Molecular Catalysis 452 (2018) 129–137

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

Polystyrene supported Zinc complex as an efficient catalyst for cyclic carbonate formation via CO_2 fixation under atmospheric pressure and organic carbamates production

Surajit Biswas[a], Resmin Khatun[a], Manideepa Sengupta[a,b], Sk. Manirul Islam[a,*]

[a] Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, West Bengal, India
[b] Refinery Technology Division, CSIR-Indian Institute of Petroleum, Dehradun, 248005, Uttarakhand, India

ARTICLE INFO

Keywords:
Polystyrene support
Heterogeneous catalyst
CO_2 fixation
Cyclic carbonate
Organic carbamates

ABSTRACT

Chemical fixation of CO_2 and synthesis of organic carbamates through phosgene –free eco-friendly pathway using a heterogeneous and sustainable catalyst is always a demanding field in synthesis chemistry. Herein, we presented the design and synthesis of a polymer support sustainable heterogeneous [PS-Zn(II)L] catalyst from modified chloromethylated polystyrene. The heterogeneous catalyst has been characterized by IR, PXRD, AAS, TG-DTA, SEM and EDX studies. The catalyst showed its efficient catalytic activity towards the formation of organic cyclic carbonate from epoxides via CO_2 fixation at room temperature under 1 atm CO_2 pressure in solvent free condition and production of organic carbamates from corresponding amines. The synthesis of carbamates in presence of this catalyst is a phosgene-free protocol where green reagent Dimethyl carbonate (DMC) is used as a carboxylating agent as well as the solvent. The catalyst is highly efficient and reusable even after five cycles.

1. Introduction

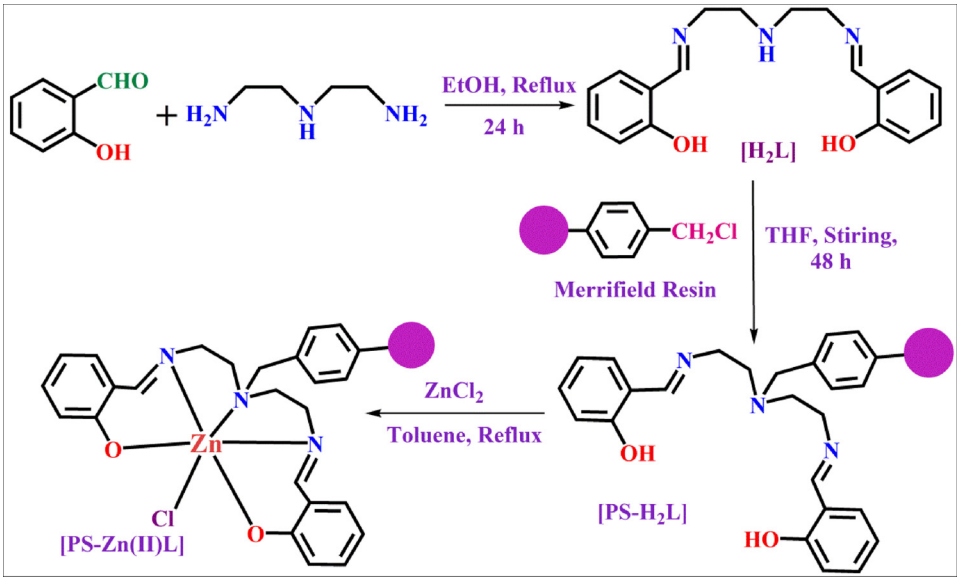
Carbon dioxide (CO_2) which is generated from human activities is one of the greenhouse gases. Thus its atmospheric concentration should be controlled by eliminating it from industrial emissions to avoid global warming which is the most dangerous environmental threat in recent years [1]. On the other side, CO_2 is a cheap and abundant recyclable carbon source. It is a very powerful, non-flammable, non-toxic C1 feedstock for organic synthesis and can sometimes replace toxic chemicals like carbon monoxide, isocyanates or phosgene [2]. It has been found that CO_2 utilization is more significant rather than its storage if economical procedures are accessible. That's why chemical fixation of CO_2 into value-added chemicals is still gaining appreciable attention. The cyclo addition of CO_2 to epoxides for the formation of cyclic organic carbonates is one of the very useful chemical transformations of CO_2. The cyclic carbonates have a wide range of applications as aprotic polar solvents, in polycarbonate precursors like Diphenyl carbonate (DPC), and Dimethyl carbonate (DMC), electrolytes in rechargeable batteries and intermediates in synthesis of fine chemicals [3]. In the conventional method, the cyclic carbonates were synthesized via a poisonous, hazardous, and corrosive route involving glycol and phosgene. Now a days these cyclic carbonates are produced through the cyclo addition of CO_2 to epoxides in presence of catalysts.

There are many homogeneous catalysts already been developed for this catalytic transformation like quaternary phosphonium/ammonium salts [4], ionic liquids [5], alkali metal salts [6], bromine [7], organo catalyst [8], metal complexes [9], peroxometalates [10] etc. But these homogeneous catalysts have the most common problems of recyclability and reusability. Alternatively, many heterogeneous catalytic systems have been also developed to overcome these problems e.g., inorganic-organic hybrid core shell microspheres [11], COFs, [12] MOFs [13] etc. But most of the catalytic system require harsh reaction conditions such as hazardous organic solvent, very high CO_2 pressure and temperature. For these aspects, it is very much desirable to explore recyclable and reusable catalytic system, which can perform its catalytic activity under atmospheric pressure, room temperature and solvent free condition. That's why; we have been designed and synthesized a polymer supported zinc metal complex which can act as an efficient heterogeneous catalyst for the synthesis of cyclic carbonate under 1 atm CO_2 pressure and room temperature in solvent free condition.

Organic carbamates are the very popular class of compounds which grasp inimitable applications in agrochemicals (as insecticides, herbicides, pesticides, fungicides *etc.*) [14] and pharmaceuticals (in form of drugs and pro-drugs) [15]. Moreover, the carbamates play a pivotal role

* Corresponding author at: Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, West Bengal, India.
E-mail address: manir65@rediffmail.com (S.M. Islam).

https://doi.org/10.1016/j.mcat.2018.04.009
Received 25 December 2017; Received in revised form 24 March 2018; Accepted 9 April 2018



Scheme 1. Schematic presentation of synthesis of [PS-Zn(II)L] catalyst.

Table 1
Elemental analysis of [PS-H_2L] ligand and [PS-Zn(II)L] catalyst (in weight%).

Compound	Colour	C	H	N	O	Cl	Zn	N/Zn[b]	O/Zn[b]	Cl/Zn[b]
[PS-H_2L]ligand	Light yellow	83.33	8.44	2.44	1.82	1.18				
[PS-Zn(II)L]catalyst	Pale yellow	76.68	8.35	2.47	1.84	2.94	3.70 3.68[a]	3.11(3)[c]	2.03(2)[c]	0.87(1)[c]

[a] Reused catalyst.
[b] mole ratio between nitrogen, oxygen or chlorine and zinc.
[c] ideal mole ratio value.

against various diseases, like anti-viral, anti-malarial, anti-HIV, anti-cancer, anti-progestational, anti-fungal, anti-estrogenic, anti-bacterial, anti-tubercular, anti-osteoporosis, anti-diabetic, anti-inflammatory, anti-obesity, anti-filarial, anti-helminths, anti-convulsant, anti-Alzheimer drugs and CVS, CNS active agents [15a,f,16]. The compounds are very competent in the peptide chemistry for the protection of amino group [17], in the organic synthesis as intermediate [18] and in the combinatorial chemistry as linker [19]. The carbamates have also been widely utilized in the synthesis of molecules of biological significance and structurally diverse synthetic intermediates [20].

These compounds are generally manufactured from the reaction of corresponding amine and phosgene or phosgene derivatives [21]. But the process is not environmentally friendly and produced toxic and unwanted waste materials. For that reason, some greener protocols for the synthesis of these compounds have been developed in recent years such as catalytic oxidative carbonylation of amines [22], carbonylation of nitroaromatics [23], methoxy carbonylation through carbonate [24], and by reaction of urea with symmetrical carbonates [25]. The carbonylation process involves the toxic CO and the latest process of urea and carbonates has bound to access the limited number of carbamates derivatives [25]. Therefore, probably the most attractive route for the synthesis of organic carbamates is the methoxy carboxylation of amine using dimethyl carbonate (DMC) in presence of a catalyst. In green chemistry, DMC is a very versatile building block for organic synthesis and produced carbamates from amine in the one-step process. For this purpose, a number of catalysts have been developed for the synthesis of carbamates from dialkyl carbonates and amines including phosphoric acid [26], lead salts [27], MCM-41-TBD [28], $Yb(OTf)_3$ [29], Zn salt containing catalysts [30], ZrO_2/SiO_2 [31], $Zn(OAc)_2$-[bmim]PF_6 [32], acid functional ionic liquids [33], IL-Co Catalyst [34]. But most of the above mention catalysts are homogeneous in nature as a result reusability and recyclability of those catalysts are very problematic and also very cost effective. Moreover, the catalysis procedure required the temperature greater than 100 °C and long reaction duration. Hence, design and synthesis of heterogeneous catalyst are essential for the efficient production of organic carbamates from amine and DMC under mild condition. Herein, we are able to synthesize a polymer-supported Zinc catalyst which is very efficient for the synthesis of organic carbamates from amine and DMC under mild condition.

In this paper, we have reported the synthesis, characterization of an organically modified polystyrene supported Zinc catalyst and its efficient dual catalytic activity towards the synthesis of cyclic carbonate at room temperature under 1 atm CO_2 pressure and solvent-free condition as well as the production of organic carbamates under mild condition from corresponding amine and DMC.

2. Experimental section

2.1. Materials

Chloromethylated polystyrene and epoxides were procured from Sigma-Aldrich. Amines were purchased from Merck (India). The reagents were used as received without any purification and solvents were distilled and dried through standard procedure prior to use.

2.2. Characterization techniques

The elemental analysis was carried out on Exeter Analytical Inc. model: CE 440. FTIR spectra were done on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. Mettler Toledo TGA/DTA 851 instrument was used for Thermogravimetric (TGA) analysis. The morphology of samples was measured using a scanning electron microscope