



# Editorial Catalytic Carbonylation Reactions

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# 1. Overview

In the last few years, the development of catalytic carbonylation reactions has increased greatly. In fact, carbonylation processes nowadays represent the most direct and efficient method for the installation of the carbonyl group into an organic substrate, using the simplest and readily available carbonyl source, that is carbon monoxide [1]. Aside from gaseous CO, several methods have also been developed in which carbon monoxide is conveniently generated in situ from suitable solid precursors, or that employ CO surrogates, such as formates or carbon dioxide [2].

# 2. Special Issue Contributions

In this Special Issue, important contributions in this exciting field of catalytic processes are reported, which further demonstrate the applicability of carbonylation reactions in the direct synthesis of high value added carbonylated products from simple starting materials. In particular, five papers have been published, three reviews and two original research articles.

# 2.1. Review Contributions

The first review (by Raffaella Mancuso, Nicola Della Ca', Lucia Veltri, Ida Ziccarelli, and Bartolo Gabriele) is an account of the research carried out in Gabriele's group during the last few decades on the use of palladium iodide-based catalysts in carbonylation reactions [3]. The authors have reviewed the achievements in this field using PdI<sub>2</sub> in conjunction with either KI or other ligands (thiourea, in particular) as catalysts. These have been demonstrated to be able to realize several different types of carbonylation reactions, including substitutive, additive, and oxidative carbonylation reactions. Particularly important results have been obtained in the oxidative carbonylation of alkynes, which have allowed to obtain important carbonyl derivatives (such as diesters, diacids, anhydrides) in one step starting from very simple building blocks (the alkyne, CO, water or alcohols and external nucleophiles, and molecular oxygen as external oxidant) with formation of water as benign coproduct. When applied to suitably functionalized acetylenic derivatives, this strategy has permitted to synthesize functionalized carbonylated heterocycles, difficult to obtained through alternative, non-catalytic and non-carbonylative routes.

The second review (by Renato Dalpozzo, Nicola Della Ca', Bartolo Gabriele, and Raffaella Mancuso) deals with another very important topic, that is, the use of carbon dioxide as a CO surrogate for the catalytic incorporation of the carbonyl group into an organic substrate, with formation of functionalized heterocycles [4]. The important of converting  $CO_2$  into high-value-added materials can hardly be overemphasized, considering the large availability of  $CO_2$  (produced in huge amounts by human activities and main responsible of the so-called "greenhouse effect" [5]) and the necessity to reconvert the  $CO_2$  ("spent carbon") into an organic product ("working carbon"). The review, in particular, focused on recent advances (since 2017 to 2020) in the catalytic conversion of  $CO_2$ , to cyclic carbonates, carbamates, and ureas.



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**Copyright:** © 2021 by the author. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). The third review (by Francesco Galiano, Roberto Castro-Muñoz, Raffaella Mancuso, Bartolo Gabriele, and Alberto Figoli), presents the recent advancements in an innovative and particularly important applicative topic, that is, the use of membrane technology in catalytic carbonylation reactions [6]. Nowadays, membrane technology is widely considered as one of the most important techniques in the separation and purification processes, as membranes act as selective separation "barriers" able to selectively retain particular molecules while allowing the permeation of others [7]. The review discusses the recent progress in the use of suitably functionalized membranes in assisting catalytic chemical reactions (esterification, oxidation, hydrogenation, and carbonylation to dimethyl carbonate (DMC), in particular). Moreover, the paper also gives an account on the use of specific membrane process (such as pervaporation) for the separation and purification of products obtained from carbonylation reactions.

### 2.2. Original Contributions

In the first original research article, Ning Lin, Qiu-Xiang Wei, Li-Hua Jiang, Yan-Qiu Deng, Zhen-Wei Zhang, and Qing Chen describe a rosin-derived bifunctional squaramidecatalyzed asymmetric Michael addition of malononitrile with chalcones [8]. The authors found that the process occurs with a low catalyst loading (0.3%) to give the final product with ees up to 90%. Although not properly a carbonylation reaction, the process shows how a possible carbonylation product (such as a chalcone) [9] can be further functionalized by an organocatalytic Micheal process.

The second original research article (by Hongyuan Chuai, Penghe Su, Hongchi Liu, Baolin Zhu, Shoumin Zhang, and Weiping Huang) reports on the hydroformylation of vinyl acetate using alkali and alkaline earth cation-decorated TiO<sub>2</sub> nanotube-supported rhodium catalysts [10]. The authors have nicely shown that some newly synthesized Rh supported catalysts (obtained by decorating rhodium nanoparticles with alkali and alkaline earth cations-modified TiO<sub>2</sub> nanotubes (TNTs)) are able to promote the hydroformylation reaction of vinyl acetate to 2-acetoxypropanal with turnover frequencies (TOFs, number of moles of product formed/(number of moles of Rh  $\times$  h)) up to ca. 3580.

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