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ABSTRACT

of the dissertation for the degree of Doctor of Philosophy

**DEVELOPMENT OF A METHOD FOR OBTAINING C₂-C₃
ALKYLPHENOLS BY ALKYLATION OF PHENOLS WITH
ALCOHOLS**

Speciality: 2314.01- Petrochemistry

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GENERAL DESCRIPTION OF WORK

Research issue rationale and development rate. In terms of production scale, among the alkyl derivatives of phenol, nonyl and octylphenols are followed by its methyl, ethyl, propyl and butyl homologues.

The raw material base of low-molecular alkyl (C_1 - C_3) phenols has long been considered to be coal tar, and the concentration of phenols in it decreases with the increase of the alkyl group. Since such mixtures, consisting mainly of phenols and cresols and partly of xylenol, ethylphenol and trimethylphenols, do not satisfy the need for these products, other methods of their preparation have been developed.

Such methods are based on the processes of sulfonation, oxidative decarboxylation, oxidation, alkylation, but although some of these processes are used in industry, there is a great need for their development, improvement and reconstruction. Thus, most of these processes are characterized by multi-stage complexity, are difficult to manage and are not widely used due to high capital costs.

From an economic, technological and environmental point of view, the alkylation process takes a special place in the production of low molecular weight alkyl phenols. However, the method of obtaining various alkylphenols by alkylation of phenols with alcohols and olefins has not yet been resolved at the level of the requirements of modern petrochemistry. The creation of effective and universal catalytic systems for these processes, the development of simple continuous and low-emission methods is one of the urgent problems and always attracts the attention of scientists.

We are talking about mono-, di-, trimethyl, ethyl and propyl homologues of phenol. Because on the basis of these valuable semi-finished products resins, stabilizers, plasticizers, antioxidants, vitamins, pesticides, special liquid mixtures used in oil production and well construction are produced.

Object and subject of research. The object of research is the catalytic alkylation of phenol and its monomethyl homologues with C_1 - C_3 alcohols. The subject of research was the development of a

method for the continuous production of C₁-C₃-alkylphenols in the presence of a catalyst based on manganese-modified cobalt ferrite and PdCaY zeolite.

Aims and objectives of the research. Study of the alkylation reaction of phenols and monomethylphenols with C₁-C₃ alcohols in the presence of oxides and zeolite catalysts of various compositions, study of the physicochemical bases of the interaction of 2-methylphenol with methanol in the presence of an established catalytic system, development of methods for the production of 2,6-dimethylphenol, as well as mixture 2,6- and 2,4-xylenols.

In this regard, the following questions were raised and resolved in the thesis:

- Comparative study of the catalytic properties of ternary catalytic systems (MFe₂O₄·γ-Al₂O₃) containing 25 wt% MFe₂O₄ (M - Mg, Zn, Co, Cu), as well as zinc-modified cobalt ferrite (ZMCF) and manganese-modified cobalt ferrite (MMCF) catalysts in the alkylation reaction of 2-methylphenol with methanol.

- Study of the activity and selectivity of palladium-containing zeolites (Pd, H-mordenite, PdCaY, Pd-ZSM-5) in the alkylation reaction of 2-methylphenol with methanol.

- Study of the alkylation reaction of 2-, 3- and 4-methylphenols with methanol in the presence of an effective catalyst MMCF (Co_{0.9}Mn_{0.1}Fe₂O₄·γ-Al₂O₃).

- Investigation of the process of alkylation of cresols with methanol and phenol with C₁-C₃ alcohols in the presence of a modified ferrite catalyst.

- Study of the catalytic properties of PdCaY zeolite in the alkylation reaction of cresols with methanol and ethanol.

- Study of the regularities of the process of obtaining 2,6-dimethylphenol by alkylation of 2-methylphenol with methanol in the presence of the MMCF catalyst, development of a kinetic model of the process and theoretical technological optimization.

- Study of stable working time and regeneration conditions for MMCF catalyst and PdCaY zeolite, study of the effect of various diluents on the process, development of a method for continuous

production of 2,6-dimethylphenol based on 2-methylphenol and methanol.

Research methods. The alkylation process was investigated in an extraction reactor containing fixed bed ferrite and zeolites containing palladium. In addition to classical methods, modern physicochemical methods were used in the analysis and verification of the purity of raw materials and products. Chromatographic analysis was performed on Chrom-5 and Chromatex-Crystal-5001 instruments, spectral analysis on a BS487B instrument of Tesla firm (80 MHz), and for kinetic studies and optimization we used the MATLAB software.

Basic theses for defence:

- comparative analysis of the results of cobalt ferrites modified with zinc and manganese, which differ in activity and selectivity among the obtained ferrite catalysts, in the alkylation reaction of 2-methylphenol with methanol;
- study of the catalytic properties of palladium-containing zeolites in the alkylation of 2-methylphenol with methanol and the results of alkylation of cresols with methanol and ethanol in the presence of the selected PdCaY;
- preparation of individual xylenol isomers and target mixtures of isomers by alkylation of 2-, 3-, and 4-methylphenols with methanol in the presence of an effective MMCF catalyst;
- peculiarities of phenol alkylation with C₁-C₃ alcohols in the presence of a modified ferrite catalyst;
- kinetic studies, kinetic model and theoretical technological optimization of the 2,6-dimethylphenol production process based on 2-methylphenol and methanol in the presence of the MMCF catalyst;
- influence of diluents on the stable lifetime of catalysts in the production of 2,6-dimethylphenol based on 2-methylphenol and methanol and development of a continuous method;
- high catalytic and operational properties of PdCaY in the process of obtaining a mixture of 2,6- and 2,4-dimethylphenols by alkylation of 2-methylphenol with methanol.

Scientific novelty of the research. The activity and selectivity of ferrite catalysts (MFe₂O₄·γ-Al₂O₃; M – Mg, Zn, Co, Cu) and

palladium-containing zeolites (Pd, H-mordenite, PdCaY, Pd-ZSM-5) were first studied in the alkylation of 2-methylphenol with methanol. The high *o*-selectivity of the manganese-modified cobalt ferrite catalyst ($\text{Co}_{0.9}\text{Mn}_{0.1}\text{Fe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$) and its versatility in the alkylation of phenols with alcohols have been established. Selective synthesis of *o*-alkylphenols became possible due to the interaction of 2-, 3- and 4-methylphenols with methanol and ethanol and alkylation of phenol with propanols. The selectivity of the corresponding target products (2,6-dimethylphenol, 2,4-dimethylphenol, 2,5- and 2,3-dimethyl mixtures) obtained by the interaction of cresols (ortho-, para-, meta) with methanol is 89.8-94.0%, the yield is 32.8-37.7%, the selectivity of 2-ethyl-6-methyl mixture obtained by alkylation of 2-, 3-, 4-methylphenols with ethanol is 86.5-90.5%, and the yield is 33.4-40.3%. Alkylation of phenol with 1- and 2-propanol in the presence of a ferrite catalyst gives 2-propyl (isopropyl) phenol with the selectivity of 87.0-88.5% and the yield of 43.9-47.4%. PdCaY from the investigated palladium-containing catalysts makes it possible to obtain a mixture of 2,6- and 2,4-dimethylphenols (molar ratio 0.9:1.0) based on 2-methylphenol and methanol more selectively (91.5%) and with a higher yield (43.9%). Other isomers and mixtures of diisomers of dimethylphenols are obtained by the reaction of cresols with methanol using PdCaY, and the target ethyl derivatives are obtained by alkylation with ethanol. As a result of kinetic studies of the alkylation reaction of 2-methylphenol with methanol with the participation of the MMCF catalyst, the kinetic parameters were calculated and a theoretically substantiated kinetic model of the 2,6-dimethylphenol production process was developed.

Theoretical and practical significance of the research. A process has been developed for the production of alkyl ($\text{C}_2\text{-C}_3$) phenols based on phenol, cresol, xylenols, and $\text{C}_1\text{-C}_3$ alcohols using the MMCF catalyst and PdCaY zeolite. As a result of kinetic studies, optimization curves were constructed between operating parameters and extreme criteria on the basis of the obtained adequate kinetic model of the alkylation process of 2-methylphenol with methanol and a flexible process flow diagram of the continuous production of 2,6-dimethylphenol was presented. The production of $\text{C}_2\text{-C}_3$ -alkylphenols

by the proposed method competes with existing methods, and its use in industry can make the production of these valuable semi-finished products more profitable.

Approbation and implementation of research. The results of the dissertation were presented at the following scientific conferences: International Scientific Conference "Functional Monomers and Special Polymeric Materials, Problems, Prospects and Practical Views" (Sumgait, 2017), X International scientific-practical conference of young scientists "Actual problems of science and technology" (Ufa, 2017), International scientific-practical conference "Oil refining and innovative development prospects of petrochemistry", dedicated to the 110th anniversary of academician V.S. Aliyev (Baku, 2018), the Fifth International Scientific Conference "Advances in Synthesis and Complexing" (Moscow, 2019).

13 scientific works on the topic of the dissertation have been published. 7 of them are articles and have been published in prestigious foreign journals (5 in foreign journals). Published scientific works fully reflect the content of the dissertation.

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

Personal participation of the author. The applicant is the responsible executor at each stage of solving the questions posed in the dissertation, the practical implementation of the research, the analysis, the analysis of the obtained results, the writing of abstracts and articles, the dissertation.

The total volume of the Dissertation with the volume of structural parts of the Dissertation. The dissertation consists of an introduction, 5 chapters, results and a list of references. The total volume of the dissertation is 161 pages, including 31 figures, 27 tables and a bibliography of 134 titles. The total volume of the dissertation (excluding figures, tables, graphs and bibliography) is 192092characters.

The main content of the dissertation. The introductory part substantiates the relevance of the topic, provides brief information

about the purpose and objectives of the work, scientific novelty, theoretical and practical significance, the main provisions of protection, approbation, structure and volume of work.

In the first chapter, the use of low-molecular-weight alkyl phenols is studied, and scientific works carried out in the field of methods for their preparation using the alkylation process are interpreted, critically analyzed and systematized.

The second chapter contains scientific information about the used raw materials and its physical properties, experimental devices and rules, methods of product analysis, as well as the composition and production of catalysts.

In the third chapter, the main results of the study of the alkylation reaction of phenols with C₁-C₃ alcohols in the presence of zeolites containing ferrite and palladium are presented.

In the fourth chapter, the results of kinetic studies of the process of alkylation of 2-methylphenol with methanol in a differential reactor and theoretical technological optimization based on the obtained kinetic model are presented.

In the fifth chapter, studies of the stable life of catalysts, the effect of diluents in the environment on their performance properties, and the results of the development of a flexible method for the production of C₂-C₃-alkylphenols are presented.

MAIN CONTENT OF THE WORK

Phenol, 2-, 3- and 4-methylphenols, 2,3- and 2,5-dimethylphenols, methanol, ethanol, 1- and 2-propanols were used as raw materials in the experiments, their purity was determined by chromatographic analysis and determination of physicochemical parameters.

Alkylation of 2-methylphenol with methanol in the presence of ferrite catalysts. Formerly, the reaction of alkylation of 2-methylphenol with methanol was studied in the presence of various catalysts. These catalyst systems include catalysts selected for their effectiveness in other alkylation processes and obtained in our department, including ferrites and palladium-containing zeolites.

Initially, the catalytic properties of various ferrite catalysts were studied to obtain 2,6-dimethylphenol in high yield and selectivity by the alkylation reaction of 2-methylphenol with methanol. For this, an iron ferrite ($\text{FeFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$) catalyst, a manganoferrite ($\text{MnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$) catalyst, a zinc ferrite ($\text{ZnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$) catalyst, a cobalt ferrite ($\text{CoFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$) catalyst, a zinc-modified cobalt-ferrite ($\text{Co}_{0.9}\text{Zn}_{0.1}\text{Fe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$) catalyst, and a manganese-modified cobalt ferrite ($\text{Co}_{0.9}\text{Mn}_{0.1}\text{Fe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$) catalyst were taken. In catalytic systems, the atomic ratio of the divalent metal to iron (III) was 1:2.33, and the mass fraction of the active component (MFe_2O_4) in the ternary system was 25.0 wt%. The experiments were carried out under the following conditions: temperature – 370°C, volumetric velocity or specific load of this raw material (ν) – 0.8 hr⁻¹, molar ratio of 2-methylphenol to methanol (ν) – 1:0.75.

The yields of 2,6-dimethylphenol and the conversion of 2-methylphenol were taken as a comparative criterion, which were calculated according to the converted and starting 2-methylphenol. Analysis of the obtained results (Table 1) made it possible to establish the following:

– Simple ferrites have lower technological characteristics than modified catalysts. Selectivity for 2,6-dimethylphenol decreases in the following order:

MMCFC > ZMCFC > $\text{CoFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ > $\text{FeFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ > $\text{MnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ > $\text{ZnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$.

Depending on the yield of the target product, the activity of the catalysts increases in a given order:

$\text{MnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ > $\text{ZnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ > ZMCFC > $\text{CoFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ > $\text{FeFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ > MMCFC

Higher conversion is achieved in the presence of $\text{FeFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ and in the presence of MMCFC. A low conversion rate is typical for the $\text{MnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ catalyst.

– As for the composition of alkylates, more complex mixtures are formed in the presence of the catalysts $\text{MnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$, $\text{ZnFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ and $\text{FeFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$. The selectivity for other xylenols (mixtures of 2,4- and 2,5-isomers) obtained in the presence of these

catalysts is 13.0%, 16.7% and 10.2%, respectively. The 2,5-isomer is not found in xylenols formed in the presence of other catalysts.

– In all cases, the alkylates also contain the 2,4,6-isomer of trimethylphenol, the yield of which, calculated according to the converted *o*-cresol, is 1.5-4.0%.

Table 1. Results of alkylation of 2-methylphenol with methanol in the presence of various ferrite catalysts. Reaction conditions: T – 370°C, $\nu = 0.8 \text{ hr}^{-1}$, $\nu=1:0,75 \text{ mol/mol}$

Indicator name	FeFe ₂ O ₄ · γ -Al ₂ O ₃	CoFe ₂ O ₄ · γ -Al ₂ O ₃	ZnFe ₂ O ₄ · γ -Al ₂ O ₃	ZMCFC	MMCFC	MnFe ₂ O ₄ · γ -Al ₂ O ₃
Alkylate yield, wt%	88.0	88.5	89.5	91.5	92.0	88.0
Yields calculated according to the converted 2-methylphenol, including						
2.6-dimethylphenol	85.8	88.8	80.5	89.0	92.0	81.0
Other dimethylphenols	10.2	8.5	16.7	8.6	6.5	13.0
Yield, calculated according to starting 2-methylphenol, of 2.6-dimethylphenol, %	33.5	32.9	25.7	31.1	35.5	19.4
2-Ethylphenol conversion, %	39.0	37.0	32.0	35.0	38.6	24.5
Methanol conversion, %	96.0	88.0	90.0	82.0	78.8	100

– In terms of the yield of the obtained alkylates (92.0%), the MMCF catalyst predominates. There is another important result of this catalyst. The yield, calculated according to converted methanol, of 2,6-dimethylphenol is 68.0%, and the total yield of methylation products is 75.0%. As can be seen, unlike other catalysts, the lowest methanol conversion in the MMCF catalyst results in a yield of 8-17.6% higher than other catalysts.

As a result of the analysis of all this, it was deemed expedient to select and use the MMCF catalyst for the selective and advantageous synthesis of 2,6-dimethylphenol by the alkylation reaction of 2-methylphenol with methanol.

Alkylation of 2-methylphenol with methanol in the presence of palladium-containing zeolites. Of particular importance are the studies carried out to determine the catalytic properties of some palladium-containing zeolites in the alkylation reaction of 2-methylphenol with methanol, the composition, structure, acid-base properties of which differ sharply from ferrite catalysts. Thus, in contrast to ferrites, these catalyst systems not only ortho-directors, but also make it possible to obtain other important xylenol isomers. Modified zeolites such as Pd, H-mordenite, PdCaY, Pd-ZSM-5 were taken as catalysts, and the weight content of palladium was 1.0 wt%. The modulus ($\text{SiO}_2/\text{Al}_2\text{O}_3$) in Pd,H-mordenite was $x=18$, $x=40$ in Pd ZSM-5, and the cation exchange rate in PdCaY was 85%. The activity and selectivity of the catalysts, as well as the molar ratio of the 2,6-isomer to the 2,4-isomer in the resulting mixture of xylenols, were taken as comparative indicators. First of all, it should be noted that the alkylation of 2-methylphenol with methanol in the presence of all three catalysts gives mainly 2,6- and 2,4-xylenolols (Table 2).

When Pd, H-mordenite is used, the overall selectivity for these isomers is 87.5%, while in the case of Pd-ZSM-5 zeolite this indicator is 90.8%. Total selectivity, calculated according to converted 2-methylphenol, of 2,6- and 2,4-dimethylphenols higher (91.5%) in the presence of PdCaY. On the other hand, the alkylate with a higher weight content of the 2,4-isomer in the mixture of 2,6-

Table 2. Results of alkylation of 2-methylphenol with methanol in the presence of palladium-containing zeolites. Reaction conditions: $T = 370^\circ\text{C}$, $v = 0.6 \text{ hr}^{-1}$, $\nu=1.0:0.75$ mol/mol and 2,4-dimethylphenols is also obtained using the PdCaY zeolite.

Indicator name	Catalyst		
	Pd,H- mordenite	PdCaY	Pd-ZSM-5

Alkylate yield, wt%	89.5	91.5	90.0
Yields calculated according to converted 2-methylphenol, including			
2.6-dimetilfenol	44.0	45.5	50.0
2.4-dimetilfenol	43.5	47.0	40.8
2.5-dimetilfenol	2.5	1.5	2.0
2.4.6-trimetilfenol	8.5	3.5	6.0
Total yield, calculated according to starting 2-methylphenol, of 2.6- and 2.4-dimethylphenols, %	34.1	43.9	40.0
Conversion of 2-methylphenol, %	39.0	47.5	44.0
Methanol conversion, %	90.0	82.5	93.5

In this case, the molar ratio of the 2,4- and 2,6-isomers is 1:0.97. This ratio is 1:0.81 for Pd-ZSM-5 and 1:1 for Pd,H-mordenite catalyst. In contrast to the PdCaY zeolite, the sequential alkylation of 2,6- and 2,4-dimethylphenols in palladium-modified mordenite and pentacil proceeds faster, and the 2,4,6-trimethylphenol concentration in the resulting alkylates increases by ~2 times. In addition, it was found that the concentration of 2,5-dimethylphenol, another isomer of xylene, was partially increased compared to PdCaY in the presence of these catalysts.

These conditions lead to a significant decrease in the total selectivity of 2,6- and 2,4-dimethylphenols, which are the target isomers in the alkylation reaction. Among the studied catalysts the higher conversion of 2-methylphenol belongs to PdCaY (47.5%).

In Pd-ZSM-5 this indicator is 44.0%, and in Pd,H-mordenite - 39.0%. Methanol conversion is higher in the presence of Pd-ZSM-5 (93.5%), but most of it is spent on side reactions. This also occurs in small amounts in Pd,H-mordenite. The lowest alcohol conversion is achieved in the presence of PdCaY. The total selectivity, calculated according to converted methanol, of 2,6- and 2,4-xylenols in the presence of this catalyst, is significantly higher than that of other zeolites (61.5%). Regarding the total yield of 2,6- and 2,4-

dimethylphenols, which are the main indicators, it appears that the PdCaY zeolite is more active than other zeolites. Thus, the total yield, calculated according to the starting 2-methylphenol, of 2,6- and 2,4-xylenols in the case of PdCaY is 43.9%, exceeding Pd-ZSM-5 by 3.9%, Pd, H-mordenite by 9.9%.

Preliminary studies have shown that the PdCaY zeolite is of greater practical importance for the synthesis of 2,6- and 2,4-dimethylphenols by the interaction of 2-methylphenol with methanol.

Further detailed studies were carried out in the presence of an efficient MMCF catalyst and PdCaY zeolite.

Alkylation of cresols with methanol and ethanol in the presence of the MMCF catalyst. The alkylation reaction of cresols with methanol in the presence of the MMCF catalyst was studied in the following range of operating parameters: $T - 310-400^{\circ}\text{C}$, $v - 0.4-1.2\text{hr}^{-1}$, $\nu=1.5-1-1-1.5$.

Alkylates formed by the reaction of 2-methylphenol with methanol contain unconverted methanol and 2-methylphenol, the resulting 2-methylanisole, 2,6-dimethylphenol, other xylenol isomers, including 2,4-dimethylphenol, and mainly 2,4,6- isomer from trimethylphenols (Table 3). The amount of gaseous products is small and consists of formaldehyde, methyl formate and carbon oxides.

The products of the alkylation reaction of 3-methylphenol with methanol contain 3-methylanisole, 2,5- and 2,3-dimethylphenols and trimethylphenols, mainly 2,3,6-isomers (Table 3). Alkylates also include unconverted 3-methylphenol and methanol. The composition of the gaseous products corresponds to the composition of the gas mixture formed by the interaction of 2-methylphenol with methanol.

Table 3. Comparative results of the alkylation reaction of methylphenols with methanol in the presence of the MMCF catalyst. Reaction conditions: $T - 370^{\circ}\text{C}$, $v - 0.8\text{hr}^{-1}$, $\nu=1:0.75\text{ mol/mol}$

Alkylate composition and indicator name	Composition of raw materials		
	2-methylphenol methanol	3-methylphenol methanol	4-methylphenol methanol

Received, in wt.%, including			
Unconverted methanol	3.5	3.0	3.1
2-, 3- and 4-methylanisole	-	0.3	0.5
Unconverted cresol	51.3	50.0	50.5
2.6-dimethylphenol	33.5	-	-
2.5- dimethylphenol	0.4	18.5	-
2.3- dimethylphenol	-	17.0	3
2.4- dimethylphenol	2.2	-	33.5
Other dimethylphenols	-	1.2	2.5
Trimethylphenols	0.2	0.6	0.5
Water	6.7	7.2	7.0
Gas + loss	2.1	2.2	2.4
Cresol conversion, %	35.6	40.1	39.5
Methanol conversion, %	78.8	81.8	81.2
Yields calculated according to converted cresol, %			
2.6- dimethylphenol	92.0	-	-
2.4- dimethylphenol	5.8	-	89.8
2.5- dimethylphenol	0.6	49.0	-
2.3- dimethylphenol	-	45.0	-

Alkylates obtained by alkylation of 4-methylphenol with methanol contain 4-methylanisole, 2,4-dimethylphenol, the 2,5-isomer from other xylenols, and 2,4,6-trimethylphenol (Table 3). The products of side reactions of methanol, as mentioned above, are the main component of the gas mixture. At low temperatures (310-340°C), parallel alkylation is observed at the oxygen (O-) and carbon (C-) atoms in the 2-methylphenol molecule. As the temperature rises ($\geq 370^\circ\text{C}$), carbon methylation appears as the main direction of the process. In fact, 2-methylanisole is not obtained under these conditions (Table 3).

This is repeated when 3-methylphenol or 4-methylphenol reacts with methanol. In other words, the alkylation reaction of all three isomers of cresol with methanol at $\geq 370^{\circ}\text{C}$ occurs via the mechanism of electrophilic substitution at the *o*-position of the carbon atom in the methylphenol nucleus. As a result, 2,6-dimethylphenol based on 2-methylphenol and methanol, 2,4-dimethylphenol based on 4-methylphenol methylation are obtained with high selectivity. The yield, calculated according to converted cresol, of the 2,6-isomer is 92.0%, and the yield of 2,4-dimethylphenol is 89.8%. As for 3-methylphenol, it should be noted that methylation occurs competitively, because both carbon atoms in the *o*-position in its molecule are empty. The total yield of the resulting mixture of 2,5- and 2,3-dimethylphenols is 37.7%, the total selectivity is 94.0%, and the molar ratio of 2,5- and 2,3-isomers is 1:0.9. Under these conditions ($T = 370^{\circ}\text{C}$, $\nu = 0.8 \text{ hr}^{-1}$, $\nu=1:0.75 \text{ mol/mol}$), the yield of 2,6-dimethylphenol and 2,4-dimethylphenols obtained by the interaction of 2- and 4-methylphenols with methanol is 32.8 and 35.5%, respectively.

The interaction of cresols with ethanol was studied with the aim of confirming the universality of the properties of the selective alkylation catalyst MMCF on the example of other alcohols.

The reaction products obtained from the alkylation of 2-methylphenol with ethanol include *o*-cresol ethyl ester, 2-ethyl-6-methylphenol (2E6MP), 2,4-diethyl-6-methylphenol (2,4-DE6MP), and other monoethyl derivatives 2-methylphenol.

The reaction of 3-methylphenol with ethanol gives mainly 2-ethyl-5-methylphenol (2E5MP), 2-ethyl-3-methylphenol (2E3MP), ethyl 3-methylphenol and other monoethyl derivatives of *m*-cresol.

Alkylation products of 4-methylphenol with ethanol include *p*-cresol ethyl ester, 2-ethyl-4-methylphenol (2E4MP), 2-methyl-4-ethylphenol (2M4EP), 2,6-diethyl-4-methylphenol (2.6 DE4MP), 3-ethyl 4-methylphenol (3E4MP).

It can be seen from the analysis of the results obtained that the alkylation reaction of cresol with ethanol also proceeds mainly by the mechanism of electrophilic substitution in the carbon atom of the *o*-position in the nucleus. The proportion of alkylation at the oxygen

atom is small and sharply decreases with increasing temperature. Ethanol side reactions include dehydrogenation and partial intermolecular dehydration reactions.

Comparative results on the yield and selectivity of the target products obtained by the alkylation reaction of cresols with methanol and ethanol are shown in Figure 1.

As can be seen, the results of the alkylation reaction of cresols with methanol and ethanol attract attention. In both cases, the *o*-direction property of the MMCF catalyst is obvious. The selectivity of the target products obtained under the same reaction conditions ($T = 370^{\circ}\text{C}$, $v = 0.8 \text{ hr}^{-1}$, $\nu=1:0.75 \text{ mol/mol}$) is slightly higher in the presence of methanol than that of ethanol. The selectivity of the target products obtained by the interaction of cresols with methanol (2,6-dimethylphenol, a mixture of 2,5- and 2,3-dimethylphenols and 2,4-dimethylphenol) is 89.8-94.0%, the selectivity of the main ethyl derivatives of cresol formed by the interaction of monomethylphenols with ethanol (2E5MP, 2E6MP, 2E6MP) is in the range of 86.5-90.5%. As for the yield of similar target products, the yield of suitable compounds obtained by alkylation of cresols with methanol ranges from 32.8-37.7%, and the yield of target products obtained as a result of alkylation of monomethylphenols with ethanol ranges from 33.4-40.3%.

Analysis of these results shows that the reactor block can act as a universal reaction apparatus when the alcohol in raw materials is methanol or ethanol, without changing the reaction mode in the presence of the MMCF catalyst. In other words, by changing the isomer of cresol and alcohol, it is possible to obtain the above-mentioned isomers of dimethylphenols and target *o*-ethyl derivatives of cresol with high technological parameters (yield, selectivity, conversion of monomethylphenol). It is possible to organize the production of these valuable products by making small improvements in the subsequent processing of the obtained products and by setting up a rectification unit.

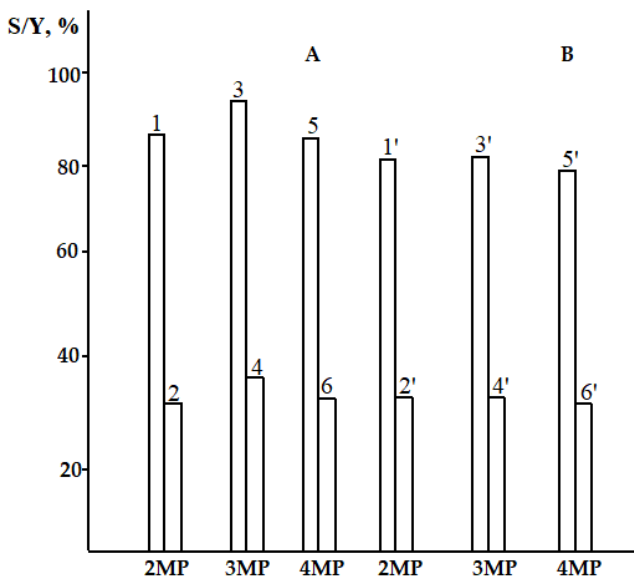


Figure 1. Selectivity for the target product obtained by alkylation of 2-, 3- and 4-methylphenols with methanol (A) and ethanol (B) (1, 3, 5 and 1', 3', 5'), and their yields (2, 4, 6 and 2', 4', 6'). Reaction conditions: $T - 370^{\circ}\text{C}$, $\nu - 0.8 \text{ hr}^{-1}$, $\nu=1:0.75 \text{ mol/mol}$.

1, 2 – 2,6-dimethylphenol, 3, 4 – mixture of 2,5 and 2,3-dimethylphenols, 5, 6 – 2,4-dimethylphenol, 1', 2' – 2-ethyl-6-methylphenol, 3', 4' – mixture of 2-ethyl-5-methylphenol and 2-ethyl-3-methylphenol, 5', 6' – 2-ethyl-4-methylphenol.

Alkylation of phenol with propanol in the presence of various catalysts. As a logical continuation of the study, the activity and selectivity of the MMCF catalyst in the alkylation of phenol with propanol were tested, and these results were compared with the results obtained with other catalysts.

Ferrites and palladium-containing zeolites were used as catalysts.

The yields, calculated according to starting phenol, of 2-propyl and 2-isopropylphenols obtained by alkylation of phenol with 1- and 2-propanols in the presence of the studied catalysts, are shown in Figure 2. It can be seen from the analysis of the results that branching of the alkyl group in the molecule of 2-alkylphenols obtained in the

presence of o-alkylating catalysts $\text{CoFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$ and MMCF systems, their yield decreases by 3.3-4.5%. A slight decrease in these yields is also observed in the presence of Pd-ZSM-5- and Pd,H-mordenite. In contrast to these catalysts, the yield of 2-isopropylphenol obtained in the presence of a PdCaY catalyst is 4.6% higher than the yield of 2-propylphenol. Selectivity to 2-propyl or 2-isopropylphenols obtained by the reaction of phenol with propanols is most often observed in the MMCF catalysts, amounting

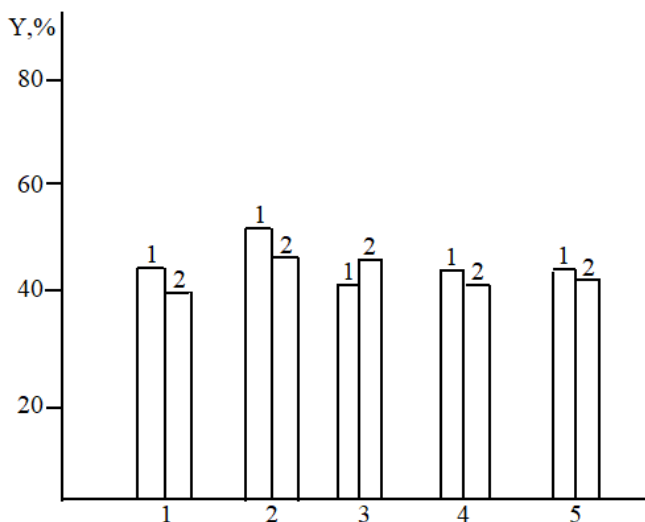


Figure 2. Yields of 2-propylphenol (1) and 2-isopropylphenol (2) obtained by alkylation of phenol with propanol and isopropanol in the presence of various catalysts. 1 – Cobalt ferrite catalyst, 2 – MMCF, 3 – PdCaY, 4 – Pd,H-mordenite, 5 – Pd-ZSM-5. Reaction conditions: $T - 350\text{ }^\circ\text{C}$, $v - 0.8\text{ hr}^{-1}$, $v=1:1\text{ mol/mol}$.

to 88.5 and 87.0%, respectively. And the lowest values are for the Pd-ZSM-5 zeolite and the selectivity of this catalyst according to o-alkylation is 68.0 and 66.5%, respectively. The MMCF catalyst is still characterized by higher yields in the synthesis of 2-propylphenol (47.3%). Higher yields for 2-isopropylphenol were obtained in the presence of PdCaY (46.2%).

Thus, the MMCF catalyst makes it possible to obtain *o*-propyl and *o*-isopropyl phenol derivatives by the alkylation method, and the results obtained are of practical importance.

Alkylation of cresols with methanol and ethanol in the presence of PdCaY zeolite. Unlike the *o*-alkylation catalysts used in the alkylation reaction of cresols with methanol, the PdCaY zeolite also exhibits special properties in the preparation of other xylene isomers in this process. Preliminary studies have shown that the interaction of 2-methylphenol and methanol forms a mixture of 2,6- and 2,4-dimethylphenols with a selectivity of 92.5%. This is a fairly high value for a single conversion of 2-methylphenol (47.5%).

In this regard, we considered it important to carry out special studies for a more detailed study of the catalytic properties of this catalytic system.

The effect of temperature, volumetric velocity, and molar ratio of raw material components on the yield of products obtained in the reaction of alkylation of cresols with methanol and conversion of cresol has been studied.

For example, when the concentration of methanol in the starting raw material is 16.7 wt%, the conversion of cresols decreases and the total selectivity of the obtained target xylenol isomers increases. Thus, the total selectivity of the mixture of 2,6- and 2,4-dimethylphenols obtained in the presence of 2-methylphenol was 92.0%, the selectivity of 2,4-dimethylphenol formed by the reaction of 4-methylphenol with methanol was 86.0 % and the total selectivity of a mixture of 2,5- and 2,3-dimethylphenols obtained by alkylation of 3-methylphenol with methanol was 90.0%. With regard to the yield of the corresponding xylenols, calculated according to starting cresol, it should be noted that in the case of 2-methylphenol, the yield of a mixture of 2,6- and 2,4-xylenol is 35.0%, the yield of 2,4-dimethylphenol obtained from 4-methylphenol is 33.5%, the yield of a mixture of 2,5 and 2,3-xylenols obtained by alkylation of 3-methylphenol is 37.4%.

The fact that the concentration of alcohol in the raw material is 30.8 wt% negatively affects the productivity of the process in all three cases.

As you can see, the above results are of practical importance and make it possible to synthesize a mixture of 2,6- and 2,4-dimethylphenols, 2,5- and 2,3-xylenols and individual 2,4-dimethylphenol by the alkylation reaction of 2-, 3- and 4-methylphenols with methanol in the presence of PdCaY zeolite in high yield and selectivity.

Then the catalytic properties of the PdCaY zeolite were studied in detail in the alkylation reaction of 2-, 3-, and 4-methylphenols with ethanol. The composition of the obtained products is close to the composition of the catalyzate obtained in the presence of the MMOKF catalyst.

In figure 3 shows the effect of the specific load on the selectivity and yield of the target products obtained in the reaction of alkylation of monomethyl homologues of phenol with ethanol. As can be seen, at a low value of the specific load (0.3hr^{-1}), the yields, calculated according to converted cresol, of the target products obtained by the interaction of all three cresols with ethanol are the lowest. At this value of the volumetric velocity, the yields, calculated according to the starting cresol, are higher in all three cases. Thus, the total yield of 2E6MP and 2M4EP obtained from 2-methylphenol and ethanol is 47.0%, the yield of a mixture of 2E5MP and 2E3MP obtained from 3-methylphenol and methanol is 44.4%, the yield of 2E4MP, formed by alkylation of 4-methylphenol ethanol is 50.0%. In this case, the selectivity for the target products is 81.0, 74.0 and 80.0%, respectively. An increase in the specific load to 0.9hr^{-1} reduces the reaction rate by reducing the contact time, increases the selectivity of the target products and reduces their yield.

For example, the yield of 2E6MP and 2M4EP mixture obtained from 2-methylphenol and ethanol decreases to 39.5%. However, the

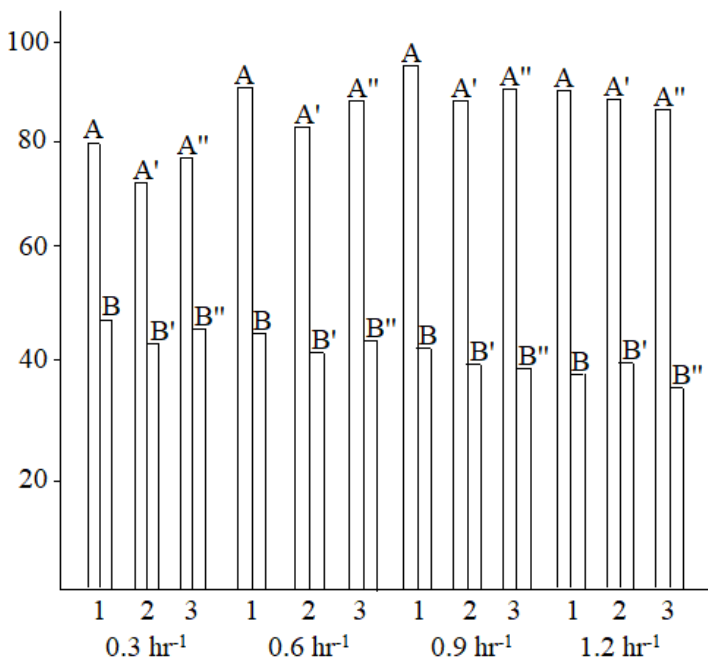


Figure 3. Effect of volumetric velocity (specific load) on the alkylation reaction of cresols with ethanol in the presence of PdCaY. 1,2-methylphenol, 2,3-methylphenol, 3,4-methylphenol. A, B – total yield of 2E6MP and 2M4EP mixture calculated according to converted (A) and starting (B) 2-methylphenol, %; A', B' – total yield of 2M5EP and 2E3MP mixture calculated according to converted (A') and starting (B') 3- methylphenol, %; A'', B'' – yield of 2E4MP calculated according to converted (A'') and starting (B'') 4-methylphenol, %.

selectivity of their formation increases to 94.0%. The yield of a mixture of 2E5MP and 2E3MP obtained by alkylation of 3-methylphenol with ethanol decreased by 7.5% to 36.9%, and the selectivity increased by 15.0% to 89.0%. Such changes are also characteristic of 4-methylphenol. In the case of v -0.9 hr⁻¹, the selectivity for 2E4MP, obtained by its interaction with ethanol, increases by 12.0% to 92.0%, and the yield decreases by 9.5% to 40.5%.

An increase in the specific load to 1.2 hr^{-1} changes the yield and selectivity of the target products obtained by alkylation of cresols with ethanol in a similar manner, but in a small amount.

The results obtained in the alkylation of cresols with ethanol under certain conditions are of practical importance and show that the ability of the PdCaY zeolite to *o*- and *p*-alkylation is high.

The characteristics of the phenol alkylation reaction with methanol, ethanol, and propanol in the presence of the MMCF catalyst depend on the reaction conditions, the composition of the alcohol used and its content in the reaction mixture. When analyzing the obtained results, the following arises:

- As the molecular weight of the alcohol used as an alkylating agent increases, the conversion of phenol under similar reaction conditions increases. In the presence of methanol, the conversion of phenol is $32 \div 45.0\%$, when ethanol is taken for alkylation under the same conditions, it is $34.5\text{-}48.5\%$. When the reaction with propanols is carried out under more favorable conditions ($T - 350^\circ\text{C}$, $v - 0.8 \text{ hr}^{-1}$), the high degree of phenol conversion is 53.5% in the presence of 1-propanol and 50.5% in the case of alkylation with 2-propanol. It should be noted that in a mixture of phenol with propanols, the equimolar ratio is preserved, the molar ratio of phenol to methanol and ethanol in the process of alkylation with other alcohols is taken as $1: 0.75\div 1$. The alkylation temperature with the last two alcohols was 370°C , and the volumetric velocity was 1.2 hr^{-1} . Another interesting result is that the branching of the structure of propanols reduces the one-time conversion of phenol.

- The main product of the alkylation reaction of phenol with all three alcohols is 2-alkylphenol. These features, which characterize the MMCF catalyst, are the main line of research [2, p.173]. The yield of 2-alkylphenol calculated according to the converted phenol is $78.0\text{-}87.0\%$ depending on the reaction conditions when alkylating with methanol, $79.5\text{-}87.5\%$ when alkylating with ethanol, 88.5% during the interaction of phenol with 1-propanol, 87.0% when phenol is alkylated with 2-propanol. It should be noted that the selectivity of 2-alkylphenol changes insignificantly depending on the composition and structure of the alcohol, but it should be noted that the value of this

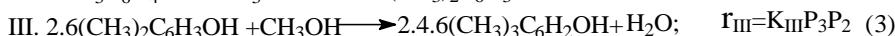
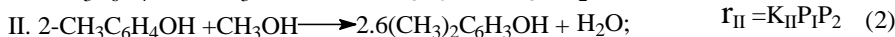
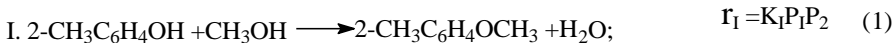
indicator, calculated according to the converted alcohol, differs more. Thus, the yield of 2-alkylphenol, calculated according to the converted alcohol, varies from 52.0 to 73.0% and decreases with an increase in the molar mass of the alcohol. In other words, as the molar mass of alcohol increases, the content of by-products in the presence of the MMCF catalyst increases and the propensity to alkylate decreases. Compared to zeolites, this occurs weaker.

–Another attractive result is a decrease in the rate of sequential alkylation with an increase in the molar mass of alcohol. This pattern manifests itself in the equimolar ratio of components in the raw material, as well as when the partial pressure of methanol is twice as high as that of phenol. Thus, the selectivity of 2,6-dimethylphenol obtained by the interaction of phenol with methanol is 9.5-22.0%, the selectivity for 2,6-diethylphenol obtained by alkylation of phenol with ethanol is 7.5-11.5%, the yield of 2,6-dipropylphenol obtained by the reaction of 1-propanol with phenol, calculated according to the converted phenol, is 5.0-8.5%, and the selectivity of 2,6-diisopropylphenol, formed when 2-propanol is used as an alkylating agent, is 8.0 -10.0%.

–As the molecular weight of the alcohol used as the alkylating agent increases, the yield of 2-alkylphenol increases. Thus, under the studied conditions, the yield of 2-alkylphenol, calculated according to the starting phenol, was 27.8-35.1% in the formation of 2-methylphenol, 30.1-38.6% in the formation of 2-ethylphenol, 40.0-47.3 % in the formation of 2-propylphenol, when the target product is 2-isopropylphenol, it was 38.5-43.9%. In the analysis of propanols, branching of the molecule reduces the yield of the formed alkylphenol.

Similar dependences are observed in the alkylation of cresols with methanol, ethanol, and propanol. This confirms that the MMCF catalyst studied by us exhibited similar catalytic properties during alkylation with all three alcohols.

Kinetic model and optimization of alkylation of 2-methylphenol with methanol in the presence of MMCF catalyst. Based on the results of kinetic studies carried out in a differential reactor, the routes of the process of obtaining 2,6-dimethylphenol were determined.



The first route is the oxygen alkylation of 2-methylphenol, the second and third routes are carbon alkylation, and the fourth route is a side reaction of methanol. P_1 , P_2 , P_3 are the partial pressures of 2-methylphenol, methanol and 2,6-dimethylphenol, respectively.

For the purpose of preliminary study and verification of the model, the activity and especially the selectivity of the MMCF catalyst in the alkylation of 2-methylphenol was analyzed, and the results obtained, albeit indirectly, confirm the type of kinetic equations in terms of quantity. This analysis is in good agreement with the stoichiometric basis of the process (I-IV) and the step-by-step process scheme (12 steps).

Based on the results of the experiments and the proposed model, the rate constants were calculated, the value of which was determined on the basis of existing programs by minimizing the root-mean-square errors. The values of activation energy on the corresponding routes are: $E_{\text{I}}=31.2$ kJ/mol; $E_{\text{II}}=105.2$ kJ/mol; $E_{\text{III}}=64.5$ kJ/mol; $E_{\text{IV}}=35.5$ kJ/mol.

Changing the kinetic order in equations (1-4) and restoring the table of stoichiometric coefficients to obtain a more favorable basis leads to more erroneous results. The obtained kinetic model is theoretically substantiated and satisfactorily describes the main conversions occurring on the catalyst surface. It justifies itself in a wide range of operating parameters and is important for industry.

The kinetic model played a major role in optimizing the process of producing 2,6-dimethylphenol.

The factors to be optimized were selected and constraints imposed as follows:

$$\begin{aligned} 600 &\leq T \leq 700 \text{ K} \\ 0.5 &\leq \theta \leq 2.5 \text{ mol/mol} \\ 0.02 &\leq P_1 \leq 0.04 \text{ MPa} \end{aligned}$$

$$0 \leq \tau \leq 20 \text{ sec}$$

Here T – the absolute temperature of the process, θ – the molar ratio of 2-methylphenol to methanol, PI – the sum of the partial pressures of 2-methylphenol and methanol in the system, τ – the contact time.

The variable step for each input parameter was taken as follows: 25 (T), 1 (θ), 0.01 (PI), 4 (τ). Unlike other methods, a scanning method was used to optimize the process, which provides a global optimum of the objective function.

Calculations of possible options based on the kinetic model and well-known programs (Matlab, etc.) were carried out, and the spectra of solutions were obtained. Graphical dependencies are then built that can provide a lot of useful information about the process, which also determines the process management strategy.

For example, at different contact times and at different values of the sum of the partial pressures of 2-methylphenol and methanol in the system, dependence curves were plotted reflecting the effect of temperature on the selectivity of 2,6-dimethylphenol formation, they were processed, and Figure 4 was obtained, which reflects the generalized the surface area of the temperature dependence of the selectivity of 2,6-xylene formation, which reflects the generalized surface for the case when $\theta=0.5$.

Similar studies were carried out for other parameters and the dependence curves were obtained, reflecting the optimal conditions for the process of alkylation of 2-methylphenol with methanol and extreme technological criteria. The results of theoretical

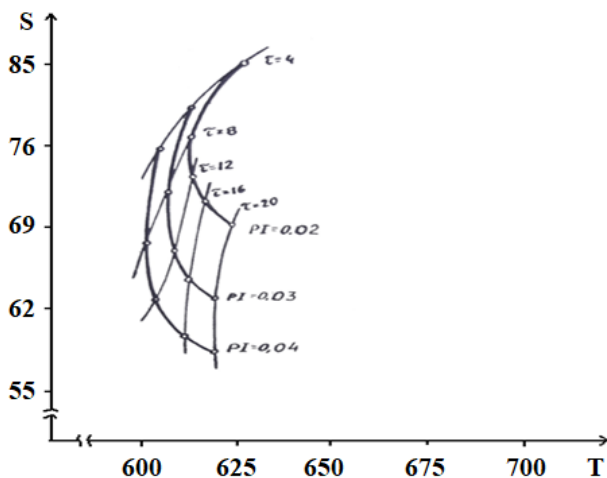


Figure 4. Temperature dependence of the optimal selectivity values for the formation of 2,6-dimethylphenol at different contact times and at different values of the sum of the partial pressures of 2-methylphenol and methanol in the starting mixture ($\theta=0.5$)

technological optimization can be considered practically significant, since there are few errors between the optimal conditions for the production of 2,6-dimethylphenol, determined in two ways, and the maximum values of the criteria.

Study of the stable operating time of catalysts and the development of a flexible method for obtaining C₂-C₃-alkylphenols. The creation of continuous technology is one of the key factors in the development of heterogeneous catalytic processes. Establishing a stationary mode is of particular importance to ensure the continuity of the process.

In the case of a non-stationary mode of operation, shutdown and repair of the reactor, which is the main reaction apparatus, the long duration of the process depends on maintaining the stationary mode. This is mainly due to the stable operating time of the catalytic system used in catalytic processes.

Taking this into account, the stable operating time of MMCF catalyst and PdCaY zeolite in the alkylation reaction of 2-methylphenol with methanol was studied. First of all, this reaction was

studied in the presence of various diluents. Nitrogen gas, water vapor, a mixture of nitrogen and water vapor, and hydrogen with different partial pressures were used in the system as diluents.

The stable operating time of both catalysts is longer in a hydrogen atmosphere. Thus, the MMCF catalyst can operate in a stationary mode for 400 hours, and the PdCaY zeolite for 250 hours in a stream of hydrogen (600 liters of hydrogen/liter of catalyst).

Hydrogen is practically not used in the alkylation process, but is directly involved in the formation of the catalyst and improving its operational properties. Oxidative regeneration of inactive catalysts was carried out under specified conditions ($T = 450^{\circ}\text{C}$, hourly air consumption per 1 liter of catalyst was 600 liters), the regeneration time was 5-8 hours.

Based on the research results, a flexible principle technological scheme is also provided. Individual isomers and isomers mixtures of alkyl ($\text{C}_2\text{-C}_3$) phenols can be obtained with high technological criteria by changing the starting phenol, methylphenols and alcohols, as well as the catalyst.

CONCLUSIONS

1. Among the ferrite catalysts ($\text{MFe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$; M – Mg, Zn, Co, Cu) used in the alkylation reaction of 2-methylphenol with methanol and containing 25.0 wt% of the active ingredient (MFe_2O_4), cobalt ferrite and its manganese-modified sample ($\text{Co}_{0.9}\text{Mn}_{0.1}\text{Fe}_2\text{O}_4 \cdot \gamma\text{-Al}_2\text{O}_3$) is more efficient [4, 6].

2. The MMCF catalyst, which performs selective alkylation in the *orto*-direction and possesses universal properties, has the same catalytic properties for the alkylation of cresols with methanol. The selectivity and yield for 2,6-dimethylphenol obtained from 2-methylphenol and methanol under the indicated conditions are 92.0 and 32.8%, the yields of 2,4-dimethylphenol obtained by alkylation of 4-methylphenol with methanol, calculated according to the converted and primary 4-methylphenol are 89.8 and 35.5%, respectively, the total selectivity and total yield for 2,5 and 2,3-dimethylphenols obtained by the reaction of 3-methylphenol with methanol are 94.0 and 37.7% respectively [10, 11, 13].

3. The *o*-alkylating property of the MMCF catalyst makes it possible to obtain practical results by selectively synthesizing the corresponding *o*-ethyl derivatives by alkylating cresols with ethanol and selectively synthesizing 2-propylphenol and 2-isopropylphenol by alkylating phenol with 1- and 2-propanols, respectively [3, 13].

4. Among the palladium-containing zeolites (Pd,H-mordenite, PdCaY, PdZSM-5) used in the alkylation reaction of 2-methylphenol with methanol, PdCaY shows a higher total selectivity (91.5%) and total yield (43.9%) in obtaining mixture 2, 6- and 2,4-dimethylphenols, while the molar ratio of 2,6 and 2,4-isomers is 0.9:1. The *o*- and *p*-directing properties of the PdCaY zeolite in electrophilic substitution reactions are also reflected in the alkylation of 3- and 4-methylphenols with methanol and cresols with ethanol [7, 8].

5. Side reactions partially occurring in the presence of MMCF catalyst and PdCaY zeolite during alkylation of 2-methylphenol with methanol include parallel O-alkylation and sequential C-alkylation in cresol, and the differences include the formation of small amounts of dimethylether in the presence of zeolite and methyl formate in the presence of ferrite, as well as the partial complexity of the composition of trimethylphenols obtained using PdCaY. Selective isomerization of 2,5-dimethylphenol to the more required 3,5-dimethanol (51.5-55.8%) was carried out in the presence of a bifunctional catalyst (Pd, HSVM) [2, 5, 8].

6. Based on the non-selective conversion of methyl anisoles to the appropriate xylenols under alkylation conditions, it was found that there is no ether mechanism for the formation of dimethylphenols, and this was confirmed by kinetic studies. The kinetic model, which satisfactorily describes the conversions taking place in the catalytic process in terms of character and quantity, attracts attention by its adequacy. Theoretical technological optimization was carried out by the scanning method on the basis of a kinetic model obtained in the presence of the MMCF catalyst, and practically significant curves of dependence between operating parameters and extreme technological indicators were constructed [5, 12].

7. A continuous (250 and 400 hours) method for obtaining 2,6-dimethylphenol in the presence of a MMCF catalyst and a mixture of 2,6- and 2,4-dimethylphenols in the presence of PdCaY zeolite has been developed and its principle technological scheme is shown [1, 9].

The main results of the dissertation are published in the following scientific works:

1. Agayev, A.A., Muradov, M.M., Murshudlu, N.A., Huseynova, I.H. Feasibility study of the process of obtaining methylphenol on the basis of phenol and methanol with the participation of modified ferrite catalyst // International scientific conference on "Sustainable Economic Development: Problems, Prospects", – Sumgait: – April 27-28, – 2016, – p. 160.

2. Agayev, A.A. Preparation of 2.3.6-trimethylphenol by alkylation of 2.3- and 2.5-dimethylphenols with methanol / A.A. Agayev, H.N. Shirinova, I.E. Garayeva, N.A. Murshudlu // Bashkir Chemical Journal, – Ufa: – 2016. v. 23, no. 2, – p. 8-11.

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4. Murshudlu, N.A., Shirinov, P.M., Mustafaev, M.M., Agayev, A.A. Obtaining an oxide catalyst for the interaction of 2-methylphenol with ethanol // X International Scientific and Practical Conference of Young Scientists "Actual Problems of Science and Technology-2017", – Ufa: – April 14 - May 19, – 2017, – p. 148-149.

5. Muradov, M.M. Conversion of methanol and dimethylether in the conditions alkylation of 2-methylphenol / M.M. Muradov, İ.G. Guseinova, N.A. Murshudlu, A.A. Aghayev // International Journal of Current Research, – India: – 2017. v.7, issue 7, – p. 54511-54513.

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13. Murshudlu, N.A., Muradov, M.M., Agayev, A.A. Ortho-alkylating catalyst with phenolic C₂-C₃ alcohols // 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: – 2-4 October, – 2019, – p.173.



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