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Catalytic synthesis of organic cyclic carbonate through CO_2 fixation and production of β amino alcohol via ring opening of epoxides under green condition by polystyrene embedded Al(III) catalyst

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Abstract

Development of low cost, eco-friendly heterogeneous catalyst for the production of value added organic compounds has been drawn a considerable attention to the synthetic chemists in recent era. Keeping the above idea in our mind, we have design and synthesized a polymer anchored Al(III) composite from modified Merrifield resin. The composite was characterized properly by FT-IR spectra, SEM, EDAX, elemental analysis, ICP-AES and PXRD studies. The low cost material is very efficient heterogeneous catalyst for the production of fine organic chemicals such as organic cyclic carbonates and 2-amino alcohols under green and mild reaction conditions. Organic cyclic carbonates were synthesized through the insertion of carbon dioxide into epoxides at room temperature under solvent free condition. The developed protocol of catalytic synthesis of cyclic carbonates is sustainable, eco-friendly and cost-effective. Moreover atmospheric carbon dioxide is utilized here. Besides, the catalyst is very much efficient to produce 2-amino alcohol from ring opening of epoxides by nucleophilic attack of amine under solvent free condition and at room temperature. This polymer anchored Al(III) can be recovered and reused easily. The catalyst preserved its catalytic intensity even after use of eight successive catalytic cycles.

Key words: Poloystyrene support, Aluminium, Carbon dioxide, cyclic carbonate, β -amino alcohol.

Introduction

For sustainable development a sensible resource management is necessary. The level of sustainability is not satisfactory in case of feedstock of chemical industry. Until now coal, crude oil and natural gas are the prime resource of carbon. Along with biomass, CO_2 can be used as renewable carbon economy. The amount of CO_2 is continuously increased from the pre-industrial time. Now CO_2 is responsible for green house effect and abnormal climate change of the earth. Combustion of fossil fuel is responsible for increasing carbon dioxide in the atmosphere, which in turn causes green house effect and increases global warming [1].

Currently world is producing major part of energy needed for mankind by combustion of fossil fuel such as coal, oil and natural gas. Though after enormous efforts to develop alternatives renewable energy sources, these fossil fuels remain as predominant energy source. To maintain carbon dioxide level in atmosphere it is necessary to control CO_2 emission in atmosphere and to introduce efficient carbon capture and storage (CCS) systems. Through CCS carbon dioxide is separated, purified, pressurized and dumped underground or under sea storage [2]. This stored and dumped carbon dioxide can be utilized in large scale production of different chemicals by carbon capture and

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utilization, (CCU) [3]. As CO_2 is readily available, non toxic and recyclable it is used as one carbon building block (C-1) for organic synthesis. In recent years one of the research interests is to utilize the carbon dioxide to an available feedstock for the production of organic fine chemicals [4].

Carbon dioxide is thermodynamically stable and kinetically inert because it is the most oxidised form of carbon. For this reason activation and utilisation of CO_2 is not easy. Generally highly reactive substrates or drastic reaction conditions are employed for CO_2 activation and this is the limitation of such methods. Strong carbon nucleophilic reagents like organolithiums, Grignard reagents are used to create C-C bond with CO_2 . CO_2 can be catalytically coupled with high energy substrate like epoxides and aziridines to produce poly carbonates/polycarbamates and cyclic carbonates/cyclic carbamates. Over past decades transformation of CO_2 in organic synthesis have been achieved and gradually improving its efficiency.

There are several strategies were invented to reduce the amount of CO_2 in atmosphere. Incorporation of CO_2 into epoxides to produce carbonates is one of them and is playing a significant roll in organic synthesis. Cyclic carbonates are very important synthetic target as they have a wide range of established and potential applications. They are utilised in lithium ion battery as electrolyte solvent, in many reaction they are used as environment friendly polar aprotic solvents, in the synthesis of many fine chemicals they are the intermediates [5]. Cyclic carbonates are also used as raw materials in paints and oils. As cyclic carbonates can undergo ring opening polymerization, Polycarbonates and polyurethanes, are synthesized from cyclic carbonates [6]. Cyclic carbonates with five membered ring can act as an alkylating reagent for aromatic amines, thiols and phenols at high temperature. This ring opening is used in polymer modification, pre-polymer synthesis and super absorbent polymers production [7].

Traditionally cyclic carbonates were manufactured through a hazardous, poisonous, and corrosive pathway involving phosgene and glycol. Recently these carbonates are synthesized by cyclo-addition of carbon dioxide to epoxides in presence of suitable catalysts. Many homogeneous catalysts already been employed for this catalytic fixation such as alkali metal salts [8], quaternary phosphonium/ammonium salts [9], bromine [10], ionic liquids [11], metal complexes [12], polyoxometalate [13], organo catalyst [14] etc. But homogeneous catalysts have general disadvantage of recyclability and reusability. On the other hand, many heterogeneous catalytic systems also developed e.g., MOFs [15], COFs [16], inorganic-organic hybrid core shell microspheres [17] etc. to beat those problems. But the catalytic system requires inconsiderate reaction conditions such as very high carbon dioxide pressure, temperature and poisonous organic solvents. 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 aluminium metal complex which can act as an efficient heterogeneous catalyst for the synthesis of cyclic carbonate under 1 atm CO₂ pressure and room temperature in solvent free condition.

 β -Amino alcohol is very attractive intermediates for the synthesis of some important biologically active natural as well as synthetic products including chiral auxiliaries [18]. These take part in pivotal role of organic synthesis, pharmaceuticals and medicinal chemistry. β -blockers are widely used as insecticidal agents [19] and also in treatment of various human disorders, such as heart failure, cardiac arrhythmias, sympathetic nervous system disorders and hypertension etc. [20]. In classical method, these compounds were produced through aminolysis of epoxides by heating in presence of excess amine. But the method has lots of disadvantages, like excess inorganic base required, large reaction duration, for deactivated aromatic amines low nucleophilicity observed, and use of elevated

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temperature may not be the standard condition for sensitive functional groups molecules [21]. In recent year synthesis of β -amino alcohol through ring opening of epoxides with amine in presence of catalyst gaining a lots of attention to the scientific community [22]. Different types of Lewis base such as NbCl₅ [23], SmI₂ [24], ZrCl₄ [25], RuCl₃ [26], Y(NO₃)₃.6H₂O [27], Sc(OTf)₃ [28] etc. have been used as catalyst for manufacturing this compounds. Under mild and improved reaction conditions metal halides [29] silica perchloric acid [30], metal alkoxides [31], metal amides [32] and alumina [33] also been utilized as efficient catalyst for this compounds preparation. But due to the homogeneous catalytic nature of above mentioned catalysts and also metal toxicity; design and synthesis of eco-friendly and low cost heterogeneous catalyst is still very desirable for production of β -amino alcohols through nucleophilic ring opening of epoxides by different amines.

In this paper we sketch and synthesize a polymer embedded monometallic aluminium (III) complex which can show its catalytic activity towards the insertion of CO_2 to various epoxides to produce cyclic carbonates under atmospheric pressure and ambient temperature and solvent free condition. Again the catalyst is very efficient to produce β -amino alcohols via nucleophilic ring opening of epoxides by aromatic amines under solvent free condition and at room temperature. This polymer anchored catalyst is easily separable from reaction mixture after completion of reaction and can be reused without any significant loss in its activity.

2. Experimental

2.1. Catalyst preparation

This catalyst was easily synthesized in three steps procedure. In the first step Schiff base, 4-Acetylpyridinethiosemicarbazone was prepared. Then chloromethyl polystyrene was reacted with this Schiff base to produce polymer anchored Schiff base ligand. Finally, this polymer-anchored Schiff base ligand reacted with aluminium chloride salt in ethanol to produce polymer-anchored aluminium, $[PS-AI^{III}(L)(Cl)_3]$ catalyst (Scheme 1).

2.1.1. Synthesis of 4-Acetylpyridine thiosemicarbazone (L)

4-acetylpyridine and thiosemicarbazide were mixed in a stoichiometric ratio to synthesize the Schiff base ligand 4-Acetylpyridine thiosemicarbazone. In methanol (100 mL) 4-acetylpyridine (0.10 mol), thiosemicarbazide (0.10 mol) were mixed and heated to reflux for 2 h. A white coloured precipitate was appeared after cooling the reaction mixture. This precipitate was filtered off and washed with methanol. A white crystal appeared after re-crystallisation of the precipitate from methanol. ¹H NMR: (400 MHz, DMSO-d₆) δ 2.288 (s, 3H), 7.889 (dd, *J*=1.6 *Hz*, 2H), 8.144 (s, -NH₂), 8.446 (s, -NH₂), 8.560 (dd, *J*=1.6 *Hz*, 2H) ppm (Fig. S1); ¹³C NMR: (100 MHz, DMSO-d₆) δ 13.83, 121.13, 145.15, 145.53, 150.21, 179.69 (Fig. S2)

2.1.2. Synthesis of Polymer-Anchored Al(III) Catalyst [PS-Al^{III}(L)(Cl)₃]

Polymer-Anchored aluminium catalyst was synthesised in two steps process. 4-acetylpyridine thiosemicarbazone (1.07 g) was dissolved in DMF (20 mL) then chloromethylated polystyrene (2 g) was added to this solution and refluxed for 24 h. After completion the reaction, it was cooled to room temperature. A light yellow coloured polymer beads were obtained which was filtered and washed properly with methanol. The product was dried in vacuum. The polymer supported Schiff base (1 g) was taken in methanol (10 mL) in a round bottom flask. To this mixture, 10 ml methanolic solution of

 $AlCl_3$ (1 % w/v) was added over a period of 30 minutes and refluxed for another 9 h. Then yellow coloured aluminium loaded beads were filtered, washed with methanol and dried under vacuum.



Scheme 1. Synthesis of $[PS-AI^{III}(L)(Cl)_3]$ catalyst.

2.2. General Experimental Procedure for insertion of CO₂ to epoxides

A mixture of epoxides (10 mmol) and [PS-Al^{III}(L)Cl₃] catalyst (40 mg) were taken in a round bottom flux, tetrabutyl ammonium bromide (TBAB) (1 mmol) was added to the above mixture as a cocatalyst. The reaction mixture was stirred under one atmospheric pressure of carbon dioxide at room temperature. The progress of reaction was monitored by TLC. After completion of the reaction ethylacetate (10 ml) was added to the reaction mixture and washed with water (10 ml) for three times. Organic part was collected in a conical flux and dried over anhydrous sodium sulphate. Then organic layer was evaporated via rotary evaporator and analyzed by Varian 3400 gas chromatograph. The gas chromatograph was equipped with a 30 m CP-SIL8CB capillary column and a Flame Ionization Detector. Peak position of various reaction products were compared and matched with the retention times of authentic samples. Identity of the products was also confirmed by using NMR spectroscopy.

2.3. General Experimental Procedure of β -amino alcohols synthesis via nucleophilic ring opening of epoxides by aromatic amines in presence of [PS-Al^{III}(L)Cl₃] catalyst

In a 50 ml R.B. flask, 40 mg of $[PS-Al^{III}(L)Cl_3]$ catalyst, amine (5 mmol), epoxides (5mmol) were taken and the mixture was stirred at room temperature till completation of the reaction. Thin layer chromatography was used to check the completation of the reaction. Then the reaction mixture was poured into 30 ml chloroform and washed with water (10 ml) for three times through solvent extraction technique. Organic part was collected in a R. B. flask and dried over anhydrous Na₂SO₄. After evaporating the organic solvent part via rotary evaporator, the obtained crude product was purified through column chromatography using pet ether and ethyl acetate as eluent. The pure product was identified by NMR spectroscopy and compare with reported literature.

3. Result and discussion

- 3.1. Characterization of $[PS-Al^{III}(L)Cl_3]$ catalyst
- 3.1.1. Elemental analysis

The elemental analysis data of Schiff base ligand (L), polystyrene supported Schiff base ligand [PS-(L)] and catalyst $[PS-Al^{III}(L)Cl_3]$ are given in Table 1. The elemental data of 4-Acetylpyridine thiosemicarbazone (L) are quite similar to that of calculated values. Thus the result indicates that compound was synthesized properly. Again zinc loading on polystyrene supported Schiff base ligand is 3.8524 (calculated from ICP-AES analysis data) also mentions the successful attachment of aluminium on the support.

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Compound	Color	С	Н	N	Al
Ligand (L)	White	49.05 (49.46)	4.99 (5.19)	28.44 (28.84)	
Polymer supported ligand [PS-(L)]	Light	66.45	5.89	18.84	
	yellow				
[PS-Al ^{III} (L)(Cl) ₃] catalyst	Light	46.68	4.32	10.32	5.8524
	yellow				5.8502 ^a

Elemental composition table (in percentage weight)

Parentheses values are calculated values; ^aReused catalyst zinc loading (after 8th cycle).

3.1.1. IR spectra

IR spectra of polystyrene embedded 4-Acetylpyridine thiosemicarbazone [PS-(L)] showed one broad band centered at 3414 cm⁻¹ is due to $v(-NH_2)$ vibration (**Fig. 1**). Another band appeared at 3075 cm⁻¹ is because of v(-NH) vibration. The peak observed at 1639 and 1160 cm⁻¹ are the characteristics frequencies of v(-C=N) and v(-C=S) groups of 4-Acetylpyridine thiosemicarbazone moiety respectively [34]. In [PS-Al^{III}(L)Cl₃] catalyst these two characteristics bands shifts towards lower frequencies which clearly indicates the interactions between aluminium metal with N atom of azomethine (-C=N) group and that of Al with S atom of (-C=S) group. Two new bands also seen in the IR spectra of catalyst at 510 cm⁻¹ and 465 cm⁻¹ that can be assign as v(Al-N) and v(Al-S) respectively [34].



Fig. 1. IR spectra of polymer supported 4-Acetylpyridine thiosemicarbazone ligand [PS-(L)] and its aluminium catalyst [PS-Al^{III}(L)Cl₃].

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3.1.2. Field emission scanning electron microscopy (SEM) and energy dispersive X-ray analyses (EDX)

In order to understand the morphological changes occurs during the course of reaction for the formation of polymer supported aluminium catalyst from polystyrene embedded 4-Acetylpyridine thiosemicarbazone ligand, FE SEM analysis for single beads of the support have been carried out. The surface of chloromethylated polystyrene beads is smooth (not shown hare). After the reaction with 4-Acetylpyridine thiosemicarbazone, the surface of beads becomes slightly rough due to covalent bonding between them (**Fig 2(a)**). Again the surface of the beads appears more rough and small particles deposited on the surface after loading of aluminium metal (**Fig. 2(b**)).

Energy dispersive X-ray analyses have been monitored to know the elemental composition of both ligand and catalyst. In ligand C, N, S elements are present whereas the catalyst contains same elements along with aluminium metal (**Fig. 3**). Thus a FE SEM and EDAX analysis confirms the successful synthesis of polymer supported ligand as well as its aluminium complex.



Fig. 2. FESEM images of [PS-(L)] ligand (a) and [PS-Al^{III}(L)Cl₃] catalyst (b).



Fig. 3. EDX analyses of [PS-(L)] ligand (a) and [PS-Al^{III}(L)Cl₃] catalyst (b).

3.1.3. Powder X-ray diffraction

Powder X-ray diffraction pattern of [PS-(L)] ligand and [PS-Al^{III}(L)Cl₃] catalyst exhibit a broad spectral band in between range of 2θ (10-50) (**Fig. 4**). From this pattern we can conclude that both ligand as well as catalyst is amorphous in nature and no nanoparticle of aluminium metal was formed during the course of catalyst formation reaction [35].



Fig. 4. PXRD spectra of [PS-(L)] ligand and [PS-Al^{III}(L)Cl₃] catalyst.

3.1.3. Thermogravimetry analysis

Thermogravimetry analysis of polystyrene supported ligand and catalyst was monitored under nitrogen atmosphere. The heating rate of the analysis was kept 10 °C/minutes. Both ligand and catalyst were quite stable up to 200 °C (Fig. 5). Catalyst was relatively more stable than ligand. Complete decomposition of ligand as well as catalyst was occurred beyond 400 °C.



Fig. 5. Thermograms of [PS-(L)] ligand and [PS-Al^{III}(L)Cl₃] catalyst.

3.2. Catalytic activity

3.2.1. Catalytic fixation of CO_2 into epoxides for the formation of organic cyclic carbonates in presence of [PS-Al^{III}(L)Cl₃] catalyst

Scheme 2a represents the preparation of cyclic carbonates from epoxides through insertion of atmospheric CO_2 at room temperature under solvent free condition in presence of [PS-Al^{III}(L)Cl₃] catalyst and *tetra-n*-butylammonium bromide (TBAB) as co-catalyst. For optimization of catalytic reaction conditions, the reaction between epichlorohydrin with carbon dioxide was taken as model reaction (Scheme 2b).



Scheme 2. Synthetic paths of (a) organic cyclic carbonates and (b) epichlorohydrin carbonate through CO_2 fixation.

The effects of various parameters like amount of $[PS-AI^{III}(L)Cl_3]$ catalyst and co-catalyst, reaction duration etc. for formation of epichlorohydrin carbonate from epichlorohydrin (5 mmol) were monitored in order to optimize the reaction conditions. **Fig. 6a** showing the effects of catalyst amount on the reaction of epichlorohydrin (5 mmol) with CO₂ (1 bar) and TBAB (1 mmol). From the figure it is clear that very poor amount of substrate conversion (~10%) was observed in absence of the catalyst. In presence of 10 mg catalyst, the substrate conversion proceeds smoothly and gave 45% conversion after 6 hrs. With increasing catalyst amount the conversion of substrate into product also increases. We got maximum conversion of epichlorohydrine (100%) while 40 mg of catalyst was used.

Effect of TBAB amount on the same catalytic reaction in presence of 40 mg catalyst is depicted in **Fig. 6b**. Partial conversion of epichlorohydrin to epichlorohydrin carbonate was observed with use of more or less amount of TBAB than 1 mmol. Use of 1 mmol TBAB gave us maximum conversion (100%) of substrate after 5 hrs of reaction.

Fig. 6c describes the effect of reaction time on substrate conversion into desired carbonate. From this Figure it is confirmed that 5 hrs reaction time is sufficient for obtaining optimize yield.





Fig. 6. Effects of (a) catalyst amount (b) amount of TBAB (c) reaction duration on the conversion of epichlorohydrin.

The conversion of epichlorohydrin and selectivity of epichlorohydrin carbonate formation with respect to reaction time is given in **Fig. 7**. Throughout the reaction, the progress of selectivity of epichlorohydrin carbonate formation from epichlorohydrin remains same (i.e. 100%) but when the reaction is carried out in presence of 1 mmol TBAB without catalyst the selectivity of desired carbonate formation decreases to only 38% under optimized reaction conditions. Thus [PS-Al^{III}(L)Cl₃] catalyst definitely have an important role to improve the conversion of substrate as well as selectivity of desired product.



Fig. 7. Conversion and selectivity with respect to reaction duration over [PS-Al^{III}(L)Cl₃] catalyst.

Substrate scopes for this organic cyclic carbonates synthesis reaction through CO_2 insertion was checked with various epoxides such as epichlorohydrin, 1,2-epoxy-3-phenoxy propane, glycidol, allyl glycidyl ether, glycidyl isopropyl ether, styrene oxide, propylene oxide and cyclohexene oxide under optimized reaction conditions. Almost all the substrates showed very good conversion and selectivity towards respective desired product (**Table 2**). From our observations it was noticeable that aliphatic terminal epoxides (Table 2, entries 1-6) showed relatively better yield of the cyclic carbonates than the aromatic terminal epoxides (Table 1, entries 7,8).

Table 2

			Time	% of GC conversion	$\mathrm{TOF}^{\mathrm{b}}$
Entry	Epoxides	Product	(h)	(% Selectivity)	
1	Cl		5	100 (≥99)	11.49
		Cl			
2	2		5	100 (≥99)	11.49
3	но	O HO HO	5	97 (≥99)	11.15
4			5	95 (≥99)	10.92
5			5	95 (≥99)	10.92
6	0	0 0 0	5	93 (≥99)	10.67

Synthesis of organic cyclic carbonate through CO_2 fixation by catalysed by [PS-Al^{III}(L)Cl₃] catalyst^a



^aReaction conditions: Epoxides (5 mmol), TBAB (1 mmol), catalyst (40 mg, 0.087 mmol based on Al metal), Room temperature, No solvent;

^bTOF (Turn Over Frequency): no. of moles of the substrate being converted per mole of active site of the catalyst/time (in h).

3.2.2. Probable mechanism of catalytic synthesis of organic cyclic carbonates

The catalytic reaction mechanism for synthesis of cyclic carbonate from epoxides in presence of a bimetallic aluminium(salen) complex and TBAB was check up and established appropriately by Michael North and Riccardo Pasquale [36]. The formation of amine carbamate salts through the breaking of TBAB is also well accepted in previous reports [36, 37]. In this work although we could not recognize and separates any intermediate species, a probable mechanism is shown here (Scheme 3) with the help of reported literatures. The catalytic cycle is initiated through the epoxides activation by Lewis acidic Al centre of [PS-Al^{III}(L)Cl₃] catalyst, then nucleophilic attack of Br⁻ of TBAB creates epoxides ring-opening to make Al-bonded bromo-alkoxide. Next, alkoxide intermediate works as nucleophile and attacks carbon dioxide to make the metal carbonate intermediate. This so formed metal carbonate intermediate produced desired carbonate compound via an intra-molecular ring-closure reaction and leave the catalyst as free for next catalytic cycle.



Scheme 3. Probable mechanistic pathway of catalytic cyclic carbonates synthesis reaction.

3.2.3. Catalytic synthesis of β -amino alcohol via ring opening of epoxides in presence of [PS-Al^{III}(L)Cl₃] catalyst

Catalytic synthesis of β -amino alcohol via ring opening reaction of epoxides and amine in presence of [PS-Al^{III}(L)Cl₃] catalyst is shown in Scheme 4a. To optimize the reaction, effects of catalyst amount and reaction duration was checked by taking epichlorohydrin (1mmol) and aniline (1 mmol) at room temperature under solvent free condition (Scheme 4b).



Scheme 4. Synthetic paths of (a) β -amino alcohol and (b) 1-chloro-3-(phenylamino)propan-2-ol through ring opening reaction of epoxide.

Fig. 8a showing the effects of catalyst amount on 1-chloro-3-(phenylamino)propan-2-ol formation through ring opening of epichlorohydrin by aniline. From the figure it is clear that very poor amount of 2-amino alcohol product is formed (\sim 5%) in absence of the catalyst after 24 hr of reaction. In presence of 10 mg catalyst, the reaction proceeds smoothly and gave 58% yield of desired product after 4 hrs. With increasing catalyst amount the product yield also increases. We got maximum yield of product (96%) while 30 mg (or 35 mg) of catalyst was used.

Fig. 8b describes the effect of reaction time on yield of desired 2-amino alcohol product formation. From this Figure it is clear that 3 hrs reaction time is sufficient for obtaining optimum yield of product.





Fig. 8. Effects of (a) catalyst amount (b) reaction duration on the production of 1-chloro-3-(phenylamino)propan-2-ol from epichlorohydrin and aniline.

Scheme 5 depicts the various pathways of products formation by means of nucleophilic attacks of amine on epoxides. There is a possibility of getting two products from the reaction involving three probable routes. The advantage of our catalytic reaction is production of β -amino alcohols from nucleophilic attack at the terminal carbon of epoxides as the sole product. The reactions mechanism is very simple, straightforward and product yields are usually high.



Scheme 5. Ring opening of epichlorohydrin by nucleophilic attack of amine.

The substrate tolerance for this catalytic 2-amino alcohol production reaction was tested with different epoxides viz. epichlorohydrin, glycidol, allyl glycidyl ether, cyclohexene oxide, styrene oxide and 1,2-epoxy-3-phenoxy propane with anilines and derivatives of anilines under optimized reaction condition. The observed results are summarized in Table 3. Generally the catalyst [PS-Al^{III}(L)Cl₃] was very efficient to produce desired 2-amino alcohol product in 3 h. A facile attack by aniline at benzylic position or the less-hindered terminal carbon of styrene oxide and aryloxy epoxides respectively produced the regioselective product (Table 3, entries 5 and 6) through this catalytic reaction. Cyclohexene oxide, a meso epoxide was also took part in the epoxide ring opening reaction with aniline. With this meso epoxide we got high yields of desired product (90%) (Table 3, entry 4). Moreover both electron-donating and electron-withdrawing group substituted anilines undergoes this catalytic reaction very smoothly and furnishes very good amount of product yield (Table 3, entries 7-10).

Table 3

Synthesis of 2-amino alcohol via ring opening reaction of epoxides by amine nucleophile in presence of $[PS-Al^{III}(L)Cl_3]$ catalyst^a

Entry	Epoxides	Amine	Product	Isolated yield (%)
1	Cl	NH ₂	HO HN-CI	96
2	НО	NH ₂	HO HN-	92
3		NH ₂		91
4	0	NH ₂	OH N-	90
5		NH ₂	OH H N	97
6		NH ₂	OH H N	97
7	CI	Cl NH2	HO HN CI	91
8		CI NH2	HO HN - Cl	88



^aReaction conditions: epoxides (1 mmol), aniline (1 mmol), [PS-Al^{III}(L)Cl₃] catalyst (30 mg, 0.065 mmol based on Al metal), Room temperature, No solvent, 3 hr.

3.2.4. Comparison of catalytic activity of our synthesized catalyast with other reported systems

The efficiency of catalytic activity of $[PS-Al^{III}(L)Cl_3]$ catalyst can be proved by comparing it with other reported catalytic protocols. Here we compared organic cyclic carbonates synthesis as well as 2-amino alcohol production reactions by $[PS-Al^{III}(L)Cl_3]$ catalyst with other reported methods (Table 4) [38-48]. The result from the comparison table clearly indicates that our synthesized catalyst is very efficient in both cyclic carbonates and 2-amino alcohol formation reactions.

Table 4:

Relative catalytic activity study of [PS-Al^{III}(L)Cl₃] with other reported systems

Catalyst	Reaction conditions	Yield (%)	Ref.
PISA-350	Epichlorohydrine (6 mmol), catalyst (0.03 mmol), CO ₂ pressure (1.0 MPa), 100 °C, 4 h	98	[38]
Dinuclear Aluminum Poly(phenolate) Complexes	Epichlorohydrine (16.63 mmol), 0.3 mol% catalyst, 0.9 mol% TBAB, 1 bar CO ₂ (balloon), 85 °C, 18 h.	97	[39]
Al-HCP	Epichlorohydrine (3 mmol), 0.25 mol % catalyst, TBAB (2 mol%), CO_2 (1.0 MPa), 40 °C, 2.5 h.	97	[40]
Bimetallic Aluminium(Salphen) Complex	Epichlorohydrine (1.66 mmol)), 0.25 mol% catalyst, TBAB (0.5 mol%), CO ₂ (10 bar), 50 °C, 24 h	80	[41]
Amidinate aluminium complex	Epichlorohydrine (1.66 mmol), catalyst (0.083 mmol), and Bu_4NI (27 mg, 0.083 mmol), CO_2 (10 bar), 50 °C, 24 h.	89	[42]
Helical Aluminium Catalysts	Epichlorohydrine (1.7 mmol mmol), catalyst (17.0 μ mol), TBAB (17.0 μ mol), CO ₂ (10 bar), 50-90 °C, 16 h.	94	[43]
[PS-Al ^{III} (L)Cl ₃] catalyst	Epichlorohydrine (5 mmol), TBAB (1 mmol), catalyst (40 mg, 0.087 mmol based on Al metal), CO ₂ (1 bar), Room temperature, No solvent, 5h	≥99	This work

Vanadium- Salan Complex	Cyclohexene oxide (1.0 mmol), anilines (1.0 mmol), Catalyst (10 mol %), DCM, 0 °C, 24 h.	84	[44]
Macrocyclic Cr(III) salen complex	Cyclohexene oxide (1 mmol), anilines (1 mmol), Catalyst (0.5 mol%), DCM/MeOH, room temperature, 24 h	98	[45]
Fe(ClO ₄) ₂ .6H ₂ O and Bolm's ligand	2,3-diphenyloxirane (1.0 equiv.), aniline (1.0 equiv.), Fe(ClO_4) ₂ .6H ₂ O (5 mol %), Bolm's ligand (6 mol %), 16 h	90	[46]
Organocatalyst	Cyclohexene oxide (0.2 mmol), anilines (0.22 mmol), Catalyst (20 mol%), DCM, room temperature, 24 h,.	95	[47]
PS-AN-Ce	Cyclohexene oxide (1.5 mmol), aniline (2.25 mmol), 25 mg PS-AN-Ce catalyst, solvent free condition, room temperature, 2.5 hour.	92	[48]
[PS-Al ^{III} (L)Cl ₃] catalyst	Cyclohexene oxide (1 mmol), aniline (1 mmol), catalyst (30 mg, 0.065 mmol based on Al metal), Room temperature, solvent free, 3 hr.	90	This work

4. Heterogeneity of [PS-Al^{III}(L)Cl₃] catalyst

Heterogeneity nature of [PS-Al^{III}(L)Cl₃] catalyst was confirmed by hot filtration test and checking PXRD pattern as well as ICP-AES analysis of fresh and used catalyst. Epichlorohydrin carbonate formation reaction was carried out by stirring epichlorohydrin (5 mmol), TBAB (1 mmol) at room temperature under 1 bar CO₂ pressure in presence of catalyst (40 mg) for 2 hr. The conversion of substrate was found (58%) by GC. After 2 hr of catalytic reaction, the catalyst was separated by filtration and the filtrate was continued to stir for another 2 hr without catalyst. Finally the conversion of substrate was further verified by GC but no more conversion of epichlorohydrin was observed. ICP-AES analysis of fresh and used catalyst after first cycle suggested that both of them contains same amount of Al metal loading (i.e. 5.8524% of metal). No considerable amount decrease of metal loading was seen even after use of eight consecutive catalytic cycles (5.8502% of metal). The PXRD spectral pattern of catalyst and used catalyst was almost similar (Fig. S21). Thus all these data confirmedly assured the heterogeneity nature of [PS-Al^{III}(L)Cl₃] catalyst.

5. Recyclability of [PS-Al^{III}(L)Cl₃] catalyst

It is very meaningful for a heterogeneous catalyst to check its separation, recoverability and reusability. To monitor the recyclability of the catalyst we use cyclic carbonates formation reaction from epichlrorhydrin through CO_2 insertion in presence of [PS-Al^{III}(L)Cl₃] catalyst. The catalyst was isolated after each catalytic cycle by simple filtration process. Then separated catalyst was washed properly by methanol and acetone simultaneously. The washed catalyst was heated in oven at 80 °C for 12 hr. Then it was kept under vacuum till the use of next catalytic cycle. From fig. 9 it is clear that the [PS-Al^{III}(L)Cl₃] catalyst can be used for eight cycles without considerable amount loss of product yield. So from this data we can conclude that the catalyst is fully heterogeneous in nature.



Fig. 9. Recyclability of [PS-Al^{III}(L)Cl₃] catalyst in epichlorohydrin carbonate production reaction.

6. Conclusion

We have design and synthesized a modified polystyrene supported Al(III) catalyst. The catalyst was characterized properly by X-ray powder diffraction analysis, FT-IR spectroscopy, Elemental analysis, Thermogravimetry and ICP-AES analysis. The catalyst is very capable in fixation of carbon dioxide towards epoxides under 1 bar pressure at room temperature for the synthesis of organic cyclic carbonates. Not only that the catalyst is very effective for regioselective preparation of 2-amino alcohol via epoxides ring opening by nucleophilic attacks of aromatic amines. Both type of catalytic reactions proceeds through solvent free, hazardless and environmentally benign conditions. We expect low cost, heterogeneous and recyclable (effective after use of eight successive cycles) catalytic system may gain an attention in industrial applications in future.

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Research Highlights

- Organically modified polystyrene embedded Al(III) catalyst has been synthesized and characterized.
- The catalyst is efficient towards the synthesis of organic cyclic carbonate under solvent free and 1 bar CO₂ pressure.
- The catalyst is also very effective for the formation of 2-amino alcohol from epoxides under green condition.
- The catalyst was stable, easily separable and efficiently reusable for several cycles.

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