Technology Offer

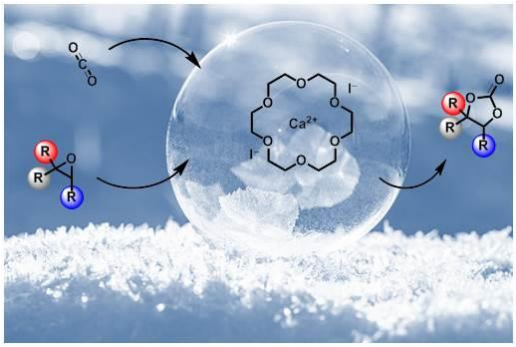
Powerful and versatile catalysts for efficient and sustainable production of a wide range of cyclic organic carbonates from a broad range of internal and external epoxides

Reference Number TO 28-00021

Challenge

Carbon dioxide (CO_2) represents the most significant and long-lived greenhouse gas in our atmosphere, which is being produced by aerobic organisms as well as - most significantly - combustion of organic materials and fossil fuels (in 2014: approx. 36 Gt). Its high availability, however, does CO_2 also make a very interesting and promising synthon, and establishing chemical processes and industries based on this renewable C1 building block would be of utmost importance to create a higher degree of sustainability. A particular challenge in this context are, however, the problems associated with CO_2 activation, as the carbon atom is present here in its most oxidized state, resulting in the molecule's high stability and low reactivity. Accordingly, a large energy input is required, leading to high costs as well as the generation and emission of additional greenhouse gases. Appropriate catalyst system can help to lower the high reaction barrier, but in general the reaction does still require rather harsh conditions.

One of the most efficient routes of chemical CO_2 fixation has been the synthesis of cyclic organic carbonates (COCs) via cycloaddition of CO_2 to epoxides. The resulting COCs represent valuable compounds, which can be broadly used as e.g. aprotic solvents, electrolytes, precursors for polycarbonates and other polymeric materials (including non-isocyanate polyurethanes, NIPUs) as well as intermediates for the production of fine chemicals and pharmaceuticals. The synthesis of COCs is usually achieved by direct coupling of CO_2 and an epoxide, requiring an appropriate catalytic system to overcome the high activation energy associated with the transformation (50-60 kcal mol-1, depending on epoxide). A vast array of metal-based and metal-free catalyst systems has been suggested for this purpose, and calculations indicate that contemporary catalyst systems may halve the activation energy. Commercial catalysts, which are currently being exploited for industrial COC synthesis, are based on non-metallic, quaternary ammonium or phosphonium salts (e.g. tetrabutylammonium bromide, TBAB), which have the advantage of low costs and simplicity. These catalysts, however, lack an acid component to activate the epoxide, and accordingly, these systems require elevated temperature and pressure, significantly reducing their carbon footprint and sustainability, and restricting the conversion of delicate substrates. The scientific literature describes some catalyst systems that facilitate a coupling of CO_2 and epoxides under mild conditions. These systems are, however, rather complex and expensive, and possess only limited reactivity and substrate specificity. Furthermore, the majority of these known systems only permit conversion of terminal epoxides, whereas the transformation of internal epoxides is still considered a huge challenge, requiring further elevated temperature and pressure, as well as prolonged reaction times.



CaI2/polyether-based catalyst

Technology

The present invention relates to an innovative catalytic system for the efficient synthesis of COCs under mild reaction conditions, significantly improving the transformation's carbon footprint and sustainability and (at the same time) facilitating the conversion of a broad range of both, internal and external epoxides (including those, featuring rather delicate structures and or functional groups). The catalytic system consists of a combination of an alkali earth metal halogenide and a polyether, whereat both components can be present either separately or in a complex.

The use of alkali earth metal salts in general, and calcium salts in particular has been only poorly investigated. For the related alkali metal salts it was shown that the introduction of polyethers (as co-catalysts) might improve the system's catalytic activity,

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but still requiring rather harsh reaction conditions (T≥ 100°C, $p(CO_2)$≥ 2 MPa) to obtain reasonable yields.
In comprehensive studies, scientist at the Leibniz Institute for Catalysis convincingly showed that alkali earth metal halogenides (particular: calcium iodide) and polyethers (particular: circular/closed crown ether or linear/open PEG) constitute a powerful and simple catalytic system for the efficient and sustainable production of COCs. The innovative catalyst system can be equally exploited for the conversion of external and internal epoxides, whereat the reactions can be performed with high yields under mild conditions (e.g. for CaI_2/18-crown-6-ether: t = 24 h, T = 23°C, $p(CO_2)$ = 0.1 MPa). Furthermore, the catalyst system shows astonishing broad substrate specificity, allowing the conversion of various classes of epoxide substrates (e.g. mono-, di- and tri-substituted) and facilitating tolerance towards various functional groups, which may be present in the epoxide substrate's side-chain(s). This, among others, also facilitates the transformation of delicate substrate, which would be unstable under harsher conditions, as well as the synthesis of novel or rare COCs, which could be particular useful as starting materials for the synthesis of polymers (e.g. NIPUs), solvents, electrolytes and/or fine chemicals.
In conclusion, the novel, highly efficient CaI_2/polyether-based catalyst system provides a powerful and versatile tool for the efficient and sustainable production of a wide range of COCs under mild conditions and from a broad range of internal and external epoxides. Key features are:

- high selectivity
- broad specificity
- high efficiency, even under mild reaction conditions
- high sustainability, due to material use of CO_2 as well as avoidance of additional emissions
- transformation of delicate substrate, facilitating accessibility of valuable, novel and/or rare COCs for multiple application
- low toxicity
- low costs

Commercial Opportunity
The proprietary technology is offered for in-licensing and/or co-development.

Development Status
The practical relevance of calcium iodide-based catalyst systems has been broadly demonstrated in lab scale for a broad range of internal and external epoxides.
Using cyclic/closed polyethers (e.g. 18-crown-6-ether) as a co-catalyst, a wide range of mono- and disubstituted terminal COCs could be synthesized at 23°C and $p(CO_2)$ of 0.1 MPa (= 1 bar) over 24 h in yields of up to 99%. The same catalyst system (CaI_2/crown ether) could be also exploited for the conversion of a broad range of internal epoxides, whereat the reactions usually proceeded over 48 h at 45°C and $p(CO_2)$ of 1 MPa (= 10 bar).
A catalyst system consisting of CaI_2 and a linear/open polyether (e.g. PEG 500 DME) generally have to be exploited at slightly elevated conditions (external epoxides: 25°C, $p(C0_2)$ = 1 MPa, 24 h; internal epoxides: 70-90°C, $p(C0_2)$ = 2-5 MPa, 24-48 h), likewise achieving yields of up to 99%.

Patent Situation
A German patent application has been filed in 2017.

Further Reading
Steinbauer, Spannenberg & Werner (2017) An in situ formed Ca^{2+}–crown ether complex and its use in CO_2-fixation reactions with terminal and internal epoxides. Green Chemistry, DOI: 10.1039/c7gc01114h
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Büttner, Longwitz, Steinbauer, Wulf & Werner (2017) Recent developments in the synthesis of cylic carbonates from epoxides and CO_2.Top Curr Chem 375: 50. DOI: 10.1007/s41061-017-0136-5
Longwitz, Steinbauer, Spannenberg & Werner (2018) Calcium-based catalytic system for the synthesis of bio-derived cyclic carbonates under mild conditions. ACS Catalysis 8: 665-672

Catalysis LIKAT Leibniz-Institut für Katalyse e.V.

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