Efficient route for oxazolidinone synthesis using heterogeneous biopolymer catalysts from unactivated alkyl aziridine and CO2 under mild conditions

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Biopolymers made of polysaccharide chains are emerging as promising materials for designing efficient, cheap, environmental friendly and recyclable heterogeneous catalysts. In this study, we synthesized a series of covalently functionalized chitosan–alkyl pyridinium halides (CS-RPX, R = ethyl, propyl, butyl, hexyl and X = Cl, Br) and evaluated their potential application as catalysts for the chemical transformation of CO2 to 4-methyl-2-oxazolidinone using 2-methyleziridine under mild reaction conditions. The catalysts were characterized using different physicochemical methods, including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), thermo gravimetric analysis (TGA), elemental analysis (EA) and field emission scanning electron microscopy (FE-SEM). 1H NMR, GC–MS, EA and FT–IR were used to confirm successful oxazolidinone formation. Cycloaddition was found to proceed through the synergistic effect of the hydroxyl and amine groups of chitosan together with the anion. The catalyst was reused five times after the cycloaddition reaction, with a loss of 2–6% in conversion and 1–3% in selectivity per cycle. The effect of different reaction parameters, such as catalyst amount, time, temperature and CO2 pressure were studied to determine the reaction conditions that resulted in the highest conversion and selectivity.

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1. Introduction

Increasing focus on research for the development of feasible alternative pathways to obtain valuable chemicals using CO2 as a C1 building block is motivated by advantages like its abundance, non-inflammability, inexpensiveness and non-toxicity [1,2]. Despite the challenge raised by the kinetic and thermodynamic stability of CO2, the synthesis of useful products like cyclic and poly carbonates from CO2 using epoxides in presence of catalyst have been well progressed and are continuously being updated [3–5]. Recently, aziridines, the highly ring-strained heterocyclic N-analogues of epoxides, are being emerged as an attractive substrate for CO2 fixation via [2 + 3] coupling to yield oxazolidinones (Scheme 1) [6–12]. Oxazolidinones are a class of 5-membered heterocyclic compounds that find applications as intermediates and chiral auxiliaries in organic synthesis and polymer synthesis [13–17], and biologically active pharmaceutical agents [18,19]. Even though the development of this process had been stagnant for the past three decades [20], researchers have more recently revisited using this approach due to increasing concerns over the development of eco-friendly processes. Moreover, among the alternative methods for oxazolidinone synthesis, viz., carbonylation of amino alcohols using phosgene or CO [21–24] and the reaction of propargylamine or propargyl alcohol with CO2 [25–27], the former one (using phosgene or CO) is considered as less attractive C1 feedstock from a green prospective in comparison to the nontoxic and abundant CO2.

A few homogeneous catalysts like inorganic salts, complexes [12,20,28–32], organic compounds, organic salts, ionic liquids [7–10,33–35], etc. have been used for the cycloaddition of aziridines with CO2. Despite being the most active homogeneous catalyst, ionic liquids are fraught with drawbacks, including the tedious process required to separate the reaction mixture at the end of synthesis. More recently, polymer supported ionic liquids [12,36] were developed in an attempt to overcome these limitations. Even though these synthetic polymers offer themselves as good platforms for rendering heterogeneity to ionic liquids, they still pose the limitation of acting only as a scaffold and do not promote or enhance the reaction. Recently, the role of vicinal hydroxyl groups in enhancing the cycloaddition of aziridines with CO2 was demonstrated by the high efficiency of polymer supported diol functionalized imidazolium ionic liquids [12].

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