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Review

# Recent developments in carbon dioxide utilization for the production of organic chemicals

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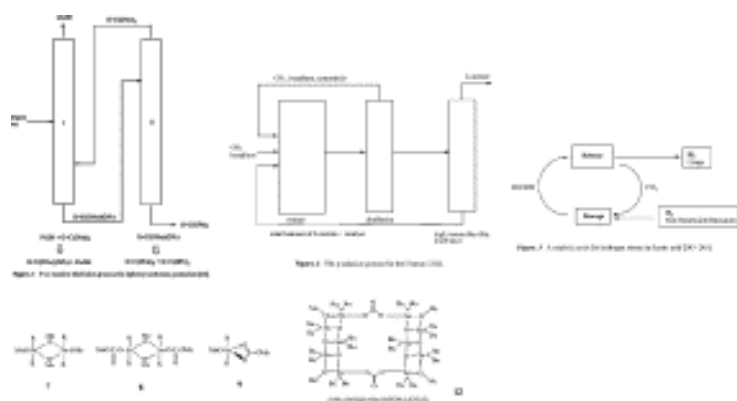
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### Abstract

Highly thermodynamically stable carbon dioxide is now used industrially as a feedstock for the carboxylation of four types of reactive substrates. The first category comprises oxygen-containing compounds, namely epoxides and alcohols. The reactions of reactive epoxides easily proceed at high yields in the presence of various kinds of transition metal compounds, non-transition metal compounds and organic compounds. However, the reactions of alcohols proceed at high yields only in the presence of a  $\text{Bu}_2\text{Sn}(\text{OMe})_2$  catalyst when dehydrating agents shift the equilibrium toward products without serious damage of catalysts by water by forming ladder compounds. The second category involves nitrogen-containing compounds, where urea is the dominant industrial product. Carbon–carbon unsaturated compounds such as aryl compounds, alkynes and alkenes

comprise the third category of substrates. The carboxylations of these substrates in the presence of metal compounds such as Cu, Ni and Pd generate the corresponding carboxylic acid derivatives. The five-membered compounds of the cyclometalated substrates can generate the corresponding carboxylic compounds using lithium, rhodium, nickel and palladium compounds as catalysts. The fourth substrate is hydrogen. We expect that the production of formic acid and methanol using hydrogen by utilizing natural energy generation such as geothermal energy and wind power will grow because these products will be in great demand in the near future.

## Graphical abstract



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## Highlights

- The types of substrate utilized by carbon dioxide are divided into oxygen-, nitrogen-containing compounds, unsaturated compounds and hydrogen.
- Syntheses of cyclic carbonates with epoxides in the presence of Cr, Ru or Co catalysts provide high TNO and TOF values.
- Reactions of alcohols with  $\text{Bu}_2\text{Sn}(\text{OMe})_2$  as catalyst and dehydrating agents proceed in high yield because the inactive site is activated by methanol.
- Many carboxylic acids can be synthesized via cyclometalation reactions with substrates such as 2-phenylpyridine.



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## Keywords

Carbon dioxide; Cyclic carbonate; Polyalkylene carbonate; Carbamic acid ester; Lactone; Formic acid

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