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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**OBTAINING OF ETHYLNAPHTHOLS BY REACTION OF
EFFECTIVE CATALYTIC ALKYLATION OF NAPHTOLS
WITH ETANOL**

Speciality: 2306.01-Organic Chemistry
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GENERAL DESCRIPTION OF WORK

The relevance of the theme and the degree of development.

Among the many derivatives of naphthols, a special place is occupied by its low molecular weight homologues. Of these compounds, methyl and ethylnaphthols are of particular importance. Because they produce vitamins, pesticides, dyes, fragrances, medicines, additives, preparations used in photography and computer technology.

The raw material base of naphthols is mainly naphthalene, obtained from oil and coal. In general, about half of the naphthalene produced in the world is used for the production of naphthol and its derivatives. Along with valuable olefins (ethylene, propylene, etc.) obtained during the chemical processing of oil, especially in the process of pyrolysis of the gasoline fraction, light and heavy pyrolysis products are formed in our country, containing a sufficient amount of naphthalene and its alkyl derivatives, the use of which is relatively limited.

The processes of oxidation, sulfonation, oxidative decarboxylation, which have been studied and used to a limited extent for the production of naphthalene based on naphthalene, are characterized by complexity, multi-stage technology and complexity of control, and therefore require the development of new effective methods. One of these methods, which attracts a lot of attention and is considered relevant, is the production of alkyl naphthols by the alkylation reaction of naphthols. Although this method is used to obtain alkyl homologues of arenes, phenols, anilines and other aromatic compounds, it has been little studied in the synthesis of the corresponding naphthol derivatives, especially ethyl homologues.

The main reason for this is the low activity, selectivity and non-stationary operation of the catalysts used in these processes. In order to eliminate them, the development of methods for the synthesis of various ethyl homologues of naphthols with the acquisition of effective catalytic systems for these processes and their effective use in the alkylation process has recently attracted increasing interest.

Object and subject of research. The catalytic alkylation of 1- and 2-naphthols with ethanol was taken as the object of study. The subject of research was the development of an effective method for obtaining ethyl homologues of naphthols in the presence of catalytic systems, which were selected among oxide-containing catalysts and modified H-mordenites and substantiated.

Aim and objectives of the research. The aim and objective of the study is to select an effective catalytic system as a result of a comparative analysis of the catalytic and operational properties of various oxide and zeolite systems in the reaction of alkylation of 1- and 2-naphthols with ethanol, to study the physicochemical foundations of the process and the development of a method for obtaining ethyl naphthols..

In this regard, the following questions were posed and resolved in the dissertation:

- Study of the activity of ferritic ($MFe_2O_4 \cdot \gamma-Al_2O_3$; M-Mg, Zn, Co, Cu) catalysts in the synthesis of ethylnaphthols by the reaction of alkylation of 1- and 2-naphthols with ethanol;

- Study of the alkylation reaction of 1- and 2-naphthols in the presence of a vanadium-chromium-aluminum oxide catalyst and analysis of their activity and selectivity in the synthesis of ethylnaphthols compared to ferrites;

- Study of the alkylation reaction of 1- and 2-naphthols with ethanol in the presence of H-mordenite and its modified samples;

- Study of the influence of the concentration of modifiers (nickel, palladium, zirconium) on the yield and selectivity of the synthesis of monoethyl-1-naphthol based on 1-naphthol and ethanol;

- Study of the activity and selectivity of nickel-, palladium- and zirconium-containing mordenites for target ethylnaphthols in the reaction of alkylation of 2-naphthol with ethanol;

- A detailed investigation of the alkylation of 1- and 2-naphthols with ethanol in the presence of a chromium, zirconium and sulfur-containing mordenite catalyst; study of the main intermediate and side transformations occurring in the process, and determination of their chemical nature;

- Carrying out kinetic studies of the reaction of alkylation of 1-naphthol with ethanol in a differential reactor, calculation of kinetic constants and development of a kinetic model;

- Study of the impact of different parameters on the alkylation reaction of naphthols with ethanol in the presence of selected chromo-zirconium, sulfur-containing H-mordenites, obtaining monoethyl-1-naphthols based on 1-naphthol and ethanol, as well as monoethyl-2-naphthols by reacting 2-naphthol with ethanol.

Research methods. The study was conducted using modern equipment, instruments and software. The experiments were carried out in an extraction type reactor, in a differential reaction apparatus, gas-liquid chromatography, NMR spectroscopy were used as a method of physicochemical analysis, MATLAB programs were used in kinetic calculations.

Main provisions for the defense:

- the catalytic properties of ferrite ($MFe_2O_4 \cdot \gamma-Al_2O_3$; M-Mg, Zn, Co, Cu) and vanadium chromium-aluminum oxide catalysts in the alkylation of 1- and 2-naphthols with ethanol were studied and compared;

- the activity and selectivity of H-mordenites modified with nickel, palladium and zirconium in the alkylation reaction of naphthols 1 and 2 with ethanol were determined, the nature of the main and side transformations was studied;

- effective alkylation of 1- and 2-naphthols with ethanol in the presence of zirconium-containing H-mordenite and chromium-zirconium-sulfur-containing composite mordenite has been carried out;

- kinetic studies of the alkylation reaction of 1-naphthol with ethanol were carried out, step-by-step scheme and routes were determined, kinetic constants were calculated and a low-error kinetic model was developed;

- the method of obtaining monoethylnaphtholes by alkylation of 1- and 2-naphthols with ethanol in the presence of chromium, zirconium and sulfur-containing H-mordenite was developed.

Scientific novelty of the research. The catalytic properties of ferrite, vanadium-chromoaluminum oxide catalysts, mordenite and

its modified samples, as well as nickel-, palladium-, zirconium-containing H-mordenites in the reaction of alkylation of 1- and 2-naphthols with ethanol were studied for the first time. As a result of a comparative analysis of the studied catalysts, among the oxide catalysts, the vanadium-chromium-aluminum system was chosen as the most active and selective catalytic system in the synthesis of monoethylnaphthols. The influence of the concentration of modifiers in mordenite on the process parameters was studied and a high yield value was obtained, calculated from the converted and initially taken naphthol, of the corresponding monoethylnaphthols in the reaction of alkylation of both naphthols with ethanol in the presence of 1.5 wt% Zr, H-mordenite. The main, intermediate and side transformations of the reaction of ethanol-1-naphthol alkylation in the presence of zirconium-containing mordenite are determined, the catalytic and operational properties of which are enhanced by the $\text{Cr}_2(\text{SO}_4)_3$ promoter, kinetic studies of the process are carried out, the main routes are refined, limiting stages are shown, kinetic constants are calculated. A kinetic model of the process occurring on the surface of a complex mordenite catalyst by a series-parallel mechanism has been obtained.

Theoretical and practical significance of the research. The catalytic properties of vanadium-chromium-aluminum oxides, ferrites and H-mordenites in the interaction of 1- and 2-naphthols with ethanol have been studied and analyzed, their activities and selectivity series have been determined. A method was developed for the synthesis of monoethyl-1-naphthols with a yield of 32.0% and a selectivity of 94.5% in the process of alkylation of 1-naphthol with ethanol, a method for obtaining a mixture of monoethyl-2-naphthols based on 2-naphthol and ethanol with a yield of 33.8% and selectivity of 94.0% in the presence of H-mordenite containing chromium, zirconium, sulfur. The use of these methods in industry can satisfy the demand for monoethylnaphthols, especially 2-ethyl-1-naphthol and 1-ethyl-2-naphthol, as well as 1- and 2-ethoxyphantalines. The resulting low-error kinetic model of the 1-naphthol alkylation process with ethanol can be used as a basis for further modeling and optimization.

Approbation and implementation of the research. Published 19 scientific papers on the topic of the dissertation, 7 articles in peer-reviewed international journals, including 2 without co-authors and 12 conference proceedings. Published works fully reflect the content of the dissertation.

The main results of the dissertation were presented at the following conferences: XXI Republican Scientific Conference of Doctoral Students and Young Researchers (Baku: 2017), International Scientific Conference "Functional Monomers and Polymeric Materials with Special Properties: Problems, Prospects and Practical Views" dedicated to the 55th anniversary of Sumgayit State University (Sumgait: 2017), International Scientific and Technical Conference "Petrochemical Synthesis and Catalysis in Complex Condensed Systems" dedicated to the 100th anniversary of Academician B.G. Zeynalov (Baku: 2017), International scientific-practical conference "Innovative prospects for the development of oil refining and petrochemistry", dedicated to the 110th anniversary of Academician V.S. Aliyev (Baku: 2018), XXII Republican Scientific Conference of Doctoral Students and Young Researchers dedicated to the 100th anniversary of the Azerbaijan Democratic Republic (Baku: 2018), Advances in synthesis and complexing The Fifth International Scientific Conference (Moscow: 2019), International scientific conference on "Actual problems of modern chemistry" dedicated to the 90th anniversary of the Institute of Petrochemical Processes named after academician Y.H. Mammadaliyev of ANAS (Baku: 2019), International scientific conference on "Prospects for innovative development of chemical technology and engineering" dedicated to the 70th anniversary of Sumgait (Sumgait: 2019).

Name of the organization where the dissertation work is carried out. The work was carried out at the Department of Petrochemistry and Chemical Engineering of Sumgayit State University.

Personal participation of the author. The applicant is a responsible executor at each stage of solving the issues raised in the dissertation, practical implementation of the study, analysis of the results, writing articles and theses, dissertation.

The total volume of the dissertation with the volume of structural parts of the dissertation. The dissertation has a volume of 147 pages and consists of an introductory part, 5 chapters, results and a bibliography of 138 titles.

The total volume of the dissertation is 172672 characters, not counting 17 figures, 30 tables and a list of references.

The main content of the dissertation. The introductory part provides brief information about the relevance of the topic, the object and subject of research, the goals and objectives of the work, scientific novelty, theoretical and practical significance, approbation, structure, volume, and substantiates.

The first chapter provides a critical analysis of scientific papers on the methods of obtaining naphthols, the study of alkylation reactions in the synthesis of their alkyl homologues. Scientific information about the procedure for conducting experiments, the used raw materials and methods for obtaining catalysts is presented **in the second chapter.**

The third chapter presents the results of studying the catalytic properties of ferrite and other oxide systems in the reaction of alkylation of naphthols with ethanol. **In the fourth chapter,** the results of the interaction of 1- and 2-naphthols with ethanol in the presence of H-mordenite and its modified samples are published. **The fifth chapter** presents the results of a detailed study of the reaction of alkylation of naphthols with ethanol in the presence of a complex mordenite catalyst containing chromium-zirconium-sulfur, which exhibits higher catalytic properties, and the scientific results obtained on the development of an effective method for producing monoethylnaphthols.

MAIN CONTENT OF THE WORK

Chemically pure 1-naphthol, 2-naphthol and ethanol were used as raw materials in the studies. The experiments were carried out in a reactor with a fixed catalyst layer, and kinetic studies in a setup with a differential reactor.

1. Methods for conducting experiments and synthesizing catalysts. Double and triple oxide systems and mordenite-type zeolites were used as catalysts. Catalysts containing $MFe_2O_4 \cdot \gamma-Al_2O_3$ (M– Zn, Mg, Cu, Co) were obtained by coprecipitation of nitrate and oxalate salts of the corresponding metals on $\gamma-Al_2O_3$ followed by drying and heating. The ratio of the atomic mass of the divalent metal to iron is 1:2.33, the concentration of the active mass (MFe_2O_4) in the catalyst is maintained at the level of 25.0 wt% according to the results of preliminary experiments.

Known methods were used in the synthesis of mordenites.

Initially, the optimal modulus (SiO_2/Al_2O_3) was determined in synthetic mordenite; nickel was found in the form of a cation impregnated with a nitrate solution on H-mordenite, zirconium in the form of a cation impregnated with a sulfate salt solution, and 20-25 wt % alumina as a hardener in catalysts.

Palladium was obtained by ion exchange using an aqueous solution of its complex salt $[Pd(NH_3)_4]Cl_2$. In the $HM+Al_2O_3$ system, its content was 0.1–2.0% of the dry mass of mordenite. A solution of chromium (III) sulfate was used in the synthesis of composite zeolites and, in parallel, modification was carried out.

2. Interaction of naphthols with ethanol in the presence of complex oxide catalysts. Such ferrites as oxide systems ($MFe_2O_4 \cdot \gamma-Al_2O_3$; M–Zn, Mg, Cu, Co), $Cr_2O_3-Al_2O_3$, $V_2O_5-Al_2O_3$ and $V_2O_5-Cr_2O_3-Al_2O_3$ have been studied, the selectivity of the reaction for the obtained monoethylnaphthols, the conversion of naphthol and the yield of the target product were taken as comparative criteria. The main products obtained by alkylation of 1-naphthol with ethanol are 1-ethoxynaphthalene and monoethylnaphthols, alkylated at the core, and the main products of the interaction of 2-naphthol with ethanol are 2-ethoxynaphthalene and monoalkylation products in the core of 2-naphthol.

In the presence of ferrite catalysts, the calculated total yield of mixtures of 1-ethoxynaphthalene, 2-ethyl, and 4-ethylnaphthol obtained by ethylation of 1-naphthol is reduced by the following order of catalysts:

$\text{CoFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3 \geq \text{ZnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3 > \text{CuFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3 \gg \text{MgFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$

Thus, the total yield in cobalt ferrite is 39.6%, while in magnesium ferrite this indicator is only 21.3%.

As for the ratio of the obtained 1-ethoxynaphthalenes and ethylnaphthalenes to each other, in magnesium and misferrites, oxygen alkylation in naphthols occurs to a sufficient extent, and the selectivity for ethoxynaphthalenes is 34.0 and 28.5%, respectively. In the case of zinc and cobalt ferrites, the advantage is the alkylation occurring in the 2-position at the core. Wherein the selectivity for ethylnaphthols is 55.5 and 64.5%, respectively. If we note the activity of the catalyst in the reaction of alkylation of 2-naphthol with ethanol in terms of the total yield of 2-ethoxyphthalene and monoethylnaphthols in terms of the initial naphthol, then a higher yield (35.5%) is observed in the presence of a copper-ferrite catalyst, and a lower yield (18.6 %) is magnesium ferrite. According to this indicator, the catalytic properties of copper, zinc, and cobalt ferrites are close. For ethyl homologues obtained by alkylation of 2-naphthol with ethanol, the overall selectivity of the reaction ranges from 76.0-84.5%. However, the molar ratio of ethoxynaphthalene to ethylnaphthol varies depending on the catalyst under the conditions studied (320°C, $\nu - 1.0 \text{ hr}^{-1}$). For example, in the presence of magnesium ferrite is 0.61:1, in the presence of cobalt ferrite 0.16:1, in the presence of copper ferrite 0.21:1, and in the presence of zinc ferrite 0.26:1.

Ferrite systems with high catalytic properties in the alkylation reaction of phenols and aromatic amines with alcohol show average results in the alkylation reaction of naphthols with alcohols, including ethanol. Therefore, further study of the possibilities of catalysis in this reaction is necessary. In this regard, other catalytic systems were used in the interaction of naphthols with ethanol.

For this purpose, the alkylation reaction of 1- and 2-naphthols with ethanol in the presence of other oxide catalysts was studied in detail. The obtaining oxide systems (in wt%) $\text{Cr}_2\text{O}_3 - 7.0, \text{Al}_2\text{O}_3 - 93.0; \text{V}_2\text{O}_5 - 3.0, \text{Al}_2\text{O}_3 - 97.0$ and $\text{V}_2\text{O}_5 - 3.0, \text{Cr}_2\text{O}_3 - 7.0, \text{Al}_2\text{O}_3 - 90.0$ were taken as catalytic systems.

The main difference from the analysis of the obtained results is the discrepancy between the specific surface of the catalysts and the conversion of 1-naphthol. In the presence of an aluminum-chromium oxide system with a larger specific surface area, the conversion of 1-naphthol is moderate and shows a result of 8.5–10.5% less than in a chromium-vanadium oxide system with a specific surface area of $\sim 25 \text{ m}^2/\text{g}$ less. This can be explained by the composition and structure of the catalysts, the shape and size of the pores, and the variety of energy properties.

When comparing the above catalysts, it is observed that, regardless of temperature, in the presence of both, the same degree of oxygen ethylation of naphthol occurs, and the selectivity of the reaction for ethoxyphthalins is practically the same. In the presence of the third catalyst, the vanadium-alumina system, the proportion of oxygen alkylation in naphthol is 2.7 times higher at 320°C , and at 360°C 7.9-9.1 times higher than that of other catalysts. However, the vanadium-alumina oxide catalyst differs from other oxides due to the low yield of ethyl naphthols. Thus, the total selectivity for mono- and diethylnaphthols formed by the electrophilic substitution reaction in the carbons in the 1-naphthol ring is less in the presence of this catalyst and is 51.5-60.5%.

Diethyl naphthols are practically not obtained by sequential ethylation in the presence of vanadium-alumina oxide system at low temperatures. Raising the temperature to 360°C increases the selectivity of the reaction for diethylnaphthalene by 1.0%.

As for the chromium alumina catalyst, it is noticeable that its alkylating ability is much higher in terms of carbon. Thus, the selectivity of the reaction for monoethylnaphthols and diethylnaphthols formed under the studied conditions is 60-68.0 and 2.0-4.0%, respectively.

A higher selectivity of mono- and diethylnaphthols in the alkylation process is achieved using a vanadium-chromium-aluminum oxide catalyst. According to the results of the experiment conducted at 360°C , the selectivity of the reaction for ethyl- and diethylnaphtholes was 80.0 and 4.5%, respectively.

In general, when analyzing the results of experiments with these catalysts, it is clear that both of them are important in the production of a mixture of ethoxynaphthalene and ethylnaphthalene. So, although the conversion of 1-naphthol in the presence of a vanadium-aluminum oxide catalyst is low (22.5-30.0%), the overall selectivity of the process for ethoxynaphthalene and monoethyl-naphthols is 87-92.0%. As for the ternary catalytic system, this indicator ranges from 83.0-87.5%. In other words, both catalysts are important in the synthesis of targeted mixtures of ethyl homologues obtained from the alkylation of 1-naphthol with ethanol. The molar ratio of

Table 1

**Results of alkylation reaction of 1-naphthol with ethanol
in the presence of various oxide catalysts
Conditions of reaction: $\nu - 1.0 \text{ hr}^{-1}$, $\nu=1:4 \text{ mol/mol}$**

Name of the indicator	Catalyst composition, in wt%					
	7.0- Cr ₂ O ₃ 93.0-Al ₂ O ₃		3.0- V ₂ O ₅ 97.0-Al ₂ O ₃		3.0-V ₂ O ₅ 7.0- Cr ₂ O ₃ 90- Al ₂ O ₃	
Specific surface of the catalyst, m ² /g	215		180		190.5	
Temperature, °C	320	360	320	360	320	360
1-Naphthol conversion, %	30.0	45.0	22.5	30.0	38.5	55.5
Yield of different groups of reaction products calculated for converted 1-naphthol, %						
Ethoxynaphthalenes	15.0	3.5	40.5	27.5	15.0	3.0
Ethyl naphthols	60.0	68.0	51.5	59.5	72.5	80.0
Diethyl naphthols	2.0	4.0	-	1.0	2.5	4.5
Alkylnaphthalenes	3.5	5.5	2.0	5.5	2.5	6.0
Oxo compounds	15.0	10.0	2.0	-	3.0	1.5
Condensation products	3.0	5.0	2.5	3.5	1.5	3.0
Concentration of 2-ethyl-1-naphthol in ethyl naphthols,%	97.0	91.5	100	99.0	98.5	92.0

ethoxynaphthalene to monoethylnaphthols obtained with the participation of the vanadium-aluminum oxide system is $0.46 \div 0.8:1$, and when using a ternary oxide catalyst, this ratio is $0.037 \div 0.208:1$.

The total yields of ethoxynaphthalene, ethyl- and diethylnaphthols calculated for the initial 1-naphthol are also of interest. Calculations showed that this indicator was 23.1-34.0% in the presence of chromium-aluminum oxide system, 20.7-26.4% in vanadium-aluminum oxide catalyst, and 34.65-48.6% in the presence of ternary oxide system.

Thus, the analysis of the results of the alkylation of 1-naphthol with ethanol shows that the ternary oxide catalyst surpasses other catalysts in terms of activity and selectivity, and the interaction of 1-naphthol with ethanol is more suitable for obtaining its ethyl homologues.

The alkylation reaction of 2-naphthol with ethanol in the presence of these catalysts was also studied.

First of all, it is noteworthy that the composition, structure and technological parameters of the products obtained from the interaction of 1-naphthol and 2-naphthol with ethanol are different. Thus, as a result of the 2-naphthol ethylation reaction, mainly 2-ethoxynaphthalene, 1-ethyl-2-naphthol, 3-ethyl-2-naphthol, 1,3- and 1,4-diethyl-2-naphthols are formed. The main part of 2-oxo compounds is 1,1-dimethyl-2-oxo-1,2-dihydronaphthalene. Traces of 1,1,3-triethyl-2-tetralone are also found in some experiments. Unlike 2-naphthol, 1-oxo-2,2-dimethyl-1,2-dihydronaphthalene is predominant in 1-oxocompounds formed by the interaction of 1-naphthol with ethanol. Both oxocompounds are thought to be involved in the production of alkyl naphthalene. Alkyl naphthalene is obtained under more severe reaction conditions and contains 1,2-diethylnaphthalene, 1-, 2-, 3- and 1,2,4-triethyl naphthalene and methyl-, ethyl naphthalene. It should be noted that the composition of the mixture of alkyl naphthalene differs little from the analogous mixture obtained from the alkylation of 1-naphthol with ethanol.

The product obtained with higher selectivity in the alkylation reaction of 2-naphthol with ethanol is 1-ethyl-2-naphthalene. The yield and selectivity of this product obtained by the electrophilic

substitution reaction for carbon in position 1 in the naphthol molecule is higher in the presence of a ternary catalytic system. Thus, the selectivity for monoethylnaphthols is 76.5% at 320°C and 81.5% at 360°C. It should be noted that in monoethylnaphthols, a mixture of two isomers (1-ethyl-2-naphthol and 3-ethyl-2-naphthol) obtained at 320°C, the concentration of 1-ethyl-2-naphthol is 97.5%, and at 360°C is 94.0%. The concentration of 1-ethyl-2-naphthol in the mixture of monoethyl-naphthols formed in the presence of other catalysts is different. For example, only one isomer (1-ethyl-2-naphthol) of monoethylnaphthol obtained by the catalyst of vanadium-alumina is found.

The concentration of 1-ethyl-2-naphthol in monoethyl-2-naphthols obtained by taking the catalytic system $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ is 94.5-96.0% depending on the temperature. It should be noted that the sufficient difference between the physical characteristics of these isomers (boiling point, melting point) does not complicate their further processing.

It is also interesting to compare the activities of the catalysts used in the reaction of alkylation of 1 and 2-naphthols with ethanol. Figure 1 shows the yields of ethoxynaphthalene and ethylnaphthols obtained in the presence of cobalt ferrite and VCA catalysts calculated according to the initial naphthol.

Analysis of these results shows that the activity of VCA catalyst for ethyl naphthols is higher than that of cobalt ferrite catalyst. Thus, this indicator, obtained as a result of the reaction of alkylation of 1-naphthol with ethanol, is 7.2% higher than that of cobalt ferrite, and 0.9% higher than the result of the interaction of 2-naphthol with ethanol. When it comes to ethoxynaphthalene yield, the opposite is true. In other words, the yield of 1-ethoxynaphthalene obtained from the alkylation of 1-naphthol with ethanol is 4.6% when cobalt ferrite catalyst is taken, and 2.6% in the case of VCA. A similar situation is observed with the interaction of 2-naphthol with ethanol. The yield of 2-ethoxynaphthalene, a product of oxygen alkylation, is 3.8% in the presence of cobaltferrite, 2.2% higher than in the presence of VCA.

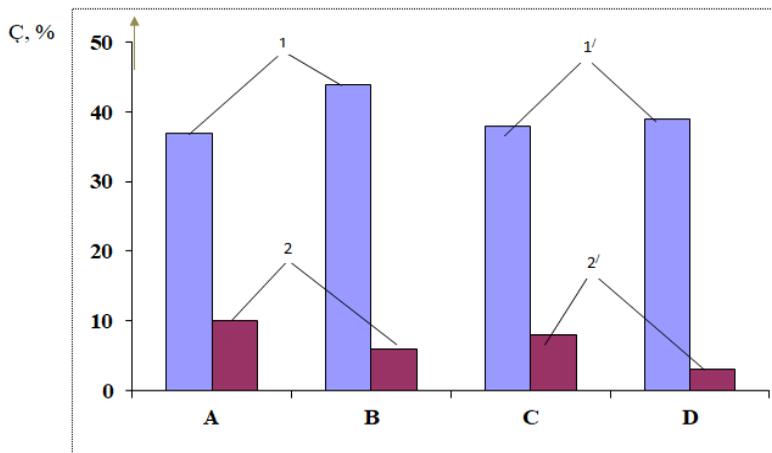


Figure 1. Yields of ethoxynaphthalenes (2, 2') and ethyl naphthols (1, 1') calculated according to the starting naphthol in the presence of cobalt ferrite (A, C) and VCA (B, D) catalysts

A, B – 1-naphthol-ethanol

C, D – 2-naphthol-ethanol

1 – yield of 2-ethyl-1-naphthol

2 – yield of 1-ethoxynaphthol

1' – yield of 1-ethyl-2-naphthol

2' – yield of 2-ethoxynaphthol

Thus, the results of the research show that cobaltferrite and especially VXA catalyst in the alkylation reaction of 1- and 2-naphthols with ethanol allow to obtain high yield and selectivity of corresponding alkylation products 2-ethyl-1-naphthol and 1-ethyl-2-naphthol according to carbon and are of practical importance.

3. Alkylation of naphthols with ethanol in the presence of mordenites. The alkylation reaction of naphthols with ethanol was studied in the presence of samples with modules of 18, 24 and 32 as a result of decationization and dealuminization of mordenites, the ratio of silicon oxide to aluminum oxide in the initially taken Na-mordenite was 10.

An increase in the rate of dealuminization in H-mordenite also increases the concentration of 2-methyl-1-naphthol in the resulting

monoethyl-naphthol mixture. The concentration of the first isomer in the mixture of 2-ethyl-1-naphthol and 4-ethyl-1-naphthol is 89.8% in H-mordenite with $x=10$ and 94.0% in zeolite with $x=24$.

Further increase of the modulus in H-mordenite has little effect on the results of the alkylation reaction of 1-naphthol with ethanol. It is likely that in mordenites with modules 24 and 32, the adsorption volume of the reagents and the size of the pores of the catalyst, as well as the number and strength of acid centers, change slightly. As can be seen, in both cases, most indicators are very close. Thus, it was possible to regulate the catalytic properties of H-mordenites with modules 24 and 32.

It is known that when aluminum is removed from zeolite, the total number of proton acid centers decreases, but their strength begins to increase. As a result, the acid-base properties of the catalytic system are regulated and its selectivity and activity in the catalytic system increases. As for the H-mordenites used in the alkylation reaction of 1-naphthol with ethanol, the fact that the sample with $x=24$ has more optimal acid-base properties confirms the above mentioned. This mordenite does not need to be subjected to further dealuminization.

In order to increase the performance properties, catalytic activity and selectivity of H-mordenite catalyst, it was modified with various ions (nickel, palladium, zirconium). For this purpose, the concentration of modifiers in H-mordenite was increased to 2.0 wt%, and the tendency of change the yields of obtained monoethyl-1-naphthols calculated according to converted and initially taken 1-naphthol was analyzed. For a more accurate and comparative analysis of this dependence, shown in figure 2, the y-axis shows similar values obtained from this reaction in the presence of H-mordenite ($x=24$).

When the concentration of the modifier in H-mordenite is 0.5 wt%, the selectivity for monoethylnaphthols in palladium and zirconium-modified zeolites increases to 76.1 and 78.0%, respectively. Further increase in the concentration of palladium is advisable. Thus, the selectivity for monoethylnaphthols obtained in the presence of 1.0% Pd, H-mordenite is 82.0%, and the subsequent

increase in concentration practically does not increase this figure (1.5 Pd, H-mordenite - 81.5%) and on the contrary, even reduces (80.0%) when palladium concentration is 2.0 wt%. In the presence of zirconium, increasing its concentration to 1.5 wt% increases the selectivity for the target product to 86.5%.

A further increase in the modifier leads to an increase in selectivity only 1.5%. In the case of H-mordenite catalysts, increasing the concentration of the modifier to 0.5 wt% reduces the selectivity of monoethylnaphthols from 74.5% to 71.5% compared to H-mordenite, in contrast to other catalysts and subsequent increase in nickel concentration changes this indicator, first to 73.0% (1.0 wt% Ni, H-mordenite) and then to 78.0% (1.5 wt% Ni, H-mordenite). Increasing the concentration of nickel in mordenite to 2.0 wt% has little effect on this indicator (78.5%).

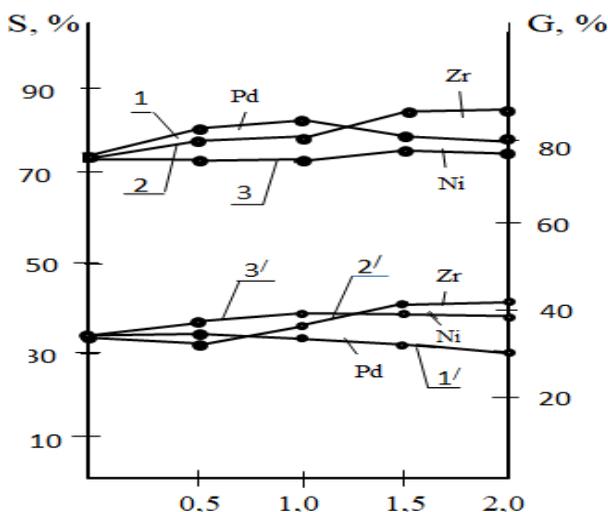


Figure 2. The effect of the modifier concentration in mordenite on the yields of monoethyl-1-naphthols, which obtained from the alkylation reaction of 1-naphthol with ethanol, calculated according to the converted (1,2,3) and initially taken (1', 2', 3') 1-naphthol: 1, 1' - Pd, H-mordenite, 2, 2' - Zr, H-mordenite, 3, 3' - Ni, H-mordenite

Similar patterns are observed for the yield of monoethylnaphthols obtained from 1-naphthol and ethanol in the presence of palladium-zirconium and nickel mordenites. Thus, when the concentration of zirconium in mordenite is increased to 0.5 wt%, then the yield of monoethylnaphthols calculated for 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. In Ni,H-mordenite this indicator is 39.5%, and in zirconium zeolite it increases to 37.5%. A further increase in the concentration of palladium in the catalyst (1.5-2.0 wt%) reduces the yield of monoethyl naphthols first to 34.0% and then to 32.5%. The subsequent increase in the concentration of the modifier in the other two catalysts has a specific effect on the yield of the target product. Thus, the yield of monoethyl naphthols in 1.5 wt% Ni, H-mordenite is practically unchanged, but increasing the concentration of the modifier in the catalyst to 2.0 wt% leads to a partial reduction in yield (2.0%). As a result of increasing the concentration of the modifier in zirconium H-mordenite to 1.5 wt%, the yield of monoethylnaphthols increases significantly and is 41.1%.

Similar studies were performed on the alkylation reaction of 2-naphthol with ethanol (figure 3).

As a result of research, compared with H-mordenite, zeolites with a density of 1.5 wt% were selected as zeolites among samples modified with nickel and zirconium, and among mordenites modified with palladium Pd, H-mordenite with a density of 1.0 wt% as more active and selective catalytic systems. Additional studies have been carried out on the regulation of the catalytic and performance properties of mordenites used in the reaction of alkylation of 1 and 2-naphthols with ethanol, and for this purpose the influence of various promoters has been studied. Cobalt, chromium and nickel sulfates were used to obtain mordenite compositions, and modification with chromium (III) sulfate was found to be more effective.

The incorporation of chromium(III) sulfate into the zirconium-containing H-mordenite acts as an activating promoter. Although it is

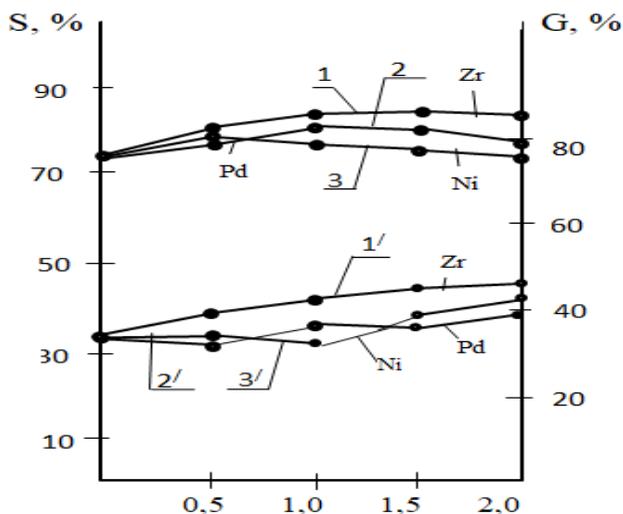


Figure 3. The effect of the modifier concentration in mordenite on the yields of monoethyl-2-naphthols, which obtained from the alkylation reaction of 2-naphthol with ethanol, calculated according to the converted (1,2,3) and initially taken (1 /, 2 /, 3 /) 2-naphthol: 1 / - Zr, H-mordenite, 2, 2 / - Pd, H-mordenite, 3, 3 / - Ni, H-mordenite

likely that new active sites will be formed by affecting the electronic structure of the active phase, it is likely that the acid-base properties of existing catalytic sites are mainly regulated. On the other hand, as a result of the migration of atoms and ions in the crystallites in the catalyst during modification, complex parameters such as the stability and lifetime of mordenites also improve. The increase in durability due to the prevention of initiation is inherent in all three mordenite catalysts. However, modification in zirconium mordenite leads to the formation of dimensional crystallites that are closer to the optimal catalytic properties, and leads to the realization of the alkylation process with the achievement of high technological parameters.

Studies have been carried out in the presence of zirconium-containing mordenite catalyst to clarify the nature of the transformations that occur during the alkylation of 1-naphthol with

methanol. For this, the main and side transformations of ethoxynaphthalene, ethanol during alkylation, the interaction of oxo compounds with ethanol were studied, and the main pathways of the process were determined based on the obtained results (table 2). 1-naphthol (1), ethanol (2), 2-ethyl-1-naphthol (3), 1-ethoxynaphthalene (4), 1,2-diethylnaphthalene (5), ethyl acetate (6), hydrogen (7) were taken as key substances in kinetic studies carried out in a wide range of regime parameters, a 12-stage scheme and limiting stages of the process are given, which are fully compatible with the stoichiometric base.

Taking into account the selected limiting stages, the values of the kinetic constants $K_I=K_2$, $K_{II}=K_5$, $K_{III}=K_7$ $K_{IV}=K_{10}$ were initially determined graphically. Their values were calculated using a system of equations 1-4 and specified by minimizing the sum of the squares of the differences obtained compared to the observed copies.

$$r_I = \frac{K_I P_1 P_2}{(1 + b_1 P_1 + b_2 P_3)^2} \quad (1)$$

$$r_{II} = \frac{K_{II} P_1 P_2}{(1 + b_1 P_1 + b_2 P_3)^2} \quad (2)$$

$$r_{III} = \frac{K_{III} P_3 P_2}{(1 + b_1 P_1 + b_2 P_3)^2} \quad (3)$$

$$r_{IV} = \frac{K_{IV} P_2}{1 + b_1 P_1 + b_2 P_3} \quad (4)$$

The main kinetic parameters are given in table 2.

b_1 , b_2 are the adsorption coefficients of 1-naphthol and 2-ethyl-1-naphthol on the catalyst surface, respectively.

The unit of measurement for K_I , K_{II} , K_{III} is g/cm^3 (kat) hours \times kPa^2 , and for K_{IV} is g/cm^3 (kat) hours \times kPa . In order to be a more favorable basis, the fractional presentation of kinetic equations and

the construction of a table of stoichiometric coefficients in a different form led to more errors.

Table 2

Main kinetic parameters

Route	lnk ₀	E, kkal/mol	lnb ₀	Q, kkal/mol
1-C ₁₀ H ₇ OH + C ₂ H ₅ OH → →1-C ₁₀ H ₇ OC ₂ H ₅ + H ₂ O	0.8990	10.711	-4.51	3.3
1-C ₁₀ H ₇ OH + C ₂ H ₅ OH → → 2-C ₂ H ₅ -1-C ₁₀ H ₆ OH +H ₂ O	9.705	18.100	-4.64	2.20
2-C ₂ H ₅ -1-C ₁₀ H ₆ OH + C ₂ H ₅ OH + 2[H] → →1.2-(C ₂ H ₅)C ₁₀ H ₆ + 2H ₂ O	8.888	19.400	-	-
C ₂ H ₅ OH → 0.5C ₄ H ₈ O ₂ + H ₂	2.320	10.051	-	-

4. Comparative catalytic properties of catalytic systems used in the alkylation reaction of naphthols with ethanol. The composition, yield, selectivity of products obtained from the interaction of naphthols with ethanol are different and depend directly on the composition, structure, acid-base properties of the used catalysts. This applies to the alkylation reaction of both naphthols with ethanol. The comparative tables (3 and 4) of the highest results obtained in the presence of different catalytic systems are given below. Table 3 shows the high results of 1-naphthol alkylation, and table 4 of 2-naphthol alkylation with ethanol obtained for each catalyst and the reaction conditions under which this result was obtained. The catalytic systems shown in the tables were contacts that showed higher activity and selectivity in the presence of this group of catalysts and were selected based on the experiments carried out in the previous chapters. These include 25-CoFe₂O₄ and 75-Al₂O₃ from ferrites (in wt %), 3.0-V₂O₅, 7.0-Cr₂O₃, 90-Al₂O₃ from other studied oxide catalysts, samples of H-mordenite modified with 1.5% nickel, 1.5% zirconium and 1.0% palladium, as well as composite H-mordenite (CM) containing 0.3% Cr₂(SO₄)₃, 1.5% zirconium.

In the reaction of alkylation of 1-naphthol with ethanol, the product of O-alkylation is 1-ethoxyphthaline, the products of C-monoalkylation are 2-ethyl- and 4-ethyl-1-naphthols and 2,4- and 2,3-diethylnaphthols. Alkylates also include ethyl and methyl homologues of naphthalene, which are formed as a result of complex transformations such as dehydroxylation - alkylation occurring under harsh conditions of alkylation of 1-naphthol with ethanol. The concentration of oxo compounds obtained under the studied conditions and in the presence of used catalysts is negligible.

O-alkylation in the presence of cobaltferrite and VCA catalysts occurs sufficiently (32.0-15.0%) at 320°C. The selectivity of the reaction for 1-ethoxynaphthalene in the presence of mordenites is low (0.7-2.0%). The C-monoalkylation reaction of 1-naphthol occurs with a selectivity of only 64.5% when ferrites are used. In the presence of mordenites, this indicator is high (except for Ni, H-mordenite). For example, in zirconium-containing H-mordenite this indicator is 86.5%, and in composite mordenite it is 92.5%. It should be noted that the concentration of 2-ethyl-1-naphthol in monoethyl-1-naphthols is 96.0 and 97.3%, respectively, in the above-mentioned mordenites. Another advantage of composite mordenite is that the selectivity of alkyl naphthalene in the obtained alkylates is only 1.5% and no dialkyl naphthols are formed. Thus, in zirconium mordenite, the selectivity for alkyl naphthalene is 6.5%, and in the case of VCA, which has shown satisfactory selectivity for monoethyl-1-naphthols (80.0%), it is 6.0%. Diethylnaphthols (1.5-4.5%) formed in the presence of these catalysts also complicate the further processing of alkylate. 80% of 1-naphthol, which is highly converted at 360°C in the presence of VCA, is spent on the production of monoethyl-1-naphthols. This is 12.5% less than in the case of CM. Comparing the values of zirconium-containing mordenite with VCA, the selectivity for monoethyl-1-naphthols is 6.5% higher in the case of mordenite, and the yield of 2-ethyl-1-naphthol is only 1.4% lower than in VCA. It should also be noted that alkylation in the presence of VXA is carried out at a higher temperature (360°C) and this catalyst has a much shorter working life than mordenite.

From the analysis of the results obtained from the alkylation of 2-naphthol with ethanol in the presence of the above-mentioned catalysts, it is clear that the regularities observed in 1-naphthol are largely repeated in this case. But there are also some differences. In this reaction, more active and selective properties are exhibited by copper ferrite from ferrites.

From the analysis of the obtained results it is clear that alkylation in the 2-naphthol-ethanol-catalyst system occurs for both O- and C-atoms. O-alkylation in 2-naphthol, as in 1-naphthol, proceeds with a selectivity of 11.0-14.5% at 320°C in the presence of ferrite and VCA catalysts. In mordenites, its speed and targeting are significantly reduced and are obtained at 340°C with a selectivity of 2.5-3.5%. C-alkylation products of 2-naphthol include monoethyl-2-naphthols (1-ethyl- and 3-ethylnaphthols) and diethylnaphthols (1,3-1,4-diethylnaphthols). The yields of monoethyl-2-naphthols calculated according to converted 2-naphthol are 70.0% at low temperatures (320°C) in the presence of copper ferrite and 76.5% in the presence of VCA. An increase in temperature (360°C) in the latter case increases this indicator to 81.5%. As for H-mordenites, the selectivity of the reaction for monoethyl-2-naphthols is 84.5% in zirconium-modified mordenite and 91.0% in composite mordenite. The concentration of 1-ethyl-2-naphthol in a mixture of monoethyl-2-naphthols is 100% in the presence of $\text{CuFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$, 94.0-97.5% in the presence of VCA, and more in the presence of CM from mordenites (95.5%).

With regard to the conversion of 2-naphthol, it should be noted that its conversion in the presence of ferrite and VCA catalysts is 3.5-8.5% less than in the presence of 1-naphthol. When comparing mordenites, the conversion of 2-naphthol increases by 2.0-12.5% compared to 1-naphthol, and this increase is more observed in zirconium-modified mordenite. An undesirable transformation during the interaction of 2-naphthol with ethanol is the formation of alkylnaphthalenes. This side reaction occurs significantly in the

presence of oxides, especially copper ferrite (5.0%), and in the presence of VCA (6.5%) at high temperatures (360°C).

In the case of mordenites, all three modified catalysts have sufficient selectivity for alkylnaphthalenes (6.0–9.5%). As for CM, in 2-naphthol the rate of this transformation is limited, as in 1-naphthol, which increases the selectivity for target products, i.e. monoethyl-2-naphthol.

Table 3

Results of alkylation reaction of 1-naphthol with ethanol in the presence of various catalysts

Conditions of the reaction and the obtained indicators	Catalyst composition, in wt%						
	25-CoFe ₂ O ₄ 75- γ -Al ₂ O ₃	3.0-V ₂ O ₅ 7.0-Cr ₂ O ₃ 90- γ -Al ₂ O ₃		1.5 Ni,H- mor- denite	1.5 Zr,H- mor- denite	1.0 Pd,H- mor- denite	0.3 Cr ₂ (SO ₄) ₃ 1.5 Zr,H- mordenite
Temperature, °C	320	320	360	340	340	340	340
Volume velocity, hr ⁻¹	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mole ratio of 1-naphthol to ethanol	1:4	1:4	1:4	1:6	1:6	1:6	1:4
Yields calculated according to converted 1-naphthol, in%, including							
Monoethyl-1-naphthols	64.5	72.5	80.0	78.1	86.5	82.0	92.5
1-ethoxynaphthalene	14.0	15.0	3.0	1.5	1.0	0.7	2.0
Alkyl naphthalene	7.0	2.5	6.0	9.5	6.5	10.0	1.5
Diethyl-1-naphthols	3.0	2.5	4.5	3.0	1.5	2.4	-
Conversion of 1-naphthol, %	50.5	38.5	55.5	50.0	47.5	42.5	34.0
Concentration of 2-ethyl-1-naphthol in monoethyl-1-naphthol mixture, %	93.5	98.5	92.0	91.5	96.0	94.2	97.3
Yield of 2-ethyl-1-naphthol, %	30.4	27.5	40.8	35.7	39.4	32.8	30.6

The yield of 1-ethyl-2-naphthol calculated according to converted 2-naphthol, i.e. the selectivity of the studied catalysts decreases in the following order:

CM > 1.5ZrHM > VXA > 1.0PdHM > 1.5NiHM > CuFe₂O₄·γ-Al₂O₃

The yield of formed 1-ethyl-2-naphthol calculated according to the initial 2-naphthol decreases in the following order:

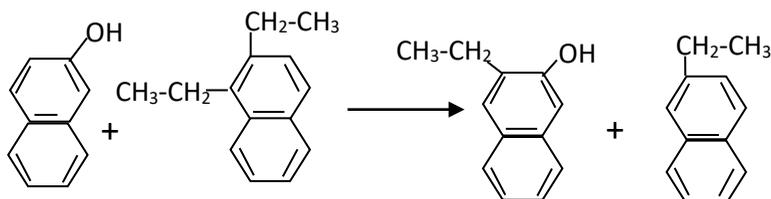
1.5ZrHM > 1.5NiHM > VXA > 1.0PdHM > CM > CuFe₂O₄·γ-Al₂O₃

Table 4

Results of alkylation reaction of 2-naphthol with ethanol in the presence of various catalysts

Conditions of the reaction and the obtained indicators	Catalyst composition, in wt%						
	25-CuFe ₂ O ₄ 75-γ-Al ₂ O ₃	3.0-V ₂ O ₅ 7.0-Cr ₂ O ₃ 90-γ-Al ₂ O ₃	1.5 Ni, H-mordenite	1.5 Zr, H-mordenite	1.0 Pd, H-mordenite	0.3 Cr ₂ (SO ₄) ₃ 1.5 Zr,H-mordenite	
Temperature, °C	320	320	360	340	340	340	340
Volume velocity, hr ⁻¹	1.0	1.0	1.0	1.0	1.0	1.0	1.0
Mole ratio of 2-naphthol to ethanol	1:4	1:4	1:4	1:6	1:6	1:6	1:4
Yields calculated according to converted 2-naphthol, in%, including							
Monoethyl-2-naphthols	70.0	76.5	81.5	77.0	84.5	81.0	91.0
2-ethoxynaphthalene	14.5	11.0	1.5	3.5	3.0	2.5	3.0
Diethyl naphthols	1.5	3.0	4.0	3.4	2.0	3.5	1.0
Alkyl naphthalene	5.0	3.0	6.5	9.5	6.0	7.0	1.5
Conversion of 2-naphthol, %	42.0	35.0	50.0	56.5	60.0	50.0	36.0
Concentration of 1-ethyl-2-naphthol in monoethyl-2-naphthol mixture, %	100	97.5	94.0	90.0	93.5	87.0	95.5
Yield of 1-ethyl-2-naphthol, %	29.4	26.0	38.3	39.1	47.4	35.2	31.3

The total selectivity for the mixture of alkyl naphthalene obtained in the alkylation reaction of 1- and 2-naphthols with ethanol in the



presence of mordenite catalysts is 1.5-10.0%, depending on the catalysts. The selectivity of a mixture of these compounds in alkylates obtained in the presence of oxide catalysts is also in the indicated range. The involvement of ethylnaphthalene in the realkylation process can be considered economically, technologically and environmentally efficient. In general, this method, based on the following reaction equation, has emerged as an interesting type of chemical transformation.

The chemical process was carried out in the presence of Pd-HSVM and KM catalysts under defined conditions ($T = 400^{\circ}\text{C}$, $P = 0.5 \text{ MPa}$, $v = 1.5 \text{ hr}^{-1}$, $v=1:2$) in benzene medium and it was found that transethylation occurs with higher results in composite mordenite. Thus, the yield of monoethylnaphthols calculated according to the converted 1- and 2-naphthols is 94.3 and 84.5%, respectively, and the one-time conversion of naphthols is 13.0 and 17.5%, respectively. The yield of monoethyl-1-naphthol calculated according to the converted 1.2-dimethylnaphthalene is 81.0%, and the yield of monoethyl-2-naphthol is 79.0%. The conversion of diethyl naphthalene is 15.5% in the interaction with 1-naphthol and 17.5% in the transethylation of 2-naphthol. An important aspect of this study is the achievement of the targeted use of alkyl naphthalene, which is obtained as a by-product of the alkylation reaction and has little use.

Thus, on the basis of detailed studies, it is possible to obtain different ethyl homologues of naphthols with high yield and selectivity by changing the composition of catalysts containing oxides and mordenite, the reaction conditions and the isomer of the initial naphthol. Determination of main and side transformations of 1- and 2-naphthols alkylation reaction with ethanol in the presence of obtained composite mordenite and zirconium-containing H-mordenite, kinetic studies, calculation of kinetic constants, development of an adequate kinetic model, development of methods for obtaining purposeful ethyl homologues of naphthols in the presence of selected catalysts with a stable regime clearly demonstrates the complete solution of the problem and is

characterized by innovation in the scientific work carried out in this direction.

CONCLUSIONS

1. Among the studied ferrite catalysts ($\text{MFe}_2\text{O}_4 \cdot \gamma \cdot \text{Al}_2\text{O}_3$, M-Mg, Zn, Co, Cu), the catalyst containing 25 wt% cobalt ferrite exhibits higher activity and selectivity in the interaction of 1-naphthol with ethanol, and a catalytic system with the same concentration of ferrite copper in the reaction of alkylation of 2-naphthol with ethanol.

2. The total yields of mono- and diethylnaphthols obtained on the basis of 1-naphthol and ethanol in the presence of an oxide catalyst of a certain composition, calculated according to the converted and initial 1-naphthol, are 84.5 and 46.9%, respectively. The total selectivity of mono- and diethylnaphthols obtained from the alkylation of 2-naphthol with ethanol in the presence of this catalyst is 85.5%, and the total yield is 42.7%.

3. The concentration of 2-ethyl-1-naphthol in monoethylnaphthols obtained by C-alkylation in the interaction of 1-naphthol with ethanol in the presence of a VCA catalyst is 92.0-98.5%, and the concentration of 1-ethyl-2-naphthol in monoethylnaphthols formed by the same mechanism from alkylation of 2-naphthol with ethanol is 97.5%.

4. When modifying H-mordenite with nickel, zirconium and palladium with a more favorable modulus ($\text{SiO}_2/\text{Al}_2\text{O}_3=18-24$), the influence of their concentrations (0.5-2.0 wt%) on the parameters of the alkylation process of naphthols with ethanol, on the occurrence of basic and side transformations have been established. It was shown that the presence of 1.5% zirconium and nickel, 1.0% palladium makes it possible to achieve better results, and it was found that among the modified mordenites 1.5Zr, H-mordenite has higher catalytic properties.

5. Regularities of the alkylation reaction of 1-naphthol with ethanol in the presence of zirconium-containing mordenites were determined. It has been established that parallel O- and C-alkylation,

sequential C-alkylation occur in the process, oxo compounds are obtained from naphthols, although insignificantly, and ethylation occurs, accompanied by dehydroxylation in the reaction medium. Limited side effects of ethanol in bifunctional H-mordenites include the production of diethyl ether (Ni, H-mordenite) by its intermolecular dehydration, the formation of acetaldehyde by dehydrogenation (Zr, H-mordenite), and the production of ethyl acetate (CM) from its interaction with alcohol.

6. The routes of the process of alkylation of 1-naphthol with ethanol in the presence of zirconium-containing mordenites were determined, kinetic constants were calculated, a low-error kinetic model was developed that adequately described the main and side transformations on the catalytic surface.

7. As a result of the comparative analysis of the alkylation of naphthols with ethanol, 92.5% selectivity is obtained from 1-naphthol and ethanol in the presence of the proposed H-mordenite composition, and 91.0% monoethylnaphthols are obtained from the alkylation of 2-naphthol with ethanol. In the first case, the concentration of 2-ethyl-1-naphthol in the mononaphthol mixture is 97.3%, and in the second case, the proportion of 1-ethyl-2-naphthol is 95.5%.

8. The intended use of a mixture of mono- and diethyl naphthalene homologues obtained as a by-product in the reaction of alkylation of naphthols with ethanol and with a small areas of use was achieved, and a selective (84.5-94.3%) synthesis of ethylnaphthols was carried out by transethylation of naphthols with ethylnaphthalenes.

THE MAIN PROVISIONS OF THE DISSERTATION ARE CONSIDERED IN THE FOLLOWING SCIENTIFIC WORKS

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