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CONVERSION OF 1,4-BUTANEDIOL TO FURAN COMPOUNDS ON COBALT CATALYSTS IN THE LIQUID PHASE

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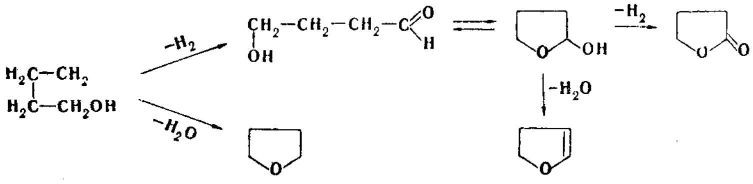
The transformation of 1,4-butanediol on cobalt catalysts applied to kieselguhr in the liquid phase under periodic and continuous conditions was investigated. When the reaction is carried out under periodic conditions, the principal reaction products are 2,3-dihydrofuran, tetrahydrofuran, and γ-butyrolactone. An increase in the selectivity of the formation of 2,3-dihydrofuran as the temperature is raised was established. 2,3-Dihydrofuran is obtained in 63-73 mole % yields under optimum conditions. 2,3-Dihydrofuran is converted to tetrahydrofuran when the process is carried out under continuous conditions on a tableted cobalt catalyst.

Relatively little study has been devoted to the catalytic transformations of 1,4-butanediol to furan compounds on cobalt-containing catalyst. It has been shown [1, 2] that 1,4-butanediol is converted to 2,3-dihydrofuran with high selectivity on such catalysts promoted by magnesium and zinc ions and by other additives in the liquid phase. The reaction proceeds via the parallel-consecutive scheme



The first parallel steps in the process are dehydration of 1,4-butanediol to tetrahydrofuran and dehydrogenation of 1,4-butanediol to γ-hydroxybutyraldehyde, which exists in equilibrium

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TABLE 1. Results of the Synthesis of 2,3-Dihydrofuran on a Mixture of Co Catalysts Applied to Kieselguhr under Periodic Conditions (at a nitrogen pressure of 1 atm)

Temp., °C	Nitrogen volume rate, h^{-1}	1,4-Butanediol : catalyst : stearic acid : H_2SO_4 wt. ratio	Yield, mole %		Conversion of the raw material, %	Efficiency of the formation of 2,3-dihydrofuran, g/kg-h
			2,3-dihydrofuran	tetrahydrofuran		
210	1577	1 : 0,09 : 0,02 : 0	1,33*	1,56	not det.	112
225	1492	1 : 0,09 : 0,01 : 0	63,2	14	90	5018
225	1041	1 : 0,11 : 0 : 0	49,1	13,5	76	1630
226	914	1 : 0,14 : 0 : 0,014	48,2	28	90,1	1475
227†	345	1 : 0,46 : 0,02 : 0	73,3	34	93	710
239	1174	1 : 0,1 : 0,02 : 0	59,5	9,6	89	2509
239	1342	1 : 0,07 : 0,08 : 0	54,2	25	85,3	1252

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*Based on the raw material used in the experiment.

†The experiment was carried out with a different batch of the catalyst.

with 2-hydroxytetrahydrofuran. The latter undergoes dehydrogenation to γ-butyrolactone and dehydration to 2,3-dihydrofuran.

In the present research we studied the selectivity of the formation of 2,3-dihydrofuran and other furan compounds as a function of the reaction conditions. We established that the selectivity of the formation of 2,3-dihydrofuran increases as the temperature is raised when the process is carried out at atmospheric pressure on an industrial Co catalyst applied to kieselguhr under flow conditions, whereas the selectivity of the formation of tetrahydrofuran decreases (Table 1). At 210°C the 2,3-dihydrofuran:tetrahydrofuran ratio was one, whereas at 225°C it was 4.6. The yield of the latter under these conditions reaches 63-75 mole % based on the converted raw material. As the temperature is raised to 239°C, the yields of 2,3-dihydrofuran decrease somewhat and amount to 54.2-59.5 mole %. Thus it is recommended that the experiment is carried out at 225-230°C, at which temperatures the maximum selectivity of the formation of 2,3-dihydrofuran is reached.

The effect of sulfur and stearic acid on the course of the process was checked. Under comparable experimental conditions it was established that the introduction of concentrated sulfuric acid (at a 1,4-butanediol:H_2SO_4 ratio of $1{:}1.7 \cdot 10^{-2}$) does not have a positive effect on the course of the reaction. Pronounced resinification of the reaction mixture is observed vis-à-vis a comparable yield of 2,3-dihydrofuran when sulfuric acid is present.

The addition of stearic acid under comparable experimental conditions leads to a considerable increase in the yield of the desired product (by 13% or more). The degree of resinification of the reaction medium is considerably smaller when stearic acid is used than when sulfuric acid is used. However, the amount of foaming increases markedly when stearic acid is added to the reaction mixture, and this complicates attempts to carry out the process in a periodic-action reactor.

A substantial change in the selectivity of the formation of furan compounds is observed when the process is carried out on a tableted cobalt catalyst applied to kieselguhr under pressure and under continuous conditions (Table 2). Under these conditions the yield of 2,3-dihydrofuran does not exceed 14.3%. The principal reaction products are tetrahydrofuran and γ-butyrolactone. The yield of the tetrahydrofuran is 46.4 mole % at 300-320°C, a nitrogen pressure of 20 atm, and a 1,4-butanediol volume rate of 0.4 h^{-1}. The yield of tetrahydrofuran decreases as the temperature is lowered. In contrast to this, the selectivity of the formation of γ-butyrolactone depends to a relatively small extent on the temperature. The maximum yield of γ-butyrolactone (42.6%) is obtained at 270°C, a pressure of 20 atm, and a 1,4-butanediol volume rate of 0.16 h^{-1}. An increase in the temperature to 300-320°C leads to a decrease in the yield of γ-butyrolactone to 28.1 mole %.

In order to ascertain the reasons for the low selectivity of the formation of 2,3-dihydrofuran when the process is realized under continuous conditions we investigated the catalytic transformation of 2,3-dihydrofuran under these conditions. We found that 2,3-dihydrofuran is transformed to tetrahydrofuran with a high degree of conversion (up to 80%). The latter constituted evidence that tetrahydrofuran is formed as a result of not only dehydration of 1,4-butanediol but also as a result of successive transformation reactions

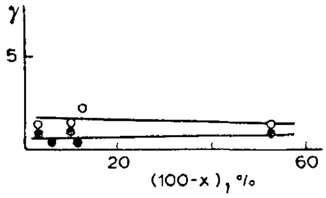

Fig. 1. Dependence of the relative selectivities on the unchanged 1,4-butanediol at 250°C, a 1,4-butanediol volume rate of 0.09-0.44 h^{-1}, and a nitrogen circulation of 0-67 h^{-1}: ○ $-\frac{GBL}{THF}$, ● $-\frac{THF}{GBL}$.

TABLE 2. Transformations of 1,4-Butanediol on a Mixture of Cobalt Catalysts Applied to Keiselguhr (tableted) under Continuous Conditions (with an OL-105/01 apparatus)

Temp., °C	Nitrogen circulation, h^{-1}	Vol. rate of butanediol, h^{-1}	Nitrogen pressure, atm	Yield, mole %			Conversion of raw material, %
				2,3-dihydrofuran	tetrahydrofuran	γ-butyrolactone	
250	200	0,44	25	—	8,98	41,6	93,58
250	67	0,24	5	3,85	24,4	37,05	89,69
250	Without circulation	0,44	5	—	27,09	36,1	47,29
270	Same	0,16	20	1,93	27,0	42,59	100
300—320	200	0,4	20	14,25	46,39	28,13	78,87

of 2,3-dihydrofuran on the cobalt catalyst. The hydrogen formed in the dehydrogenation of 1,4-butanediol to γ-hydroxybutyraldehyde and in the dehydrogenation of 2-hydroxytetrahydrofuran to γ-butyrolactone evidently participates in the hydrogenation of 2,3-dihydrofuran to tetrahydrofuran. The role of the successive transformations of 2,3-dihydrofuran is displayed to a great degree during their realization under continuous conditions on tableted catalysts.

The possibility of the formation of tetrahydrofuran (THF) from γ-butyrolactone (GBL) and vice versa was evaluated by the method of relative selectivities [3, 4]. The dependence of the relative selectivities (γ) on (100 − x)* shown in Fig. 1 provides evidence that the above-mentioned reactions involving the conversion of γ-butyrolactone to tetrahydrofuran and of tetrahydrofuran to γ-butyrolactone do not proceed at appreciable rates. Our results do not contradict the parallel-consecutive scheme proposed by Dimroth and co-workers [1, 2]. However, the conversion of 2,3-dihydrofuran to tetrahydrofuran takes place in addition to the transformations specified by the aforementioned scheme.

In order to avoid the subsequent conversion of 2,3-dihydrofuran and to increase the selectivity of its formation it is necessary to ensure the rapid removal of the 2,3-dihydrofuran from the reaction mixture. To achieve these ends the process is optimally carried out under periodic conditions at atmospheric pressure with removal of the resulting 2,3-dihydrofuran from the reaction mixture during the reaction by distillation.

EXPERIMENTAL

The catalytic transformation of 1,4-butanediol was investigated at 210-310°C and at a 1,4-butanediol volume rate of 0.1-0.44 h^{-1}. The experiments at atmospheric pressure under periodic conditions were carried out with the aid of the glass apparatus described in [1]. The catalytic transformation of 1,4-butanediol under pressure and under continuous conditions was carried out with an OL-105/01 dual reactor (Hungary). A mechanical mixture of two industrial cobalt-containing catalysts [a cobalt-magnesium catalyst applied to kieselguhr (I) and a cobalt catalyst for the synthesis of butyl alcohols (II); I:II = 2:3]. The tableted catalyst was prepared by compressing a moistened mixture of the powdered catalysts (unreduced) mentioned above and graphite [the catalyst:graphite:water ratio was 1:0.03:

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*Where x is the degree of conversion of 1,4-butanediol to products.

(0.07–0.1)]. The catalyst was activated prior to the experiments in a stream of hydrogen at 400°C for 4 h.

Analytical-grade 1,4-butanediol was used. The reaction products were condensed in a mixture of dry ice and acetone. The condensate was analyzed by gas—liquid chromatography (GLC) with a Varian Aerograph-2800 chromatograph with Cilicon DC-702 applied to Cellite-545 in 30% amounts as the stationary phase. The detector was a flame-ionization device, the vaporizer temperature was 220°C, the carrier-gas (helium) flow rate was 60 ml/min, and the column temperatures were 90 and 150°C. Isoamyl alcohol was used as the internal standard.

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ISOTOPE EXCHANGE OF HETEROCYCLIC COMPOUNDS WITH D_2O IN THE PRESENCE OF TRANSITION METALS

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During a study of deuterium-hydrogen exchange of two-ring condensed heterocycles in the presence of a Pt catalyst it was observed that the degree of deuteration decreases in the order benzofuran ≫ naphthalene > benzothiophene. It was found that the degree of deuteration of 2-acetylbenzofuran is 80%, whereas for 2-propylbenzofuran it is only 8%. The degree of deuteration of hydrogenated derivatives decreases in the order coumarin > chromene > dihydrocoumarin; the formation of polydeuterated derivatives is observed for coumarin, whereas products of replacement of one hydrogen atom by deuterium predominate for chromene and dihydrocoumarin.

In the present research we investigated H—D exchange with D_2O of a number of heterocyclic compounds in the presence of Pt, Cu, Fe, Co, and Ni blacks.

In contrast to benzene [1], which undergoes intensive exchange with D_2O, furan and thiophene undergo exchange considerably less vigorously under similar conditions (see Table 1), and they can be arranged in the order benzene > thiophene > furan with respect to their degree of deuteration.

The "introduction" of another benzene ring in the molecules named above changes the picture substantially. Benzofuran, benzothiophene, and naphthalene are arranged in the order benzofuran ≫ naphthalene > benzothiophene with respect to their degree of deuteration.

The difference in the behavior of one-ring and two-ring compounds can be explained within the framework of the concepts of π-complex adsorption [1]. During π-complex adsorption benzene is flatly disposed on the surface and participates actively in the adsorption—desorption process [1]. Furan and thiophene, due to the strong interaction of the n electrons of the heteroatoms with the metal, evidently are vertically oriented on the surface [2, 3], and this leads to a significant decrease in the degree of deuteration.

In the case of two-ring systems the presence of two aromatic rings will increase the strength of π-complex adsorption [1], and, as noted above, this should give rise to a de-

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