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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

SYNTHESIS OF ETHYLENE CARBONATE BY THE REACTION OF CARBON DIOXIDE WITH ETHYLENE OXIDE IN THE PRESENCE OF NEW ZINC PHENOLATE CATALYSTS

Speciality:	3349.01 – Chemistry and technology of gas processing processes
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GENERAL CHARACTERISTICS OF THE WORK

Relevance of the topic and the degree of elaboration. Carbon dioxide is a by-product of burning natural resources (oil, gas, coal, etc.) as energy sources, as well as emissions from various chemical industries. Carbon dioxide, a greenhouse gas that negatively affects the climate of our planet, which makes the problem of CO_2 utilization more and more acute. One of the options for the utilization of CO_2 is the possibility of using it as a carbon source for the synthesis of chemicals, which is reflected in various numerous international research programs[1]. These studies form the basis of "green chemistry" technologies and mainly include the synthesis of various derivatives of carboxylic acids, lactones, polycarbonates, cyclic organic carbonates, etc.

Organic carbonates have a fairly large market (about 1.8 million tons/year) and are widely used as solvents, selective reagents, intermediates (for the synthesis of drugs and agricultural products), fuel additives, monomers for polymer synthesis. The existing technologies for the synthesis of organic carbonates involve the use of phosgene, a rather toxic and expensive substance, which leads to serious environmental problems. Therefore, the development of new, environmentally friendly processes, especially with the use of various epoxides and CO_2, is an extremely topical issue.

In modern processes, organometallic compounds and complexes, classical Lewis or Bronsted acids, and metal-containing phthalocyanines are used as catalysts for the synthesis of cyclic carbonates based on epoxides and CO_2. It is very rare to find the use of metal oxides as catalysts. But the catalysts used, along with low activity and low efficiency, reveal such disadvantages as the need to use an additional solvent due to the poor solubility of the catalysts in the reaction medium, the high sensitivity of the catalyst to pollutants, and the reaction at high temperatures.

Therefore, the development of new, more efficient catalysts that

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[1] Alper, E., CO_2 utilization: Development in conversion processes / Alper, E., Orhan, O.Y. // Petroleum, - 2017, 3 (1), - p. 109-126.

make it possible to carry out the process of synthesis of cyclic carbonates under any reaction conditions (in a homogeneous or heterogeneous medium, with the participation of aqueous epoxide and under favorable temperature conditions) is extremely important and is of great scientific and practical importance.

Goals and objectives of the study. The main goal of this work is the development of fundamentally new, cheap and “green” catalytic systems for the synthesis of cyclic carbonates. For this purpose, the process of obtaining ethylene carbonate based on the cycloaddition reaction of carbon dioxide and ethylene oxide in the presence of zinc phenolate or zinc phenolate/ion-liquid catalysts was studied.

Research objects. Both “pure” dry and wet (moisture-containing) ethylene oxide and carbon dioxide were used as initial compounds. Synthesized zinc phenolates based on methylene-bis, thio-bis and dithio-bis phenols, as well as ionic liquids based on amines (N-methyl-2-pyrrolidone, alkyl or dialkylamines, etc.) as cations and acetic acid, hydrobromic acid and zinc chloride, etc. as anions. The solvent was methylene chloride, toluene, chlorobenzene, etc.

Research methods. When performing the work, an integrated approach was used to solve the tasks set, which consisted in an organic combination of methods for working with gaseous substances under pressure and synthetic chemistry, with modern methods of physical and chemical analysis.

NMR, IR-spectroscopy, and gel-permission chromatography were used to determine the composition and physicochemical characteristics of the synthesized catalysts and ethylene carbonate.

The main provisions of the defense. To achieve the goal of dissertation, it was necessary to solve the following tasks:

- Synthesis and study of the main physico-chemical properties of zinc phenolate catalysts based on methylene-bis, thio-bis and dithio-bis phenols and zinc chloride;
- Synthesis and study of the main physico-chemical properties of bromine-containing, acetate and zinc chloride ionic liquids using N-methyl-2-pyrrolidone, imidazoles, alkyl- and dialkyl amines, etc. as cations and acetic acid, hydrobromic acid and zinc chloride as anions;

- Study of the activity and selectivity of various zinc phenolate and ionic liquid catalysts in the cycloaddition reaction of ethylene oxide and carbon dioxide;
- Study of the influence of various factors (catalyst and ethylene oxide concentrations, mixing speed of the reaction mixture (stirrer rotation speed), CO_2 pressure, temperature and reaction time) on the yield and selectivity of ethylene carbonate, as well as on the productivity of the catalyst and the TOF process.
- Testing the process of synthesis of ethylene carbonate by the cycloaddition reaction of ethylene oxide and carbon dioxide in a high-pressure laboratory plant using optimal catalysts and reaction conditions;
- Study of the possibility of purification of the obtained ethylene carbonate and the study of its basic physical and chemical properties.

Scientific novelty of the research. For the first time: various new zinc phenolate (methylene-bis-, thio-bis- and dithio-bis zinc phenolates) and/or zinc phenolate/ionic-liquid (amino bromide, acetate and zinc chloride) catalysts have been developed and proposed; the process of obtaining ethylene carbonate by the cycloaddition reaction of ethylene oxide and carbon dioxide in the presence of the proposed catalysts was studied. It is shown that the developed new catalysts, in contrast to the existing ones, along with high activity, selectivity and productivity, also have the ability to carry out the cycloaddition reaction using not only “pure”, but also “water-containing” ethylene oxide (Patent of the Republic of Azerbaijan № İ 2020 0031, 11.05.2017 and № İ 2023 0036, 11.03.2022).

Theoretical and practical significance of the research. The developed new zinc phenolate catalysts, along with the ethylene carbonate synthesis reaction, can also be used in the synthesis of a number of cyclic carbonates (propylene carbonate, butylene carbonate, styrene carbonate, etc.) by the cycloaddition reaction of the corresponding epoxides with carbon dioxide. The obtained cyclic carbonates are used as solvents, intermediates and active components in various chemical reactions, in cosmetics, agriculture, etc. The process for producing ethylene carbonate, developed taking into account the data obtained in this thesis, can be recommended for use in the Petkim company (SOCAR-Turkiye, Izmir, Turkiye), taking into account the production of ethylene oxide (wet) and its by-product - carbon dioxide.

Personal presence of the author. The main results of the dissertation were obtained personally by the author, or with his direct participation, including planning, organizing, conducting theoretical and experimental research, interpreting the data obtained and generalizing them. All data are systematized and analysed, designed and prepared in the form of publications and scientific reports with the active participation of the author.

Aprobation and application. The main results of the work were presented at republican and international scientific conferences: 3rd International Turkic World Conference on Chemical Sciences and Technologies, Baku, 10-13 September, – 2017; S.Sultanovun 90 illik yubileyinə həsr olunmuş konfrans, 3 oktyabr, AMEA NKPİ, Bakı, – 2017; //“Funksional monomerlər və xüsusi xassəlıi polimer materiallar: problemlər, perspektivlər və praktik baxışlar” Elmi Konfransı, AMEA PMİ, Sumqayıt, 15-16 Noyabr, – 2017; 7th Rostocker International Conference: “Thermophysical Properties for Technical Thermodinamics”, University of Rostock, Germany, 26-27 July, – 2018; Akademik V.S.Əliyevin 110 illik yubileyinə həsr olunmuş Beynəlxalq Elmi-Praktiki Konfrans, AMEA NKPİ, Bakı, Azərbaycan, Sentyabr, – 2018; International Scientific Conference “Innovative Development Perspectives of Chemical Technology and Engineering”, Sumgait, İPM of ANAS, 28-29 November, – 2019; “Müasir təbiət və iqtisad elmlərinin aktual problemləri”, H.Əliyevin 96-cı ildönümünə həsr olunmuş Beynəlxalq Elmi Konfrans, Gəncə Dövlət Universiteti, 02-03 May, – 2019; The International Scientific Conference “Actual Problems of Modern Chemistry” Dedicated to the 90th Anniversary of the Academician Y.H.Mammadaliyev Institute of Petrochemical Processes, October 2–4, – 2019; “Kimya və biologiyanın aktual problemləri” H.Əliyevin 97-ci il dönümünə həsr olunur Beynəlxalq Elmi Konfrans (onlayn), Gəncə Dövlət Universiteti, 12 noyabr, – 2020; Tələbə və gənc tədqiqatçıların II beynəlxalq elmi konfransı, Bakı Ali Neft Məktəbi, 13-28 aprel, – 2021; N.İ.Seyidovun 90 illiyinə həsr olunmuş Konfrans, 19-20 May,

– 2022, AMEA NKPİ, Bakı, s., akademik A.H.Əzizovun 80 illik yubileyinə həsr olunmuş Konfrans, Noyabr, – 2023, Bakı ş.

Scientific articles. Based on the scientific results of the work, 23 scientific works were published, of which 6 are scientific articles (3 articles are mono-authorized), 15 are conference and symposium theses, and 2 is a patent of the Republic of Azerbaijan.

Reliability of scientific results. The reliability of the results presented in the dissertation is ensured by the use of well-known methods for the synthesis of cyclic carbonates by carrying out the cycloaddition reaction of CO_2 with ethylene oxide in a metal reactor without pressure or under pressure using the proposed catalysts and is due to the use of a complex of modern physico-chemical research methods: IR-, NMR- spectroscopy, GPC, etc.

Name of the organization where the dissertation work is carried out. The dissertation work was carried out at the Institute of Petrochemical Processes named after acad. Yu.H. Mamedaliev of the National Academy of Sciences of Azerbaijan in accordance with the program of research works (State registration № № 0106 AZ 00018 and № 0113 AZ 2034).

The total volume of the dissertation with a sign, indicating the volume of the structural units of the dissertation separately. The dissertation work consists of an introduction, a brief review of the literature with a statement of the problem, 5 chapters, a list of cited literature from 205 references. The dissertation is presented on 188 pages, including 52 drawings, 47 diagrams, 22 tables and 2 applications, consists of 172675 signs.

In the introduction (10640 signs), the relevance of the presented dissertation work is substantiated, the purpose and objectives of the study, scientific novelty, practical value and areas of application of the results are formulated.

The first chapter (36540 signs) is devoted to a literature review, which describes the current state of the synthesis of cyclic carbonates by the cycloaddition reaction of ethylene oxide and carbon dioxide using zinc and zinc/ion-liquid catalysts. Additionally, Appendix 1 provides references on the synthesis of ethylene carbonate using ion-liquid catalysts.

The second chapter (28560 signs) describes the methods of experiment and analysis of the catalyst components and the products obtained by modern physical and chemical methods, the selection, purification and preparation of starting materials, and the method of carrying out the cycloaddition reaction under pressure.

The third chapter (48760 signs) shows the results for:

- study of the influence of various factors (catalyst and ethylene oxide concentrations, reactor stirrer rotation speed, carbon dioxide pressure, reaction temperature and time, etc.) on the activity and productivity of the catalyst in the cycloaddition reaction of "pure" ethylene oxide with carbon dioxide using zinc phenolate, as well as "water-containing" ethylene oxide with carbon dioxide in the presence of zinc phenolate / ion-liquid catalyst.

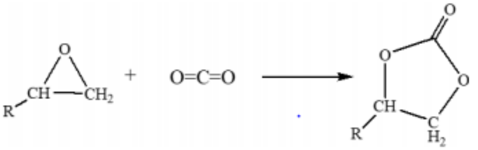
In the fourth chapter (16470 signs) the possibility of synthesis of ethylene carbonate on a high-pressure laboratory unit using zinc phenolate and zinc phenolate / ion-liquid catalysts is considered by the cycloaddition reaction of both "pure" and "wet" ethylene oxide with carbon dioxide.

In the fifth chapter (27690 signs), the technological scheme of the production of ethylene carbonate by the cycloaddition reaction of ethylene oxide and carbon dioxide in the presence of the developed zinc phenolate containing ionic liquid catalyst is considered and a feasibility study of the proposed process is carried out.

The results (4015 signs) summarize the main scientific results obtained during the work on dissertation.

MAIN CONTENT OF THE WORK

The synthesis of valuable products based on carbon dioxide (CO_2) is a promising way to reduce the concentration of harmful "greenhouse gases" in the atmosphere [14]. The synthesis of cyclic carbonates by the cycloaddition reaction of CO2 with epoxy compounds is one of the most promising directions in CO_2 utilization.



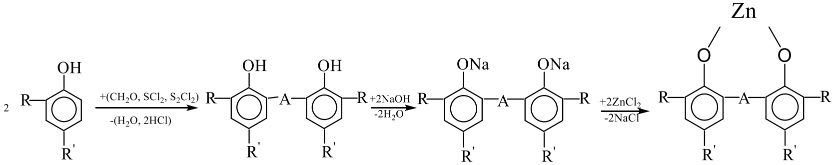
Almost all catalytic systems currently used in the synthesis of cyclic carbonates (metal salts or complexes and organocatalysts - phosphonium and ammonium salts, alcohols and phenols) have such disadvantages as low stability and activity, the need to use a cocatalyst, high cost, etc. [14].

The simplest and most readily available catalysts for the synthesis of various cyclic carbonates are zinc compounds, among which the zinc halide/quaternary ammonium salt systems, zinc bromide or chloride with tetrabutylammonium iodide ($ZnBr_2$/TBAI), homogeneous and heterogeneous zinc(II)-pyridine catalytic systems, which carry out the reaction at 25-140°C and a CO_2 pressure of 0.1-1.0 MPa, with a yield of 50–65%, but with satisfactory TOF values of 680-1000 h^{-1} [16]. Despite the high stability and satisfactory activity of most zinc complexes, the difficulty of synthesizing these compounds and their multicomponent nature make them expensive, which limits their wide industrial application.

In recent decades, numerous studies have been carried out on CO_2 binding with epoxides for the synthesis of cyclic carbonates with the participation of ionic liquids (ILs) as a catalyst [16], which significantly improved the understanding of how to efficiently activate CO_2 and C–O bonds in epoxides.

It is known that tetrabutylammonium salts and some imidazole-based ILs are environmentally friendly, metal-free, alternative catalysts for the process of CO_2 utilization with the formation of cyclic carbonates [16]. However, these catalysts often only work effectively at high temperatures (>120°C) and pressures (>10 bar CO_2), which makes the processes difficult to achieve in terms of a positive CO_2 balance. To increase the reactivity of these catalysts, Lewis acidic metal cocatalysts, such as zinc compounds, are most often added, which have a favorable effect on the reaction rate [16]. Therefore, the synthesis and application of readily available zinc and IL compounds with high activity, selectivity, and productivity in the reaction of obtaining cyclic carbonates from CO_2 and epoxides (in particular, ethylene carbonate, EC) is an urgent task of scientific and practical importance.

The starting bis-alkylphenol components of the ZnY catalyst (where Y= methylene-bis, thio-bis, and dithio-bis alkylphenols) were synthesized by the Mannich condensation reaction of the corresponding alkylphenol with CH_2O, or SCl_2, or S_2Cl_2, in the presence of a KU-2 catalyst. ZnY, used as a catalyst, was synthesized by the substitution reaction of the starting bis-alkylphenols with NaOH (or KOH) and the exchange reaction of the resulting sodium (potassium) salt with ZnCl2, according to the scheme:



where, A = $–CH_2–$, –S– or –S–S– groups; R = H, C_1-C_8 alkyl groups or $(C_2H_5)_2$-N-CH_2– (diethylaminomethyl) group; R` = H, C_1-C_8 alkyl groups.

The ILs of the general formula RLX used in the work (where, R=H or C_1-C_8 alkyl groups; L= N-methylpyrrolidonium [NMP], methylimidazolium [MIM], pyridinium [Py], or alkylaminium cationic groups; X= Br, $ZnCl_2$, $CHCOO^-$, CH_3COO^- anionic groups) were synthesized according to the general scheme:

$$L + RX \rightarrow RLX$$

Equimolar amounts of L and compound RX (1-alkyl bromide, zinc chloride, formic or acetic acid, where, R= H or C_1-C_8 alkyl groups; X= Br–, CHCOO–, CH3COO–) in an appropriate solvent (or no solvent) placed in a three-necked round bottom flask, mixed thoroughly and heated to 70-100°C for 4-48 hours under nitrogen atmosphere. The resulting viscous liquid is cooled to room temperature, and in order to remove unreacted starting compounds, it is washed several times with small portions of ethyl acetate (or diethyl ether), then the main product is dried in vacuum at 80°C. It turns out IL RLX with yields of 85.0-98.0%.

Synthesis of ionic liquids of the formula $R_2L_2X_2ZnY$ (where, R= H or C_1-C_8 alkyl groups; L= NMP, IM, Py or alkylamine cationic groups; X= Br or $ZnCl_2$; Y= methylene-bis, thio-bis or dithio-bis alkylphenolate group) is carried out in a nitrogen atmosphere by the reaction of the corresponding ionic liquids of the general formula RLX ([RNMP]X, [RMIM]X, [RPy]X or [RAlkAm]X, where, R=H or C_1-C_8 alkyl groups; X= Br, $ZnCl_2$) with the corresponding zinc phenolates of the general formula ZnY (where, Y = methylene-bis, thio-bis or dithio-bis alkylphenolate groups) according to the scheme:

$$2RLX + ZnY \rightarrow R_2L_2X_2ZnY$$

In a three-necked flask, a solution of the corresponding zinc phenolate of the general formula ZnY (0.1 mol) in toluene is added to a solution of an ionic liquid of the general formula RLX (0.2 mol) in methylene chloride and stirred for 3 hours at a temperature of 70-100°C. After cooling to room temperature, the residue is filtered off, washed several times with ethyl acetate (or diethyl ether) and dried under vacuum at 80°C. The yield of IL $R_2L_2X_2ZnY$ is 95.0–99.0%.

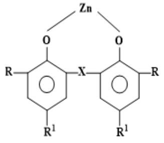
All experiments on the synthesis of ethylene carbonate by the reaction of ethylene oxide with carbon dioxide under pressure were carried out in a stainless steel autoclave. To do this, in order to remove air, the autoclave was filled three times with carbon dioxide up to 1.0 MPa and the pressure was released. Then, the required amount of catalyst in solvent and ethylene oxide in a CO_2 flow were loaded into the autoclave, and the required pressure was built up with CO_2. The autoclave was heated to the desired temperature for the duration of the reaction, and the pressure was released. After completion of the reaction, to separate the catalyst, the reaction mixture was cooled to room temperature and passed through silica gel (eluent CH_2Cl_2).

The structures of all starting compounds, bis-alkylphenols, synthesized catalysts, and the target product were confirmed by ^{1}H-NMR, ^{13}C-NMR, and IR spectroscopy. NMR spectra were recorded on a Bruker-Fourier spectrophotometer at frequencies of 300 MHz (for ^{1}H-NMR) and at a frequency of 101 MHz (for ^{13}C-NMR). DMSO-d6, $CDCl_3$, CD_3OD, D_2O, or CD_2Cl_2 were used as solvents. IR spectra were recorded on a Lumos FT-IR Microscope spectrophotometer manufactured by Bruker (Germany) at 400-4000 cm^{-1}.

Four different approaches were used in the work: first, the activity and selectivity of the synthesized various methylene bis, thiobis, and dithiobis alkyl phenolates of zinc (ZnY) were studied in the synthesis of cyclic ethylene carbonate in order to select the optimal zinc phenolate catalyst and optimal conditions; then, under similar reaction conditions, the activity and selectivity of the synthesized various RLX ILs of various compositions (N-methylpyrrolidonium zinc chloride, N-methylpyrrolidonium halides, N-methylpyrrolidonium formate, N-methylpyrrolidonium acetate, tetrabutylamminium bromide, imidazolium halides, diethylaminoacetate, etc.) and the choice of the optimal IL and reaction conditions was carried out; further, in the ethylene carbonate synthesis reaction, the activity and selectivity of binary catalysts Zn-phenolate + IL (ZnY + RLX) were tested using the selected optimal zinc phenolate and IL catalysts, or using $R_2L_2X_2ZnY$ IL catalysts synthesized on their basis.

Investigation of the activity of various zinc phenolate ZnY catalysts in the cycloaddition reaction of ethylene oxide and carbon dioxide

As zinc phenolate catalysts for the synthesis of ethylene carbonate, various methylene- bis, thio-bis, and dithio-bis alkyl phenolates of zinc of the general formula have been studied:

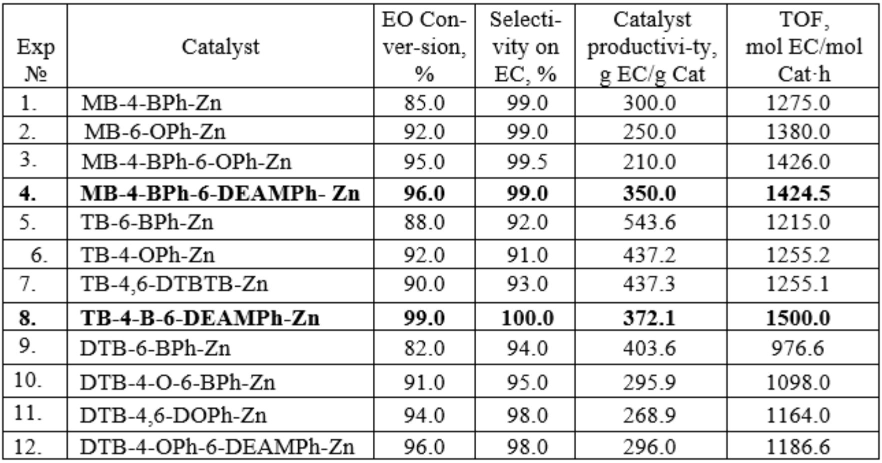


where, X= CH_2, S, S-S groups; R= H, C_1-C_8 alkyl groups or $(C_2H_5)_2$–N-CH_2 (diethylaminomethyl) group; R^{1}= H, C_1-C_8 alkyl groups.

The results of experiments on the synthesis of ethylene carbonate from CO_2 and EO are summarized in Table 1. As can be seen from the table, all used zinc alkyl phenolates exhibit high activity and selectivity. The productivity of the catalyst and the TOF of the process are in the ranges of 210.0-437.0 g EC/g Cat and 976.6-1500.0 mol EC/mol Cat.h, respectively.

Table 1.

Activity of methylene-bis, thio-bis, dithio-bis alkyl phenolates of zinc in the synthesis of ethylene carbonate based on EO and CO_2. Reaction conditions: [EO] = 3.0 mol/l; [Cat] = $1.0 \cdot 10^{-3}$ mol/l; P_{CO2} = 5.0 MPa; T = 80°C; τ = 60 min, solvent is methylene chloride



Exp №	Catalyst	EO Con-ver-sion, %	Selecti-vity on EC, %	Catalyst productivi-ty, g EC/g Cat	TOF, mol EC/mol Cat·h
1.	MB-4-BPh-Zn	85.0	99.0	300.0	1275.0
2.	MB-6-OPh-Zn	92.0	99.0	250.0	1380.0
3.	MB-4-BPh-6-OPh-Zn	95.0	99.5	210.0	1426.0
4.	**MB-4-BPh-6-DEAMPh- Zn**	**96.0**	**99.0**	**350.0**	**1424.5**
5.	TB-6-BPh-Zn	88.0	92.0	543.6	1215.0
6.	TB-4-OPh-Zn	92.0	91.0	437.2	1255.2
7.	TB-4,6-DTBTB-Zn	90.0	93.0	437.3	1255.1
8.	**TB-4-B-6-DEAMPh-Zn**	**99.0**	**100.0**	**372.1**	**1500.0**
9.	DTB-6-BPh-Zn	82.0	94.0	403.6	976.6
10.	DTB-4-O-6-BPh-Zn	91.0	95.0	295.9	1098.0
11.	DTB-4,6-DOPh-Zn	94.0	98.0	268.9	1164.0
12.	DTB-4-OPh-6-DEAMPh-Zn	96.0	98.0	296.0	1186.6

Thio-bis-4-butyl-6-diethylamino-methyl phenolate of zinc (TB-4-B-6-DEAMP-Zn) was chosen as the optimal catalyst, in the presence of which the EO conversion is 99.0%, the EC selectivity is 100.0%, and the catalyst productivity is 372.1 g EC/g Cat and TOF of the process is 1500.0 mol EC/mol Cat· h.

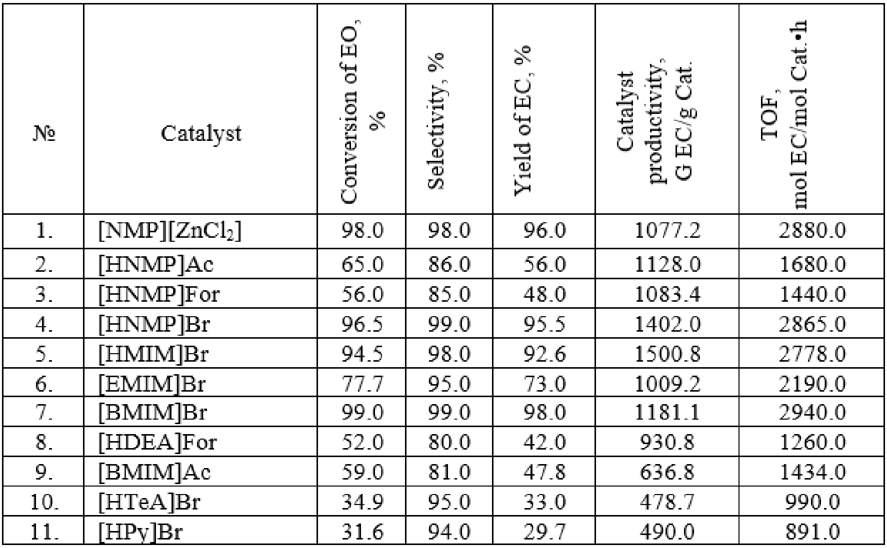
Study of the activity of various RLX ionic liquid catalysts in the synthesis of ethylene carbonate by the cycloaddition Reaction of ethylene oxide and carbon dioxide

Were used N-methyl-2-pyrrolidonium zinc chloride ([NMP][$ZnCl_2$]), N-methyl-2-pyrrolidonium acetate ([HNMP]Ac), N-methyl-2-pyrrolidonium formate ([HNMP]For), N-methyl-2-pyrrolidonium bromide ([HNMP]Br), 1-methyl-imidazolium bromide ([HMIM]Br), 1-ethyl-3-methylimidazolium bromide ([EMIM]Br), 1-butyl-3-methyl-imidazolium bromide ([BMIM]Br), 1-butyl-3-methyl-imidazolium acetate ([BMIM]Ac), diethylammonium formate

([HDEA]For), triethylammonium bromide ([HTeA]Br) and pyridinium bromide ([HPy]Br). The results obtained are summarized in Table. 2.

Table 2.

Activity and selectivity of various ionic liquids in the reaction of ethylene carbonate synthesis. Reaction conditions: [EO]= 3.0 mol/l; [Cat]= $1.0 \cdot 10^{-3}$ mol/l; P_{CO2}= 5.0 MPa; T= 80°C; τ = 60 min, stirrer rotation speed – 350 rpm, solvent – methylene chloride.



№	Catalyst	Conversion of EO, %	Selectivity, %	Yield of EC, %	Catalyst productivity, G EC/g Cat.	TOF, mol EC/mol Cat.•h
1.	[NMP][ZnCl$_2$]	98.0	98.0	96.0	1077.2	2880.0
2.	[HNMP]Ac	65.0	86.0	56.0	1128.0	1680.0
3.	[HNMP]For	56.0	85.0	48.0	1083.4	1440.0
4.	[HNMP]Br	96.5	99.0	95.5	1402.0	2865.0
5.	[HMIM]Br	94.5	98.0	92.6	1500.8	2778.0
6.	[EMIM]Br	77.7	95.0	73.0	1009.2	2190.0
7.	[BMIM]Br	99.0	99.0	98.0	1181.1	2940.0
8.	[HDEA]For	52.0	80.0	42.0	930.8	1260.0
9.	[BMIM]Ac	59.0	81.0	47.8	636.8	1434.0
10.	[HTeA]Br	34.9	95.0	33.0	478.7	990.0
11.	[HPy]Br	31.6	94.0	29.7	490.0	891.0

As can be seen, the ILs [HNMP]Ac, [HNMP]For, [EMIM]Br, [HDEA]For, [BMIM]Ac, [HTeA]Br, and [HPy]Br exhibit relatively low catalytic activity and selectivity in the synthesis of ethylene carbonate. In their presence, the EO conversion is 31.6-77.7%, the EC selectivity is 80.0-95.0%, the catalyst productivity is 478.7-1128.0 g EC/g Cat, and the TOF of the process is 891.0-2190.0 mol EC/mol Cat·h.

The ILs [NMP][ZnCl$_2$], [HNMP]Br, [HMIM]Br, [BMIM]Br exhibit high activity and selectivity. In their presence, the EO conversion and EC selectivity are in the ranges of 94.5-99.0% and 98.0-99.0%, respectively. The productivity of the catalyst and TOF are also high: 1077.2-1500.8 g EC/g Cat and 2778.0-2940.0 mol EC/mol Cat·h, respectively.

Study of the synthesis of ethylene carbonate in the presence of optimal catalysts ZnY+RLX or $R_2L_2X_2ZnY$

In order to elucidate possible synergism in the activity and selectivity of zinc phenolate and IL catalysts in the cycloaddition reaction of EO and CO_2 were investigated the binary catalysts RLX+ZnY (where R=H or C_1-C_8 alkyl groups; L= [NMP], [MIm], [Py] or alkylamine cations; X= Br^-, $CHCOO^-$, CH_3COO^- anions, Zn= metal, Y= methylene-bis, thio-bis and dithio-bis alkylphenolate groups). The experiments were carried out under the following conditions: $[RLX]=2.5\cdot10^{-4}$ mol/l, $[ZnY]=2.5\cdot10^{-4}$ mol/l, $[EO]=3.0$ mol/l; $P_{CO2}= 5.0$ MPa; T= 80°C; $\tau= 60$ min, stirrer rotation speed - 350 rpm, solvent - methylene chloride. The results of the study are summarized in Table 3.

As can be seen from the table, at low concentrations of the initial components ($2.5\cdot10^{-4}$ mol/l of each component instead of $1.0\cdot10^{-3}$ mol/l in the previous experiments of Tables 1 and 2), binary catalysts exhibit sufficiently high activity and selectivity, which, undoubtedly proves the presence of a synergistic effect in their joint action in the reaction of the synthesis of ethylene carbonate. In their presence, high EO conversions of 95.0-99.0%, EC selectivities of 97.0-100.0%, and high productivity of the catalyst and TOF of the process are achieved in the range of 1000.0-1428.0 g EC/g Cat and 5238.0-5940.0 mol EC/mol Cat·h, respectively (Table 3).

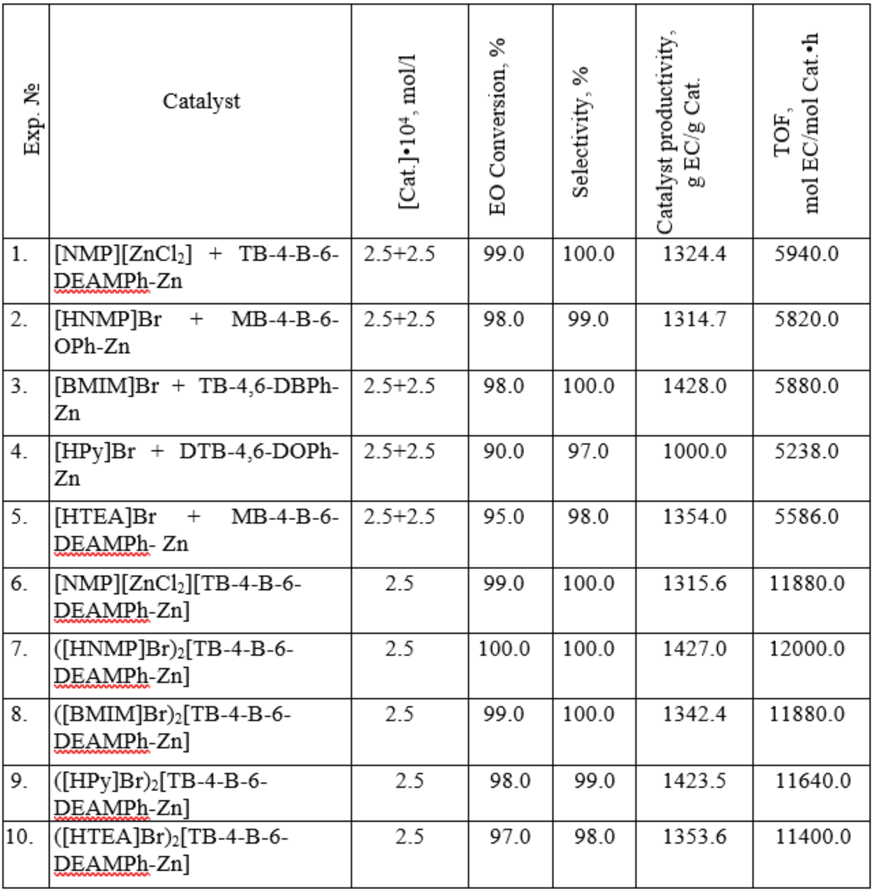
A similar dependence is also observed when using IL catalysts $R_2L_2X_2ZnY$ (where, R=H or C_1-C_8 alkyl groups; L= NMP, IM, Py or alkylamine cationic groups; X= Br or $ZnCl_2$; Y=methylene-bis, thio-bis or dithio-bis alkylphenolate groups) synthesized from these components.

Synthesis of ethylene carbonate by the reaction of water contained ethylene oxide and carbon dioxide using selected optimal catalysts

Due to the high degree of danger and high cost of the process of isolation and storage of pure ethylene oxide, it is usually used in the synthesis of ethylene glycols, or it can be isolated in the form of an aqueous solution with a concentration of up to 50%.

Table 3.

Synthesis of ethylene carbonate in the presence of RLX+ZnY or $R_2L_2X_2ZnY$ catalysts



Exp. №	Catalyst	[Cat.]$\cdot 10^4$, mol/l	EO Conversion, %	Selectivity, %	Catalyst productivity, g EC/g Cat.	TOF, mol EC/mol Cat.•h
1.	[NMP][ZnCl$_2$] + TB-4-B-6-DEAMPh-Zn	2.5+2.5	99.0	100.0	1324.4	5940.0
2.	[HNMP]Br + MB-4-B-6-OPh-Zn	2.5+2.5	98.0	99.0	1314.7	5820.0
3.	[BMIM]Br + TB-4,6-DBPh-Zn	2.5+2.5	98.0	100.0	1428.0	5880.0
4.	[HPy]Br + DTB-4,6-DOPh-Zn	2.5+2.5	90.0	97.0	1000.0	5238.0
5.	[HTEA]Br + MB-4-B-6-DEAMPh- Zn	2.5+2.5	95.0	98.0	1354.0	5586.0
6.	[NMP][ZnCl$_2$][TB-4-B-6-DEAMPh-Zn]	2.5	99.0	100.0	1315.6	11880.0
7.	([HNMP]Br)$_2$[TB-4-B-6-DEAMPh-Zn]	2.5	100.0	100.0	1427.0	12000.0
8.	([BMIM]Br)$_2$[TB-4-B-6-DEAMPh-Zn]	2.5	99.0	100.0	1342.4	11880.0
9.	([HPy]Br)$_2$[TB-4-B-6-DEAMPh-Zn]	2.5	98.0	99.0	1423.5	11640.0
10.	([HTEA]Br)$_2$[TB-4-B-6-DEAMPh-Zn]	2.5	97.0	98.0	1353.6	11400.0

Therefore, in further experiments, the possibility of using ethylene oxide and carbon dioxide with different water content from the production process of mono ethylene glycol (MEG) in the Petkim company (SOCAR, Azerbaijan) was tested.

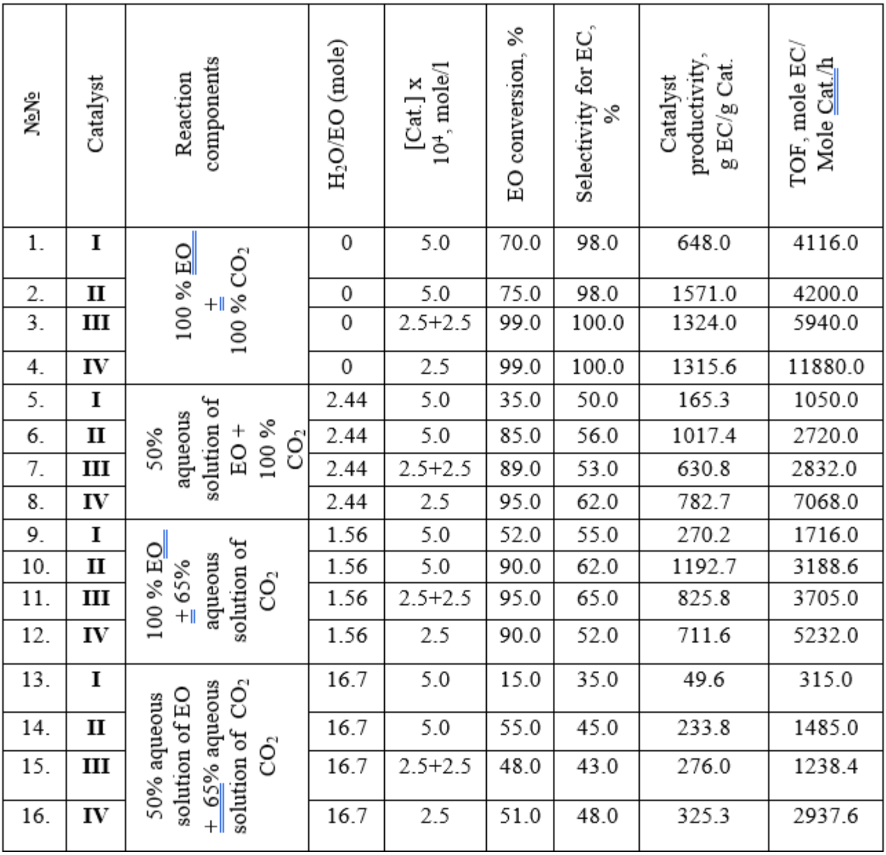
Based on the research results, a series of experiments on the synthesis of ethylene carbonate was carried out using EO and CO_2 with a different amount of water with the participation of selected catalysts:

– zinc phenolate catalyst – TB-4-B-6-DEAMF-Zn (catalyst I);
– ionic liquid catalyst – [NMP][$ZnCl_2$] (catalyst II);
– zinc phenolate+ionic liquid catalyst – TB-4-B-6-DEAMP-Zn + [NMP][$ZnCl_2$] (catalyst III);
– zinc phenolate containing ionic liquid catalyst – [TB-4-B-6-DEAMP-Zn][$(NMP)_2(ZnCl_2)_2$] (catalyst IV).

Comparative research results are given in Table 4.

Table 4

Results of the synthesis of ethylene carbonate by the cycloaddition reaction of ethylene oxide and carbon dioxide with different water content. Reaction conditions: [EO] = 3.0 mole/l; P_{CO2} = 5.0 MPa; T = 80°C; τ = 60 min.



№№	Catalyst	Reaction components	H_2O/EO (mole)	[Cat.] x 10^4, mole/l	EO conversion, %	Selectivity for EC, %	Catalyst productivity, g EC/g Cat.	TOF, mole EC/ Mole Cat./h
1.	**I**	100 % EO + 100 % CO_2	0	5.0	70.0	98.0	648.0	4116.0
2.	**II**		0	5.0	75.0	98.0	1571.0	4200.0
3.	**III**		0	2.5+2.5	99.0	100.0	1324.0	5940.0
4.	**IV**		0	2.5	99.0	100.0	1315.6	11880.0
5.	**I**	50% aqueous solution of EO + 100 % CO_2	2.44	5.0	35.0	50.0	165.3	1050.0
6.	**II**		2.44	5.0	85.0	56.0	1017.4	2720.0
7.	**III**		2.44	2.5+2.5	89.0	53.0	630.8	2832.0
8.	**IV**		2.44	2.5	95.0	62.0	782.7	7068.0
9.	**I**	100 % EO + 65% aqueous solution of CO_2	1.56	5.0	52.0	55.0	270.2	1716.0
10.	**II**		1.56	5.0	90.0	62.0	1192.7	3188.6
11.	**III**		1.56	2.5+2.5	95.0	65.0	825.8	3705.0
12.	**IV**		1.56	2.5	90.0	52.0	711.6	5232.0
13.	**I**	50% aqueous solution of EO + 65% aqueous solution of CO_2 CO_2	16.7	5.0	15.0	35.0	49.6	315.0
14.	**II**		16.7	5.0	55.0	45.0	233.8	1485.0
15.	**III**		16.7	2.5+2.5	48.0	43.0	276.0	1238.4
16.	**IV**		16.7	2.5	51.0	48.0	325.3	2937.6

As can be seen from the table, in the presence of catalyst I (TB-

4-B-6-DEAMP-Zn) when using EO with a content of 50% water (H_2O:EO= 2.44, mol), the EO conversion sharply decreases to amounts of 35.0% against 70.0%. At the same time, both a decrease in the selectivity for EC (from 98.0% to 50.0%), the productivity of the catalyst (from 648.0 g EC/g Cat. to 165.3 g EC/g Cat.) and TOF of the process (from 4116.0 mol EC/mol Cat.·h to 1050.0 mol EC/mol Cat.·h) are observed.

The results obtained indicate a partial destruction of the structure of the zinc phenolate catalyst with the participation of water in the system, which leads to an observed decrease in the EO conversion and EC selectivity. In this case, side reactions proceed with the formation of formaldehyde, ethylene glycols (mono-, di-, tri-), 2-methyl-1,3-dioxolane, 2-methoxyethanol, etc.

It was found that when using the IL catalyst II ([NMP][$ZnCl_2$]), the EO conversion slightly increases (85.0%), but the selectivity for EC (56.0%), catalyst productivity (1017.4 g EC/g Cat.) and TOF of process (2720.0 mole EC/mole Cat.·h) are unsatisfactory.

When using a combination of a zinc phenolate and IL catalyst (catalyst III), at concentrations of each catalyst component of $2.5 \cdot 10^{-4}$ mole/l, an EO conversion of 89.0% and an EC selectivity of 53.0% are achieved, which is significantly lower than similar indicators when using pure EO (99.0% and 100.0%, respectively), but more than with catalysts I and II. The productivity of the catalyst and the TOF of process is 630.8 g EC/g Cat. and 2832.0 mole EC/mole Cat.·h, respectively, which is also lower than in the case of using pure EO, but more than with the participation of catalysts I and II. The data obtained indicate a synergistic effect in the combined use of zinc phenolate and IL catalyst.

The use of zinc-containing IL (catalyst IV) results in an EO conversion of 95.0% and an EC selectivity of 62.0%, with a catalyst productivity of 782.7 g EC/g Cat. and TOF of the process 7068.0 mole EC/mole Cat.h. Although these values are much higher than for the reaction with catalysts I, II and III, when compared with the process values obtained using pure OE, they are significantly lower (99.0%, 100.0%, 1315.6 g EC/g Cat. and 11880.0 mole EC/mole Cat.·h, respectively).

When using pure EO and CO_2 with a water content of 35.0% (H_2O:OE = 1.56, mole), more encouraging results are achieved. Thus, in the presence of catalyst I, the EO conversion is 52.0%, the EC selectivity is 55.0%, the catalyst productivity is 270.2 g EC/g Cat. and TOF of the process is 1716.0 mole EC/mole Cat.h. With the participation of IL catalyst II, the following results are provided: EO conversion – 90.0%; selectivity for EC – 62.0%; catalyst productivity – 1192.7 g EC/g Cat. and TOF of the process – 3188.6 mole EC/mole Cat.h. With the participation of catalyst III, a significant improvement in these data is observed – 95.0%, 65.0%, 825.8 g EC/g Cat., 3705.0 mole EC/mole Cat.·h, respectively.

Relatively better process values are achieved with Catalyst IV: 98.0%, 70.0%, 911.6 g EC/g Cat. and 8232.0 mole EC/mole Cat.·h, respectively, which can be explained along with the synergistic effect, also by the resistance of catalyst IV to the action of water in the reaction zone.

When using EO with a water content of 50.0% and CO_2 with a water content of 35.0%, the process performance deteriorates significantly:

– catalyst I: EO conversion – 15.0%; selectivity for EC, 35.0%; catalyst productivity - 49.6 g EC/g Cat. and TOF of the process – 315.0 mole EC/mole Cat.·h;

– catalyst II: EO conversion – 55.0%; selectivity for EC, 45.0%; catalyst productivity – 233.8 g EC/g Cat. and TOF of the process – 1485.0 mole EC/mole Cat.h;

– catalyst III: EO conversion – 48.0%; selectivity for EC – 43.0%; catalyst productivity – 276.0 g EC/g Cat. and TOF of the process – 1238.4 mole EC/mole Cat.h;

– catalyst IV: EO conversion – 51.0%; selectivity for EC – 48.0%; catalyst productivity – 325.3 g EC/g Cat. and TOF of the process – 2937.6 mole EC/mole Cat.·h.

Considering the abovementioned, in order to determine the reaction conditions for the cycloaddition reaction of EO and CO_2, providing the best process performance in the presence of water and finding its optimal content in the reaction zone, a series of experiments was carried out at various ratios of H_2O:EO in the range of 0-3.0

(mole) (water content 0-55.0%) with the participation of the established optimal catalyst IV. The results obtained are shown in Fig. 1. As can be seen, with an increase in the H_2O:EO ratio from 0 to 0.1 (mole) (the water content in the reaction zone is 0-3.9%), the EO conversion increases from 70.0% to 90.0%. An increase in the H_2O:EO ratio to 0.15 (water content – 5.8%) leads to an increase in the EO conversion to 96.0%. With a further increase in this ratio to 3.0 (mol) (water content – 55%) the EO conversion increases to 97.0-98.0%.

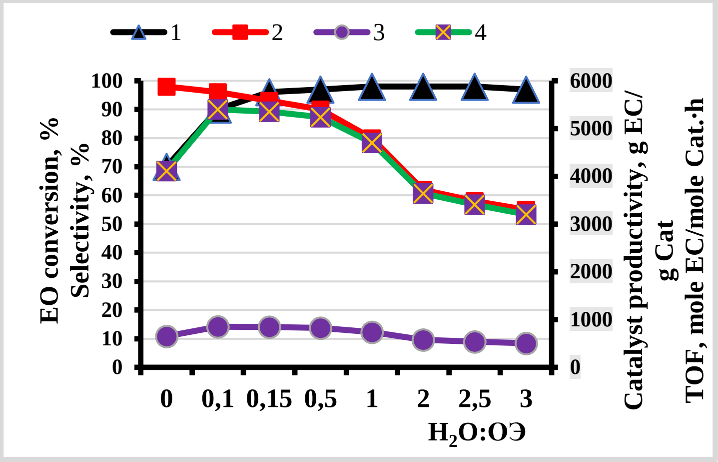


Fig. 1. Dependence of EO conversion (1 - ▲), selectivity for EC (2 - ■), catalyst productivity (3 - ●) and TOF of the process (4 - ×) on the H_2O:EO.

It has been established that an increase in the H_2O:EO ratio in the range of 0-3.0 (mole) is accompanied by a sharp decrease in the selectivity for EC from 98.0% to 55.0%. The observed increase in the EO conversion (from 70.0% to 98%) and a decrease in the selectivity for EC are accompanied by a decrease in both the catalyst productivity from 850.0 to 504.0 g EC/g Cat. and the TOF of the process from 5400.0 to 3201.0 mole EC/mole Cat.h .

Fig. 2 shows the dependence of the yield of ethylene carbonate on the reaction time in the presence of catalyst IV at various H_2O:OE ratios: 1–0; 2–0.1; 3–0.5; 4–1.0; 5–2.0; 6–3.0.

As can be seen, under the conditions: [Cat.]=2.5·10-4 mole/l,

[EO]= 3.0 mole/l, P_{CO2}= 5 MPa, T=80°C, in the absence of water (curve 1) with increasing reaction time up to 180 min moderately increases the yield of EC up to 75%. An increase in the H_2O:EO ratio to 0.1 (mole) leads to an increase in the EC yield to 87.0% (curve 2). At a ratio of H_2O:OE= 0.5 (mole), an increase in the yield of EC to 100% is observed (curve 3). With a further increase in the water content to 29.0% (H_2O:OE= 1.0, mole), a slight decrease in the EC yield is observed, which is 98.0% at a reaction time of 60 min, and 93.0% at a reaction time of 180 min.

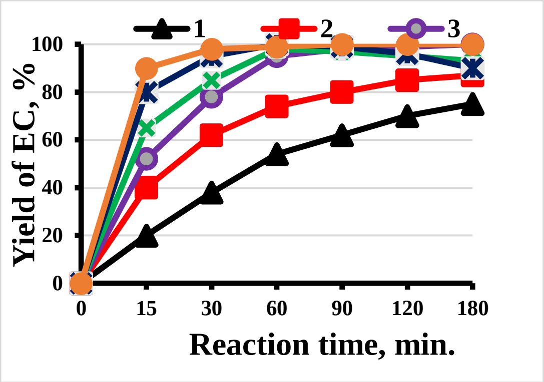


Fig. 2. Ethylene carbonate yield vs. reaction time in the presence of catalyst IV at various H_2O:OE ratios: 1 - 0; 2 - 0.1; 3 - 0.5; 4 - 1.0; 5 - 2.0; 6 - 3.0.

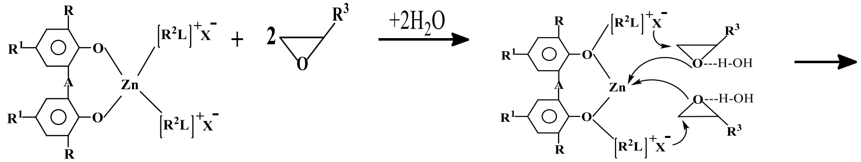
The H_2O:OE = 2.0 (mole) (water content in the EO 45.0%) and H_2O:EO = 3.0 (mole) (water content 55.0%) could be considered as optimal, at which 100% and 99% are reached in 60 min. But yield of EC decrease to 87.0% with an increase in the reaction time to 180 min.

Based on the obtained results, the optimal ratio of H_2O:EO in the reaction zone can be considered as an data in the range of 1.0-2.0 (mole) (water content in the EO is 30-45%), which ensures the yield of EC in the range of 98.0-100.0% with the optimal reaction time of 60 min.

Considering the above, in the reaction of EC synthesis by cycloaddition of EO and CO_2, it is proposed to use zinc phenolate containing IL catalyst – [TB-4-B-6-DEAMP-Zn][$(NMP)_2(ZnCl_2)_2$] (catalyst IV), ethylene oxide with content of water 30-45% and pure carbon dioxide under optimal reaction conditions: [Cat.]=2.5·10^{-4} mole/l, [EO]=3.0 mole/l, P_{CO2}=5 MPa, T=80°C, τ=60 min.

Proposed mechanism of the cycloaddition reaction of ethylene oxide and carbon dioxide in the presence of water

The proposed reaction mechanisms for the synthesis of ethylene carbonate using zinc phenolate, IL and zinc phenolate/IL catalysts are given in the thesis. This subsection presents the proposed mechanism for the cycloaddition reaction of ethylene oxide and carbon dioxide in the presence of water using the optimal catalyst [TB-4-B-6-DEAMP-Zn][(NMP)2 (ZnCl2)2] (catalyst IV), the scheme of which shown in Fig. 3. As can be seen, water (as the acid site) and the Lewis base halide anion (as the base site) first coordinately attack different parts of the epoxide. The coordination of the H atom of the water molecule with the O atom of the epoxide via a hydrogen bond leads to the polarization of the C–O bonds, and at the same time, the halide anion performs a nucleophilic attack on the less sterically hindered β-carbon atom of the epoxide. As a result, the epoxy ring opens easily (I). Then an interaction occurs between the oxygen anion and CO2, forming an alkenyl carbonate anion (II), which is converted to a cyclic carbonate as a result of intramolecular substitution of the halide in the next stage (III). In the reaction, water as a Lewis acid plays a similar function of opening the epoxy ring, so that the Lewis base can exhibit excellent activity in the absence of the Lewis acid. The results obtained allow to suggest that water and the Lewis base anion have a synergistic effect of opening the epoxy ring, contributing to the acceleration of the formation of cyclic alkylene carbonates.



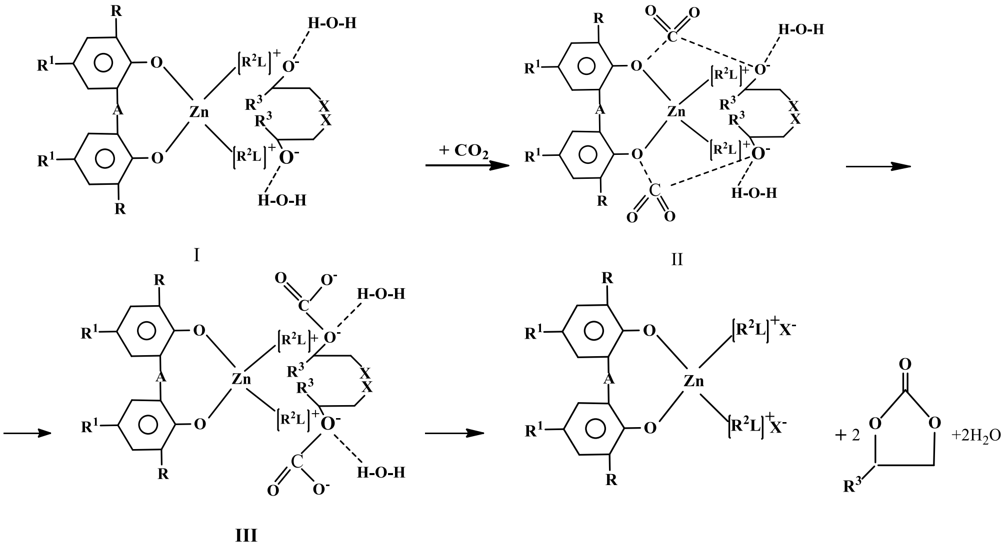


Fig. 3. Proposed mechanism for the synthesis of ethylene carbonate in the presence of water

Principal technological scheme for the production of ethylene carbonate

In order to find out the possibility of organizing the process of EC production using the proposed catalysts, was considered the technological schemes for its production in two versions with a capacity of 10.0 thousand tons/year: 1) autonomous production of ethylene carbonate by the reaction of ethylene oxide and carbon dioxide; 2) EC production process integrated with the ethylene oxide reactor.

Fig. 4 shows a schematic flow diagram of the autonomous production of ethylene carbonate by the cycloaddition reaction of ethylene oxide and carbon dioxide. Optimum amounts of ethylene oxide, carbon dioxide and catalyst in a solvent are continuously fed into the reactor-mixer (1). Under optimal process conditions and the optimal rotation speed of the stirrer, the cycloaddition reaction of EO and CO_2 is carried out.

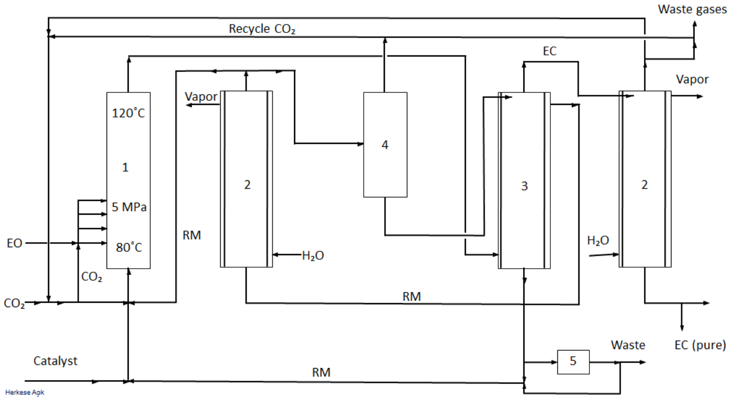


Fig. 4. Schematic flow diagram of autonomous production of ethylene carbonate. 1 - reactor-mixer; 2 – evaporator with heating jacket; 3 – heat exchanger for steam production; 4 - pressure reliever; 5 – catalyst regenerator. RM - reaction mixture.

Upon reaching the reaction time at the top of the reactor-mixer (1), the reaction mixture (RM) is sent to the evaporator (2), from above which the mixture of EC and CO_2 enters the heat exchanger (3). Carbon dioxide is regenerated and sent to the reactor-mixer (1) for reaction with EO. Pure ethylene carbonate is sent to the commodity shop.

The RM exiting from the bottom of the evaporator (2) with the catalyst is sent to the catalyst-regenerator (5), where the catalyst is separated from by-products and, together with the reaction mixture, enters the reactor-mixer (1) to continue the process. Similarly, from the top of the evaporator (2) part of the RM is fed into the second heat exchanger for the production of steam (3), and then from the top of this heat exchanger (3) to the reactor-mixer (1). Fresh portions of the catalyst, ethylene oxide and carbon dioxide are simultaneously fed into the reactor-mixer (1) and the continuous reaction cycle is repeated.

The integrated process, in which the ethylene oxide reactor is connected to the ethylene carbonate production process through absorption and stripping steps, is described according to the scheme shown in Fig. 5.

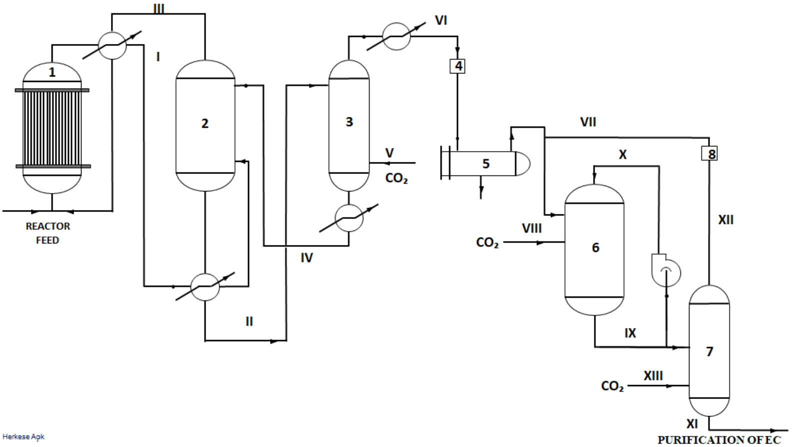


Fig. 5. Ethylene carbonate production process integrated with ethylene oxide reactor. 1 - EO reactor, 2 - absorber, 3 - stripper column, 4, 8 - compressors, 5 - condenser, 6 - EC reactor, 7 - EO stripper column.

The flow leaving the EO reactor (1) passes through the pipeline (I) into the absorption column (2) containing ethylene carbonate as an absorbent (temperature 25-50°C). The non-absorbed ethylene oxide is returned via line (III) to the EO reactor (1). The EC absorbent, containing dissolved EO and CO_2, is sent through pipeline (II) to the desorption column (3), where it is heated to a temperature of 90-150°C and contacts with an inert boil-off gas (CO_2 or N_2) introduced through line (IV) at temperature around 110°C. The desorbed gases (EO and CO_2) are removed via pipeline (VI), and the absorbent (EC) is returned via pipeline (IV) to the absorber (2). The desorbed gases are compressed by the compressor (4) to a pressure of 1.0-5.0 MPa and sent through the condenser (5) (temperature 0-25°C) to condense water before being fed through the pipeline (VII) to the EC reactor (6), which contains the proposed catalyst. The pressure in the reactor (6) is maintained at the level of 1.0-5.0 MPa, which is somewhat lower than that of the incoming gases. Additional CO2 is fed through line (VIII) to the reactor (6). Ethylene carbonate is removed via pipeline (IX), excess CO_2 is returned via pipeline (X) to the EC reactor (6), and the dissolved unreacted EO is removed from the EC in the stripping column (7), into which CO_2 is supplied as stripping gas via pipeline (XIII) . The latter is also used as a source of make-up CO_2 and returns to the reactor (6) through the pipeline (XII) passing through the compressor (8), where the gas pressure is increased to a level sufficient to overcome the pressure in the EC reactor (6), into which they are fed into as reagents, while the main EC product is sent through the pipeline (XI) to the purification stage. The cleaned finished product, ethylene carbonate, is sent to the tarring line and after that to the storage barn.

Material balance and feasibility study of the ethylene carbonate production process

Initial data of the process of obtaining ethylene carbonate:

– unit productivity for the end product EC ($C_3H_4O_3$)	– 30.0 t/day;
– water content in the technical EO	– 30.0 %;
– water content in the technical CO_2	– 0 %;
– EO conversion	– 95.0 %;
– CO_2 conversion	– 50.0 %;
– selectivity for the EC	– 96.0%;
– optimal yield of EC	– 1250.0 kq EC/hour (91.2 %);
– catalyst productivity	– 465.0 g EC/g Cat.;
– TOF of the process	– 4210.0 mole EC/mole Cat.·h
– *Reaction for calculate:*	$C_2H_4O + CO_2 \longrightarrow C_3H_4O_3$

Taking into account the initial data, the material balance of the process was calculated (Table 5) and a feasibility study was carried out for the production of ethylene carbonate based on ethylene oxide and carbon dioxide using the developed zinc phenolate containing IL catalyst.

According to preliminary calculations, the total cost of the target product for the proposed technology is 1455.33 AZN/t. The price of ethylene carbonate in the world market is about 1400 USD/ton, or, taking into account the current exchange rate of USD/AZN, 2380 AZN/t. Taking into account the cost of delivering goods to the Republic of Azerbaijan, as well as customs duties, the cost of ethylene carbonate will vary from 2400 to about 2600 AZN/t. Thus, the organization of the production of ethylene carbonate will save an average of 1,000 AZN/t, which is equivalent to about 10 million AZN/year.

Table 5

Summary material balance of the ethylene carbonate production process

Name	% (mass)	Amount, t/year.	Name	% (mass)	Amount, t/year
1. Taken:			**2. Received:**		
Technical EO	36.19	6 582	Ethylene carbonate	54.98	10 000
Technical CO2	61.06	11 106	Unreacted EO	1.39	253
Catalyst	0.12	22	Unteacted CO_2	26.39	4 800
Solvent for catalyst	2.63	478	Catalyst	0.09	16
			Water	12.75	2319
			By-products	2.20	400
			Total	97.80	17 788
			3.Losses:	2.20	400
Total:	**100.0**	**18 188**	**Total:**	**100.0**	**18 188**

Conclusions

1. The main physical and chemical properties of zinc phenolate catalysts based on methylene-bis, thio-bis and dithio-bis phenols and zinc chloride, as well as various ionic liquids with bromine, acetate and zinc chloride anions and N-methyl-2-pyrrolidonium, imidazolium, alkyl- and dialkylammonium cations were synthesized and studied [1, 3, 10, 20, 22, 23].

2. The effectiveness of the synthesized zinc phenolate and ionic liquid catalysts in the ethylene carbonate synthesis by the ethylene oxide and carbon dioxide cycloaddition reaction was determined by studying the influence of various factors, determining the conversion of ethylene oxide, the yield and selectivity of ethylene carbonate, the productivity of the catalyst and the TOF of process [1, 2, 4-13, 15, 17-19, 21, 22].

3. It was found that in the presence of zinc phenolate catalysts ZnY (where, Zn = metal, Y = methylene-bis, thio-bis and dithio-bis alkyl phenolate groups) under the conditions: $[Cat] = 1.0 \bullet 10^{-3}$ mole/l; $[EO] = 3.0$ mole/l; $P_{CO2} = 5.0$ MPa; $T = 80°C$; $\tau = 60$ min, the stirrer rotation speed is 350 rpm, it is possible to synthesize ethylene

carbonate with a selectivity of 98.0–99.5%, an EC yield of 80.4-98.5%, with ethylene oxide conversions of 80.0–98.0%, catalyst productivity of 245.7-448.9 g EC/g Cat. and TOF of the process – 2328.0-2850.0 mole EC/mole Cat.·h [2, 7, 8, 12, 18].

4. In the presence of RLX ionic liquid catalysts (where, R = H or C_1-C_8 alkyl groups; L= $[NMP]^+$, $[MIm]^+$, $[Py]^+$ or $[AlkAm]^+$ cations; X = $Br^–$, $HCOO^–$, $CH_3COO^–$ anions), under the same conditions, ethylene carbonate is obtained with a selectivity of 80.0-95.0% [15-19, 21].

5. When using a binary catalyst zinc phenolate+ionic liquid (ZnY+RLX) under the conditions: [RLX] = $2.5 \cdot 10^{-4}$ mole/l, [ZnY] = $2.5 \cdot 10^{-4}$ mole/l, [EO] = 3.0 mole/l; P_{CO2} = 5.0 MPa; T = 80°C; τ = 60 min, stirrer rotation speed 350 rpm, the following process data are achieved: selectivity – 97.0-100.0%, EC yield – 87.3-99.0%, EO conversion – 90.0-99.0%, catalyst productivity – 1000.0-1428.0 g EC/g Cat and TOF of process – 5238.0-5940.0 mole EC/mole Cat·hour [15-19, 21].

6. Best process performance is achieved using a zinc phenolate containing ionic liquid catalyst $R_2L_2X_2ZnY$ (where, R = H or C_1-C_8 alkyl groups; L = N-methylpyrrolidone [NMP], imidazolium [Im], pyridine [Py], or alkylammonium [AlkAm] cationic groups, X= Br or $ZnCl_2$ anions, Y= methylene-bis, thio-bis or dithio-bis alkyl phenolate groups). Under optimal conditions: $[R_2L_2X_2ZnY]$ = $2.5 \cdot 10^{-4}$ mole/l, [EO]= 3.0 mole/l; P_{CO2} = 5.0 MPa; T= 80°C; τ= 60 min, stirrer speed – 350 rpm, ethylene carbonate is obtained with EO conversion 97.0-100.0%, selectivity for EC – 98.0-100.0%, catalyst productivity – 1315.6-1427.0 g EC/g Cat and TOF of process – 11400.0-12000.0 mole EC/mole Cat.·h [16-19, 21].

7. On the basis of the experimental results obtained, the proposed mechanism of the cycloaddition reaction of ethylene oxide and carbon dioxide in the presence of synthesized various catalysts (ZnY, RLX, ZnY+RLX and $R_2L_2X_2ZnY$) is considered. In particular, the proposed mechanism for the synthesis of EC in the presence of a zinc phenolate containing ionic liquid catalyst ($R_2L_2X_2ZnY$) includes the stages of coordination of 2 moles of ethylene oxide with the Lewis acid Zn to form a metal-epoxy complex, nucleophilic attack by the X–

anion (in particular, the halide (Br) anion) of an ionic liquid onto a less hindered carbon atom of epoxide with ring opening and the formation of an oxy-anionic structure, coordination of 2 moles of CO_2 by interaction with Br^- and O^- anions, and then with the formation of EC due to intramolecular cyclic elimination [18].

8. Using the catalysts ZnY, RLX, ZnY+RLX, as well as the selected optimal catalyst $R_2L_2X_2ZnY$, ethylene carbonate was synthesized based on water-containing EO and CO_2. Under the conditions: $[R_2L_2X_2ZnY] = 2.5 \cdot 10^{-4}$ mole/l; [EO]= 3.0 mole/l; P_{CO2} = 5.0 MPa; T= 80°C; τ= 60 min, stirrer rotation speed – 350 rpm, it is possible to synthesize ethylene carbonate with EO conversion of 51.0-99.0%; selectivity for EC – 48.0-100.0%; the productivity of the catalyst – 325.3–1315.6 g EC/g Cat and the TOF of the process – 11400.0–12000.0 mole EC/mole Cat.·h [17-19, 21].

9. The basic technological scheme was considered, the material balance was drawn up, and a feasibility study was carried out for the production of ethylene carbonate using the proposed optimal catalyst $R_2L_2X_2ZnY$ [20, 22, 23].

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