



C₃-symmetric zinc complexes as sustainable catalysts for transforming carbon dioxide into mono- and multi-cyclic carbonates

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ARTICLE INFO

Keywords:

Carbon dioxide fixation
Multi-cyclic carbonates
Zinc complexes
Bifunctional catalysts
Counter anions

ABSTRACT

In this study, we report a single-step preparation method for the synthesis of a series of C₃-symmetric zinc complexes containing both a Lewis acidic zinc center and a nucleophilic halide counter ion for coupling CO₂ with epoxides. The Zn-complexes were shown to be effective one-component bifunctional catalysts and displayed high catalytic activity and selectivity for the transformation of CO₂ into cyclic carbonates under mild conditions. This strategy is simple, efficient, environmentally benign, and does not require an additional cocatalyst or solvent, and the catalyst can be easily recovered and reused several times without significant loss in catalytic activity. The CO₂ coupling reaction proceeded on broad range of substrates and exhibited good tolerance to functional groups, and the cyclic carbonate products were isolated in high yields. On the basis of the experimental results, a plausible reaction mechanism was proposed, and the high catalytic activity was explained.

1. Introduction

Over the past decades, developing environmentally benign and sustainable catalysts is still an active area of research for the efficient transformation of carbon dioxide (CO₂) into economically high value-added products of chemicals or fuels [1–6]. Abundance, low cost, nontoxicity and nonflammability make CO₂ a potentially renewable C1 feedstock for the chemical industry [7–9]. Therefore, the chemical conversion of CO₂ into valuable products is highly important from the utilization of CO₂ resource [10–12]. However, the kinetic and thermodynamic stability of CO₂ significantly limits its utility in chemical reactions. Therefore, highly reactive substrates and catalysts are required to activate CO₂ [13,14]. To date, a variety of methods have been successfully developed to convert CO₂ into different products [15–22]. Among these methods, the industrially important process of coupling CO₂ with epoxides is of particular interest as a promising and green route to produce 100 % atom-economical cyclic carbonates products, which have wide-ranging commercial applications, such as polar aprotic solvents, raw materials for fine chemicals and polymer synthesis, and electrolytes in lithium-ion batteries [23–25]. So far, various catalyst systems, including metal-based catalysts and organocatalysts, have been developed for the selective synthesis of cyclic carbonates [26–33]. These active catalytic systems typically function via two key steps, the activation of the C–O bond of an epoxide via coordination with a Lewis acidic metal center followed by epoxide ring-opening by a

nucleophilic cocatalyst. Several homogeneous binary catalytic systems for this transformation have been successfully reported involving combinations of metal-based complexes and cocatalysts, such as onium salts or Lewis bases (Scheme 1a) [34–43].

Consequently, considerable effort has been expended to develop one-component bifunctional metal catalyst systems that can promote cyclic carbonate formation without cocatalysts and mild conditions. In such catalysts, a Lewis acidic metal center and a nucleophilic cocatalyst are assembled in the same molecule. At first, the covalently attached onium salts such as quaternary ammonium salts, quaternary phosphonium salts, and ionic liquid salts that facilitate the role of nucleophilic cocatalyst, which has been attached to a ligand scaffold of catalyst (Type I) [44–49]. These catalysts exhibit higher catalytic activity than a binary catalyst system because of enhanced intramolecular cooperation between a Lewis acidic center and a nucleophilic halide anion [49]. Another class of bifunctional catalyst systems has been designed, where a Lewis metal center and a ligand carrying a sterically hindered organic base as a nucleophile within the same structure were used to promote the coupling of CO₂ with epoxides (Type II) [50–54]. The cooperative effect of the Lewis metal center and organic base as a nucleophilic cocatalyst exhibited higher catalytic activity than a system without a Lewis base. Despite the advantages in the designing of catalysts, however, bifunctional catalysts have not been widely studied because of several synthesis steps, time-consuming purification and high catalyst preparation costs. Therefore, development of efficient and

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<https://doi.org/10.1016/j.apcatb.2020.119395>

Received 12 June 2020; Received in revised form 27 July 2020; Accepted 3 August 2020

Available online 15 August 2020

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