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Ethylene Carbonate Production by Cyclocondensation of Ethylene Glycol and Urea in the Presence of Metal Oxides and Metal Acetylacetonates

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Abstract—A promising method for the production of ethylene carbonate is the cyclocondensation of ethylene glycol and urea in the presence of a catalyst. In this study, the catalytic effect of oxides and acetylacetonates of various metals on the occurrence of this reaction has been examined. It has been shown that cobalt acetylacetonate is the most effective catalyst. The effect of reaction conditions (temperature, pressure, contact time, and catalyst concentration) on the main parameters of catalytic conversion has been studied.

Keywords: ethylene carbonate, ethylene glycol, urea, metal oxides, metal acetylacetonates

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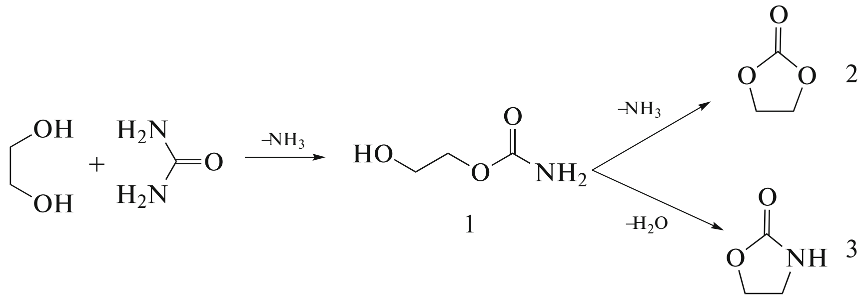
Ethylene carbonate (EC) is an ester of ethylene glycol and carbonic acid; EC is commonly used as a polar solvent because it has a molecular dipole moment of 4.9 D. In the liquid state, EC is capable of dissolving many polymers, polyester fibers, and resins. It is a good solvent for acrylonitrile polymers and copolymers and is used in the production of polyacrylonitrile fiber. Since EC has a high dipole moment, it is also used as a highly permeable component of electrolytes in lithium batteries and in the production of inks, dyes, inorganic salts, lubricants, fuel additives, and auxiliaries in the textile industry [1]. Ethylene carbonate is a low-toxicity biodegradable material.

Pioneering studies on the synthesis of cyclic carbonates were conducted in the early 1930s [2, 3]; the first patent was received more than 50 years ago [4]. There are several currently available methods for synthesizing cyclic carbonates, particularly EC: the carboxylation of epoxides, the oxidative carboxylation of olefins, the reaction of cyclic ketals with CO_2, the reaction of CO_2 with diols, the cyclocondensation of urea and respective diols, and the reaction of CO_2 or urea with glycerol.

The cyclocondensation of dihydric alcohols and urea is one of the most convenient and environmentally safe methods for producing cyclic carbonates. The reaction scheme is given in [5]. At the first stage, ethylene glycol and urea react to form 2-hydroxyethyl carbamate (1), which undergoes further cyclization to form the desired product EC (2) and 2-oxazolidone (3):



The process occurs under mild conditions in the presence of simple catalyst systems. In this case, catalysts based on oxides of various metals are commonly used [6–8]. The authors of [9] described the catalytic activity of zinc acetate; the possibility of using zinc chloride and magnesium chloride to produce propyl-

Table 1. Catalyst systems used in the study

No.	Oxide	Acetylacetonate
Alkaline earth elements		
1	ZnO	Zn(acac)$_2$
2	MgO	Mg(acac)$_2$
d-Block elements		
3	Fe_2O_3	Fe(acac)$_3$
4	Cr_2O_3	Cr(acac)$_3$
5	CoO	Co(acac)$_2$
Rare earth elements (REEs)		
6	La_2O_3	La(acac)$_3$
7	Gd_2O_3	–
8	Er_2O_3	–
Supported catalysts		
9	Silica gel	–
10	H-TsVM	–
11	15%Co/silica gel	–
12	15%Co/H-TsVM	–

ene carbonate was shown in [10]. Thus, the expansion of the range of compounds that are used as catalysts for the production of cyclic carbonates through the reaction of urea and diols and the identification of the most effective catalysts is an urgent task facing the researchers.

The aim of this study was to examine the EC synthesis via the cyclocondensation of ethylene glycol and urea in the presence of a wide range of oxides and acetylacetonates of various elements.

EXPERIMENTAL

Oxides of various elements and respective acetylacetonates were used as cyclocondensation catalysts. The list of the catalysts is given in Table 1. Commercially available oxides were used. Before use, the oxides were calcined in an air stream at a temperature of 300°C for 1 h. Acetylacetonates of respective elements were synthesized as described in [11]. Supported catalysts were prepared by twofold incipient wetness impregnation using two supports—KSKG silica gel and H-TsVM zeolite—at a cobalt content of 15 wt %. To this end, a support preliminarily dried in an air stream at a temperature of 400°C was impregnated with an aqueous solution of cobalt nitrate; after that, it was dried on a steam bath and then calcined in an air stream at a temperature of 450°C to decompose cobalt nitrate and remove the moisture and decomposition products.

Cyclocondensation was conducted under reduced pressure in a flask equipped with a reflux condenser and an external jacket for heating the reaction mixture to a desired temperature. Reduced pressure in the reaction system was generated using a vacuum pump and controlled with a mercury pressure gage. Stirring was conducted using a magnetic stirrer. In all experiments, the urea/ethylene glycol molar ratio was 1/1. Catalyst concentration in the reaction system was 3 wt %; system pressure, 50 mmHg; reaction time, 3 h; and temperature, 140°C, unless otherwise indicated.

The feed components and cyclocondensation reaction products were analyzed by GLC on a Kristallyuks 4000M chromatograph using a CP-Wax58 capillary column (50 m), a flame ionization detector, and helium as a carrier gas. The concentration of the precursors and reaction products was determined by the internal standard method using *n*-butanol as the internal standard.

RESULTS AND DISCUSSION

Reaction between ethylene glycol and urea can occur in the absence of a catalyst; however, in this case, the ethylene glycol conversion is no more than 20% and EC can be formed with a selectivity of 76% (Table 2). The introduction of an oxide catalyst leads to an increase in the ethylene glycol conversion. Thus, oxides of alkaline earth elements (zinc, magnesium) exhibited almost the same activity in the EC production reaction. It should be noted that the cyclocondensation of 2-hydroxyethyl carbamate to form 2-oxazolidone occurs only in the presence of these oxides. In the case of other studied oxides, the formation of 2-oxazolidone was not observed. In the presence of oxides of iron, cobalt, and chromium, ethylene glycol conversion did not achieve high values; however, in the case of chromium oxide and cobalt oxide, the EC selectivity was 92 and 100%, respectively.

REE oxides also exhibited activity in the studied reaction. It was found that the catalytic activity decreases with increasing ordinal number of REE. In the presence of lanthanum(III) oxide, ethylene glycol conversion was 67%, while in the case of erbium(III) oxide, the conversion did not exceed 37%. Another feature of the catalytic action of REE oxides is that the ability to mediate cyclocondensation decreases with increasing ordinal number, as evidenced by increasing 2-hydroxyethyl carbamate selectivity in the series of REE oxides (Table 2).

In all cases, the use of metal acetylacetonates led to an increase in the ethylene glycol conversion compared with the use of oxides. In the case of zinc acetylacetonate, the composition of the resulting products significantly changed; the 2-oxazolidone selectivity achieved 24%. Oxazolidones constitute one of the new groups of synthetic antimicrobial drugs used for the treatment of infections caused by multidrug-resistant

Table 2. Data on the cyclocondensation of ethylene glycol and urea in the presence of metal oxides and metal acetylacetonates

No.	Catalyst	*K*(EG)*, %	*S*(EC)*, %	*S*(P1)*, %	*S*(P2)*, %
1	–	20	76	24	0
		Oxides			
2	ZnO	67	63	28	9
3	MgO	68	70	22	8
4	Fe_2O_3	45	59	41	–
5	Cr_2O_3	36	92	8	–
6	CoO	28	100	–	–
7	La_2O_3	67	97	3	–
8	Gd_2O_3	56	93	6	–
9	Er_2O_3	37	88	12	–
		Acetylacetonates			
10	$Zn(AcAc)_2$	68	42	34	24
11	$Mg(AcAc)_2$	75	94	6	–
12	$Fe(AcAc)_3$	57	58	42	–
13	$Cr(AcAc)_3$	42	94	6	–
14	$Co(AcAc)_2$	72	100	–	–
15	$La(AcAc)_3$	59	90	10	–

* *K*(EG) is the ethylene glycol conversion; *S*(EC), EC selectivity; *S*(P1), 2-hydroxyethyl carbamate selectivity; and *S*(P2), 2-oxazolidone selectivity.

Gram-positive cocci [12]; therefore, the reaction of diols with urea can become a promising inexpensive method for the preparation of compounds of this group.

The most interesting result was obtained in the case of cobalt acetylacetonate. Ethylene glycol conversion was about 2.5 times higher than that in the case of cobalt oxide, while the selectivity for the target product—EC—remained unchanged at a level of 100%. Further studies on the effect of synthesis conditions on the features of occurrence of the reaction between ethylene glycol and urea were conducted in the presence of cobalt acetylacetonate.

Figure 1a shows the effect of temperature on ethylene glycol conversion and EC selectivity. An increase in temperature leads to a significant increase in the degree of conversion of ethylene glycol and a change in the EC selectivity. At temperatures below 140°C, the formation of 2-hydroxyethyl carbamate, in addition to EC, is observed.

A decrease in the system pressure has a positive effect on the occurrence of the reaction (Fig. 1b). It should be noted that, at pressures above 110 mmHg, EC selectivity abruptly decreases to values below 50%. Reaction time also affects the ethylene glycol conversion (Fig. 1c). An increase in the contact time leads to an increase in the ethylene glycol conversion, while the EC selectivity remains unchanged at a level of 100%. A similar dependence is observed with a change in the catalyst concentration in the reaction system (Fig. 1d). Ethylene glycol conversion increases with increasing cobalt acetylacetonate content in the system, while the target product selectivity is not affected by a change in the catalyst concentration.

It is known that the deposition of a catalytically active component on the surface of a porous support leads to an improvement of catalytic conversion param-

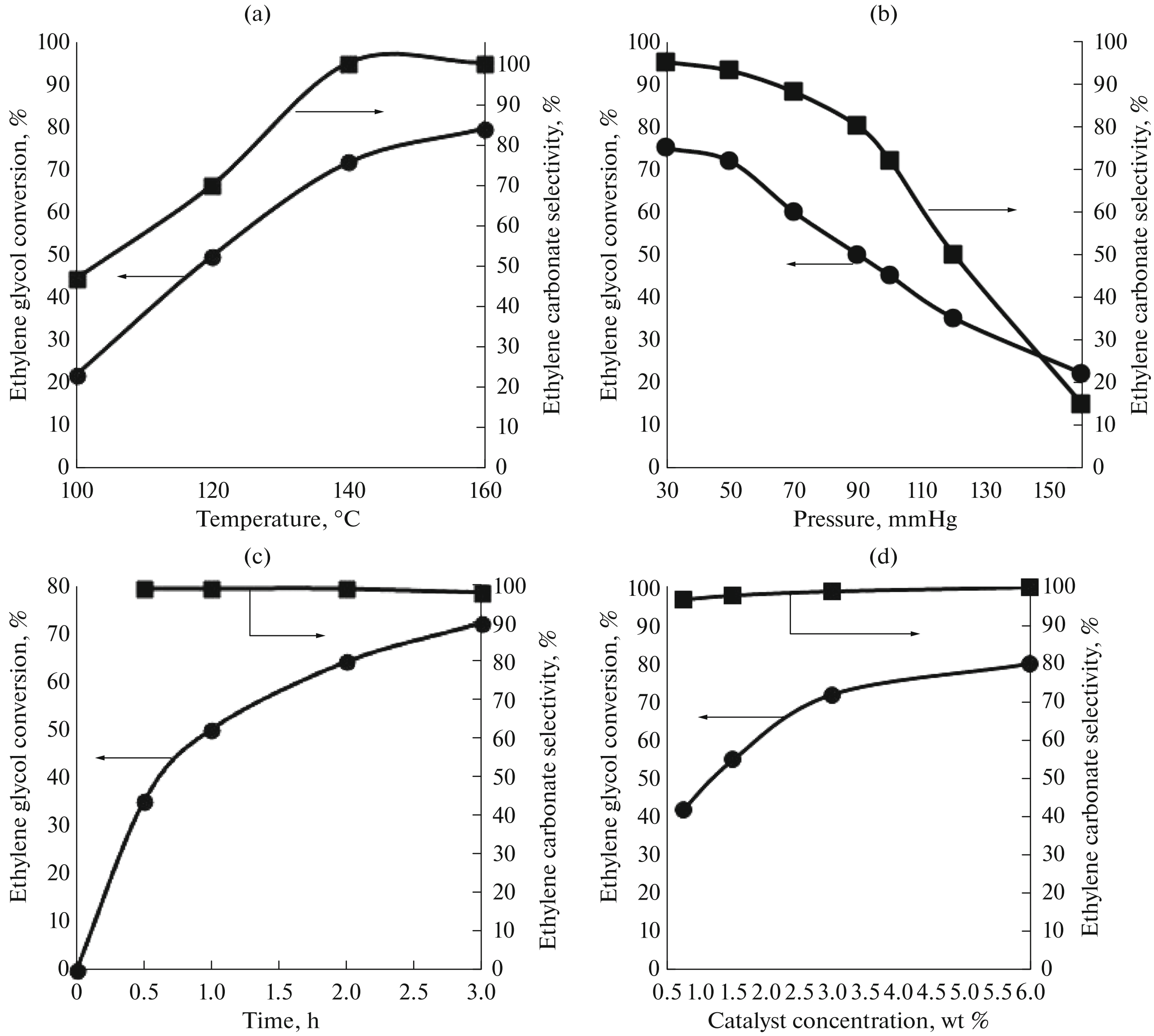


Fig. 1. Effect of cyclocondensation reaction conditions on ethylene glycol conversion and EC selectivity in the presence of $Co(acac)_3$: effect of (a) temperature, (b) pressure, (c) contact time, and (d) catalyst concentration on ethylene glycol conversion and EC selectivity.

eters. Two supports—KSKG silica gel and H-TsVM zeolite—were used in this study.

In the individual state, the supports were not highly active in cyclocondensation; EC conversion was at the level provided by the noncatalyzed process (Table 3). The supporting of cobalt oxide leads to a significant increase in the atomic catalytic activity. Thus, in the case of the 15% Co/silica gel and 15% Co/H-TsVM catalysts, the catalytic activity in terms of cobalt is 9 and 8 times higher than that in the case of cobalt oxide, respectively.

CONCLUSIONS

Features of the reaction between ethylene glycol and urea in the presence of oxides and acetylacetonates of various metals have been studied. It has been shown that oxides of alkaline earth, rare earth, and *d*-elements exhibit catalytic activity in this reaction. The use of acetylacetonates of these elements as catalysts or their supporting leads to an increase in the activity and selectivity in the cyclocondensation reaction. The best results have been obtained for cobalt acetylacetonate. The variable process parameters—temperature, pressure, time, and cobalt acetylaceto-

Table 3. Data on the cyclocondensation of ethylene glycol and urea in the presence of supported catalysts

No.	Catalyst	*K*(EG)*, %	*S*(EC)*, %	*S*(P1)*, %	*S*(P2)*, %
1	Silica gel	28	81	19	–
2	H-TsVM	25	74	26	–
3	15%Co/silica gel	51	100	–	–
4	15%Co/ H-TsVM	43	100	–	–

* *K*(EG) is the ethylene glycol conversion; *S*(EC), EC selectivity; *S*(P1), 2-hydroxyethyl carbamate selectivity; and *S*(P2), 2-oxazolidone selectivity.

nate concentration—have a significant effect on the ethylene glycol conversion and EC yield.

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