

## Review

## Transition metal mediated coupling of carbon dioxide and ethene to acrylic acid/acrylates

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## ABSTRACT

The search for renewable alternative energy sources and energy storing possibilities has gained significant importance during the last decades, due to depleting fossil carbon sources, the continuously increasing human population and a generally increasing interest in environmental issues. Carbon dioxide, for example, can be captured directly at its source and thus made available for chemical industry. Homogeneous catalysis in solution is an attractive alternative to established heterogeneous procedures to utilize the C<sub>1</sub> building block CO<sub>2</sub> as an abundant and cheap starting material. Therefore, the development of cost efficient routes to bulk chemicals like acrylic acid and acrylates has significant interest for industry. In order to progress more rapidly in such a research field a combination of experiment and computational calculations is often considered as beneficial. This review presents a comprehensive overview on the synthesis of acrylates and acrylic acid, starting from CO<sub>2</sub>, focusing on synthetic insights as well as current findings in theoretical studies. Mechanistic studies are outlined and rational approaches to a full catalytic cycle presented using various molecular transition metal catalysts. In addition, the first catalytic transformations of carbon dioxide and ethene to acrylic acid are presented.

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## 1. Introduction

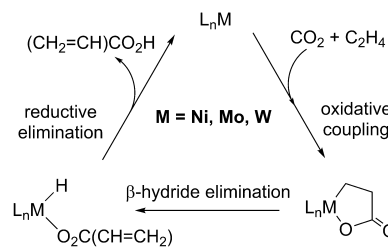
Considering that CO<sub>2</sub> emissions will continue to increase due to the energy and materials demand of the growing world population, CO<sub>2</sub> accumulation leads to a greater interest in new storage and recycling possibilities. CO<sub>2</sub> concentrations have increased by 40% since pre-industrial times and to levels unprecedented for at least the last 800,000 years, possibly as long as 20 million years. Human contribution to this carbon overload occurs primarily by burning fossil fuels and also deforestation. It has to be stated, however, that the atmospheric CO<sub>2</sub> levels of prehistoric times were usually considerably higher than in most recent earth history (during the time of human evolution). Nevertheless, the atmospheric CO<sub>2</sub> concentration grew by more than 100 ppm since the beginning of the industrial age from ca. 275 ppm in 1750 (and at least for the previous 10 ka) to reach the 400 ppm level in the atmosphere this year.

Therefore, it is not far fetched to utilize CO<sub>2</sub>, which is a versatile C<sub>1</sub> feedstock for chemical synthesis. CO<sub>2</sub> is abundant, cheap and non-toxic. Its thermodynamic stability as well as kinetic restrictions due to steric reasons, however, pose the primary barrier to its application. A great deal of research is underway to find methods that would be economically viable for industrial applications. Presently CO<sub>2</sub> is used in the industrial production of bulk chemicals like salicylic acid, urea, cyclic carbonates and polypropylene carbonate. Investigations on catalyst development are continuing for other processes, which are thermodynamically unfavorable, such as reduction of CO<sub>2</sub> to CO, CH<sub>4</sub> or methanol. It has to be emphasized, however, that a chemical utilization of CO<sub>2</sub>, leading to its recycling in a more than negligible amount on an atmospheric scale (the atmosphere contains ca. 3000 Gt of CO<sub>2</sub>, ca. 36 Gt are added each year by human activities) would work only on a really large order of magnitude, e.g. by transforming CO<sub>2</sub> to methanol or similar liquid fuels that might supplant the currently used fossil fuels for combustion engines. To achieve such a goal, cheap energy would be needed to bridge the gap between the energy rich liquid fuels and the much more stable CO<sub>2</sub>.

So far, only processes of much smaller scale are operational or close to be operational. Conversion of CO<sub>2</sub> and alkenes to acrylates could nevertheless be regarded as a breakthrough for industrial applications. This process would be sustainable and economical, as applications of acrylates are ubiquitous, particularly as monomers. Moreover, in the acrylic acid value chain coatings, adhesives, construction chemicals, hygiene products and paints are only a few examples of important daily life products. Currently, industrial synthesis of acrylates is carried out by the oxidation of propylene. Production costs of the acrylate end product are ruled by the costs of propylene, a chemical based on non-renewable carbon sources. Hence, a potential alternative route to acrylic acid or acrylates by the coupling of CO<sub>2</sub> and ethene is of considerable interest.

The synthesis of acrylates has been studied employing various (transition) metal complexes, however, a really efficient catalytic cycle has not yet been accomplished [1]. The essential steps of a hypothetical catalytic cycle – broadly discussed in the literature – are oxidative coupling of the substrates to form metallalactones, followed by β-hydride elimination forming a hydridoacrylate, and thereafter reductive elimination of the acrylate to regenerate the M(0) species (Scheme 1). The β-hydride elimination step is hindered due to high stability of the metallalactones in some cases, whereas high bond-dissociation energies of the M–H and M–O moieties in the hydridoacrylate intermediates present substantial kinetic barriers to the elimination of acrylic acid in others.

Nevertheless, several successful studies have been reported on transition metal mediated CO<sub>2</sub>/C<sub>2</sub>H<sub>4</sub> coupling reactions leading to the formation of acrylic acid/acrylates. Especially nickel mediated coupling reactions of CO<sub>2</sub> with various alkenes have been in the



Scheme 1. Outline of the hypothetical catalytic cycle.

focus of recent reviews [1–3]. This review aims to summarize the advances made so far in studying the coupling reaction of carbon dioxide with ethene with homogeneous/molecular catalysis methods. In order to broaden the scope of metals used in this catalytic transformation, various approaches using different transition metals have been examined and are presented in some detail. Most studies could not achieve a closed catalytic cycle, but they hold key insight and information on the use of different metal catalyst systems, which are important for further investigations on this conversion.

## 2. Nickel mediated CO<sub>2</sub> ethene coupling catalyst systems

### 2.1. Pioneering work

Earliest reports on coupling reactions of CO<sub>2</sub> and ethene originate from Hoberg et al. in the 1980s (Scheme 2) [4–8]. The Ni mediated reactions result in the formation of stable, isolable γ-nickelalactones and represent the first isolation of an intermediate in the reaction of CO<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>. Stability of the nickelalactones depends on the ligand coordinated to the Ni center; e.g. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), 1,2-bis(dicyclohexylphosphino)ethane (dcpe) and bipyridine (bpy). The nickelalactones undergo alkene substitution on reaction with other alkenes, indicating a reversible system. Acid hydrolysis leads to protonation of the ligand on the nickelalactone and to the formation of various carboxylic acids.

### 2.2. Synthetic and mechanistic details on nickel mediated coupling of CO<sub>2</sub> and ethene

In 2006, Walther et al. presented a putative catalytic cycle of Ni mediated coupling of CO<sub>2</sub> and ethene involving the γ-lactone as an intermediate, leading to acrylic acid as a product (Scheme 3) [9]. The first evidence of a β-hydride transfer was described in this report during attempts of reacting nickelalactones with donor ligands, presumed to be potential activators of the β-hydride elimination reaction.

Simple ligand exchange reactions are observed in most cases (Scheme 4): 1,2-bis(diphenylphosphino)ethane (dppe) forming a thermally stable nickelalactone, whereas 1,3-bis(diphenylphosphino)propane (dppp) and 1,4-bis(diphenylphosphino)butane (dppb) lead to unstable nickelalactones, that subsequently form Ni(0) complexes upon warming to 60 °C.

However, in the reaction of 1,1-bis(diphenylphosphino) methane (dppm) with nickelalactone a binuclear complex is formed, where the Ni centers are linked by a Ni–Ni single bond and three bridging ligands (Scheme 4). Investigations were carried out to further elucidate the mechanism. In a 1:2 reaction of dppm and [(py)<sub>2</sub>Ni(CH<sub>2</sub>CH<sub>2</sub>COO)] (py = pyridine) the complex [(py)(dppm)Ni(CH<sub>2</sub>CH<sub>2</sub>COO)] is isolated. It was postulated as the first addition product, which converts to [(dppm)<sub>2</sub>Ni(CH<sub>2</sub>CH<sub>2</sub>COO)] in the presence of excess dppm. β-Hydride elimination subsequently leads to an intermediate Ni–H complex. The methylene

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