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Study of processes occurrıng between ethylnaphthalenes and 1-naphthol

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Abstract. The work is devoted to the study of an additional method for the synthesis of monoethylnaphthols by the reaction of transethylation of 1-naphthol with ethyl- and diethylnaphthalene, which are by-products of alkylation of 1-naphthol with ethanol and has a small area of application.In the catalytic process carried out in the presence of modified H-mordenite based on 1-naphthol and ethanol, along with the target products (1-ethoxynaphthalene, monoethyl-1-naphthols), up to 10.0% ethyl homologues of naphthalene are obtained. In this regard, the interaction of 1-naphthol with diethylnaphthalenes in the presence of Pd-HSVM and composite mordenite was studied, the effect of pressure on the process, which was identified as an important factor, was studied. In the presence of 1.0 wt % palladium pentasil (x=40), a positive effect of a pressure of 0.5 MPa on the results was noted, the selectivity for monoethyl-1-naphthols was 85.0%, and in the presence of H-mordenite containing zirconium, chromium and sulfur, this indicator was 94.3% under the same conditions. An increase in pressure adversely affects the course of the reaction and increases the rate of other transformations in the process, such as isomerization and disproportionation.

Keywords: *1-naphthol, 1,2-diethylnaphthalene, transethylation, zeolite, monoethylnaphthol, yield, selectivity, conversion*.

1. Introduction

Among the studied methods for the preparation of ethyl derivatives of naphthols, the interaction with mono- and diethylnaphthalenes containing reactive ethyl groups cannot be considered traditional [1]. It is this method of synthesis that was set by us as a goal and studied. It should be considered that ethylnaphthalene obtained as a by-product of the alkylation of naphthols with ethanol can increase the efficiency of the process by converting into target products in the presence of naphthols.

The study of the composition of the catalyzates obtained by the interaction of 1-naphthol with ethanol in the presence of the Zr,H-mordenite catalyst [1-3] and the analysis of the reaction parameters prove that the process is complex and occurs with a large number of transformations (Table 1). In the alkylation reaction of 1-naphthol with ethanol, the O-alkylation product is 1-ethoxynaphthalene, and the C-monoalkylation products are 2-ethyl- and 4-ethyl-1-naphthols, as well as 2,4- and 2,3-diethylnaphthols. Alkylates include ethyl and methyl homologues of naphthalene, formed as a result of complex transformations such as dehydroxylation – alkylation, when the alkylation reaction of 1-naphthol with ethanol occurs under harsh conditions. The fact that the main products of the reaction are ethylnaphthols at low temperatures (300-340°C) and alkyl (C_1-C_2) homologues of naphthalene at high temperatures (360-420°C), as well as the presence of 1-ethoxynaphthalene [4] and oxo compounds of various structures in the catalyzates confirms what we have said. For this reason, identifying the main and secondary transformations occurring in the process, as well as detecting sequential and parallel reactions, seem to be one of the important tasks.

In general, the use of methyl- and polymethylbenzenes as transalkylants and phenol as substrates has been previously studied [5-8], and the results obtained have attracted little practical attention.In experiments carried out in this direction, toluene, xylenes, trimethylbenzenes, even hexamethylbenzene were used as transalkylators, and it was found that the conversion occurs with the production of isomers of cresol [9] and methylbenzenes with one less number of methyl groups in the phenol-polymethylbenzene system.

These studies mainly emphasized the use of zeolite catalysts and the activity of benzene homologues with a large number of methyl groups in transalkylation. These reactions accelerated with increasing temperature, and it was found to be partially limited in a vacuum. The raw material base of polymethylbenzenes can be fractions of primary oil refining, catalytic cracking and platforming distillates. It is also important to note that, since the applications of toluene and other methyl homologues are small, it seems more attractive to obtain a mixture of benzene and valuable cresol by their transmethylation.

However, there are features that characterize the study of such transformations in the naphthol-ethylnaphthalenes system. First of all, when analyzing the composition of alkylates obtained in the presence of mordenites [10-12], it becomes clear that a certain amount of ethyl- and diethylnaphthalenes is formed in the process, and their involvement in the realkylation process can be considered efficient from an economic and technological point of view.

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Table 1. Comparative results of reactions of interaction of 1-ethoxynaphthalene and 1-naphthol with ethanol in the presence of Zr, H-mordenite. Reaction conditions: υ=1.0 st^{-1}, ν=1:5 mol/mol

Indicator name	Name of the methylating reagent					
	1-ethoxynaphthalene	1-naphthol	1-ethoxynaphthalene	1-naphthol	1-ethoxynaphthalene	1-naphthol
Temperature, °C	300	300	340	340	380	380
Obtained, wt%, incl.						
1-ethoxynaphthalene	69.0	7.3	47.0	1.0	25.5	-
1-naphthol	4.0	70.6	2.8	53.7	2.0	29.7
2-ethyl-1-naphthol	5.9	18.5	7.0	37.8	6.8	50.8
4-ethyl-1-naphthol	1.0	0.7	1.5	2.3	2.0	4.5
Dimethylnaphthols	-	-	-	-	0.5	2.4
1-oxo-2,2-diethyl-1,2-dihydronaphthalene	3.0	1.9	2.8	1.0	1.6	-
Naphthalene	1.5	-	1.6	-	4.0	2.4
1,2-diethylnaphthalene	9.5	1.0	20.0	2.3	25.0	7.1
Other alkyl (C_1-C_2) naphthalenes	2.7	-	14.1	1.2	29.2	1.9
Unidentified substances	3.4	-	3.2	0.7	3.4	1.2
Total	100	100	100	100	100	100
Conversion of 1-naphthol, %	-	24.7	-	40.3	-	67.5
Conversion of 1-ethoxynaphthalene, %	27.4	-	46.7	-	72.2	-

As a result of the conducted studies [13-14], it was found that the yield of mono- and diethylnaphthalene calculated according to converted 1-naphthol was 9.5% in Ni,H-mordenite, 6.5% in Zr,H-mordenite, and 6.5% in Zr, H-mordenite 10.0%. % in Pd,H mordenite, and in CM it is much less - 1.5%.

2. Materials and methods

The alkylationreaction of 1-naphthol with ethanol was studied in an extraction type reactor with a fixed layered catalyst; the analysis of the obtained products was carried out by chromatographic and spectral methods. Chromatec Crystal-5000 device was used as a gas chromatograph.The analysis of naphthol and its alkyl homologues and ethylnaphthalenes was carried out in a combined calon (3.6m x 0.4mm), the first 1/3 of the calon was filled with Apiezon M on Celite 545, and the remaining part was filled with Carbowax 20M on Chromosorb W. The analysis was carried out according to a predetermined program in the temperature range of 150-250°C in the mode of increasing the temperature by 8°C per minute. Helium was taken as a carrier gas and its consumption was 60 ml/min.PMR spectra were recorded on a Bruker Fourier (300 MHs) spectrometer. CCl_4 was used as the solvent, and hexamethylenedisiloxane as the internal standard.

The interaction of 1-naphthol with 1,2-diethylnaphthalene was studied in the presence of two types of catalysts: palladium-containing pentasil and composite mordenite. The content of palladium in pentasil was 1.0 wt%, and the composition of mordenite (x=24) includes zirconium, chromium and sulfur. As a result of preliminary experiments, the conditions for this reaction were taken as follows: T – 400°C, υ = 1.5 hr^{-1}, molar ratio of naphthol to 1,2-diethylnaphthalene (ν) = 1:2.

Benzene was used as a diluent, and the ratio of its components as raw materials to the mole ratio was changed between 1÷2. Taking into account that the transformation occurring in the naphthol-1,2-diethylnaphthalene system under the indicated conditions is unimportant at atmospheric pressure, the effect of pressure on the catalytic process was studied and its value varied within 0.1-1.0 MPa.

3. Results and discussion

The results of the interaction of 1-naphthol with 1,2-diethylnaphthalene are given in table.

Table 2. Results of the interaction of 1-naphthol with 1,2-diethylnaphthalene. Reaction conditions: T – 400°C, υ = 1.5 hr^{-1}, ν = 1:2 mole/mole

Indicator name	Composition of the catalyst					
	Pd-HSVM			CM		
Pressure, MPa	0.1	0.5	1.0	0.1	0.5	1.0
Yield of monoethylnaphthols calculated according to converted 1-naphthol, %	80.5	85.0	77.0	90.0	94.3	83.0
Yield of monoethyl-1-naphthol calculated according to converted 1,2-diethylnaphthalene, %	75.5	74.0	70.0	78.0	81.0	71.0
1-Naphthol conversion,%	15.5	19.0	22.5	11.5	13.0	16.5
1.2-Diethylnaphthalene conversion, %	18.0	21.5	27.0	14.0	15.5	20.0

In the catalyzates obtained by the interaction of 1-naphthol with 1,2-diethylnaphthalene, a mixture of 2-ethyl-1-naphthol and ethylnaphthalene is found as the main product. The molar ratio of 1- and 2-ethylnaphthalenes in this mixture is 0.6:0.4, respectively.The catalyzates also contain 4-ethyl-1-naphthol, naphthalene, 2,4-diethyl-1-naphthol, and complex condensation products.In the catalytic process, the main transformation occurs according to the following scheme.

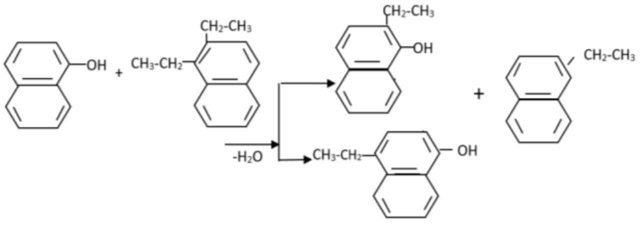

Figure 1. The main transformation schemes

As can be seen from the table, the transethylation of 1-naphthol with diethylnaphthalene occurs more selectively in the presence of CM catalyst compared to Pd-HSVM zeolite, and the yield of the mixture of 2-ethyl-1-naphthol and 4-ethyl-1-naphthol calculated according to the converted 1-naphthol is 83.0-94.3%. The overall selectivity for monoethyl derivatives of 1-naphthol in the Pd-HSVM catalyst is 77.0-85.0%.In both cases, increasing the pressure in the system to 0.5 MPa increases the selectivity, this increase is 4.5% in the presence of pentasil and 4.3% in the presence of CM.

An increase in pressure to 1.0 MPa leads to a decrease in selectivity for naphthol monoethyl homologues by 8.0-77.0% in the presence of Pd-HSVM and by 11.3-83.0% in the presence of CM.Similar changes are found when analyzing the total yield of monoethyl-1-naphthols calculated according to the converted 1,2-diethylbenzene. This decrease is from 75.5 to 70.0% in the presence of Pd-HSVM and from 78.0 to 71.0% in the presence of CM. Increasing the pressure in the process from 0.1 to 1.0MPa also increases the conversion of the initial components. On the Pd-HSVM catalyst, this increase was 7.0% in 1-naphthol from 15.5 to 21.5% and in 1,2-diethylnaphthalene from 18.0 to 27.0%.

Although increasing the pressure to 1.0 MPa increases the conversion of both starting components, it causes a significant decrease in the selectivity for the target product and a partial increase in the number of side transformations, such as isomerization and disproportionation. The reaction products contain 3-ethyl-1-naphthol, 1-naphthol methyl derivatives, and alkylnaphthalenes of a more complex composition, although in small amounts.

The main reaction products at low temperatures (300°C) are 1-ethoxynaphthalene and 2-ethyl-1-naphthol, and in the temperature range of 340-380°C, 1-naphthol-orthoethyl derivative. With increasing temperature (>380°C), the formation of alkyl derivatives of naphthalene in the catalyzates accelerates. The yield of 2-ethyl-1-naphthol in terms of converted naphthol at a temperature of 340°C and a value of 1.0 st^{-1} volume of this raw material is 87.6%, and at a temperature of 400°C 71.0%. This increase in temperature increases the selectivity of the reaction by 12.0 for alkylnaphthalenes to 13.5%. In general, as a practical result of the research, it was found that ethyl and especially diethylnaphthalene, formed at high temperatures (>340°C) during the alkylation reaction of 1-naphthol with ethanol, have the transethylation property. In the presence of Pd-HSVM and CM catalysts under specified conditions (T–400°C, P–0.5 MPa, volumetric flow rate of the given raw material –1.5 hr^{-1}, molar ratio of 1-naphthol to 1,2-diethylnaphthalene 1÷2) depending on the catalyst, it is possible to synthesize monoethyl-1-naphthols from 1-naphthol and 1,2-diethylnaphthalene with a selectivity of 85.0–94.3% and a yield of 12.3–16.1% upon repeated operation.

In the presence of mordenites modified with palladium, zirconium and nickel, similar regularities are observed regarding the yield of monoethylnaphthols formed on the basis of 1-naphthol and ethanol. Thus, when the concentration of zirconium in mordenite is increased to 0.5 wt%, the yield of monoethylnaphthols calculated based on the initial 1-naphthol decreases from 33.5% to 31.5% compared to H-mordenite. When palladium- and nickel-modified mordenites are taken, the yield increases to 34.0 and 37.4%, respectively.Increasing the concentration of the modifier to 1.0 wt% increases the yield to 34.9% in the case of palladium zeolite. This indicator is 39.5% in Ni, H-mordenite, and 37.5% in zirconium zeolite. The subsequent increase in the concentration of palladium in the catalyst (1.5-2.0 wt%) decreases the yield of monoethylnaphthols first to 34.0% and then to 32.5%.In the other two catalysts, the subsequent increase in the concentration of the modifier affects the yield of the target product in its own way. Thus, the yield of monoethylnaphthols in 1.5 wt% Ni, H-mordenite practically does not change, but increasing the concentration of the modifier in the catalyst to 2.0 wt% causes a partial (2.0%) decrease in the yield. As a result of increasing the density of the modifier in zirconium H-mordenite to 1.5 wt%, the yield of monoethylnaphthols increases significantly and is 41.1%.

Based on the conducted research, it was found that compared to H-mordenite, zeolites with a concentration of 1.5 wt% from samples modified with nickel and zirconium, and 1.0 wt% Pd in palladium-modified mordenites, H-mordenite was chosen as a more active and selective catalytic system. In the alkylation process in the presence of modified mordenite catalysts, the conversion of 1-naphthol decreases in the following order.

Ni, H-mordenite > Zr, H-mordenite > Pd, H-mordenite. As a final result, 1.5 wt% Zr, H-mordenite was selected as a more active and selective catalyst in the alkylation reaction of 1-naphthol with ethanol, and it was determined that it can be of practical importance in obtaining of monoethyl-1-naphthols, especially 2-ethyl-1-naphthol.

Ethyl ether of naphthol obtained by the Williamson method from the interaction of the sodium salt of naphthol with diethyl sulfate, ethyl bromide or ethanol is widely used in perfumes and cosmetics. Chinese scientists report the positive effect and future of the compound formed by ethylnaphthols on the Chitosan electrode modified with nanosilver acetylene in the development of new types of biosensors.

For the first time, the catalytic properties of mordenite and its modified samples, including H-mordenites containing nickel, palladium, and zirconium, were studied in the alkylation reaction of 1-naphthols with ethanol. As a result of the analysis of the indicators of the investigated catalysts, a more active and selective catalytic system was selected in the synthesis of monoethylnaphthols. The influence of the density of modifiers in mordenite on the process indicators was studied and the high value of the conversion of suitable monoethylnaphthols in the alkylation reaction of naphthol with ethanol and calculated based on the initial naphthol was obtained in the presence of 1.5 wt% Zr, H-mordenite.

Taking into account the further development of biologically active compounds and chiral ligands and the synthetic acquisition of new classes of compounds, scientists have carried out an effective synthesis of naphthol and its derivatives. As a future perspective, the use of naphthol derivatives from this class in the treatment of a number of diseases (oncological, convulsive), their application as antibacterials, and their use as starting components in the synthesis of some green catalysts is emphasized.

4. Conclusions

C_1-C_2 alkyl derivatives of naphthols are used in the production of additives, dyes, K vitamins used in veterinary medicine. The methods of obtaining these products based on the oxidation, sulfonation, oxidative decarboxylation processes of naphthalene and alkylnaphthalenes, as well as the dehydrogenation reaction of tetralones, are not widespread due to a number of defects (multi-stage, presence of external production, increased capital costs). One of the promising methods for obtaining alkylnaphthols is based on our method.

Thus, as a result of the conducted research, it was found that zirconium H-mordenite has stable operational properties in the alkylation reaction of 1-naphthol with ethanol for up to 300 hours, and it is necessary to carry out the process in a nitrogen environment. Under the specified conditions, the complete recovery of its activity through the oxidative regeneration of this zeolite and the high value of yields in the alkylation process were achieved in the presence of 1.5 wt% Zr, H-mordenite.

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Этилнафталиндер мен 1-нафтол арасындағы процестерді зерттеу

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Аңдатпа. Жұмыс 1-нафтолды этанолмен алкилдеудің жанама өнімдері болып табылатын және қолдану аясы аз 1 - нафтолды этил және диэтилнафталинмен трансэтилдену реакциясы арқылы моноэтилнафтолды синтездеудің қосымша әдісін зерттеуге арналған. 1-нафтол және этанол негізіндегі модификацияланған H-морденитттің қатысуымен жүргізілетін каталитикалық процесте мақсатты өнімдермен бірге (1-этоксинафталин, моноэтил-1-нафтолдар) 10.0% - ға дейін нафталиннің этил гомологтары алынады.Осыған байланысты PD-HSVM және композициялық морденитттің қатысуымен 1-нафтолдың диэтилнафталиндермен өзара әрекеттесуі зерттелді, маңызды фактор ретінде оқшауланған процеске қысымның әсері зерттелді. 1.0 массаның қатысуымен палладий пентасилінің % (x=40) алынған нәтижелерге 0.5 МПа қысымның оң әсері байқалды, моноэтил-1-нафтолдар бойынша селективтілік 85.0% құрады, ал құрамында цирконий, хром және күкірт бар H-морденитттің қатысуымен бұл көрсеткіш дәл осындай жағдайларда 94.3% құрады. Қысымның жоғарылауы реакция барысына теріс әсер етеді және изомеризация және диспропорция сияқты процестегі басқа түрленулердің жылдамдығын арттырады.

***Негізгі сөздер**: 1-нафтол, 1,2-диэтилнафталин, трансэтилдену, цеолит, моноэтилнафтол, шығу, селективтілік, конверсия.*

Исследование процессов, происходящих между этилнафталинами и 1-нафтолом

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Аннотация. Работа посвящена изучению дополнительного метода синтеза моноэтилнафтолов путем реакции трансэтилирования 1-нафтола этил- и диэтилнафталином, которые являются побочными продуктами алкилирования 1-нафтола этанолом и имеет небольшую область применения. В каталитическом процессе, проводимом в присутствии модифицированного H-морденита на основе 1-нафтола и этанола наряду с целевыми продуктами (1-

этоксинафталином, моноэтил-1-нафтолами) получают до 10.0% этиловые гомологи нафталина. В связи с этим изучено взаимодействие 1-нафтола с диэтилнафталинами в присутствии Pd-HSVM и композиционного морденита, изучено влияние давления на процесс, которое было выделено как важный фактор. В присутствии 1.0 масс.% пентасила палладия (x=40) отмечено положительное влияние давления 0.5 МПа на полученные результаты, селективность по моноэтил-1-нафтолам составила 85.0 %, а в присутствии H-морденита, содержащего циркония, хром и серу, этот показатель составил 94.3% при тех же условиях. Повышение давления отрицательно влияет на ход реакции и увеличивает скорость других превращений в процессе, таких как изомеризация и диспропорционирование.

Ключевые слова: *1-нафтол, 1,2-диэтилнафталин, трансэтилирование, цеолит, моноэтилнафтол, выход, селективность, конверсия.*

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