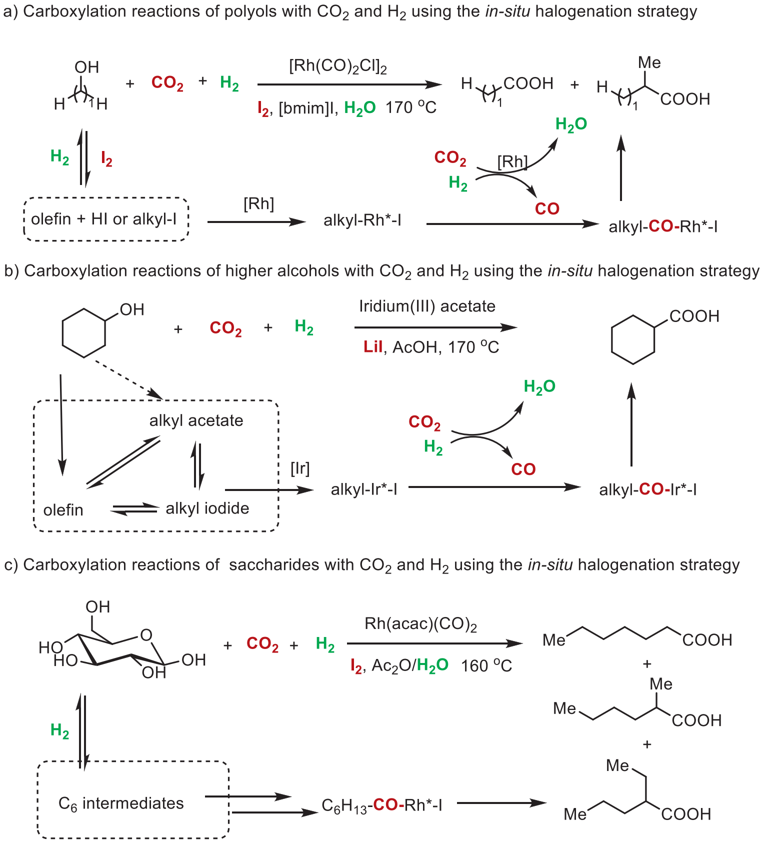
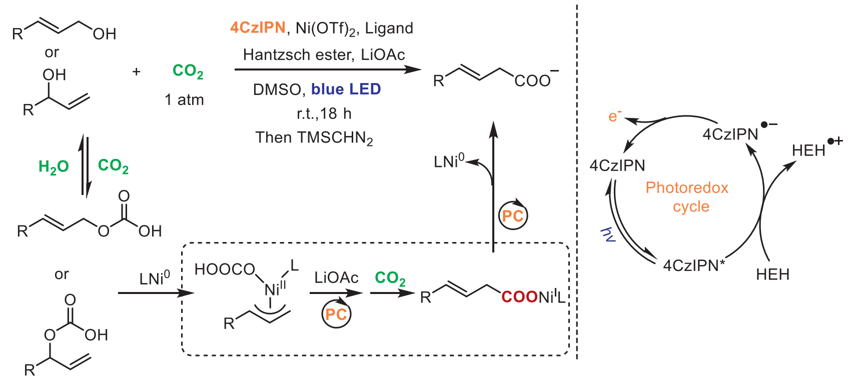
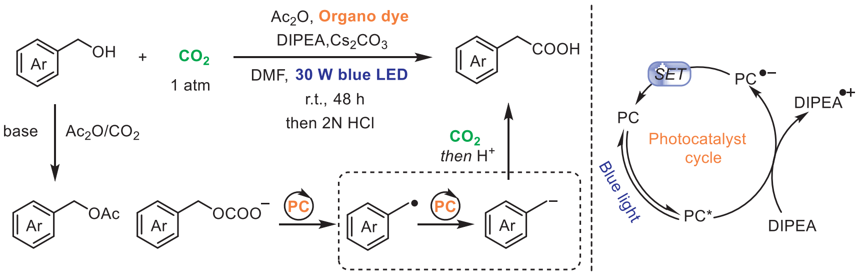


Fig. 4. Carboxylation reactions of alcohols with CO_2 and H_2 using the *in-situ* halogenation strategy.

a) Carboxylation of *a, ß*-unsaturated alcohols with CO_2 using the photocatalysis strategy



b) Carboxylation of activated benzyl alcohols with CO_2 using the photocatalysis strategy



c) Carboxylation of boryl radical activated benzyl alcohols with CO_2 using the photocatalysis strategy

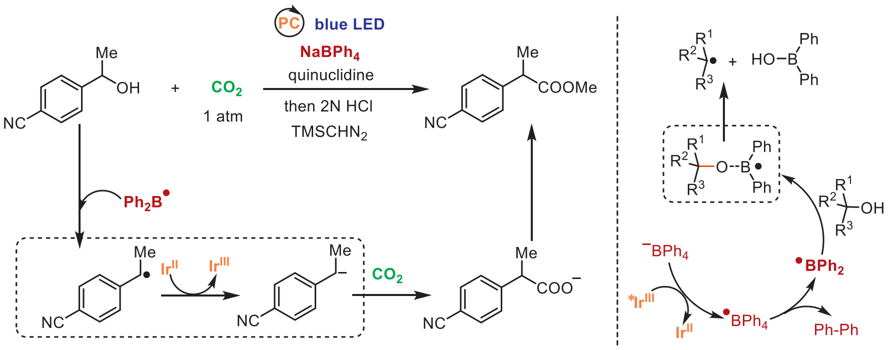


Fig. 5. Carboxylation of α,β-unsaturated alcohols and/or benzyl alcohols with CO_2 using the photocatalysis strategy.

hols, and corresponding acetates were found during the reaction process. These outcomes establish a solid research foundation for valorization of both CO_2 and biomass.

Based on systematic control experiments, similar mechanisms were proposed for both reactions. Initially, the reverse water-gas shift process converted CO_2 and H_2 into CO and water. Simultaneously, the alcohol substrates underwent conversion into olefin and/or alkyl iodide intermediates, which served as potential alkyl reagents. The alkyl groups then underwent oxidative addition with an active metal species (M = Ir or Rh), followed by the insertion of CO generated *in-situ*. This step resulted in the formation of alkyl-CO-M-I intermediates. Subsequently, reductive elimination occurred, leading to the formation of alkyl-CO-I species. Finally, in the presence of water, these species were converted into the corresponding target carboxylic acids.

These halogenation approaches have made significant advancements in the CO_2 chemistry. However, they are still limited by the requirement for high temperatures (170 °C), high pressure (70 bar), and the use of several indispensable additives, which can result in challenging issues such as catalyst deactivation, poor selectivity, and an ambiguous understanding of the catalytic mechanism. Therefore, it is crucial to address these challenges in the future.

4. Photocatalysis strategy

Inspired by photosynthesis in nature, methodologies based on photochemistry have also been developed for the carboxylation of alcohols. A photoredox/nickel dual catalysis approach for the carboxylation of allylic alcohols with CO_2 was successfully developed by Xi *et al.* using photoredox/nickel dual catalysis, producing exclusively linear acids with good *Z*/*E* stereoselectivity (Fig. 5a) [37]. Notably, water readily activates the alcohols with CO_2, leading to the *in-situ* formation of an intermediate allylic hydrogen carbonate, followed by the oxidative addition of CO_2 [28]. This protocol exhibited good tolerance towards a range of aryl and alkyl allylic alcohols, as well as propargylic alcohols, under visible light at room temperature.

In a groundbreaking study reported by Yu and coworkers (Fig. 5b), they utilized organic dyes, such as 2,4,5,6-tetrakis(diphenylamino)-isophthalonitrile (4DPAIPN) or 2,4,6-tris-(diphenylamino)-3,5-difluorobenzonitrile (3DPA2FBN), as photocatalysts to effectively catalyze the conversion of benzyl alcohols into carboxylic acids under visible light at room temperature [38]. After irradiation, a key intermediate, benzylic carbanion, was formed from the benzylic alcohols. The *in-situ* activation by acetic anhydride significantly enhanced the catalytic efficiency.

Subsequently, the carbanion underwent nucleophilic attack on CO_2, followed by protonation, resulting in the desired products. While *in-situ* esterification reactions were involved in both cases (Fig. 5a and b), we are inclined to categorize them as utilizing the photocatalysis strategy since photocatalysts are essential for these transformations. Xia and colleagues further extended the photocatalytic strategy for the carboxylation of benzyl alcohols using sodium tetraphenylborate ($NaBPh_4$) and an Ir-photocatalyst ($Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$) (Fig. 5c) [39]. Under mild visible light photoredox conditions, the neutral diphenyl boryl radical readily bonded to the oxygen atom of the alcohols to achieve *in-situ* activation. The B–O adducts then underwent homolysis of the C–O bond, generating a benzyl radical intermediate, which further transformed into the benzylic carbanion through single electron transfer reduction. Both protocols exhibited excellent compatibility with a wide range of substrates and demonstrated good tolerance towards various functional groups, accommodating primary, secondary, and even tertiary C–O bonds in diverse benzyl alcohols.

5. Conclusion and outlook

Until recently, the carboxylation of alcohols with CO_2 has received limited attention. This perspective aims to provide an overview of this topic and highlight three main strategies for activating the C–O bond.

Unlike the *in-situ* esterification strategy, only limited allylic and benzyl alcohol substances could be transferred into carboxylic acids, the *in-situ* halogenation approach offers attractive methods for carboxylating simple alcohols into various carboxylic acids using clean H_2 instead of metallic reducing agents, which simplifies the work-up process. However, this approach comes with inherent shortcomings, such as the use of corrosive additives, high temperatures and pressures, as well as possible catalyst deactivation. The combination of CO_2 capture and its catalytic conversion may show promise for the future of CO_2 chemistry. Catalysts with CO_2 adsorption capacity, such as porous organometallic polymers [40–42], could potentially lower pressures and inhabit the possible catalyst deactivation. Moreover, the design of suitable ligands through electronic or steric effects may enhance catalyst stability and improve selectivity of the reaction.

As a more sustainable strategy, photocatalysis enables the carboxylation of alcohols with CO_2 under much mild reaction conditions with a wide range of substrates, including allyl and benzyl alcohols. In the case of inactive aliphatic alcohols, sulfides. such as carbon disulfide or dimethyl sulfide could be utilized to achieve satisfactory outcomes [43,44]. Currently, the separation and purification of the resulting mixture are still challenges, developing suitable solid molecular photocatalytic materials, based on carbon nitride [45] and covalent organic frameworks [46], with excellent recycling capabilities, may accelerate the development of valorization of CO_2 with alcohols.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

Financial support from the National Natural Science Foundation of China (No. 22271060), the Department of Chemistry at Fudan University, and Nanjing Forestry University are gratefully acknowledged.

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