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Alkylene Carbonates Synthesis by the Reaction of Carbon Dioxide and Ethylene Oxide in the Presence of Zink Phenolates

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Abstract: The cycloaddition reaction of carbon dioxide (CO_2) and ethylene oxide (EO) for the synthesis of ethylene carbonate (EC) was successfully conducted in a high-pressure reactor in the presence of synthesized thio-bis-alkyl phenolate-Zn catalysts in methylene chloride solvent, without using any co-catalysts. The optimum reaction condition was found at: [Cat]= $1.0 \cdot 10^{-3}$ mol/l; [EO]= 3.0 mol/l; P_{CO2}= 6.0 MPa; T= 120ºC; τ= 2.0 h and 350 rpm stirring speed in the presence of 2,2`-thio-bis-6-ethylaminomethyl-4-tert-octyl phenolate-Zn (TB-6-EAM-4-OPh-Zn) catalyst. In these conditions EO conversion, yield and selectivity of EC, catalyst productivity and TOF were 96.0%, 99,0%, 95.0%, 372.1g of EC/g Cat. and 1424.5mol EC/mol Cat.•h, respectively.

Keywords: alkylene carbonates, carbon dioxide, ethylene oxide, zink phenolates

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1 Introduction

In the synthesis of many organic products a huge amount of both inorganic and organic waste is formed. The problems of the purity of air, water and conservation of nature are the urgent problems of humanity. In this case, environmentalists are right - who want to destroy these harmful wastes. But, at the same time, it is necessary to arm yourself with the Principles of "Green Chemistry" to completely secure chemical production [1].

One such waste is carbon dioxide. The main sources of industrial emissions of carbon dioxide (CO_2) are the production of electricity from fossil fuels, such as oil, natural gas and coal, as well as from timber. A huge amount of CO_2 is also formed in chemical processes, in the production of cement and as a result of automobile exhausts. This adverse effect has led to a concentration of CO_2 in the atmosphere over the past 200 years increased from 250 ppm to 367 ppm [2, 3]. The growing concern with global warming and its effects on climate change is almost certain to drive government regulation to reduce the amount of greenhouse gases allowed to be emitted into the atmosphere. Although CO_2 is not the worst greenhouse gas, it is by far the most released with the current world-wide emission rate of approximately 28 gigatons of CO_2 per year. Therefore, scientists consider it necessary to further reduce carbon dioxide emissions to the atmosphere [2, 3].

Using CO_2 can replace various solvents in chemical processes due to its specific physical and chemical properties. This minimizes the risk of environmental pollution that occurs when environmentally harmful volatile organic compounds (VOCs) are used as solvents [4-8].VOCs emissions, which are often used as solvents in industrial processes, are environmentally harmful and therefore replacing VOCs with environmentally safer "green solvents", such as ionic liquids or alkylene carbonates, is very relevant [9-15].

CO_2 is also seen partly as a renewable raw material and the chemical utilization of CO_2 as a carbon resource in chemistry reactions is an important topic [16-21]. These are the synthesis of many derivatives: carbamates (**10**), carboxylated allylic derivatives (**11**), acetic acid (**12**), dialkyl carbonates (**13**), polypyrrones (**14**), lactones (**15**), polyuretanes (**16**), propionic acid (**17**), CO_2 addition to styrene (**18**), carboxylation of aromatic halogenides (**19**), receiving carbon acids from alkenes (**20**), ethylene (**21**), etc.

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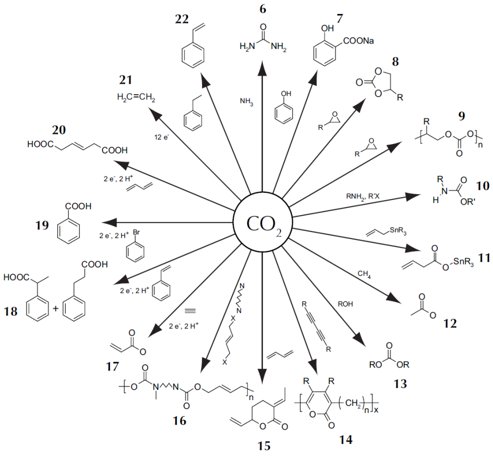
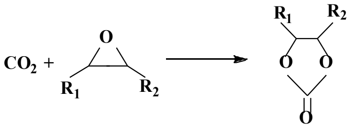
[16-21] (Scheme 1).

Synthesis of cyclic alkylene carbonates (AC) by the reaction of CO_2 with various alkylene oxides (such as, ethylene oxide, propylene oxide, butylene oxide, styrene oxide, etc.) (**8**) is a step towards the production of alkylene carbonates according to the principles of “green chemistry”[22-31] (Scheme 2).



Scheme 1: Using of CO_2 as C_1 building block in organic synthesis.



Scheme 2: Synthesis reaction of alkylene carbonates.

Cyclic carbonates are excellent “green” solvents for cosmetics and in various chemical processes due to their unique properties, high solubility, and non-toxicity [32]. They also can use as an intermediate in the production of fine chemicals such as plastics, and pharmaceutical materials [33].

The production of five-membered cyclic carbonates from CO_2 has been industrialized since the 1950s. The history of coupling CO_2 with epoxide has been known since 1969 when Inoue et al. combined $ZnEt_2$, water, CO_2, and propylene oxide (PO) to yield a small quantity of polymeric material [34]. A wide range of catalysts have been explored for the generation of cyclic carbonates using CO_2. The most effective of these were found to be organometallic and salen complexes, metal oxides, alkali metal salts, supported phase catalysts, phosphines, quaternary onium salts, ionic liquids and metal organic frameworks [22-31]. Catalysis based on (salen)metal complexes have seen significant progress. Salen-metal catalysts originally evolved from the metal porphyrinate catalysts. They have measured one of the highest TOFs for homogeneous metal-based catalysts. In particular, a TOF of 100-500 mol AK/mol Cat•hour was observed [28, 29].

Most of the catalysts described in the literature have significant drawbacks, among which low stability, activity, selectivity and productivity, the need to use co-catalyst, high cost [30, 31]. Therefore, the research and development of fundamentally new, easy synthesized, low cost and "green" catalytic systems for the synthesis of cyclic carbonates has undoubted scientific and practical interest. The recent challenges in cyclic carbonate synthesis have focused on limiting the use of inorganic catalysts or replacing them with new, environmentally benign free metal media in a view to develop “green” chemical synthesis.

In the present work, the cycloaddition reaction of carbon dioxide with ethylene oxide to produce ethylene carbonate was efficiently catalyze by Zn-thio-bis-alkylphenolates.

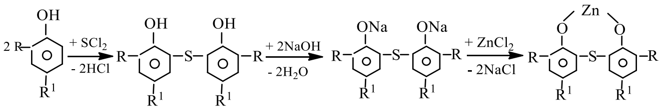
2 Experimental

2.1Materials and Reagents

All the starting phenolic compounds used, zinc chloride, SCl_2 and solvent (methylene chloride), etc. are produced by Sigma-Aldrich and were used without further purification. Silica gel 60 silica gel with particle size 0.063-0.100 mm produced by Merck was used for the column chromatography. Ethylene oxide and carbon dioxide 99.8% pure, produced by Merck, were used in the work.

2.2 General Method for the Synthesis of Zn-Catalyst and Ethylene Carbonate

The starting components for the preparation of the catalysts, thio-bis-alkylphenols, were synthesized according to a known procedure [35, 36], by the condensation of the corresponding phenols with SCl_2 in the presence of KU-2 catalyst. The Zn-thio-bis-alkylphenolate catalysts were synthesized through the reaction of the starting thio-bis-alkylphenols with NaOH (or KOH) and the exchange reaction of the resulting sodium salt with $ZnCl_2$, according to the scheme:



Scheme 3: Synthesis reactions of Zn-thio-bis-alkyl-phenolates. R= H atom, C_1-C_8 alkyl radicals or $(C_2H_5)_2$-N-CH_2-diethylaminomethyl group; R^1 = H, C_1-C_8 alkyl radicals.

Physico-chemical data of synthesized Zn-thio-bis-alkylphenolates are shown in Table 1.

All the reactions for the production of ethylene carbonate were carried out in a mechanically stirred high pressure reactor (autoclave - model, India) equipped with a pressure gauge, stirrer, thermocouple and a heating mantle and controller. To remove the air, the autoclave was filled three times with carbon dioxide of 1.0 MPa and then the pressure

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was dropped. The necessary amount of catalyst in the solvent and ethylene oxide in the CO_2 stream was loaded into the autoclave. Then the necessary pressure of CO_2 was collected. The autoclave was heated to the desired temperature for the duration of the reaction. The autoclave was then cooled to room temperature and the pressure was released. After completion of the reaction, to separate the catalyst, the reaction mixture was passed through silica gel (Eluent-CH_2Cl_2). When the products of the reaction were purified, column chromatography was used, the eluent was EtOAc/Hexane=1:3. As the reaction solvent, methylene chloride was mainly used. The product obtained from the filtered reaction mixture was then analyzed using gas chromatography (GC).

2.3 Methods for Analysis of Starting Reagents and Products

The structure of all starting phenol compounds, synthesized catalysts and the ethylene carbonate product were described and confirmed by ^{1}H-NMR, ^{13}C-NMR, in some cases by high-resolution mass spectrometry and IR-spectroscopy. The ^{1}H-NMR spectra were recorded on Bruker Avance 400 spectrometers at 400 MHz. The ^{13}C spectres were recorded on a Bruker Avance 400 device at a frequency of 101 MHz. DMSO-d6, $CDCl_3$, CD_3OD, D_2O and CD_2Cl_2 were used as solvents. IR-spectra were recorded on the FTIR Shimadzu IR Prestige-21 spectrometer. Shimadzu GC-2014 gas chromatograph (GC) was used to analyze the reaction mixture and internal standardization method was used for quantification of all the components present in the reaction mixture. The melting points were measured in open capillary tubes and were not corrected. Elemental analyses were carried out in the Laboratory No. 12 of IPCP of ANAS.

3 Results and Discussion

The effect of various parameters such as catalyst types, catalyst and ethylene oxide concentration, CO_2 pressure, reaction temperature and time has been studied to find the optimum conditions and the best preferred catalyst for the reaction.

3.1 Effect of Different Catalysts Type

Several synthesized new Zn-phenolate catalysts were tested in order to study the catalytic activity and selectivity for the production of EC from the reaction of EO and CO_2 using a high-pressure reactor.

Table 2 shows the effect of different catalysts which including various Zn-thio-bis-alkylphenolates on the conversion of EO and on the yield and selectivity of EC.

It can be seen from Table 2 that every Zn-phenolates show high effect in cycloaddition reaction, but TB-4-O-6-EAMPh-Zn and TB-4-B-6-EAMPh-Zn catalysts gave highest conversion of EO (~95.0-96.0%), EC yield (~92.2-95.0.0%), selectivity (~97.0-99.0%) and TOF (~1382.8-1424.5 mol EO/mol Cat·hour). Based on this study, TB-4-O-6-EAMPh-Zn catalyst was found to be the best performed catalyst for synthesis of EC and all further studies were conducted using this catalyst.

3.2 Effect of Stirring Speed

The cycloaddition reaction of EO and CO_2 was carried out at different stirring speed of 250-650 rpm. The results are shown in Figure 1,a. It was found that there were no significant changes in the conversion of EO (~93.0-96.0%), yield (~89.3-95.0) and selectivity of EC (~96.0-99.0) when the stirring speed was increased from 250 to 450 rpm considering the experimental error of ±3%. Since there exists no external mass transfer resistance, it could be concluded that good homogeneous distribution of catalyst was possible even at low stirrer speed of 350 rpm (energy efficient process). Therefore, all the subsequent experiments were carried out at a stirring speed of 350 rpm.

3.3 Effect of Catalyst Concentration

The synthesis of EC was studied with different concentrations of TB-4-O-6-EAMPh-Zn catalyst at 120ºC and 6.0 MPa CO_2 pressure. The results are presented in Figure 1,b. It can be seen from Figure 1,b, that an increase in catalyst concentrations in interval $2.5 \cdot 10^{-4}$-$1.0 \cdot 10^{-3}$ mol/l increases EO conversion (45.0-96.0%), yield (31.5-95.0%) and selectivity of EC (70.0-99.0). Future increasing of [Cat.] in interval $1.0 \cdot 10^{-3}$-$2.0 \cdot 10^{-3}$ mol/l accompanied by increasing of EO conversion (from 96.0 to 99.0%), but in that time are decreased the yield of EC (from 94.1 till 93.1%) and selectivity of EC (from 98.0 till 94.0%). Based on this study, catalyst concentration of $1.0 \cdot 10^{-3}$ mol/l was chosen as optimum and all further experiments were conducted at this catalyst concentration.

3.4 Effect of Ethylene Oxide Concentration

The synthesis of EC was studied with different concentrations of ethylene oxide and at TB-4-O-6-EAMPh-Zn catalyst concentration of $1.0 \cdot 10^{-3}$ mol/L, 120ºC and 6.0 MPa CO_2 pressure. It can be seen from Figure 2,a, that an increase in ethylene oxide concentrations in interval 1.0-6.0 mol/L decrease the conversion of EO in the interval 98.0-83.0%. By increasing of EO concentration from 1.0 to 3.0 mol/L the yield and selectivity of EC is increased in the interval 91.1-95.0% and 93.0-95.0%, respectively. Further increasing in [EO] till 6.0 mol/l accompanied by decreasing of EC yield and selectivity till 70.6% and 85.0%, respectively. Based on this study, ethylene oxide concentration of 3.0 mol/l was chosen as optimum and all further experiments were conducted at this EO concentration.

3.5 Effect of Reaction Temperature

Cycloaddition reaction of EO and CO_2 was carried out at different reaction temperature to study its effect on EO conversion and EC yield and selectivity. Figure 2,b shows the temperature dependence on the yield and selectivity of EC and on the EO conversion. For this study, all experiments

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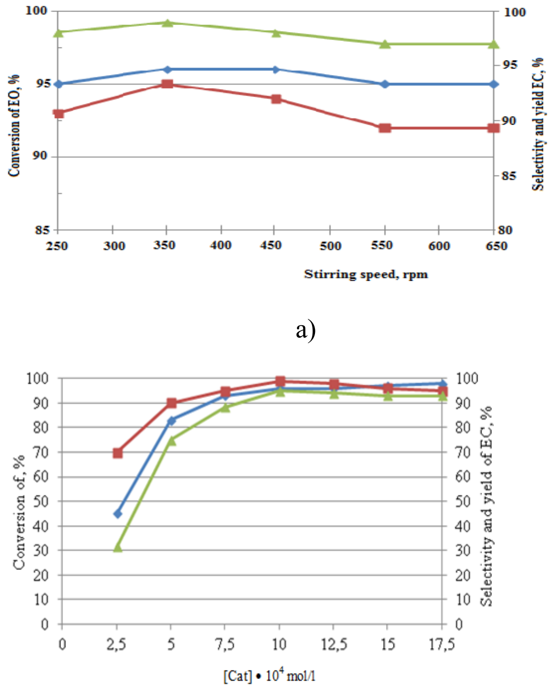
were carried out at [Cat]·10^{-3} mol/L; CO_2 pressure - 6.0 MPa; reaction temperature - 120°C; reaction time - 2.0 h; stirring speed 350 rpm. It can be observed from Figure 2,b, that an increase in reaction temperature from 80.0°C till 120°C increases EO conversion (80.0-97.0-95.0%) and EC yield (73.6-95.0-86.5%) and selectivity (92.0-99.0-91.0%) with maximum at 120°C. However, in the further increasing of the reaction temperature from 120°C till 200°C the conversion of EO was increased to 99.0%, the yield and selectivity of EC were decreased to 89.0% and 90.0%, respectively, when compared to the experiment conducted at 120°C. All the subsequent experiments for EC synthesis were carried out at 120°C.



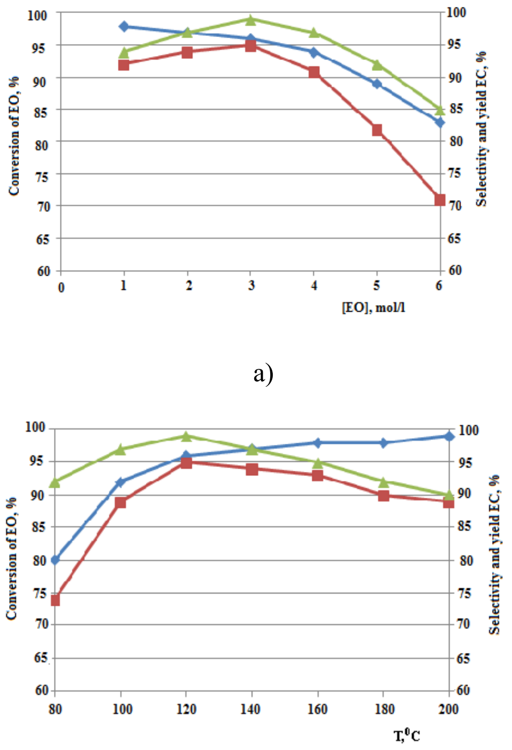
a)

b)

Fig. 1: Effect of stirring speed (a) and catalyst concentration (b) on the conversion (◊) of ethylene oxide (EO) *versus* selectivity (Δ) and yield (□) of ethylene carbonate (EC). Experimental conditions: Catalyst - TB-4-O-6-EAMPh-Zn; [EO]= 3.0 mol/l; P_{CO2}= 6.0 MPa; T= 120°C; τ= 2.0 h; a) [Cat]= 1.0·10^{-3} mol/l; b) stirring speed 350 rpm.

3.6 Effect of Carbon Dioxide Pressure

The reaction of EO and CO_2 to produce EC was investigated at different CO_2 pressure. For this study, the experiments were carried out at 120°C, [Cat]=1.0·10^{-3} mol/l; [EO]= 3.0 mol/l; reaction time- τ= 2.0 h; stirring speed 350 rpm. Figure 3,a shows the effect of CO_2 pressure on conversion of EO and on the yield and selectivity of EC formation. It can be observed from Figure 3,a, that an increase in CO_2 pressure increases EO conversion and yield and selectivity of EC. At a CO_2 pressure of 1.0-6.0 MPa, the conversion of EO and the yield and selectivity of EC were ~60.0-96.0%, ~54.0-95.0% and ~90.0-99.0%, respectively. However, at a CO_2 pressure of 10.0 MPa, the EO conversion, yield and selectivity of EC decreased to 85.0%, ~79.0% and ~93.0%, respectively.



a)

b)

Fig. 2: Effect of ethylene oxide concentration ([EO]) (a) and reaction temperature (T) (b) on the conversion (◊) of ethylene oxide (EO) *versus* selectivity (Δ) and yield (□) of ethylene carbonate (EC). Experimental conditions: Catalyst - TB-4-O-6-EAMPh-Zn; [Cat]= 1.0·10^{-3} mol/l; P_{CO2}= 6.0 MPa; τ= 2.0 h; stirring speed 350 rpm.; a) T= 120°C; b) [EO]= 3.0 mol/l.

The reasons for such outcomes from this study are inconclusive. Based on the experimental results, it can be concluded that 6.0 MPa CO_2 pressure was the optimum CO_2 pressure and all the subsequent experiments for the EC synthesis were performed at a CO_2 pressure of 6.0 MPa.

3.7 Effect of Reaction Time

A series of experiments were carried out by varying the reaction time to determine the optimum reaction time for synthesis of EC using TB-4-O-6-EAMPh-Zn catalyst. All experiments for this study were conducted at [Cat]=1.0·10^{-3} mol/l; [EO]= 3.0 mol/l; T= 120°C and stirring speed 350 rpm. Figure 3,b illustrates that an increase in reaction time increases EO conversion as well as yield and selectivity of EC. EO conversion of ~96%, ~95.0% yield and ~99.0%

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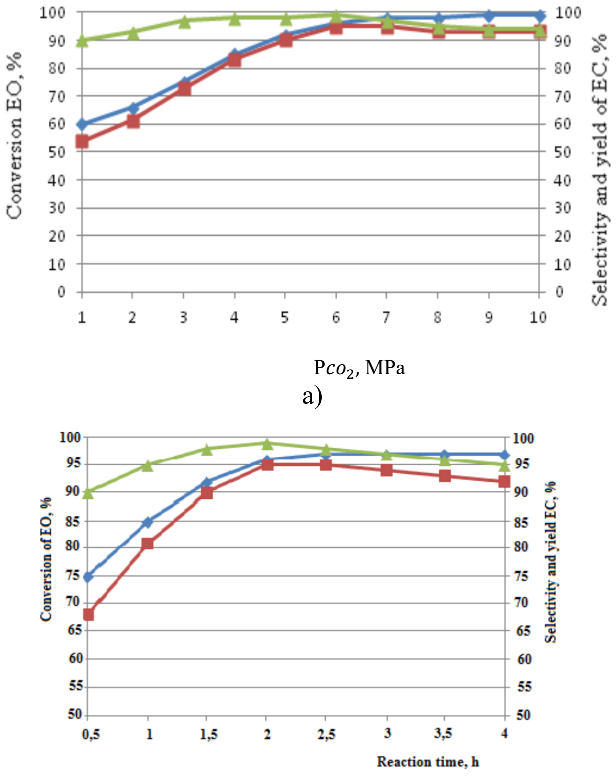
selectivity of EC was observed for reaction time of 2 h. However, when the reaction was carried out beyond 2.0 h, i.e., 4.0 h, the conversion of EO as well as yield and selectivity of EC were similar to that obtained at 2.0 h. It can be concluded that the reaction reaches equilibrium at 2.0 h and the reaction time beyond 2.0 h would not be beneficial for this reactive system. Based on this study, reaction time of 2.0 h was considered to be the optimum and all further investigations were carried out at a reaction time of 2.0 h.



a)

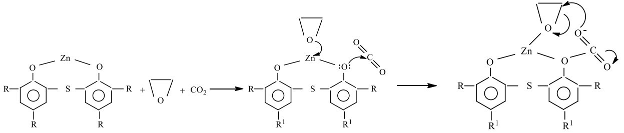
b)

Fig. 3: Effect of carbon dioxide pressure (P_{CO2}) a) and reaction time (τ) (b) on the conversion (◊) of ethylene oxide (EO) *versus* selectivity (Δ) and yield (□) of ethylene carbonate (EC). Experimental conditions: Catalyst - TB-4-O-6-EAMPh-Zn; [Cat]=$1.0 \cdot 10^{-3}$ mol/l; [EO]= 3.0 mol/l; T= 120ºC; T= 120ºC; stirring speed 350 rpm; a) τ= 2.0 h; b) P_{CO2}= 6.0 MPa.

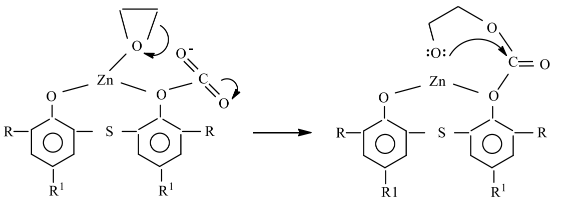
3.8 Possible Reaction Mechanism for Syntheses of Ethylene Carbonate in the Presence of Zn-thio-bis Alkylphenolate Catalyst

The use of various catalysts to synthesize cyclic carbonate from the cycloaddition reaction of CO_2 and epoxides is currently attracting interest in the last few decades in view of environmental, green chemistry and technical advantages. A few mechanistic studies have been proposed for the cycloaddition of epoxides and CO_2 in the presence of homogeneous and heterogeneous catalysts [37-39]. In most cases, the studies were demonstrated by means of characterization with various spectroscopic and analytical instruments. As such, path for the specific reaction mechanism typically depends on the nature of the catalytic system, type of epoxides (substrates) and reaction conditions [40]. The proposed reaction mechanism for the ethylene carbonate syntheses from reaction of epoxides and CO_2 in the presence of Zn-thio-bis alkylphenolate catalysts is shown in Figure 4 (a, b, c).

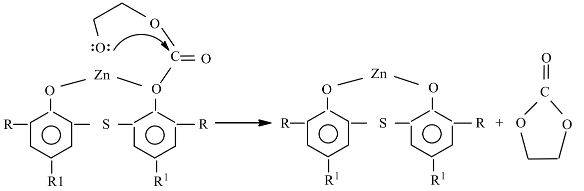
a) Initiation by involving of epoxide and CO_2 on catalyst:



b) Ring opening of epoxide to form oxy-anion specie:



c) Ring closure and elimination of cyclic organic carbonate.



Zn is a metal (acidic site) atom and O is oxygen (basic site) atom of Zn-phenolate catalyst.

Figure 4. Possible reaction mechanisms for ethylene carbonate syntheses over Zn-phenolate catalyst.

In the proposed mechanism, Zn-phenolate catalyst contain both Lewis acid and Lewis base site for the electrophilic and nucleophilic activation of epoxides and CO_2. The metal atom acts as a Lewis acid site for the electrophilic activation, while oxygen atom acts as a Lewis basic site for nucleophilic activation. Cycloaddition reaction is initiated by involving of CO_2 on the Lewis basic sites to form a carboxylate anion and epoxide was activated by involving on the Lewis acidic site. The carbon atom of epoxide is attacked by a carboxylate anion that leads to the ring opening of epoxide to form oxy-anion specie. Dissociation of metal-oxide (catalyst) from the oxy-anion specie leads to a ring closure and elimination of cyclic carbonate as a product. The very less amount (~1.0-10.0%) of side products associated with cycloaddition reaction of CO_2 and epoxide includes isomers of epoxide such as acetone and propionaldehyde, and dimers of epoxide including 2-ethyl-4-methyl-1,3-dioxolane and their derivatives.

As it seems from results of experiments, effect of various reaction parameters such as catalyst type, catalyst and ethylene oxide concentration, CO_2 pressure, reaction time,

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reaction temperature, etc. was discussed in this article. It was found that an increase in reaction time increases EO conversion and EC yield and selectivity. Experimental results showed that an increase in reaction temperature above 120ºC and CO_2 pressure beyond 6.0 MPa decreases EC yield. The optimum reaction condition was found at: [Cat]= $1.0\cdot10^{-3}$ mol/l; [EO]= 3.0 mol/l; P_{CO2}= 6.0 MPa; T= 120ºC; τ= 2.0 h and 350 rpm stirring speed in the presence of TB-4-OPh-6-EAM-Zn catalyst. In these conditions EO conversion, yield and selectivity of EC, catalyst productivity and TOF were 96.0%, 99.0%, 95.0%, 372.1 g of EC/g Cat. and 1424.5 mol EC/mol Cat.•h, respectively.

4 Conclusions

The market demand for organic carbonates has dramatically increased in recent years due to the significance of organic carbonate as intermediates in several industrial applications. Greener and sustainable catalytic reaction of epoxide and carbon dioxide (CO_2) to produce organic carbonates is receiving a growing attention from chemical industries in terms of technical advantages of heterogeneous and homogeneous processes.

In this work, several thio-bis-alkylphenolate-Zn catalysts were synthesized and investigated for the syntheses of ethylene carbonate from cycloaddition reaction of ethylene oxide and CO_2 in methylene chloride solvent, without using any co-catalysts. The experiments have been conducted in a batch high pressure reactor. The effect of various parameters e.g. catalyst type, catalyst and ethylene oxide concentrations, reaction time and reaction temperature, CO_2 pressure on the efficiency of ethylene carbonate synthesis has been discussed. The optimum reaction condition was found at: [Cat]= $1.0\cdot10^{-3}$ mol/l; [EO]= 3.0 mol/l; P_{CO2}= 6.0 MPa; T= 120ºC; τ= 2.0 h and 350 rpm stirring speed in the presence of 2,2`-thio-bis-4-tert-octyl-6-ethylaminomethyl phenolate-Zn (TB-4-O-6-EAMPh-Zn) catalyst. In these conditions EO conversion, yield and selectivity of EC, catalyst productivity and TOF were 96.0%, 99,0%, 95.0%, 372.1 g of EC/g Cat. and 1424.5 mol EC/mol Cat.•h, respectively.

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