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# Nanoheterogeneous Catalytic Cotransformation of Polyatomic Alcohols and Carbamides

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**Abstract**—The interaction of ethylene glycol and glycerol with carbamide in the presence of nanosized cobalt oxide obtained by the decomposition of cobalt(II) acetylacetonate in diphenyl ether is studied. The average size of the nanosized catalyst particles is 8–10 nm. The effect of nanoheterogeneous catalysis on the cyclocondensation of polyatomic alcohols with carbamide is investigated. A high capacity of the nanosized catalyst in this process is found 150 g(cyclic carbonate)/(g(catalyst) h), which is more than 100 times higher than the capacity of conventional catalysts.

**Keywords:** organic carbonate, ethylene carbonate, glycerol carbonate, ethylene glycol, glycerol, carbamide, nanosized oxide, nanoheterogeneous catalysis

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Cyclic organic carbonates belong to the class of esters of carbonic acid and polyatomic alcohols; they are widely used in different fields of the economy as high-polarity solvents, disinfectants, and additives to fuels [1]. There are many approaches to producing cyclic carbonates. The main industrial method to produce them is the catalytic carboxylation of epoxides [2]. This method is not environmentally benign; therefore, the development of new effective methods for production of cyclic carbonates is a topical problem. It was shown that the interaction of polyatomic alcohols and carbamide makes it possible to effectively obtain cyclic carbonates [3–5]. Moreover, this method enables conversion of the by-product of biodiesel production—glycerol—to a high-margin product, and carbamide is a commercially available compound [6–8].

The scheme illustrating the interaction of polyatomic alcohols with carbamide is presented in Fig. 1. The process proceeds at an elevated temperature and reduced pressure and is mediated by a catalyst. At the first stage, one hydroxyl group of polyatomic alcohol interacts with a carbamide amino group, whereupon the corresponding hydroxycarbomate is formed. Then the intramolecular cyclization of hydroxycarbomate proceeds in two ways to produce the target product cyclic carbonate or oxazolidone derivative. Oxazolidone derivatives are widely used as new-generation antibiotics against gram-positive bacteria.

It was shown in [5] that the cobalt-containing catalyst systems have the highest selectivity for ethylene

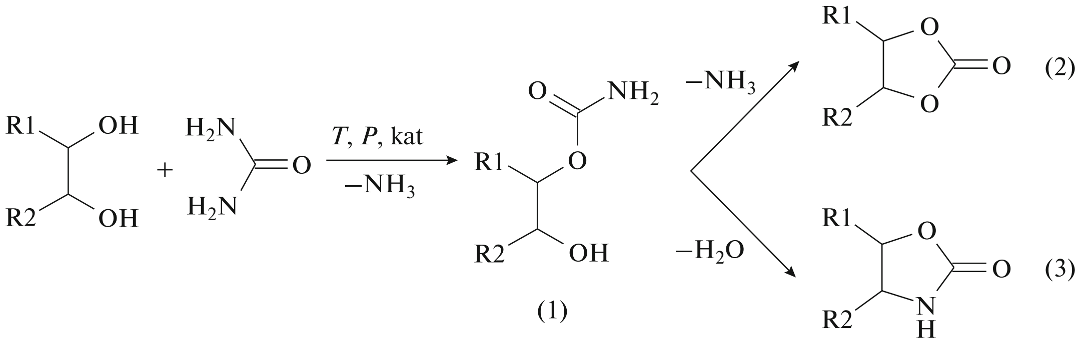


**Fig. 1.** Interaction of polyatomic alcohols with carbamide: (1) hydroxycarbomate, (2) organic carbonate, and (3) oxazolidone derivative.

carbonate for the interaction of ethylene glycol and carbamide. But these catalysts do not always exhibit a high activity. It is known that transfer of the reaction to the nanoheterogeneous regime makes it possible to increase the catalyst capacity by several times [9]; therefore, the investigation of polyatomic alcohol interaction with carbamide under nanoheterogeneous catalytic conditions is of both scientific and practical interest.

The purpose of the present work is to explore the combined transformation of ethylene glycol or glycerol and carbamide in the presence of nanosized cobalt oxide obtained by the thermolysis of cobalt acetylacetonate in diphenyl ether.

## EXPERIMENTAL

Commercial ethylene glycol, glycerol, and carbamide were used as reagents in catalytic tests. The precursor of nanosized cobalt oxide was cobalt(II) acetylacetonate synthesized as described in [10].

Nanosized cobalt oxide was obtained by the decomposition of cobalt(II) acetylacetonate in diphenyl ether (DPE) in a manner similar to [11]. For this purpose, 0.5 g of cobalt(II) acetylacetonate was dissolved in 10 mL of DPE. Forty milliliters of DPE was heated to the required temperature under intensive stirring by a magnetic stirrer in an oil bath in a two-neck round-bottom flask equipped with a reflux condenser. Then the solution of cobalt(II) acetylacetonate was rapidly added to the heated diphenyl ether using a syringe. This mixture was intensely stirred for 2 h to attain complete thermolysis and to form the nanosized particles. Thereafter the mixture was cooled and analyzed. As reference catalysts, we used cobalt oxide, which was obtained by the decomposition of cobalt nitrate at 400°C in an air stream, and the supported catalyst 15% $Co_3O_4/SiO_2$, which was produced by incipient wetness impregnation of the KSKG trademark silica gel by cobalt(II) nitrate solution followed by calcination in an air stream at 400°C. The comparative experiments were performed using these catalysts with a particle size of 50–100 μm.

Cyclocondensation was carried out at a reduced pressure in a flask equipped with a reflux condenser and an external jacket for heating of the reaction mixture to the required temperature. The reduced pressure in the reaction system was formed using a vacuum pump and controlled by a mercury manometer. The system was stirred by a magnetic stirrer. The cyclocondensation reaction conditions were as follows: 120–180°C, 30–160 mmHg, reaction time of 1–4 h, and polyatomic alcohol/carbamide ratio = 0.5–2. The concentration of the nanosized cobalt oxide in all catalytic tests was 500 ppm.

The initial components and cyclocondensation products were analyzed by gas-liquid chromatography on a Kristalyuks-4000M chromatograph equipped with a CP-Wax58 capillary column (50 m) and a flame ionization detector. Helium was used as a carrier gas. The concentration of the initial compounds and reaction products was determined using the internal standard method (*n*-butanol).

The size of particles and the morphology of the synthesized nanosized cobalt oxides were studied by transmission electron microscopy (TEM) on a Tecnai Spirit 120 kV microscope. The test samples were dispersed in methanol using ultrasound, whereupon they were deposited on a copper support and dried.

The X-ray phase analysis was carried out on a Rigaku X-ray diffractometer equipped with an Ultima IV theta-theta goniometer. $CoK_\alpha$ radiation with a scanning step of 0.02° and an exposure time of 1 s was used. The range of angle measurements was $2\theta = 30°–90°$.

The X-ray patterns of the products obtained were indexed by the homology method using the data taken from the international database ICDD PDF-4. The crystal lattice parameters were refined by means of the XRD tabular processor (RTP) software program.

## RESULTS AND DISCUSSION

During the thermolysis of cobalt(II) acetylacetonate in diphenyl ether used as a dispersion medium, spherical nanosized cobalt oxide with an average particle size of 8–10 nm is formed. Figure 2 illustrates the TEM images of the nanosized cobalt oxide.

X-ray phase analysis showed that the thermolysis of cobalt(II) acetylacetonate resulted in formation of mixed cobalt oxide $Co_3O_4$ which crystallizes in the cubic syngony (*Fd*3*m* space group, refined unit cell parameters: $a = 6.9850 \pm 0.0009$). The X-ray pattern of nanosized cobalt oxide (Fig. 3) is characterized by the widening of diffraction peaks. This indicates that the sizes of oxide crystallites are within the nanosized range.

The influence of conditions of organic carbonate synthesis from polyatomic alcohols and carbamide in the presence of the nanosized carbon oxide was studied. All dependences obtained for ethylene glycol and glycerol have the same pattern (Fig. 4). In all catalytic tests, selectivity for the target carbonates was almost 100%; in the case of ethylene glycol, ethylene carbonate was obtained, and in the case of glycerol, glycerol carbonate was obtained.

As expected, a rise in temperature leads to an increase in the conversion of polyatomic alcohol. The conversion significantly increases in the temperature range from 120 to 150°C; above 150°C, the alcohol conversion changes insignificantly. It should be noted that the interaction of glycerol with carbamide proceeds more intensely compared with ethylene glycol. A decrease in pressure in the reaction system favorably affects these processes, since ammonia, which is continuously formed during the reaction, must be

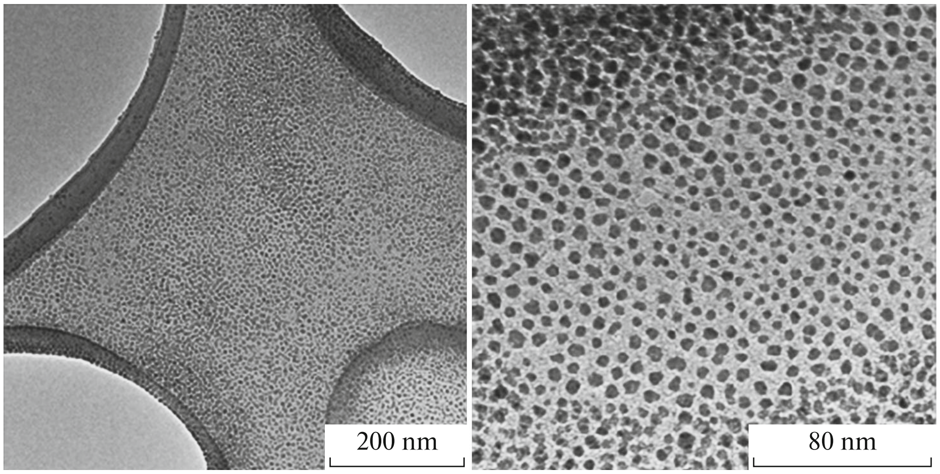


**Fig. 2.** TEM images of nanosized cobalt oxide obtained by the thermolysis of cobalt acetylacetonate in DPE.

removed from the reaction zone. In the case of glycerol, a decrease in pressure leads to an almost linear rise in its conversion throughout the studied pressure interval. For ethylene glycol, the conversion dependence on pressure follows an S-shaped pattern. The reaction time also affects the yield of the target product. With a rise in the contact time from 1 h to 3 h, the ethylene glycol or glycerol conversion increases linearly. Further rise in the contact time leads to insignificant changes in conversion. Dependences illustrating the effect of the molar ratio of the initial reagents on polyatomic alcohol conversion show a maximum at the molar ratio polyatomic alcohol/carbamide = 1. This fact provides evidence for the stoichiometric interaction of the reagents.

Taking into account the above data, we found that the optimum conditions of glycerol or ethylene glycol interaction with carbamide are as follows: 150–160°C, 30–50 mmHg, reaction time of 3 h, and polyatomic alcohol/carbamide molar ratio = 1. Under these conditions the efficiency of the nanosized cobalt oxide was comparable with the efficiency of micron-sized cobalt oxide (50–100 μm) and cobalt oxide supported on silica gel. The results of the comparative studies are presented in Table 1.

The interaction of polyatomic alcohols with carbamide can also proceed without catalysts; however, in this case, the conversion does not exceed 30%, and the selectivity for the target products is no more than 80%. Introduction of the cobalt catalysts in the reaction system makes it possible to selectively synthesize organic carbonates. The traditional oxide or supported catalysts have a capacity of about 1 g(cyclic carbonate)/(g(catalyst) h). The capacity of the nanosized catalyst is more than 100 times higher than the capacity of traditional catalysts. This difference is caused exclusively by a high activity of the nanocatalysts, whereupon achievement of an acceptable level of raw material conversion needs a substantially lower catalyst concentration in the reaction system.

The interaction of the polyatomic alcohols by the example of ethylene glycol and glycerol with carbamide in the presence of the nanosized cobalt oxide ($Co_3O_4$) with an average particle size of 8–10 nm has been studied in the present paper. It has been shown that temperature, pressure, contact time, and molar ratio of the reagents affect the synthesis of ethylene carbonate and glycerol carbonate under the conditions of nanoheterogeneous catalysis, and the optimal conditions for producing these products have been determined. The application of the nanosized cobalt oxide as a catalyst in the synthesis of cyclic carbonate from polyatomic alcohols and carbamide makes it possible to implement this process with high efficiency and selectivity for the target products, which may be synthesized with capacity above 150 g(cyclic carbonate)/(g(catalyst) h).

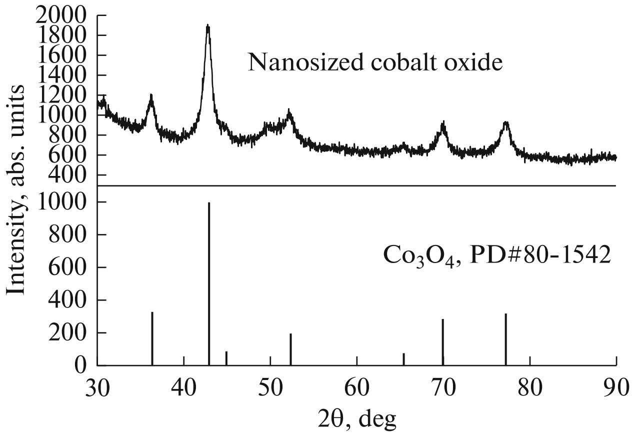


**Fig. 3.** X-ray pattern of nanosized cobalt oxide.

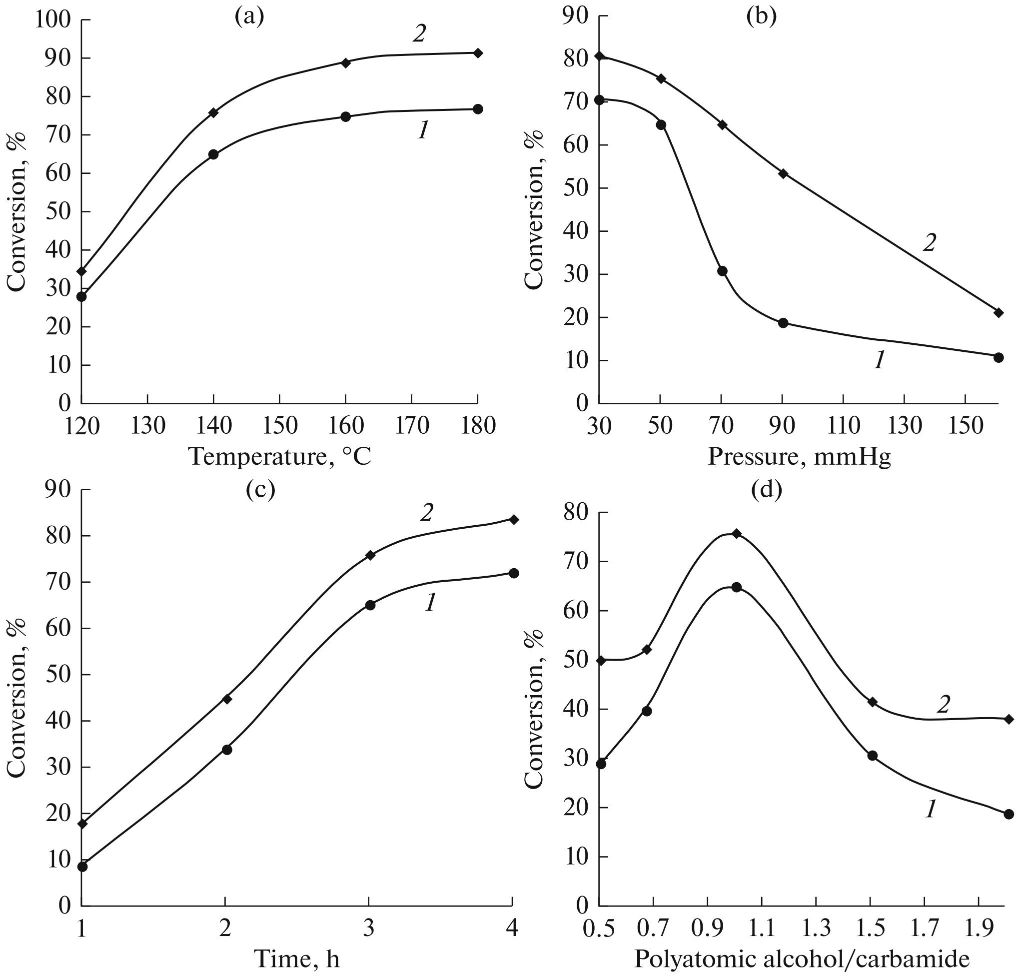
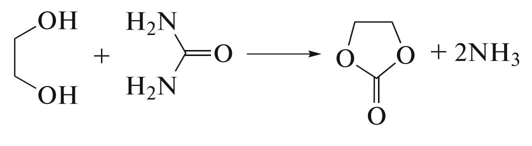
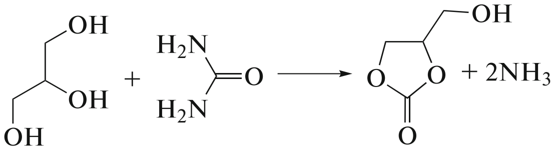


**Fig. 4.** Influence of reaction conditions on the conversion of polyatomic alcohols (*1*) ethylene glycol and (*2*) glycerol: (a) temperature, (b) pressure, (c) time, and (d) polyatomic alcohol/carbamide molar ratio.

**Table 1.** Comparison of cobalt oxide catalysts in the interaction of ethylene glycol and glycerol with carbamide (synthesis conditions: 140°C, 50 mmHg, 3 h, nanosized catalyst concentration of 0.1 wt %, micron catalyst concentration of 10 wt %)

| Catalyst | Con. (EG), % | S (EC), % | Cap., g/(g(cat) h) | Con. (Gl), % | S (GC), % | Cap., g/(g(cat) h) |
|---|---|---|---|---|---|---|
| |  | | |  | | |
| Without | 20 | 76 | – | 24 | 80 | – |
| Nano-$Co_3O_4$ | 65 | 100 | 153.3 | 76 | 100 | 162.2 |
| $Co_3O_4$ | 28 | 100 | 0.66 | 33 | 100 | 0.71 |
| 15% $Co_3O_4/SiO_2$ | 51 | 100 | 1.21 | 52 | 100 | 1.11 |

Con.(EG) denotes ethylene glycol conversion; S(EC) denotes selectivity for ethylene carbonate; Cap. denotes catalyst capacity; Con.(Gl) denotes glycerol conversion; S(GC) denotes selectivity for glycerol carbonate.

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