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PRODUCTION OF PROPYLENE CARBONATE FROM CO_2 USING BIFUNCTIONAL HALOMETALLATE CATALYSTS $[Bu_4N]_n[MCl_4]$

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ABSTRACT

This study investigates the efficiency of bifunctional catalysts $[Bu_4N]_n[MCl_4]$ (where M = Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) in the reaction between CO_2 and propylene oxide for the synthesis of the respective cyclic carbonate. Among the tested catalysts, $[Bu_4N]_2[CoCl_4]$ was the most effective, achieving up to 77% conversion with 100% selectivity for propylene carbonate. The results indicate that the choice of the metal ion is crucial for catalytic performance. Moreover, the simplicity of synthesis and low cost of these catalysts make them viable for industrial applications. The next step involves optimizing the reaction conditions and evaluating the catalysts' efficiency with different substrates.

Keywords: Bifunctional catalyst; Carbon Dioxide; Cyclic Carbonate; Epoxide.

INTRODUCTION

The pressing challenge of climate change has underscored the importance of controlling atmospheric greenhouse gases, particularly carbon dioxide (CO_2). CO_2 emissions reached a staggering 37.9 Gt in 2018, with projections suggesting a potential rise to 600–1550 ppm by 2030 due to increased energy demands [1,2]. This scenario has intensified research into utilizing CO_2 as a carbon source in chemical processes, aiming to transform this abundant greenhouse gas into valuable products.

Despite significant advancements in this field, current industrial processes only utilize an amount equivalent to about 1% of CO_2 emissions, with major applications including the synthesis of urea, inorganic carbonates, and methanol [3,4]. Among the various routes for CO_2 utilization, the cycloaddition of CO_2 with epoxides to form cyclic carbonates stands out due to its potential for producing high-value products such as solvents for electrolytes in lithium-ion batteries, aprotic solvents, and fuel additives [5,6].

Cyclic carbonates, synthesized via the reaction between CO_2 and epoxides, offer a promising pathway for CO_2 fixation. This reaction not only addresses the issue of greenhouse gas emissions but also provides a sustainable route to valuable chemicals. Traditional methods often rely on toxic reagents like phosgene, but the direct use of CO_2 represents a greener alternative. The development of efficient catalytic systems is critical to making this process viable on an industrial scale [7].

The focus of this study is on bifunctional catalysts, specifically $[Bu_4N]_n[MCl_4]$, for the cycloaddition of CO_2 with propylene oxide. Bifunctional catalysts are particularly advantageous because they combine multiple catalytic sites within a single entity, enhancing both the activation of CO_2 and the epoxide substrate, thus improving overall reaction efficiency [8]. Recent studies have demonstrated that catalysts based on zinc complexes and ionic liquids exhibit excellent performance, highlighting the potential of these systems for large-scale applications [9].

This work aims to explore the catalytic efficiency, selectivity, and mechanistic aspects of $[Bu_4N]_n[MCl_4]$ bifunctional catalysts in the synthesis of cyclic carbonates. Through this study, we hope to contribute to the development of more sustainable and efficient catalytic processes for CO_2 utilization, aligning with global efforts to mitigate climate change.

MATERIALS AND METHODS

Catalyst Synthesis

The Fe^{3+} catalyst, $[Bu_4N][FeCl_4]$ (where Bu_4N = tetrabutylammonium), was synthesized according to reference [10], by directly adding an alcoholic solution of tetrabutylammonium chloride $[Bu_4N]Cl$ to an alcoholic solution of $FeCl_3 \cdot 6H_2O$ under constant stirring, resulting in the formation of a precipitate, which was then filtered, vacuum-dried, and characterized.

The other catalysts of the type $[Bu_4N]_2[MCl_4]$ (where M = Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) were synthesized by directly adding tetrabutylammonium chloride to a metallic chloride salt [MCl_2] in tetrahydrofuran solution under constant stirring, leading to the formation of a precipitate, which was filtered, vacuum-dried, and characterized.

Catalyst Characterization

The formation of the [MCl_4]$^-$ anions was confirmed by high-resolution mass spectrometry (HRMS). Additionally, the samples were characterized by Fourier-transform infrared spectroscopy (FTIR), confirming the presence of functional groups related to the tetrabutylammonium cation, elemental analysis (CHN), and thermogravimetric analysis (TGA) to determine the thermal stability of the catalysts.

Cycloaddition Reactions

The cycloaddition reactions were carried out in an autoclave reactor under a pressure of 10 bar of CO_2. A total of 25 mmol of propylene oxide (PO) and 0.08 mol% of the catalyst in relation to substrate were used, at a temperature of 100°C, for 3 hours. The reaction mixtures were analyzed by hydrogen nuclear magnetic resonance spectroscopy (^{1}H NMR) to determine product conversion and selectivity. The conversion is based on the consumption of propylene oxide (PO).

RESULTS AND DISCUSSION

The results obtained for the bifunctional catalysts [Bu_4N]$_n$[MCl_4] are presented in Table 1. The tetrabutylammonium tetrachlorocobaltate(II), [Bu_4N]$_2$[$CoCl_4$], catalyst proved to be particularly efficient, achieving conversions of up to 77% with 100% selectivity for propylene carbonate, as shown in Figure 1.

The catalyst [Bu_4N]$_2$[$CoCl_4$] stood out for its high efficiency and reaction selectivity, especially when compared to the binary system $CoCl_2$/[Bu_4N]Cl and the bifunctional catalyst [Bu_4N]$_2$[$CoCl_4$] where the bifunctional system showed an approximately 100% improvement in conversion. This represents a significant result given the simplicity and speed of synthesis, as well as the low cost of obtaining the catalysts.

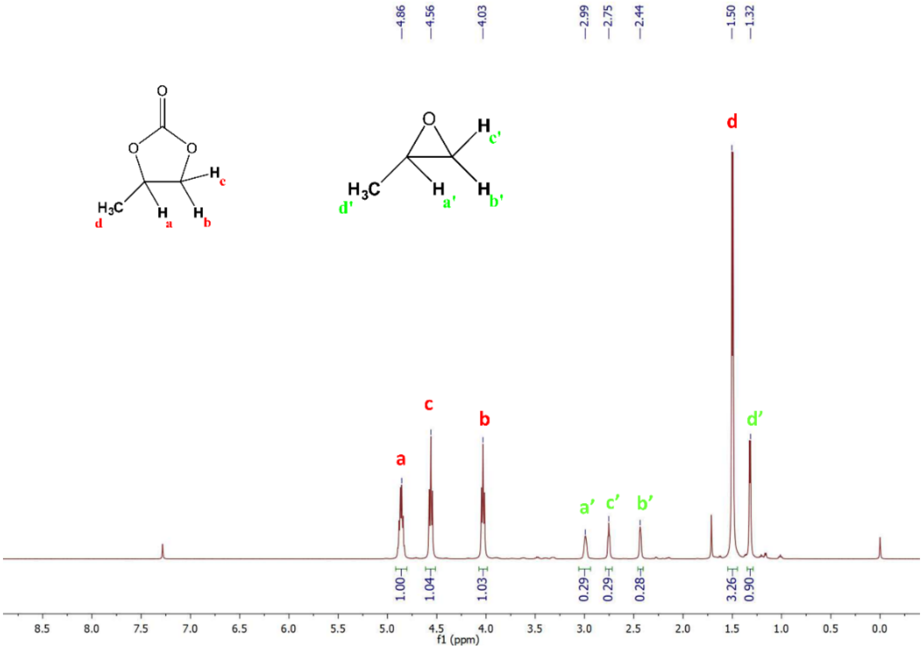

Figure 1. ^{1}H NMR Spectrum of the Reaction Mixture Catalyzed by $[Bu_4N]_2$[CoCl4].

Table 1. Catalytic Performance of $[Bu_4N]_2$[CoCl4] Bifunctional Catalysts in the Cycloaddition of CO_2 with Propylene Oxide.

Catalyst	Conversion (%)	TON^b	TOF^c
$CoCl_2{\cdot}6H_2O$*	39	1984	661
$[Bu_4N]_2[MnCl_4]$	46	2282	761
$[Bu_4N][FeCl_4]$	18	884	294
$[Bu_4N]_2[CoCl_4]$	77	3875	1291
$[Bu_4N]_2[NiCl_4]$	36	1838	612
$[Bu_4N]_2[CuCl_4]$	7	374	124
$[Bu_4N]_2[ZnCl_4]$	37	1858	619

Reaction conditions: 25 mmol PO, Catalyst (0.08 mol%), temperature (100 °C), $P_{[CO2]}$ = 10 bar, time (3 hours). ^{a}Conversion was estimated from the ^{1}H NMR spectrum of the reaction mixture. ^{b}TON = turnover number (moles of epoxide consumed)/(moles of catalyst). ^{c}TOF = turnover frequency TON.h^{-1}, *Cocatalyst (0,16 mol%).

CONCLUSION

This study demonstrated that the bifunctional catalysts $[Bu_4N]_2[CoCl_4]$ are promising for the cycloaddition of CO_2 with epoxides, showing high selectivity and efficiency. The $[Bu_4N]_2[CoCl_4]$ was the most effective catalyst, suggesting that the choice of the metal ion is crucial for optimizing the reaction. The simplicity and low production cost of these catalysts make them attractive for industrial applications in the synthesis of cyclic carbonates. Once the best catalyst is defined, the next steps of this work include catalytic optimizations to determine the best pressure, temperature, time, and catalyst loading conditions, in addition to testing its efficiency with different substrates.

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