

The Study of The Catalytic Conversion of 1-Ethoxy Naphthalene

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Abstract: *Ethanol interaction of 1-ethoxy naphthalene in alkylation conditions to determine the major and side effects of alkylation process of 1-naphthol with ethanol was investigated by Zr, H-mordenite catalyst. Comparative analysis of products derived from alkylation of 1-naphthol and 1-ethoxy naphthalene with ethanol showed that aromatic ester is not intermediate in the synthesis of 2 and 4-ethyl naphthols. Keywords: 1-naphthol, 1-ethoxy naphthalene, ethanol, alkylation, mordenite-zirconia, catalyst, 2-ethyl-1-naphthol, oxo-compounds, comparative analysis. C₁-C₁ alkyl derivatives of naphthols are used in the production of vitamins, dyes, additives (1-2). They are mainly obtained by synthetically methods, and the alkylation of 1 and 2 naphthols with alcohols are more prominent in these methods. The complexity of these methods, which has been studied with the participation of some catalysts (3-4), is characterized by the presence of side-effects. Consequently, this leads to the acceleration of technology and the emergence of environmental problems and adversely affect the cleanliness, exit, and selectivity of the products. The article presents the comparative results of the study of alkylation of 1-naphthol and 1 ethoxy naphthalene with ethanol in the participation mordenite-zirconia catalyst.*

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I. EXPERIMENTAL PART

The experiments were carried out within 1 hour the catalyst's of the laboratory equipment equipped with a flow-type reactor, and the analysis of the products was conducted by chromatographic and spectral methods. The analysis of naphthol and its ethyl homologs was performed in combined column (3.6 m x 4.0 mm). At the beginning of the column, 1/3 part was filled with 10% Apiezon M adsorbed tcelit 545 and the remaining portion 10% Karbovoks is placed on the chromosorb W, 20m in the impregnated phase. The analysis was carried out pre-programmed by way of increasing the temperature at 8° C/min at 120-240°C temperature. The consumption of helium taken as a gas carrier was 60 ml/min and the relative error was 3.0%. Spectral analysis of pure (≥ 99.0%) reaction products obtained by vacuum rectification was performed on UR-20 and M-80 devices. Synthetic mordenite (SiO₂ / Al₂O₃ x = 10 ÷ 32) containing zirconium are considered when synthesizing, the activity of the mordenite catalyst depends on the amount of sodium contained in it and the ratio of silicon oxide to mole ratio in aluminum oxide (5). On the other hand, this ratio increases as the result of aluminization, the adsorption volume and the pores increase, the number and strength of the acid centers change. Thus, the activity and selectivity of mordenite catalysts can be adjusted by change of aluminization. Increasing the ratio of SiO₂ / Al₂O₃ is possible by various methods, including increasing the contact time of zeolites and acids, increasing the number of acids refinery and increasing the acid solution. On the other hand, the addition of acid solutions can lead to the breakdown of the crystal structure of mordenite at the short contact time. It has been possible to regulate the degree of aluminization due to the slight disintegrate of the crystal structure of mordenite by changing the concentration of HCl solution (1-8 N), the temperature of processing (25-100°C) and duration (0.5-5 h). The initial Na-mordenite (x = 10) was obtained after the hydrogen and ammonium forms were processed with HCl and NH₄Cl solutions. For this purpose, first, 4 hours at 150°C with

the selected solid (1n) NH_4Cl solution, then during 5 hours at 100°C with 2 n HCl solution mordenite cationization and aluminization process was carried out. The zeolite washed with distilled water until the chlorine ions disappeared and then thermally was processed within the range of $150\text{--}600^\circ\text{C}$ for 5 hours. Its absorption volume was determined by the mass change of the mordenite sample remaining in the medium of water and benzene vapors at 24 hours. Depending on the number of processing of H-mordenite chloride acid, the aluminization degree has been obtained. Zirconium was replaced by zeolite (H-mordenite + Al_2O_3) by ion substitution and its content was 0.1-2.5% mass. At that time, its sulfate solution was used. The crystallization rate of H-mordenite is 95.0% when $x = 18$, and 90.5% when $x = 32$. Investigating the composition of the catalysts from the reaction of 1-naphthol with ethanol with the participation of Zr, H-mordenite catalyst, and the analysis of reaction parameters prove that the process is complex and numerous conversions occur (Table 1). The main reaction products of ethyl naphthols at low temperatures ($300\text{--}3400^\circ\text{C}$) and at high temperatures ($360\text{--}4200^\circ\text{C}$) are the alkyl ($\text{C}_1\text{--}\text{C}_2$) homologs of naphthalene, as well as the presence of 1-ethoxy naphthalene and various oxo compounds in catalysis confirms what we mentioned. For this reason, identification of major and side effects processes occurring in the process, and finding consistent and parallel reactions appear to be one of the important issues. -oxo-2, 2-diethyl-1, 2-dihydro naphthalene and 1-oxo-4, 4-diethyl-1, 4-dihydro naphthalene in products are derived from the interaction of 1- naphthol with ethanol. It is believed that these compounds are intermediates in the acquisition of alkyl ($\text{C}_1\text{--}\text{C}_2$) homogenous with naphthalene and 1-ethoxy naphthalene (6, 7). On the other hand, to identify the role of 1-ethoxy naphthalene in the production of 2-ethyl-1-naphthol and 4-ethyl-1-naphthol which are the targeted products is of interest. herefore, conversion of 1-ethoxy naphthalene with Zr, H-mordenite catalyst and ethanol was investigated. The main purpose of the research is to determine the position of 1-ethoxy naphthalene in the reaction mixture under given conditions which are obtained from the interaction of 1-naphthol with ethanol actually, to determine whether was obtained by the intermediate or parallel scheme. he research was carried out at a temperature of $300\text{--}3800^\circ\text{C}$. 1- ethoxy naphthalene at 1: 5 and $\nu\text{--}1.0$ st-1 at the mole ratio of ethanol. The results obtained are listed in the table. To facilitate comarison, the results of the interaction of 1 naphthol with ethanol ($\nu = 1: 5$ mol/mol) are shown in that table.ubstances in water and gases phase, other than non-reacting ethanol as well as the chemical composition of the products are 41.1-42.8 w %, with both cases brought to 100%.

Comparative analysis of the results of 1-ethoxy naphthalene and alkylation of 1-naphthol with ethanol in the participation of Zr, H- mordenite catalyst allowed to determine the following.

1. The difference between 1-ethoxy naphthalene and 1-naphthol conversion is 2.7-6.4% in the interaction with ethanol.
2. Ethylation reaction does not occur according to carbon in the nucleus, and 2-ethyl-1-methoxy naphthalene is not practically obtained. In the ethylation of 1- naphthol with ethyl ester partially deethylation is occurred and by the same time 1- naphthol obtain. The fact is that as the temperature increases, the rate of this reaction decreases partly, and the concentration of the naphthol taken in alkylation is decreased by two times and is 2.0 w % at 3800°C .

The conversion reaction of 1-ethoxy naphthalene to ethyl naphthol is by its basic transformation compared to partial. Particularly, 5.9-7.0% 2-ethyl-1-naphthol obtained from 1-ethoxy naphthalene at low temperature ($300\text{--}3400^\circ\text{C}$), 3-5 times less than this product taken by other reaction. On the other hand, leads to the molecule isomerization of 1-ethoxy naphthalene with 2-ethyl-1-naphthol. This reaction occurs slowly. This is clearly observed when investigating the chemical composition of the reaction products. So even at a temperature of 3000°C , the concentration of 2-ethyl-1-naphthol less than 2 times compared to naphthalene alkyl homologs. Increasing the temperature to 3800°C does not actually affect the concentration of the 2-ethyl-1-naphthol obtained in alkylation but partly increases the concentration of the other isomer 4-ethyl-1-naphthol. However, the mass fraction of this isomer is twice less than that of 1-naphthol and 4-ethyl-1-naphthol obtained from ethanol. At the low temperature with the presence of some catalysts (8-9), phenols and methyl phenols of cresols were obtained as intermediates, then converted into mono- and dimethylphenols. In our case, this hypothesis is not correct. Rather, at temperatures of 3200°C with the participation of catalytic systems which is the acid-base properties are adjusted and fundamental ideas about methylation of carbon in the phenol nucleus and denial of the ether mechanism (4, 10-12) may also be considered for the reaction of 1- naphthol to ethanol.

Other different aspects of the conversion of 1-ethoxy naphthalene with the presence of ethanol, among the products received, is the presence of 1-oxo-2,2-diethyl-1,2-dihydro naphthalene and naphthalene alkyl ($\text{C}_1\text{--}\text{C}_2$) concentrations of homologs is more than enough. The concentration of 1-oxo-2,2-diethyl-1,2-dihydro naphthalene derived from the interaction of 1 naphthol with ethanol at temperatures of 3000°C is twice as high as the concentration of 1-ethoxy naphthalene, it is 12 times less than the concentration of alkyl ($\text{C}_1\text{--}\text{C}_2$) homologs of naphthalene. The reaction of 1-oxo-2,2-diethyl-1,2-dihydro naphthalene on the interaction of 1-ethoxy naphthalene with ethanol and the reactions of 1,2-diethyl naphthalene and another alkyl ($\text{C}_1\text{--}\text{C}_2$)

homologs taken on its basis are predominant in other temperatures when compared to the 1-naphthol-ethanol system. It is given in the table from the analysis of the results. Thus, if 1-ethoxy naphthalene was obtained from the interaction of 1-naphthol with ethanol and subsequently subjected to transformation, then the chemical composition of the reaction products would be quite different. On the other hand, 46.7% at 3400C, 72.2% at 3800°C, the conversion of 1 ethoxy naphthalene in these conditions is negligible (3400°C) or is generally not taken (T-3800°C) in the reaction of 1-naphthol with ethanol. In conclusion, can be partially affected by the above-mentioned conversions of 1-ethoxy naphthalene, which is received in the small quantities parallel method in the interaction of 1 naphthol with ethanol at a temperature of 3400°C. In the reaction of 1-naphthol with ethanol, the role of this compound in the reaction is not large. On the other hand, the inclusion of it into the raw material which is obtained in the reaction, it will not damage the performance of the process. However, circulation in 1-ethoxy naphthalene systems that are taken at only low temperatures can prevent the subsequent increase in its quantity. As a result of this study, it was determined that 1-ethoxy naphthalene derived from the interaction of 1-naphthol with ethanol did not play the role of intermediate substance in the getting of ethyl naphthols. 1-ethoxy naphthalene ethanol and Zr was taken from the parallel mechanism are converted to alkyl (C₁-C₂) naphthalenes in the presence of H-mordenite catalyst. The received results are of exceptional importance in the process of kinetic research and the development of the kinetic model in the development of trends of the process.

Table 1. Comparative results of the interaction of 1-ethoxy naphthalene and 1-naphthol with ethanol in the presence of Zr, H-mordenite.

The reaction conditions are: $\nu = 1.0$ st-1, $\nu = 1: 5$ mol/mol

The name of the indicator	The name of the methylated reagents					
	1-epoxy-naphthalene	1 naphthol	1-epoxy-naphthalene	1 naphthol	1 -epoxy-naphthalene	1 naphthol
Temperature, °C	300	300	340	340	380	380
Obtained, by w %						
Including 1-ethoxy naphthalene	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
Dimethylenaphthols	-	-	-	-	0.5	2.4
1-oxo-2,2-diethyl-1,2-dihydro naphthalene	3.0	1.9	2.8	1.0	1.6	-
Naphthalene	1.5	-	1.6	-	4.0	2.4
1,2-diethyl naphthalene	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 1 Ethoxynaphthalene, %	27.4		46.7		72.2	

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