Synthesis of Para-(1-Methylcycloalkyl) Phenols and Their Carbonyl Derivatives

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***Abstract*— The study explores the cycloalkylation of phenol with 1-methylcyclopentene and 1-methylcyclohexene using a zeolite-based KH-30 catalyst. Key parameters such as reaction temperature, molar ratio of reagents, and space velocity were evaluated to determine their impact on product yield and selectivity. The optimal conditions were established at 120°C, with a 1:1 molar ratio of phenol to methylcycloalkenes and a space velocity of 0.6 h^{-1}. Under these parameters, the yield of p-(1-methylcyclohexyl)phenol reached 73.8% based on the used phenol, with a selectivity of 92.1%. The product yield was 71.3%, and the selectivity for 1-methylcyclopentene was 89.7%. The findings confirm that the cycloalkylation of phenol with methylcycloalkenes, catalyzed by KH-30, is a highly effective route for synthesizing p-(1-methylcycloalkyl)phenols, offering both high selectivity and significant product yield. The acylation reactions of synthesized para-cyclohexylphenols with acetyl chloride were investigated, and optimal conditions for the process were investigated. New application areas for synthesized acetophenones were identified.**

Keywords*— *phenol, 1-methylcyclohexene, 1-methylcyclopentene, alkylation, catalyst, para-cycloalkylphenol, acylation, acetophenone

Introduction

Alkylphenols are among the key intermediates used in the production of antioxidants, stabilizers, oxygenates, and additives for polymeric materials, lubricants, and fuels [1-5]. Over the past two decades, liquid-phase alkylation of phenol with aliphatic hydrocarbons in the presence of zeolite-based catalysts has been successfully developed and widely implemented in industrial processes [6-11].

The use of zeolite catalysts for alkylphenol synthesis offers significant advantages over traditional alkylation methods. These include lower capital and operational costs, the absence of a corrosive medium or waste disposal issues, higher alkylphenol yields, and complete catalyst regenerability [12-15].

The studies have shown that in the presence of both homogeneous and heterogeneous acidic catalysts, predominantly para-substituted phenols are formed, with a small amount of ortho-substituted derivatives.

This work presents the results of the investigation of the cycloalkylation reaction of phenol with 1-methylcyclopentene (MCP) and 1-methylcyclohexene (MCH) in the presence of the zeolite-based catalyst KH-30.

I. EXPERIMENTAL PART

Freshly distilled phenol, 1- methylcyclopentene (boiling point 74-75°C, n_D^{20} 1.4347, ρ_4^{20} 0.7782, molecular weight 82, purity 98%), and 1-methylcyclohexene (boiling point 110-111°C, n_D^{20} 1.4500, ρ_4^{20} 0.8200, molecular weight 96, purity 99.8%) were used to obtain p-(1-methylcycloalkyl)phenols.

KH-30 catalyst, meeting the specifications of TU 2177-011-07622236-2008, was employed for the reaction.

Cycloalkylation of phenol with methylcycloalkenes was carried out on a laboratory continuous-flow plant. The continuous liquid-phase cycloalkylation was performed in a flow reactor packed with catalyst. The reaction mixture, after passing through the catalyst layer, interacts and exits the reactor as an alkylate. The resulting alkylate is then subjected to distillation and analyzed using physicochemical, spectroscopic, and chromatographic methods.

The analysis of the initial 1-methylcycloalkenes was carried out using a Fractovon chromatograph, model 2150, "Carbo Erba" (Italy), equipped with a flame ionization detector and a flexible quartz capillary column (50 m long, 0.2 mm inner diameter) with a stationary liquid phase. The analysis was performed with helium as the carrier gas, a column inlet pressure of 2.4-2.5 kg/cm², a flow division of 1:150, and a sample volume of 0.3 μL. The initial temperature was set to 30°C, and after 10 minutes, heating commenced at a rate of 2°C/min. The total analysis time was 40 minutes. Peak areas were normalized using the "System-1" integrator

(USA). The scale and tape speed were adjusted to ensure peak identification according to the reference chromatogram.

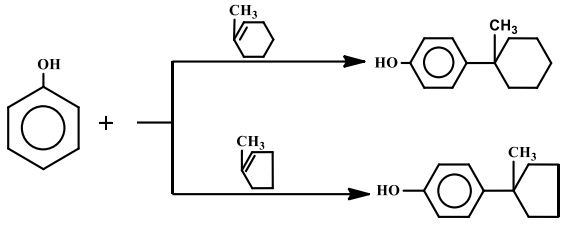
The chromatographic analysis of the alkylate was performed using an LHM-72 chromatograph with a thermal conductivity detector. The column length was 2 m, filled with Chromaton A-AW-DMS solid support, washed with acid and silanized with dimethyldichlorosilane (fraction 0.2-0.25 mm). The stationary phase was a 5% methylsiloxane elastomer SE-30. The initial column temperature was 50°C, the final temperature was 270°C, with a heating rate of 10°C/min. The carrier gas (helium) flow rate was 50 mL/min, the evaporator temperature was 365°C, the detector temperature was 300°C, and the diagram tape speed was 60 mm/h. The internal normalization method was used for calculation, based on the summation of peak areas normalized to 100%.

The decoding of alkylation products was carried out using high-performance liquid chromatography (HPLC). The stationary phase used was "Silasorb C-18", and methanol and methanol-water mixtures (5%, 10%, 15%, and 20% water content) were employed as the mobile phase. The alkylate separation was performed on "Altex-312" liquid chromatograph (USA) with columns measuring 250 × 4.1 mm. A fixed wavelength detector with a wavelength of 254 nm was used.

The separation of cycloalkylphenol mixtures and the identification of individual components were achieved on the "Silasorb C-18" sorbent, with a mobile phase flow rate of 0.5 mL/min, diagram tape speed of 30 cm/h, and a sample injection volume of 10 µL. The samples under investigation were introduced as aqueous solutions of 0.1-0.2% concentration in the mobile phase.

II. Results and Discussion

The cycloalkylation of phenol with MCH and MCP in the presence of the zeolite-based catalyst KH-30 proceeds with the formation of p-(1-methylcycloalkyl)phenols:



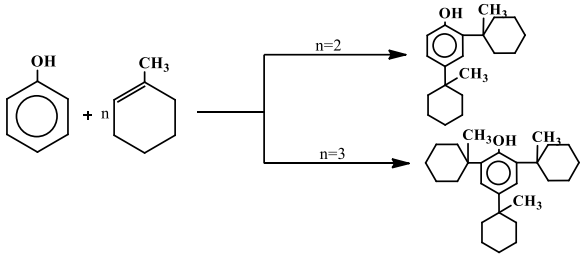
The production of p-(1-methylcycloalkyl)phenols, the effects of temperature, molar ratio of phenol to MCH (MCP), and volumetric flow rate on the yield of target products and the selectivity of the process were studied for in order to determine the optimal conditions.

For instance, the results of the cycloalkylation reaction of phenol with 1-methylcyclohexene in the presence of the KH-30 catalyst are presented in the figure.

Reaction temperatures were varied from 60 to 140°C, the molar ratio of phenol to MCH ranged from 2:1 to 1:2 mol/mol, and the volumetric flow rate was adjusted from 0.2 to 1.0 h^{-1}.

As shown in the figure, with an increase in the reaction temperature from 60 to 120°C, the yield of the target product increases from 44.2% to 73.8% (based on the phenol used), while the selectivity remains approximately at the same level, i.e., 93.4-96.2%. When the reaction temperature is increased to 140°C, the yield decreases to 67.6%, and selectivity drops to 80.7% for the target product. This is explained by the formation of other undesirable isomers at higher temperatures.

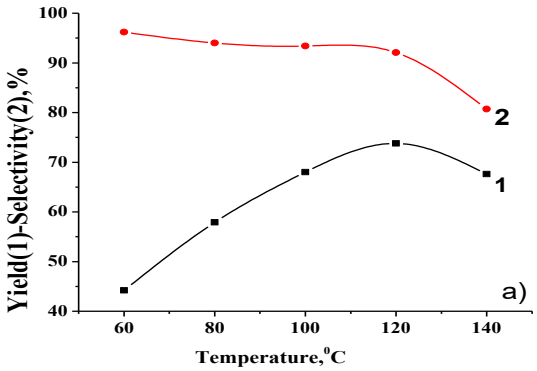
The concentration of MCH in the reaction mixture plays an important role in the production of p-(1-methylcyclohexyl)phenol. When there is an excess concentration of MCH (Figure b), the yield of the main product is 45.5%. This is the result of the formation of di- and trisubstituted methylcyclohexylphenols.

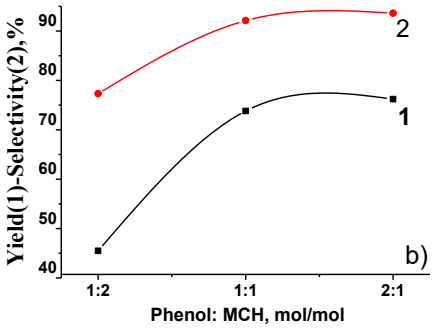


A molar ratio of phenol to MCH of 1:1, the yield of p-(1-methylcyclohexyl)phenol is 73.8%, and the selectivity is 92.1%. As the concentration of phenol in the reaction mixture increases, the yield and selectivity increase slightly (to 76.2% and 93.6%, respectively).

The yield of the target product and the selectivity of the process are acceptable (Figure c), at a volumetric flow rate of 0.6 h^{-1}.

Thus, for the cycloalkylation reaction of phenol with MCH in the presence of the zeolite-based catalyst KH-30, the optimal conditions were determined: temperature of 120°C, molar ratio of phenol to MCH of 1:1 mol/mol, and a volumetric flow rate of 0.6 h^{-1}. Under these conditions, the yield of p-(1-methylcyclohexyl)phenol is 73.8% based on the phenol used, and the selectivity is 92.1% for the target product.





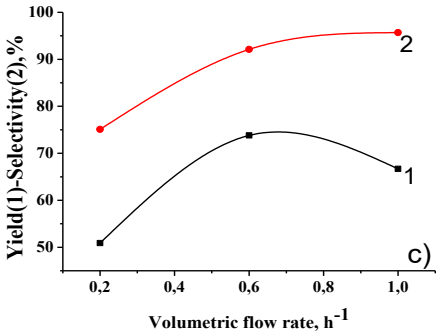


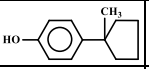
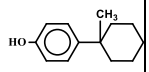
Fig. The dependence of the yield (1) of p-(1-methylcyclohexyl)phenol and the selectivity (2) of the process on temperature (a), reactant ratio (b), and volumetric flow rate (c)

Similar results were obtained for p-(1-methylcyclopentyl)phenol: under optimal conditions, the yield of p-(1-methylcyclopentyl)phenol is 71.3% of the theoretical yield, and the selectivity of the process is 89.7% for the target product. The identification of the synthesized products was carried out using IR and ^{1}H NMR spectroscopy.

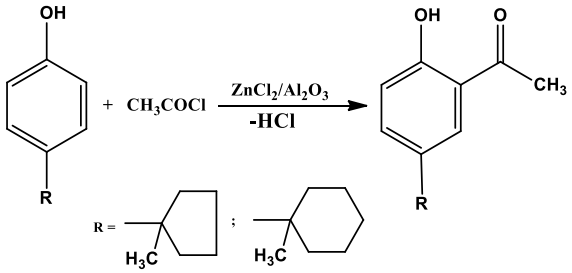
Four signals with intensity ratios of 3:10:1:4 were observed in the ^{1}H NMR spectrum of p-(1-methylcyclohexyl)phenol. The singlet at 1.12 ppm corresponds to the proton of the CH_3 group attached to the quaternary carbon atom. The multiplet with a large peak at $\delta = 1.77$ ppm and a smaller one at 1.5 ppm is characteristic of the saturated hydrocarbon ring. The OH group is confirmed by a singlet in the 5-6 ppm region. The 1,4-disubstituted benzene ring (multiplet) corresponds to the AA BB or approximated AB type spectrum, with an average chemical shift around 6.90 ppm and a spin-spin coupling constant of 8.5 ± 0.5 Hz.

The IR absorption spectrum of p-(1-methylcyclohexyl)phenol exhibits bands in the range of 1505, 1592-1610 cm^{-1}, which are attributed to the benzene ring vibrations. The bands at 3010 and 3030 cm^{-1} correspond to the stretching vibrations of $=CH_2$. A band at 825 cm^{-1} indicates out-of-plane deformation vibrations of $=CH_2$. The OH group is confirmed by the band at 1240 cm^{-1} and in the range of 3100-3500 cm^{-1}. The gem-substituted cyclohexane ring is characterized by C-H stretching bands at 2920 and 2845 cm^{-1}, as well as bands at 1108 and 1345 cm^{-1} corresponding to δCH_2 vibrations in the cycle. The methyl group is characterized by deformation vibrations at 1370 and 1460 cm^{-1}.

The table presents the physicochemical characteristics and elemental composition of p-(1-methylcycloalkyl)phenols

Structural formula	Temp., °C/10 mm Hg	Temp., °C	Mol. Mass	Elemental compositon, % $\frac{calculated}{found}$	
				C	H
	145-148	90	176	81.8 / 82.3	9.1 / 8.4
	161-164	96	190	82.1 / 82.4	9.5 / 8.8

Stage II deals with the study of acylation reactions of p-cycloalkylphenol with acetyl chloride.in the presence of a dispersed $ZnCl_2$-impregnated γ-Al_2O_3 catalyst [15-18].



The acylation reaction of *para*-cycloalkylphenols with acetyl chloride in the presence of $ZnCl_2/Al_2O_3$ catalyst [19] in three necked flaks with thermometer, stirrer and dropping funnel. According of researches, the effect of various parameters (temperature, duration of the reaction, mole ratio of reactants) ot the yield of desired products and selectivity were studied and the optimal conditions for each acylation reactions were determined: temperature at 140°C, duration: 30 min., mole ratio of reactants CAPh:AcCl 1:2:mol/mol and the yield of desired products were 63.5-67.4%.

Acetophenones have the following physico-chemical properties: 2-hydroxy-5(1-methylcyclohexyl)-acetophenone: molar mass – 232, $T_{boil.}$=166-168 °C/10 mmHg; $T_{melt.}$=114.8°C; 2-hydroxy-5(1-methylcyclopentyl)acetophenone: molar mass – 232, $T_{boil.}$=161-163 °C/10 mmHg; $T_{melt.}$=123°C; 2-hydroxy-5(3-methylcyclohexyl)acetophenones are used [20] as photostabilizers for polystyrene, as an antioxidant at M-8 motor oil, also as anti-radiation for polypropylene.

III. CONCLUSION

1. Alkylation reactions of phenol with 1-methylcyclohexene and 1-methylcyclopentene in the presence of zeolite-containing KH-30 catalyst were studied. It was found that under optimal conditions, the yield of p-cycloalkylphenol is 71.3-73.8% based on the phenol taken, and the selectivity of the process was 89.7-92.1% based on the target product.

2. Optimal conditions were found for the acylation reactions of p-cycloalkylphenols with acetyl chloride in the presence of $ZnCl_2$-impregnated γ-Al_2O_3 catalyst, and the yields of 2-hydroxy-5-alkylacetophenones were determined as 63.5-67.4%.

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