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A rational investigation of the Lewis acid promoted coupling of carbon dioxide with cyclohexene oxide: towards CO₂-sourced polycyclohexene carbonate under solvent and co-catalyst free conditions

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PURPOSE OF THE ABSTRACT

The valorization of carbon dioxide (CO₂) as a renewable C1 feedstock to produce fine chemicals or polymers is of growing interest in academic laboratories and industries in the context of sustainable chemistry.[1] In this context, the coupling of CO₂ with epoxides that leads to the formation of cyclic carbonates or polycarbonates is a highly attractive 100% atom economic reaction. Both products are valuable chemicals that should be selectively produced in order to minimize the separation and purification steps. The selectivity of this reaction is dependent on the nature of the substrate and the formation of either cyclic carbonates, polycarbonates or poly(ethers) is strongly related to the choice of an appropriate catalyst. The selectivity is also influenced by the reaction conditions (temperature, CO₂ pressure) as the activation barrier for the formation of polycarbonates is generally lower and cyclic carbonates are the thermodynamically favored products.

Thus, for the selective and efficient synthesis of polycarbonates (PC) from the copolymerization of CO₂ and epoxides, many Lewis acid catalysts such as organometallic complexes usually used in combination with a nucleophile have been developed. A recent review by Pescarmona et al. [2] offers an updated overview of the catalytic synthesis of polycarbonates, their physicochemical properties, and the growing applications of this class of green polymers. Therefore, this research field is still very active as further improvements are still needed in order to develop robust, active, and selective catalysts while respecting environmental and economic standards and improving the material properties of PC that generally displays low molar masses hence severely limiting their usefulness.

In this context, we have performed a rational investigation of the copolymerization of cyclohexene oxide (CHO) with CO₂ in the presence of commercially available Lewis acids with metal center such as Zn, Mg, Fe, Al, Ni, Sc, and Y. The influence of the pressure, the temperature, the catalyst loading and the presence of a co-catalyst or a solvent on the reaction yields, selectivity and molar masses has been evaluated for selected catalytic platforms. ZnOTf in the presence of a tosylate based co-catalyst has allowed to obtain the synthesis of PCHC in good to high yields. Then, the commercially available Zinc tosylate salt investigated under various thermodynamic conditions appears to be the most attractive simple Lewis catalyst that enables the selective synthesis of polycyclohexene carbonate with a molecular weight of about 62.1 kg/mol with about 70% yields at 343K and 4 MPa under solvent and co-catalyst free conditions. Thanks to in situ FTIR spectroscopy, we have put in evidence a specific interaction between ZnTos and CO₂. Thus, we propose that, although ZnTos is expected to activate the epoxide towards ring opening, such catalytic performance is related to the co-activation of CO₂ by ZnTos.

FIGURES

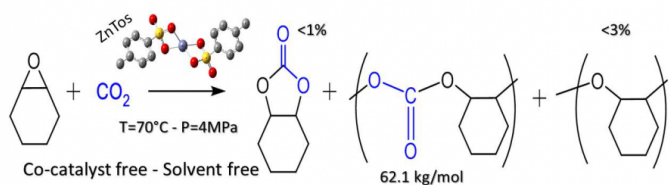


FIGURE 1

Catalytic coupling of CO₂ with cyclohexene oxide

Catalytic amount of ZnTosylate enables the synthesis of high molar mass polycyclohexene carbonate from the copolymerization of cyclohexene oxide with CO₂ under solvent and co-catalyst free conditions.

FIGURE 2

KEYWORDS

CO₂ utilization | Zinc catalyst | Cyclohexene Oxide | Polycarbonate

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