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ИЗУЧЕНИЕ ЭФФЕКТИВНОГО КАТАЛИТИЧЕСКОГО МЕТОДА ПОЛУЧЕНИЯ АЛКИЛ(C_1–C_2)НАФТОЛОВ

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STUDY OF EFFECTIVE CATALYTIC PRODUCTION METHOD OF ALKYL(C_1–C_2)NAPHTHOLS

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Реакцию алкилирования 1-нафтола метанолом и этанолом изучали в присутствии H-морденита и его модифицированных образцов. Количество модификатора (Pd, Ni, Sr) в катализаторе изменяли в диапазоне 0.1–2.0% мас. и детально изучали каталитические свойства H-морденита с модулем 24. Установлено, что выбранный катализатор SrH-морденит проявляет высокую селективность (86.5–90.5 %) и активность (39.8–41.1 %) в синтезе 2-метил-1-нафтола и 2-этил-1-нафтола.

Ключевые слова: метанол; метилнафтолы; H-морденит; нафталин; нафтолы; этанол, этилнафтолы.

The alkylation reaction of 1-naphthol with methanol and ethanol was studied in the presence of H-mordenite and its modified samples. The amount of modifier (Pd, Ni, Sr) in the catalyst was changed in the range of 0.1–2.0% mass and the catalytic properties of H-mordenite with modulus 24 were studied in detail. It was determined that the selected SrH-mordenite catalyst showed high selectivity (86.5–90.5 %) and activity (39.8–41.1 %) in the synthesis of 2-methyl-1-naphthol and 2-ethyl-1-naphthol.

Key words: ethanol; ethylnaphthols; H-mordenite; methanol; methylnaphthols; naphthalene; naphthols.

The raw material base of naphthols and low molecular weight (C_1–C_2) alcohols is available in Azerbaijan, including Sumgait city. There are enough naphthalene and its homologs in liquid pyrolysis products. Hydrocarbons of the naphthalene series have few applications. However, ~40% of the naphthalene produced in the world is used for the synthesis of naphthol and its numerous derivatives. Naphthols and their methyl and ethyl homologs are considered valuable by-products of organic synthesis. Based on them, all types of K vitamins (K_1 (2-methyl-3-phytyl-1,4-naphthoquinone), K_2 (2-methyl-3-difarnesyl-1,4-naphthoquinone), K_3 (menadione, 2-methyl-1,4-naphthoquinone), K_4 (2-methyl-1,4-diacetoxynaphthalene and menadiol (2-methyl-1,4-dioxynaphthalene), K_5 (4-amino-2-methyl-1-naphthol), K_6 (2-methyl-1.4-methylenediamine)), widely used in veterinary medicine, are produced. On the other hand, azide dyes based on methyl-and ethylnaphthols, vitamins, fragrances, glues, pesticides, medicinal substances, emulsifiers, dispersants, stabilizers, preparations used in color photography, hydraulic fluids, as well as food products, including bakery products, beverages, sweets products and additions to chewing gum as aromatizers are also produced [1].

A convenient method for methyl- and ethyl homologs of naphthols is based on the alkylation reaction of naphthols with methanol and ethanol. The production method created mainly with the

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Table 1

Catalytic properties of H-mordenite in the alkylation reaction of 1-naphthol with ethanol

Indicator Name	Modulus value in H-mordenite (SiO_2/Al_2O_3)			
	10	18	24	32
The yield of the main reaction products calculated according to the converted 1-naphthol, in %, including				
1-Ethoxynaphthalene	8.0	8.5	8.0	7.1
Monoethyl-naphthols	66.0	70.5	74.5	75.0
Diethylnaphthols	4.0	3.0	2.4	2.0
1-Oxo compounds	7.5	7.2	7.0	6.5
Methyl and ethyl homologs of naphthalene	11.0	9.0	6.5	5.0
Conversion of 1-naphthol, %	52.8	49.5	45.0	45.0
Yield of monoethyl naphthols calculated based on starting 1-naphthol, %	41.4	35.0	33.5	33.8
Concentration of 2-ethyl-1-naphthol in the mixture of monoethyl naphthols, %	89.8	92.5	94.0	94.0

presence of aluminum oxide has been operating in a number of countries (USA, Japan, China) since the end of the last century [2–4]. There is a need to improve these ortho-tonnage productions, which have low economic and technological indicators, and to create an effective catalyst. Considering these, we extensively studied the alkylation process with the presence of zeolites, including modified H-mordenites [5]. As a result of decationization and dealumination of H-mordenites, zeolites with modulus 18, 24 and 32 were synthesized. The starting H-mordenite had a silica to alumina ratio of 10. The experiments were carried out under the following reaction conditions: T = 340 °C, υ = 1.0 st^{-1}, ν = 1:5 mol/mol.

The analysis of the obtained results shows that (tab. 1) the increase in the degree of dealuminization in H-mordenite also increases the concentration of 2-ethyl-1-naphthol in the resulting monoethyl-naphthol mixture. At this time, 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 increasing the modulus in H-mordenite has little effect on the results of the alkylation reaction of 1-naphthol with ethanol. Most likely, in mordenites with moduli 24 and 32, there is little change in the adsorption volume of reagents and catalyst pore sizes, as well as the number and strength of acid centers. As you can see, most of the indicators are very close in both cases. Therefore, it was possible to adjust the catalytic properties of H-mordenites with modules of 24 and 32.

In order to increase the operating properties, catalytic activity and selectivity of the H-mordenite catalyst, its modification with various ions (nickel, palladium, zirconium) was carried out. For this purpose, the concentration of modifiers in H-mordenite was increased to 2.0% mass, and the tendency of the conversion of monoethyl-1-naphthols obtained at this time and calculated according to the original 1-naphthol was analyzed. In order to more accurately and comparatively analyze this dependence given in Fig. 1, the analogous indicators obtained from that reaction in the presence of H-mordenite (x = 24) are given on the ordinate axis.

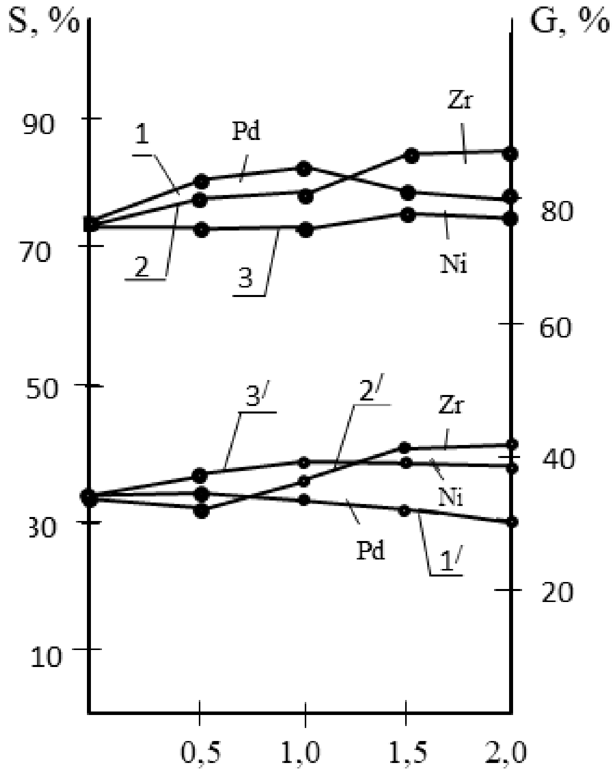

Fig. 1. Effect of modifier concentration in mordenite on calculated yields of monoethyl-1-naphthols obtained from alkylation of 1-naphthol with ethanol in terms of converted (1,2,3) and initial (1′, 2′, 3′) 1-naphthol: *1, 1′ – Pd, H-mordenite; 2, 2′ – Zr, H-mordenite; 3, 3′ – Ni, H-mordenite*

When the concentration of the modifier in H-mordenite is 0.5% mass, the selectivity to monoethylnaphthols increases and becomes 76.1 and 78.0 %, respectively, in zeolites modified with palladium and zirconium. A subsequent increase in palladium hardness is desirable. Thus, the selectivity for monoethylnaphthols obtained in the presence of 1.0% mass Pd, H-mordenite reaches 82.0%, and the

Table 2

Results of the study of the alkylation reaction of 1-naphthol with ethanol in the presence of H-mordenite catalyst modified with zirconium, palladium and nickel

Indicator Name	Catalyst content, percent mass (%)		
	1.5 – Ni, 98.5-H-mordenite	1.5 – Zr, 98.5-H-mordenite	1.0 – Pd, 99.0-H-mordenite
The yield of the main reaction products calculated according to the converted 1-naphthol, in %, including			
1-Ethoxynaphthalene	1.5	1.0	0.7
2- And 4-ethylnaphthols	78.1	86.5	82.0
Diethylnaphthols	3.0	1.5	2.4
1-Oxo compounds	5.0	1.8	3.0
Methyl and ethyl homologs of naphthalene	9.5	6.5	10.0
Conversion of 1-naphthol, %	50.0	47.5	42.5
Yield of monoethyl naphthols calculated based on starting 1-naphthol, %	39.1	41.1	34.9
Concentration of 2-ethyl-1-naphthol in the mixture of monoethyl naphthols, %	91.5	96.0	94.2

subsequent increase in density practically does not increase this indicator (1.5 Pd, H-mordenite – 81.5%), and on the contrary, even when the density of palladium is 2.0% mass reduces (80.0%). In the case of zirconium, increasing its concentration to 1.5% by mass increases the selectivity for the target product up to 86.5%. A further increase in the modifier leads to an increase in selectivity of only 1.5% [6, 7]. In the case of Ni, H-mordenite catalyst, increasing the density of the modifier to 0.5% mass, unlike other catalysts, reduces the selectivity of monoethylnaphthols compared to H-mordenite from 74.5 to 71.5 %, and the subsequent increase in the density of nickel increases this indicator to 73.0% (1.0% mass Ni, H-mordenite) and then up to 78.0% (1.5% wt Ni, H-mordenite). Increasing the concentration of nickel in mordenite to 2.0% by mass has little effect on this indicator (78.5%).

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% by mass, 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% mass 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 % mass) reduces 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% mass Ni, H-mordenite practically does not change, but increasing the concentration of the modifier in the catalyst to 2.0% mass 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% mass, the yield of monoethylnaphthols increases significantly and is 41.1%.

As a result of the conducted research, compared to H-mordenite, zeolites with a hardness of 1.5% mass from samples modified with nickel and zirconium, and 1.0% mass Pd in palladium-modified mordenites, H-mordenite was selected as a more active and selective catalytic system.

Tab. 2 shows the results obtained in the alkylation reaction of 1-naphthol with ethanol in the presence of those catalysts.

As can be seen, the composition of the products obtained from the alkylation reaction of 1-naphthol with ethanol varies slightly depending on the catalyst used. These products include 1-ethoxynaphthalene monoethylnaphthols (2- and 4-isomers), diethylnaphthols, 1-oxo compounds and methyl and ethyl homologs of naphthalene. Alkylates contain small amounts of condensation products whose composition has not been determined precisely. Zirconium mordenite catalyst shows high activity and selectivity in the ortho-alkylation reaction of 1-naphthol, while Ni,H-mordenite zeolite shows low catalytic properties. These catalytic systems are also suitable for obtaining diethyl naphthols by sequential alkylation of 1-naphthol by carbon. Regarding the composition of the obtained 1-oxo compounds, it should be noted that the density of 1-oxo-2,2-diethyl-1,2-dihydronaphthalene in the mixture obtained in the presence of Ni,H-mordenite is 88.7%, and this indicator is 96.5% in zirconium-modified zeolite.

In the mixture of 1-oxo compounds obtained in the presence of Pd,H-mordenite catalyst, the concentration of the other isomer 1-oxo-4,4-diethyl-1,4-dihydronaphthalene is 4.5%. One of the

Table 3

Comparative table of the study of the alkylation reaction of 1-naphthol with methanol and ethanol in the presence of zirconium-modified H-mordenite catalyst

$T = 340\ ^oC$, $\upsilon = 1.0\ st^{-1}$, $\nu = 1:5$ mol/mol

Indicator Name	Composition of raw materials	
	1-naphthol: methanol	1-naphthol:ethanol
The yield of the main reaction products calculated according to the converted 1-naphthol, in %, including		
1-Ethoxynaphthalene	-	1.0
1-Methoxynaphthalene	1.5	-
2- And 4-ethylnaphthols	-	86.5
2- And 4- methylnaphthols	90.5	-
Diethylnaphthols	-	1.5
Dimethylnaphthols	2.0	-
1-Oxo compounds	1.0	1.8
Methyl and ethyl homologs of naphthalene	4.0	6.5
Conversion of 1-naphthol, %	44.0	47.5
Yield of monoethyl naphthols calculated based on starting 1-naphthol, %		41.1
Yield of mono-methyl naphthols calculated based on starting 1-naphthol,%	39.8	
Concentration of 2-ethyl-1-naphthol in the mixture of monoethyl naphthols, %		96.0
Concentration of 2-methyl-1-naphthol in the mixture of monoethyl naphthols, %	98.0	

interesting results is the difference in composition and yield of methyl and ethyl naphthalene obtained during the process. In contrast to zirconium mordenite, alkylnaphthalenes formed in nickel and palladium modified zeolites contain methyl homologs. Nickel mordenite has a high selectivity (9.5%) for alkylnaphthalenes, and Zr, H-mordenite has a low selectivity (6.5%).

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

The highest value of the converted monoethyl-1-naphthols and the calculated yield of the original 1-naphthol belongs to zirconium-modified mordenite and is 86.5 and 41.1 %, respectively. In Ni, H-mordenite, these indicators are 78.1 and 39.1, respectively. When Pd, H-mordenite is taken, the selectivity for monoethyl-1-naphthols is 82.0, and the yield is 34.9%.

The selected catalytic system showed high activity and selectivity in alkylation reaction of 1-naphthol with methanol [8]. Tab. 3 shows the comparative results of the interaction of 1-naphthol with C_1 and C_2 alcohols in the presence of zirconium H-mordenite (Tab. 3).

As the molecular mass of the alkylating agent, i.e. alcohol, increases, alkylation due to oxygen increases partially. The share of alkylation increases due to carbon in the nucleus. The amount of alkyl homologs of naphthalene decreases. From the comparison of the results, it can be seen that in the presence of ethanol, the conversion of naphthol and the yield of obtained monoalkylnaphthols increase. However, the concentration of 2-methyl-1-naphthol in the mixture of monoalkylnaphthols is slightly higher than that of 2-ethyl-1-naphthol. The obtained results show that the concentration of ortho-methyl and ethyl homologs of 1-naphthol is dominant in the alkylation process. This is explained by the structure, composition, and adjustment of acid-base properties of the selected zirconium mordenite catalyst.

Thus, 1.5% mass Zr, H-mordenite ($x = 24$) was chosen as a more active and selective catalyst in alkylation reaction of 1-naphthol with methanol and ethanol. It has been determined that it is of practical importance in the production of monomethyl and monoethyl-1-naphthols, especially 2-methyl (ethyl)-1-naphthols [9].

An efficient method of obtaining alkyl homologues of 1-naphthol has been developed, patented and published in a number of prestigious journals.

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