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SYNTHESIS OF 1,4-DIOXENE FROM DIETHYLENE GLYCOL IN THE PRESENCE OF BIFUNCTIONAL COPPER-CONTAINING CATALYSTS.
EFFECT OF SUPPORT ON THE SELECTIVITY OF DIOXENE FORMATION

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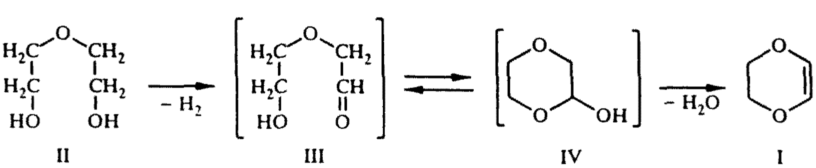
In the synthesis of 1,4-dioxene from diethylene glycol in the presence of a bifunctional copper-containing catalyst, the composition of the by-products has been studied and the effect of the support on the overall direction of the reactions has been investigated. It has been established that on Cu/SiO_2*, 1,4-dioxanone is formed together with dioxene, the yield of the former increasing with an increase in the content of copper in the catalyst. This is due to an increase in the dehydrogenating function of the latter. On the more acidic* Cu/Al_2O_3*, 1,4-dioxane is mainly obtained together with, to a lesser degree, methyl-1,3-dioxolane. This is due to the predominance of dehydration reactions followed by isomerization. Dioxene, dioxane, and methyldioxolane are formed on Cu/HNaY, and the yield of the latter increases with an increase in the degree of acidity (degree of decationization) of the zeolite. It is possible to increase the selectivity of dioxene formation substantially with the use of a catalyst with a moderately acidic zeolite, by varying its copper content and by dilution with water vapor.*

1,4-Dioxene (I) is of interest as the starting compound for the synthesis of 1,4-dioxane derivatives that are biologically active and which find application as drugs, insecticides, and acaricides [1, 2]. The most promising methods for its preparation are heterogeneous catalytic methods that have a simple process design and are able to utilize conventional production equipment and a comparatively inexpensive and readily available raw material such as diethylene glycol (II). Thus, according to one of the early methods [3], diethylene glycol is converted to dioxene I in the presence of $CuCr_2O_4$ suspended in an aqueous solution of $KHSO_4$ [3]. It is assumed that the reaction takes place through dehydration of one of the alcohol groups of diol II to form the aldehydroalcohol III, followed by dehydration of the corresponding cyclic hemiacetal IV (see Scheme 1).

Scheme 1



In this case $CuCr_2O_4$ acts as the dehydrogenation agent while $KHSO_4$ acts as the dehydration agent. It was anticipated that such reactions could be successfully carried out in the presence of bifunctional catalysts, one of which (Cu/SiO_2) was proposed in the 1960s and 1970s [4, 5]. It was also of interest to study other bifunctional catalysts with a varying ratio of acidic to dehydrogenating functions and to elucidate the effect of this ratio on the selectivity for formation of dioxene I. To this purpose the reactions of diethylene glycol II were studied on copper catalysts with supports that had different acidic properties, for example, silica gel, Al_2O_3, and zeolite NaY. The results of the experiments are listed in Table 1.

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TABLE 1. Reactions of Diethylene Glycol on Copper-Containing Catalysts with Different Supports at 280°C

Catalyst	Withdrawal time of catalyzate, h	Yield of catalyzate, wt. %	Content in catalyzate, wt. %					Conversion of II, wt. %	Yield of I, % of theor.	
			II	I	V	VI	VII		based on II added	based on II reacted
5% Cu/SiO_2	0...1	68,1	3,5	33,1	52,8	0,7	0,3	96,5	21,2	21,9
	1...2	77,6	21,1	19,4	50,4	0,2	0,2	78,9	15,4	19,5
10% Cu/SiO_2	0...1	75,6	3,8	25,5	58,3	0,8	0,3	96,2	18,6	19,4
	1...2	78,0	8,4	20,0	56,7	1,6	0,4	91,6	15,4	16,8
10% Cu/Al_2O_3*	0...0,5	36,1	—	—	—	78,5	5,0	100,0	—	—
	0,5...1	58,1	—	—	—	49,4	34,9	100,0	—	—
5% Cu/zeolite Na Y (13% Na_2O)	0...1	65,0	9,5	19,2	—	48,9	2,9	90,5	11,7	12,9
	1...2	94,6	25,1	29,4	—	27,0	4,4	75,0	29,7	39,5

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*Temperature of experiment 250°C.

TABLE 2. Effect of Decationization of Zeolite NaY on the Composition of the Products of Diethylene Glycol Conversion at 280°C

Catalyst	Yield of catalyzate, wt. %	Content in catalyzate, wt. %					Conversion of II, wt. %	Yield of I, % of theor.	
		II	I	V	VI	VII		based on added II	based on reacted II
5% Cu/NaY (13% Na_2O)	94,6	25,2	29,4	–	27,0	4,4	75,0	29,7	39,5
5% Cu/HNaY (3,6% Na_2O)	100,0	70,3	7,2	0,3	10,0	3,0	29,7	8,7	29,1
5% Cu/HNaY (1,1% Na_2O)	97,1	40,0	14,4	0,5	20,2	7,2	60,0	15,4	25,6
5% Cu/HNaY (0,7% Na_2O)	89,6	28,8	9,0	0,9	29,7	10,3	71,2	8,7	12,2

TABLE 3. Effect of Dilution of Diethylene Glycol with Water Vapor on Its Reactions in the Presence of Copper-Containing Catalysts at 300°

Catalyst	Experiment*	Withdrawal time of catalyzate, h	Yield of catalyzate, wt. %	Content in catalyzate, wt. %					Conversion of II, wt. %	Yield of I, % of theor.	
				II	I	V	VI	VII		Based on II added	Based on II reacted
5% Cu/SiO_2	A	0...1	68,1	3,5	33,1	52,8	0,7	0,3	96,5	21,2	21,9
		1...2	77,6	21,1	19,4	50,4	0,2	0,2	78,9	15,4	19,5
	B	0...1	75,6	23,7	31,2	32,5	0,3	–	76,3	17,3	22,7
		1...2	100,0	27,5	39,7	27,1	0,2	–	72,5	39,6	54,6
5% Cu/HNaY†	A	0...1	65,5	50,9	8,2	0,3	26,9	3,2	49,1	5,8	11,8
		1...2	100,0	70,3	7,2	0,3	10,0	3,0	29,7	8,7	29,1
	B	0...1	78,7	43,8	34,1	1,3	10,5	0,5	56,2	27,4	48,8
		1...2	94,4	50,2	27,4	0,5	8,2	1,0	49,8	28,7	57,7
Regenerated 5% Cu/HNaY†	A	0...1	80,0	43,4	34,2	2,3	9,3	0,5	56,6	28,2	49,7
		1...2	95,5	65,9	22,7	0,6	6,0	0,3	34,1	24,9	72,8
Twice regenerated 5% Cu/HNaY†	B	0...1	76,5	26,9	50,9	0,7	12,8	0,5	73,1	37,7	51,6
		1...2	89,1	64,4	17,5	0,6	9,3	0,5	35,6	17,6	49,2

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*A) without dilution with water vapor; B) dilution with water vapor, molar ratio of II:vapor = 1:1.

†Catalyst contains 3.6% Na_2O.

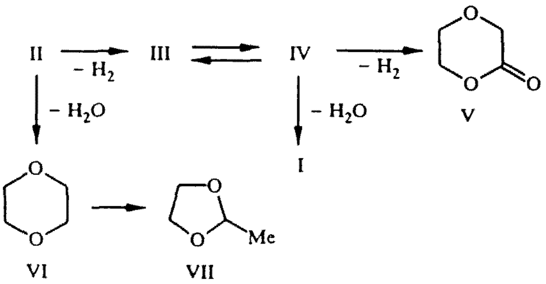
It can be seen from the results listed that on samples of Cu/SiO_2 containing 5 and 10% copper, the conversion of diethylene glycol II at 280°C reaches 79-96% with a selectivity with respect to dioxene I (yield based on reacted glycol II) of 17-22%. The main conversion product is 1,4-dioxanone (V), whose content exceeds 50% in the catalyzate. On the sample with a higher copper content the increase in yield of compound V is particularly marked (57-58%). In addition, 1,4-dioxane (VI) and 2-methyl-1,3-dioxolane (VII) are found in small quantities in the catalyzate.

On Cu/Al_2O_3 the conversion of glycol reaches 100% even at 250°C. At the same time dioxene is not formed at all and the main reaction product is dioxane VI or (with a longer experiment time) the latter mixed with methyldioxolane.

When zeolite NaY (5% Cu/NaY) is investigated as the support, the conversion of glycol II is lower (75-90%, see also experiments with Cu/SiO_2). Dioxene I, dioxane VI and a small quantity of methyldioxolane VII are present in the catalyzate. At the same time the content of product VI is similar or even higher than that of dioxene, with the result that the selectivity with respect to dioxene does not exceed 40%.

Thus, the composition of the conversion products of diethylene glycol II varies with the acidity of the support, and hence with the ratio of acidic to dehydrogenating functions of the catalyst. The possible routes for conversion of glycol II on these catalysts are shown in Scheme 2. On copper on a silica gel support, the acididity of which is low [6], product IV (see Scheme 2) probably undergoes dehydrogenation to a greater extent than dehydration, resulting in the preferential formation of dioxanone V. It should be noted that formation of the latter from diethylene glycol on Cu/SiO_2 had not been previously observed. An increase in the content of the dehydrogenating component (copper) naturally leads to an increase in the dioxanone content in the reaction mixture. On the significantly more acidic catalyst Cu/Al_2O_3 it is probable that dehydration processes occur to a greater degree, giving dioxane VI, which under the acidic catalytic conditions partially isomerizes to methyldioxolane VII. Hence, depending on the relative strength of the acidic and dehydrogenating sites, the reaction leads to the formation of products V or VI and VII. In order to obtain dioxene I, it is clearly necessary to strike a given balance between acidic and dehydrogenating functions, so that glycol II can be converted in the desired direction. This balance can be achieved by altering the dehydrogenating activity of the catalyst (for example, by varying the copper content) or by changing its acidity (for example, in the case of the zeolite-containing catalysts, through a change in the degree of decationization of the zeolite).

Scheme 2



Data on the conversion and composition of the conversion products of diethylene glycol on copper-containing zeolite catalysts with a varying degree of decationization of the zeolite (Table 2) demonstrate that the yield of dioxene decreases as it increases, which is probably due to an acceleration of acid-catalyzed dehydration and isomerization reactions. In fact, the content of dioxane VI and methyldioxolane VII in the reaction mixture increases at the same time, reaching 30 and 10% respectively for the most decationized sample (residual Na_2O content 0.7%).

It has been found that in catalytic processes where unsaturated compounds are formed, their oligomerization products are obtained in larger or smaller quantities. At higher temperatures the latter undergo partial loss of hydrogen to form condensed products (coke). The hydrogen eliminated can saturate the molecules of other unsaturated compounds that occur in the reaction mixture. According to this theory, the formation of dioxane may to a certain extent be due to the transfer of hydrogen from oligomeric products to the dioxene molecule I:

$$\mathrm{II} \longrightarrow \mathrm{I} \longrightarrow \text{oligomers} \xrightarrow{\mathrm{I}} \mathrm{VI} + \text{"coke"}$$

In hydrocarbon catalysis the formation of condensation products is inhibited by dilution of the initial hydrocarbon with water vapor [7]. This leads to a decrease in the formation of saturated hydrocarbons and hence to an increase in selectivity with respect to unsaturated compounds.

The experimental data without dilution and with dilution of the initial glycol II with water vapor on supported copper catalysts, where silica gel or zeolite NaY with a varying degree of decationization of the latter were used as the support, are shown in Table 3. It can be seen that when water vapor is employed, the yields of dioxene, as the target product, are increased. Thus, on the Cu/SiO_2 catalyst, it was possible to increase the selectivity with respect to dioxene from 20 to 55% by dilution with water vapor. A further significant increase in selectivity from the effect of dilution occurs on the Cu/HNaY sample. As can be seen from Table 3, for similar conversion rates of diethylene glycol (49 and 50%), the selectivity with respect to dioxene when water vapor was included increased from 12 to 58%, so that the yield of this product based on added glycol II rose from 6-9% to 27-29%. The relatively high (about 40%) yields are achieved only in the first 2 hours of the experiment, after which they decrease, mainly due to a reduction in conversion of diethylene glycol. It is significant that after oxidative regeneration of the catalyst is carried out, the yields of dioxene are similar to those obtained with fresh catalyst.

Thus, the acidic properties of the support have a considerable effect on the direction of conversion of diethylene glycol on copper-containing catalysts. By using a catalyst with a moderately acidic zeolite support, by varying the content of copper in it, and by diluting with water vapor, the selectivity of formation of dioxene can be increased substantially.

EXPERIMENTAL

The reaction products were analyzed by means of GLC on a 3 m × 3 mm column with 10% Apiezon L on Inerton at 80-180°C. The main reaction products were identified by GC-MS on an Incos 50 instrument (Finnigan MAT) with a 70 eV electron impact ionization potential. Separation was carried out on a glass capillary column (30 m) coated with RSL-200, with a programmed increase in temperature from 40 to 250°C. The spectra recorded during chromatography were automatically correlated with a computer "library" of 10,000 compounds, and from several variants were selected those that showed the closest match to the spectrum of the compound under study and to the chemical nature of the process.

Catalysts. Catalysts containing 5 and 10% copper were used in this study; they were prepared by saturating the supports with aqueous solutions of $Cu(NO_3)_2 \cdot 3H_2O$ followed by drying and calcination of the samples at 140 and 550°C respectively. The supports used were γ-Al_2O_3 (A-64 grade, specific surface 162 m^2/g), SiO_2 (ShSM), and also zeolite Y ($Na_2O \cdot Al_2O_3 \cdot 4.8\ SiO_2 \cdot 8.9\ H_2O$; $SiO_2/Al_2O_3 = 5.74$), which underwent partial decationization. Decationization was carried out by exchange of Na^+ ions in the zeolite for $NH_4{}^+$ ions from an aqueous solution of NH_4Cl followed by drying and calcination of the sample, during the course of which the $NH_4{}^+$ exchange ions decomposed to NH_3 and H^+. In particular, a mixture of 80 cm^3 (56.3 g) of zeolite NaY powder and 1800 ml of aqueous solution containing 31.14 g of NH_4Cl was kept for 6 h with agitation in a 2-liter flask on a boiling water bath. After precipitation of the suspension, the solution was decanted, and the precipitate was washed on a glass filter until a reaction for Cl^- ions was no longer to be seen in the filtrate. Treatment of the zeolite with ammonium chloride was repeated twice, and then the washed precipitate was dried at 120°C followed by calcination in a muffle furnace at 500°C for 6 h. Decationized zeolite with a residual Na_2O content of 3.6% was repeatedly obtained by this process. Repetition of the procedure described above using the latter gave a twice decationized sample containing 1.1% Na_2O; and using a similar procedure from it, a sample decationized three times with 0.7% Na_2O was obtained.

Experimental Method. The experiments were carried out on a continuous-flow unit with a vertical quartz reactor containing 17 cm^3 of catalyst (1-2 mm grain) and placed in a block electric furnace. The initial diethylene glycol or a mixture of it and water was pumped into the reactor and the catalyzate was collected in cooled traps. The experiments were carried out at 280-300°C with a volumetric rate for passage of glycol of 0.7 h^{-1}. Two portions of catalyzate were collected for analysis during the first hour and second hour (see Tables 1 and 3) or during the first 30 min and subsequent 30 min of the experiment (see Table 1). After the experiments, the catalyst underwent oxidative regeneration by passing through a current of air at 500°C for 3 h. The completion of regeneration was monitored from the cessation of CO_2 evolution (cessation of CO_2 absorption by Askarite).

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