Heterogeneous Catalytic Conversion of Glycerol with *n*-Butyl Alcohol

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Abstract—The etherification of glycerol with *n*-butyl alcohol at 140°C in the presence of sulfonated cation-exchange resins and zeolite catalysts in an autoclave reactor has been studied. It has been shown that styrene–divinylbenzene ion-exchange resins are effective catalysts for the production of glycerol *n*-butyl ethers: the glycerol conversion is about 98% with an *n*-butyl ether selectivity of about 88 mol % (140°C, 5 h, 5 wt % Amberlyst 36 catalyst, and 10 wt % glycerol in *n*-butanol). Zeolites Y and β in the H$^+$ form exhibit comparable specific activity (glycerol conversion of no more than 25% under similar conditions) in combination with high selectivity for glycerol di-*n*-butyl ethers (up to 28%).

Bioglycerol conversion to high value added products is an important issue in the production of biofuels and "green" counterparts of petrochemicals (petrochemicals substituents). One of the possible ways for glycerol derivatization is the production of ethers. An intriguing prospect is open by the use of *n*-butyl alcohol, which can be derived from carbohydrate-containing vegetable raw materials. Ethers of glycerol and *n*-butyl alcohol can be prepared using components only of vegetable origin; owing to this feature, these ethers are environmentally safe compounds that do not form harmful substances during decomposition and are entirely carbon-neutral during combustion.

Glycerol ethers exhibit a number of interesting physicochemical properties. First, glycerol ethers are of interest as solvents (mono- and diethers as protic solvents and triethers as aprotic solvents) for paint materials and fine organic synthesis processes because the ethers are characterized by high solubility and biodegradability and fairly high viscosity, dielectric permeability, and surface tension [1]. In addition, glycerol ethers can be promising fuel components: a significant number of studies are focused on the effect of additives of glycerol ethers (particularly cyclic) on the quality of motor fuels [2–5]. Depending on the structure of the substituent, glycerol ethers can be octane-boosting gasoline components [2] or diesel fuel components. Glycerol dimethyl ethers have a cetane number of about 58 [6]; it is only logical to assume that glycerol *n*-butyl ethers will have a considerably higher cetane number. In addition, glycerol ethers exhibit a certain surface activity [1] and may be of interest as promising hydrotropes [7]. In this case, the key advantages are amphiphilicity, the possibility of producing both protic and aprotic alkyl glycerol solvents, the possibility of "tuning" the physicochemical properties of the solvent via replacing the substituents, and finally biodegradability, which is of crucial importance for detergents. Some glycerol ethers are extensively used as components of cosmetics [8]. A common feature of the above areas of application is a high value added of the product (incommensurable with that of motor fuel components) whether it be a surfactant or an octane booster.

It has been previously reported on advances in the preparation of glycerol ethers with ethanol [9], *tert*-butanol [10], benzyl alcohol [11], 1-pentanol, 1-hexanol, 1-octanol, and 1-dodecanol [12, 13]. Gaudin et al. [13] have briefly reported a number of experiments with *n*-butanol in the presence of sulfonated cation-exchange resins exhibiting high activity and selectivity for glycerol etherification. Nandiwale et al. [14] described the reaction catalyzed by zeolites β, ZSM-5, and K-10. Sulfonated cation-exchange resins, which are sulfonated styrene–divinylbenzene polymer matrices, exhibit acid strength, acidity, and surface properties that are appropriate for the production of ethers from alcohols. On the other hand, glycerol ethers—both acyclic (e.g., *tert*-butyl) or cyclic (solketal)—can be produced with high selectivities by catalysis over zeolites Y and β [10, 15]. Therefore, zeolite catalysts, along with ion-exchange resins, have been selected as the objects of this study.

The main aims of this study are the screening of various heterogeneous catalysts in the reaction

Table 1. Properties of the test catalysts

Catalyst	Acidity, mmol H$^+$/g	Specific surface area, m^2/g	Pore volume, cm^3/g	Average pore diameter, nm	Si/Al
Zeolite β-25	1.2	680	0.62	–	12.5
Zeolite β-40	0.8	750	0.58	–	20.0
Amberlyst 35*	5.4	50	0.20	24.0	–
Amberlyst 36*	5.4	33	0.20	24.0	–
Amberlyst 70*	2.7	36	–	22.0	–

* The sulfonated cation-exchange resins in a dry state.

between glycerol and *n*-butanol and a primary analysis of the kinetics of conversion.

EXPERIMENTAL

Materials

The reactants were glycerol (special purity grade, Khimmed, Russia) and butanol-1 (reagent grade, Komponent-reaktiv, Russia). The catalysts were styrene−divinylbenzene cation-exchange resins Amberlyst 35 Wet (A-35 wet), Amberlyst 36 Dry (A-36), and Amberlyst 70 (A-70) (Rohm & Haas, Chauny, France) and zeolites β-25 and β-40 (CP811TL and CP814E, Zeolyst International, Kansas City, Kansas, United States). Prior to use, the Amberlyst 70 catalyst was dried at 100°C and a residual pressure of 10 mmHg for 2 h; the Amberlyst 35 wet catalyst was used both in the dry form (A-35 dry) after similar drying and as received (A-35 wet, 51−57 wt % water); Amberlyst 36 Dry containing about 2−3% moisture was used without further drying. The zeolites in the ammonium form were converted to the H$^+$ form by calcination at 550°C. The properties of the catalysts are shown in Table 1.

Equipment and Experimental Procedures

Experiments in a batch reactor were conducted under standard conditions. Six milliliters of a glycerol−*n*-butyl alcohol mixture (10 wt % glycerol), 250 mg of a heterogeneous catalyst (about 5 wt % per feedstock), and a magnetic stirrer were placed in a stainless steel autoclave (inner volume of 20 mL). The closed autoclave was placed on a glycerol bath at an initial temperature of 200 ± 5°C; after that, stirring was switched on; this instant was assumed to be the beginning of the reaction. In 15 min after the beginning of the reaction, the bath temperature was stabilized at 160 ± 5°C and remained at this level to the end of the experiment. The temperature inside the autoclave, which was measured by a thermocouple, stabilized at a level of 140 ± 2°C after 20 min of the reac-

tion. The duration of the runs was 15 min to 8 h. Standard experimental conditions: reaction temperature, 140°C; catalyst weighed portion, 5 wt %; and run time, 4 h. The screening of the catalyst samples was conducted under standard conditions. After the experiment, the autoclave was cooled with cold water and the catalyzate was decanted and analyzed by GLC and GC/MS.

Analysis of Products

The reaction products were analyzed on a Kristallyuks 4000 M chromatograph equipped with a flame ionization detector using a 30 m × 0.25 mm Supelcowax 10 column and helium as a carrier gas (a split ratio of 1 : 90). Temperature programming: holding at 70°C for 3 min; rise from 70 to 250°C at a rate of 10°C/min; and holding at 250°C for 9 min.

The composition and structure of the reaction products were determined by gas chromatography−mass spectrometry using a Finnigan MAT 95 XL instrument (a 30 m × 0.25 mm Varian VF-5ms capillary column; carrier gas, helium; operation mode: injector temperature, 270°C; initial chromatograph oven temperature, 30°C; and 5-min holding followed by heating to 300°C at a rate of 10°C/min; operation mode of the mass spectrometer: ionization energy, 70 eV; source temperature, 230°C; scan range, 20−800 Da at a rate of 1 s/decade of mass; and resolution, 1000). The components were identified using the reference mass spectra from the NIST/EPA/NIH 11 database. The component content was calculated from the chromatographic peak areas in the chromatogram for the total ion current without corrections for ionization efficiency.

RESULTS AND DISCUSSION

The reaction between glycerol and *n*-butyl alcohol at 140°C leads to the formation of glycerol mono-*n*-butyl ethers (m-GNBEs), which are converted to glycerol di-*n*-butyl ethers (di-GNBEs) in the second step. 1-Monoether is formed in approximately fivefold

**Table 2.** Dehydration of glycerol with *n*-butanol under standard conditions

Catalyst	X_G, %	Y_{DBE}, mol %	X_{Gly}/Y_{DBE}	S_M, mol %*	S_D, mol %*	Specific activity**	Acidity, mmol/g
A-36	94	20	4.8	75	6	17	5.4
A-35 wet	64	5	13.6	77	5	12	5.3
A-35 dry	91	14	6.7	78	4	17	5.3
A-70	49	16	3.2	78	7	18	2.7
β-25	24	6	4.2	34	26	17	1.4
β-40	16	4	3.9	39	29	20	0.8

* S_M and S_D are the selectivity for m-GNBE and di-GNBE, respectively, calculated for glycerol conversion ignoring *n*-butanol.
** Conversion (%) per number of acid sites.

excess with respect to 2-monoether (see Scheme). The main byproduct is di-*n*-butyl ether (DBE), which results from the intermolecular dehydration of *n*-butyl alcohol. The maximum yield of DBE is up to 40 mol %. In addition, minor byproducts, which can hardly be precisely identified by the GC/MS method, were detected in the composition of the reaction mixtures.
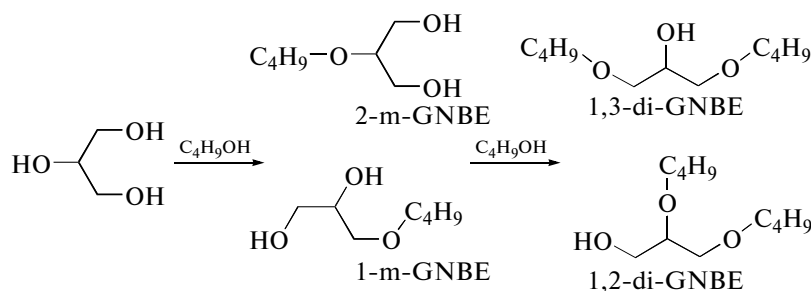
Schematic reaction between glycerol and *n*-butyl alcohol.

It can be assumed that some of these products are cyclic diglycerols of different structure, which are present in the catalyzate in trace amounts (typically up to 5 wt % per the total amount of glycerol and derivatives thereof), and theiir butyl ethers:
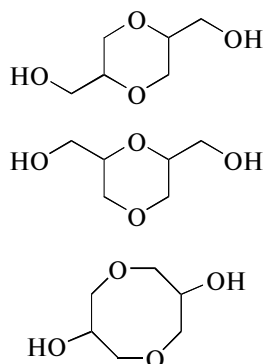
The formation of these structures suggests that butyl alcohol exhibits a low reactivity; the reaction apparently occurs according to the bimolecular mechanism. The reaction of glycerol with *tert*-butanol and benzyl alcohol, which are prone to react by the mono-molecular mechanism, occurs at significantly lower temperatures (glycerol is intensively converted even at 60–70°C) and does not lead to the formation of diglycerols [10, 11].

In contact with an acid catalyst, *n*-butanol is capable of eliminating a water molecule to form butene-1 (no more than 5 wt % in the catalyzate), which in turn reacts with glycerol and thus leads to the formation of glycerol *sec*-butyl ethers. Byproducts of this structure are also present in the reaction mixture in trace amounts (no more than 3%), along with branched isomers of DBE.

The highest activity in the formation of GNBE is found in sulfonated cation-exchange resins. Sulfonated cation-exchange resins A-35, A-36, and A-70 in a dry state exhibit close specific activities in the conversion of glycerol (Table 2) and different activities in the dehydration of *n*-butanol to DBE. In this case, the denser the structure of the resin, the lower the DBE selectivity in the presence of glycerol: the densest structure and the highest degree of crosslinking are characteristic of A-35 that contains 20% divinylbenzene and exhibits a ratio of glycerol conversion to DBE

Table 3. Dehydration of glycerol with *n*-butanol under standard conditions in the presence of A-70

T, °C	X_G, %	S_M, mol %	S_D, mol %	S_E, mol % *	Y_{DBE}, mol %	X_{Gly}/Y_{DBE}
140	18.1	81.9	7.6	89.5	4.7	3.9
160	63.8	80.7	7.1	87.8	18.4	3.5

* Total selectivity for GNBE.

yield (X_{Gly}/Y_{DBE}) of 6.7. At the same time, A-36, which contains a smaller amount of divinylbenzene (12%) and has a slightly less dense structure, is characterized by a ratio of $X_{Gly}/Y_{DBE} = 4.8$. Finally, A-70, which comprises 8% divinylbenzene, exhibits the highest relative activity with respect to DBE. The *n*-butanol concentration in the volume is an order of magnitude higher than that of glycerol; however, the ratio of active reactant concentrations inside the pores and on the surface of a heterogeneous catalyst can be dramatically different; this feature is responsible for the different selectivities of the catalytic process.

The moisture adsorbed by the surface of a cation-exchange resin has a significant effect on the catalytic activity of the resin. The specific activity of wet A-35 with respect to glycerol is 1.4 times lower than that of a dry sample; at the same time, wet A-35 exhibits the lowest selectivity for DBE. Apparently, a glycerol molecule, which exhibits a significant hydrogen bonding affinity, exhibits a higher affinity to adsorption on a hydrated surface (on the surface of a swollen polymer); this feature is responsible for the high effective surface concentration of glycerol.

The above relationships differ from (although are not contrary to) the laws of conversion of *n*-butanol to DBE in the absence of glycerol over sulfonated cation-exchange resins that have been described in [16]. The authors of the cited study have come to the following reasonable conclusion: the less dense the polymer structure, the higher the selectivity of *n*-butanol conversion to DBE. In the case of catalysis with sulfonated cation-exchange resins with an extremely dense structure (A-35), high selectivity for the elimination of water to form butene-1 is observed. At the same time, A-35 is more active than A-36 in reactions between glycerol and *tert*-butanol and less prone to decrease catalytic activity owing to swelling in water [17]. Moreover, the rate of swelling of the polymer in water is an order of magnitude higher than that in glycerol. Thus, the denser structure of sulfonated cation-exchange resins is more advantageous to provide the process selectivity because the water formed during the reaction inhibits mostly the formation of DBE and does not have an equally significant effect on the formation of glycerol ethers. If the reaction medium does not contain glycerol, two reactions compete with each other: the formation of ether and the formation of olefin by elimination of water; the latter reaction is more sensitive to the presence of water (based on the law of mass action). Thus, the combination of the degree of crosslinking of the resin and the presence of moisture in the reaction medium has dissimilar effects on the *n*-butanol conversion depending on the presence or absence of glycerol.

Styrene–divinylbenzene catalysts exhibit low thermal stability: as the allowable process temperature is exceeded, the ipso-substitution reactions of sulfo groups are sharply accelerated, resulting in a decrease in catalytic activity. For resins A-35 and A-36, the maximum operating temperature is 150°C; chlorinated resin A-70 is stable up to 190°C. For A-35 and A-36, the temperature of 140°C, at which the reaction between glycerol and *n*-butanol was studied, is close to a maximum, whereas A-70 has a "reserve" of allowable temperatures. The results of the catalytic experiments at different temperatures are shown in Table 3.

As the temperature increases from 140 to 160°C, the activity of A-70 considerably increases, while the pattern of distribution of the reaction products remains almost the same. A slightly higher X_{Gly}/Y_{DBE} ratio apparently suggests a higher activation energy of formation of DBE because it is this direction of conversion of the reactants that is more significantly affected by an increase in temperature. Since the reaction can be multiply accelerated while maintaining selectivity, we believe that A-70 is the most promising sulfonated cation-exchange resin catalyst for the reaction under study.

Zeolite catalysts exhibit specific activity comparable to that of sulfonated cation-exchange resins; however, the selectivity is completely different. First, a considerably lower amount of DBE is formed over zeolites; this fact is apparently attributed to the presence of narrow pores that are accessible to *n*-butanol molecules and inaccessible to glycerol; only DBE or butenes can be formed in these pores. At the same time, in the case of catalysis with zeolites, a high selectivity for diethers was observed: at a total selectivity for glycerol ethers of up to 76 mol %, the diether selectivity achieved 29%. The observed selectivity values can be attributed to the fact that the range under study is a low-conversion region where the kinetic factor plays an important role. As the reaction proceeds further, the diether selectivity slightly decreases in favor of monoethers: apparently, transalkylation occurs; it is characteristic of many multistage reactions. Fairly similar results on catalysis with zeolite β (SiO_2/Al_2O_3 ratio, 8.8; $T = 140{-}190$°C; $p = 0.5$ MPa,

reaction time, 4 h; ninefold molar excess of *n*-butanol; 10 wt % of the catalyst) were obtained in [14]. The glycerol conversion at 140°C did not exceed 30%; as it increased, the authors cited observed diether selectivities of up to 32%; this fact is in agreement with our results. Finally, a factor that affects the selectivity of the catalytic reaction is the hydrophobicity of the catalyst surface: it is this factor that is responsible for the higher glycerol di-*tert*-butyl ether selectivity of zeolite β compared to that of sulfonated cation-exchange resins [11].

The reaction selectivity for diethers and DBE should also be attributed to the effective (active) reactant concentrations inside the pores and on the surface of the catalyst, which are determined by a number of factors: first, the different rates of diffusion of glycerol and *n*-butanol molecules and, second, the different adsorption affinities thereof. An assumption that the active *n*-butanol concentration in the pore volume and on the surface of the zeolites is higher than in the case of A-35 and A-36 elucidates the high selectivity for DBE and di-GNBE: an excess active mass of *n*-butanol leads to a multiple alkylation of glycerol; in addition, glycerol deficiency increases the probability of active collision of two butanol molecules. Since the average pore diameter of zeolites is 0.7 nm, the access into the pores is to some extent hindered to glycerol molecules, which have a slightly larger diameter than that of *n*-butanol molecules. The diffusion of desorbed GNBE molecules is associated with even greater diffusion hindrances; it is this feature that is responsible for the high selectivity for DBE and di-GNBE.

It should be noted that the production of ethers from primary alcohols over zeolites and sulfonated cation-exchange resins has been thoroughly studied. The authors of [18] have compared the activation energy of formation of di-*n*-pentyl ether from *n*-pentanol. In the reaction catalyzed by zeolites Y and β, the activation energy of formation of the ether is slightly higher than that in the case of catalysis with sulfonated cation-exchange resins (110 ± 10 and 95 ± 5 kJ/mol, respectively); moreover, the zeolites exhibit a comparable catalytic activity at higher temperatures, i.e., above 140°C, whereas the sulfonated cation-exchange resins are active even at 120−130°C. Apparently, this fact is attributed to the lower acid strength of the zeolites: the closest activation energy is exhibited by mordenite, which is the most strongly acidic zeolite.

In the reaction between glycerol and *tert*-butanol (monomolecular mechanism), sulfonated cation-exchange resins are also more active than zeolites and provide a higher yield of glycerol *tert*-butyl ethers than zeolites Y and β do [17]. The higher activity of sulfonated cation-exchange resins compared with that of zeolites that has been observed in this study is in good agreement with the above relationships.

The kinetics of conversion of glycerol in a mixture with butanol over dried sulfonated cation-exchange resins A-35 and A-70 at 140°C is shown in Fig. 1. The
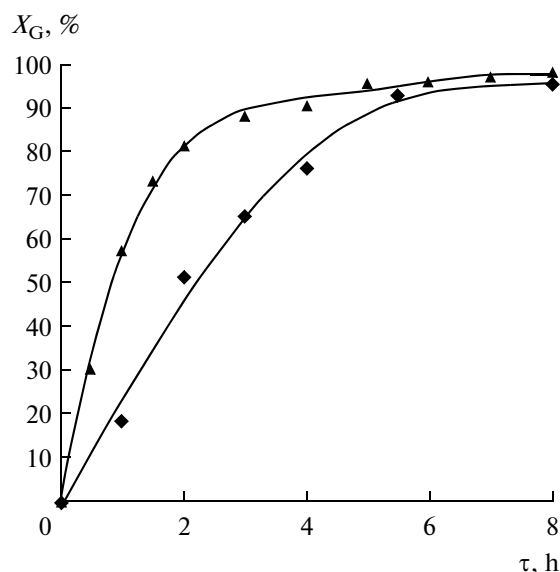

Fig. 1. Kinetic curves of glycerol conversion at $T = 140°C$ and 5 wt % of the catalyst: (◆) A-70 and (▲) A-35 dry.

glycerol conversion occurs much more rapidly over A-35; the initial turnover number per active site of A-35 is almost two times higher than the turnover number for A-70: it is 58 and 35 h^{-1}, respectively (calculated only for glycerol). The equilibrium conversion of glycerol at the time of 8 h is approximately the same for the two catalysts.

The variation in the component concentration in the reaction mixture in the case of catalysis with A-35 is shown in Fig. 2. In the reaction catalyzed by the sulfonated cation-exchange resins, transalkylation effects are not observed; the rate of formation of diethers depends on the monoether concentration in the mixture. At the time of 8 h, the reaction is still far from thermodynamic equilibrium despite the almost complete conversion of glycerol. In the further course of the reaction, it is reasonable to expect the formation of additional amounts of glycerol diethers and DBE.

Note that the formation of DBE should not be necessarily regarded as an undesirable side reaction. DBE is a "green" aprotic solvent and a promising additive to motor fuels [19, 20]; in addition, DBE can be recycled and used as an alkylating agent in a mixture with *n*-butanol.

To summarize the results of the study, we note that sulfonated cation-exchange resins A-35, Amberlyst 36, and Amberlyst 70 have proved to be effective catalysts for the production of GNBEs from *n*-butanol and glycerol. The denser the structure of the resin, the higher the ratio between the rates of formation of GNBEs and DBE; the presence of moisture adsorbed on the polymer sharply increases this ratio from 6.7 (A-35 dry) to 13.6 (A-35 wet). The reaction between *n*-butanol and glycerol (9 : 1 by weight) in an autoclave in the presence of dry A-36 at 140°C for 5 h leads to
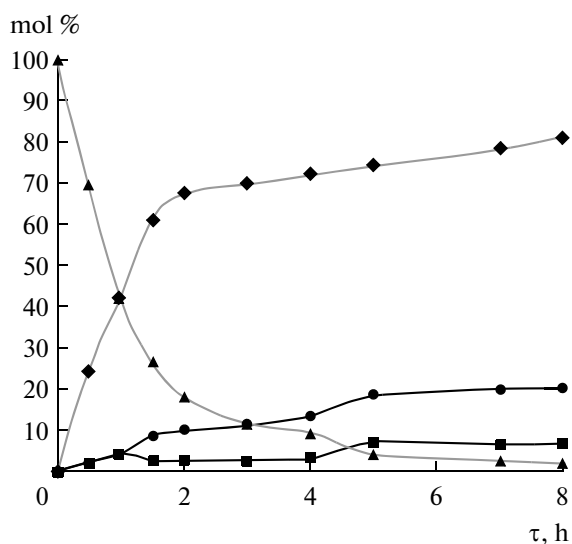
mol %

Fig. 2. Time variation in the component concentrations in the reaction mixture: $T = 140°C$; 5 wt % A-35 dry; (◆) m-GNBE, (■) di-GNBE, (▲) glycerol, and (●) DBE.

the quantitative conversion of glycerol with the GNBE selectivity of up to 88 mol %.

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