

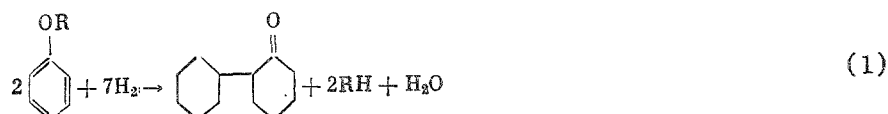
TRANSFORMATION OF PHENOL AND ITS ETHERS IN CONDITIONS
OF HYDROGENATION ON BIFUNCTIONAL ZEOLITE CATALYSTS

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The catalytic transformation of benzene, its halogenated derivatives, and toluene in the presence of H₂ and bifunctional zeolite catalysts which have a hydrogenating and alkylating effect was studied in [1-3]. Hydrodimerization of benzene and toluene takes place on these catalysts with the formation of the corresponding phenylcyclohexane derivatives. Cyclohexene, which further alkylates benzene at acid sites, is an intermediate product of the hydrodimerization of benzene [4-10].

In the hydrodimerization of phenol, anisole, and phenetole, we found a different manifestation of the bifunctionality of the catalytic systems used. The basic product of the reaction is 2-cyclohexylcyclohexanone



where R = H, Me, Et. 2-Cyclohexylcyclohexanone, used as a blowing agent for detergents and in the perfume industry [5], is currently prepared by multistage syntheses [6].

The reaction of hydrodimerization of phenol, anisole, and phenetole on bifunctional zeolite catalysts and the products and mechanism of the reaction were investigated in the present study.

EXPERIMENTAL

The catalysts were prepared from NaY zeolite containing 20 wt. % $\gamma\text{-Al}_2\text{O}_3$ binder by consecutive ion exchange in solutions of Ca and La salts according to the method in [1]; after treatment at 550°C in air, transition metal cations were also added by ion exchange. Ni and Pd were added to the zeolite from solutions of amines, and Rh was added in the form of Rh(III) chloropentamine at pH 8-9. The samples of the catalysts, with the anions completely washed off, were dried in air and again treated with heat in air at 550°C for 4 h with subsequent reduction with hydrogen at 320°C for 1 h. The reaction was conducted in anisothermal flow-type reactor in the setup described in [2]. The flow rate of H₂ was monitored with a precision of $\pm 10\%$ in the range of 0.5-30 ml/h using a flow meter [7]. Phenol was delivered in a solution of benzene, and anisole and phenetole were used with no diluent. The conditions of conducting the reaction were: 1.5-2.5 MPa, 150-170°C, volume flow rate of 0.6-1 h⁻¹ (with respect to the liquid). The catalyzate was analyzed by GLC on a LKhM-8MD chromatograph with a thermal conductivity detector in a linear programmed temperature elevation mode (90-250°C). The stationary phase was 5% silicone SE-30 on Chromaton N-AW. The individual products liberated by vacuum distillation were separated by liquid chromatography in a column packed with silica gel and identified by PMR, ¹³C NMR, and mass spectrometry. The samples of the catalysts were analyzed by chemical, atomic emission, and atomic absorption methods.

DISCUSSION OF RESULTS

Pd-, Ni-, and Rh-containing samples of zeolite catalysts were used in the reaction of hydrodimerization of phenol and its ethers (Table 1).

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TABLE 1. Zeolite Catalysts Used in the Reaction of Hydrodimerization of Phenol (anisole, phenetole)

Catalyst	Degree of cation exchange in % of total exchange capacity							Si/Al atomic ratio
	Na	Ca	La	Pd	Ni	Rh	H	
A	1,5	8,0	71,8	17,7	-	-	-	2,1
B	7,0	15,0	64,4	-	14,0	-	-	2,35
C	1,5	8,3	71,8	-	-	3,0	14,0	2,1

TABLE 2. Activity of Bifunctional Zeolite Catalysts in the Reaction of Hydrodimerization of Phenol (anisole, phenetole) (160°C, 2.0 MPa, 1 h⁻¹, H₂:starting substance = 2:1, molar)

Starting substance	Catalyst	Concentration in catalyate, wt. %						Conversion of starting substance, %	Yield of 2-cyclohexylcyclohexanone, %
		cyclohexane	phenylcyclohexane	2-cyclohexylphenol	2-cyclohexylanisole	2-cyclohexylphenetole	2-cyclohexylcyclohexanone		
Phenol: benzene = 2:1 (molar)	A	32,9	9,3	2,0	-	-	28,0	91,2	90,3
	B	1,8	12,5	8,8	-	-	25,9	84,1	82,4
	C	-	11,6	5,0	-	-	16,7	80,0	62,5
Anisole	A	3,2	1,2	-	6,0	-	25,6	36,7	69,8
	B	3,0	0,8	-	8,1	-	20,9	33,0	63,2
	C	0,9	0,5	-	2,8	-	3,5	9,4	36,9
Phenetole	A	4,1	0,9	-	-	5,0	23,6	34,2	69,4
	B	3,9	1,3	-	-	5,8	19,8	31,9	62,1
	C	1,3	0,7	-	-	2,2	4,1	11,7	35,1

Note. Catalysts: A: Pd-containing; B: Ni-containing; C: Rh-containing. Yield for unreacted phenol (anisole or phenetole).

2-Cyclohexylcyclohexanone and the products of hydrodimerization of the starting substances, particularly 2-cyclohexylphenol (in the case of phenol) and the corresponding methyl and ethyl ethers (in the case of anisole and phenetole), were separated as the basic products of the reaction. The concentration of the last products in the catalyate was significantly lower (Table 2).

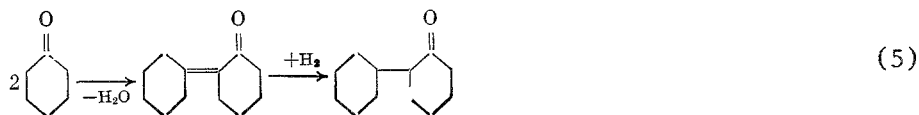
When the benzene used for dissolving the phenol was present in the starting mixture, phenylcyclohexane was formed. The analysis of the gaseous products of the reaction with anisole and phenetole revealed the formation of RH hydrocarbons (CH₄ and C₂H₆) according to Eq. (1). In addition, water (in the case of phenol) and methanol and ethanol in the case of anisole and phenetole were present in the products of the reaction. 2-Cyclohexylcyclohexanone, 2-cyclohexylphenol, and its methyl and ethyl ethers were separated from the products of the reaction by vacuum fractionation with subsequent purification and preparation of the pure individual substances by liquid chromatography on silica gel (eluent: hexane-acetone mixture). The constants of the separated substances were in agreement with the data in the literature [6, 7]. The mass spectra and ¹³C NMR spectra confirmed the structure of the substances obtained. According to [8], hydrogenolysis of ethers can take place on aluminosilicate catalysts with metal additives both with cleavage of the phenyl-O bond and the O-alkyl bond with the formation of benzene or phenol



These data form the basis for hypothesizing that when anisole or phenetole are used on zeolite catalysts containing group VIII metals, phenol is formed at high temperatures and is subsequently hydrogenated. As shown in [9], cyclohexanone is formed with a high selectivity in the hydrogenation of phenol on catalysts containing group VIII metals.

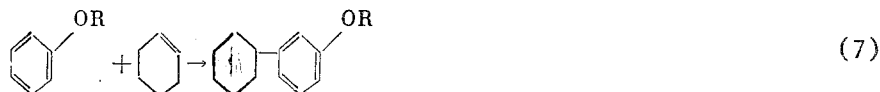


Cyclohexanone is then condensed on acid sites with the formation of water and 2-cyclohexylidenecyclohexanone, which is easily hydrogenated into 2-cyclohexylcyclohexanone



To confirm the proposed mechanism, experiments were conducted on hydrocondensation of cyclohexanone in the presence of a Pd-containing catalyst. It was found that the reaction takes place to 2-cyclohexylcyclohexanone with a quantitative yield of the latter. In the absence of H_2 , cyclohexanone is transformed into cyclohexylidenecyclohexanone on the same catalysts.

The formation of 2-cyclohexylphenol, 2-cyclohexylanisole, and 2-cyclohexylphenetole takes place as a result of alkylation of phenol and its ethers by the cyclohexene formed in the incomplete hydrogenation of benzene, which either reacts in a mixture with phenol or is obtained according to Eq. (2). This mechanism is similar to the mechanism of formation of phenylcyclohexane or hydrodimerization of benzene [4]



In comparing the activity of the catalysts in the reaction of hydrodimerization of phenol and its ethers, the same mechanisms were observed as in the case of benzene (toluene) [2]. The activity of the Pd-containing catalyst is slightly higher than the activity of the Ni-containing catalyst and is significantly higher than the activity of the Rh-containing zeolite catalyst. In particular, when anisole and phenetole are used as the starting products on sample A, the yield of 2-cyclohexylcyclohexanone attains 69.8%. Similar results were obtained on sample B, and the yield was significantly lower on sample C, apparently due to the low concentration of Rh (3% exchange in comparison to 14-17% for Ni- and Pd-zeolite) (see Table 1) and the fact that Rh is primarily located in the surface layer of the zeolite granules in the form of cluster formations. The impossibility of re-exchange of Rh with other cations after heat treatment of the Rh-containing zeolite in air at 500-600°C confirms this finding. These results are in agreement with the data in [11]. When phenol was used as the starting product, its conversion on sample B was 84.1% with an 82.4% yield of 2-cyclohexylcyclohexanone. Similar values of the conversion (91.2%) and yield (90.3%) were observed on sample A.

The formation of cyclohexane takes place as a result of hydrogenation of benzene added as a solvent for phenol or formed according to Eq. (2). In addition to the complete hydrogenation of benzene, the reaction of its hydrodimerization also takes place with the formation of phenylcyclohexane according to [2].

CONCLUSIONS

1. 2-Cyclohexylcyclohexanone is the basic product of the hydrodimerization of phenol, anisole, and phenetole in the presence of bifunctional zeolite catalysts containing palladium, nickel, rhodium, calcium, and lanthanum. The activity of the catalysts is a function of the type of cations added.

2. Hydrodimerization of phenol and its ethers takes place through the stage of hydrogenation of the starting substances to cyclohexanone on metallic sites with subsequent condensation to 2-cyclohexylidenecyclohexane on acid sites and hydrogenation of the latter to 2-cyclohexylcyclohexanone.

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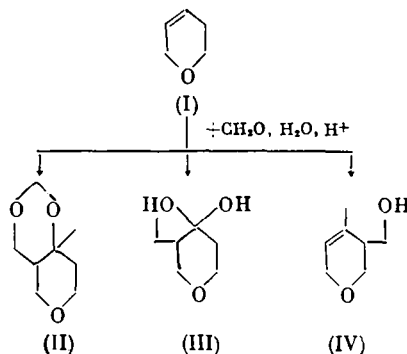
THE CHEMISTRY OF DI- AND TETRAHYDROPYRANS.

COMMUNICATION 3. ON THE ANOMALOUS BEHAVIOR OF
4-METHYL-5,6-DIHYDROPYRAN IN THE PRINS REACTIONS

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The condensation of olefins with formaldehyde under the conditions of acidic catalysis (the Prins reaction) results mainly in 1,3-dioxanes [1]. When dilute solutions of CH_2O (4-5%) are used [2], or acetic acid [3], the main products are a 1,3-diol or its diacetate. In the reaction of 4-methyl-5,6-dihydropyran (I) with a 30% aqueous solution of CH_2O , the yield of the expected dioxane in the form of a mixture of cis-trans-isomers of 10-methyl-1,3,7-trioxadecalin (II) was only 14%, while that of the diol - 3-hydroxymethyl-4-hydroxy-4-methyl-tetrahydropyran (III) - was 58% (cis- 5%, trans- 53%). Moreover, 3-hydroxymethyl-4-methyl-3,6-dihydropyran (IV) (5%) could also be isolated and identified



On the other hand, the condensation of CH_2O with other cyclic ethers (4-methylenetetrahydropyran and 4-phenyl-5,6-dihydropyran) leads to the corresponding dioxanes [4, 5]. The aim of the present work was to discover the reasons for the anomalous behavior of pyran (I) in the Prins reaction.

We found that in the reaction of 2-methyl-5,6-dihydropyran with formaldehyde, 6-methyl- and 9-methyl-1,3,7-trioxadecalins (V), (VI) are formed in an overall yield of 42% of theoretical

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