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THE RESEARCH OF NEW PREPARATION METHOD OF CRESOLS

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Abstract - *The results of the investigation of the interaction process of phenol and tetramethylbenzenes in the presence of palladium containing pentasil are shown. The activities of all three isomers of tetramethylbenzene, which can be found in primary refining fraction of petroleum or the distillates of catalytic cracking and reforming, have been determined and the interaction of 1,2,3,5-tetramethylbenzene with phenol has been widely studied. The influences of temperature, pressure and special overloading have been studied and new and selective (83%) catalytic production method of tetramethylbenzene has been proposed.*

Key Words: phenol, tetramethylbenzene, cresol, catalyst, transmethylation, selectivity, conversion

1. INTRODUCTION

The methyl homologues of phenol, especially cresols have a special place among the organic products with small and medium tonnage. On the basis of them, resins, pesticides, plasticizers and stabilizers, drugs, fragnants, vitamins are manufactured [1 - 3].

The most widely used method for the preparation of methylphenols is the alkylation of phenol with methanol. The results of the investigation of this reaction in the presence of different oxide (4-6) and zeolite (7-8) catalysts have been either applied or have been applying to practice right now. This reaction is mainly favorable for the synthesis of orto- (o-) and para (p-) cresols and it is not used practically for the production of m- isomer.

Other methods are also used in order to produce 3 – methylphenol and dicresol mixture (m- and p-) in which the concentration of m-cresol is bigger. One of them is based on the interaction of the phenol with methyl and polymethylbenzenes. If it is taken into consideration that the electron density is bigger in o- and p- positions for phenol molecule, it will be obvious that the transmethylation reaction in phenol-methyl (polymethyl) system has an enough speed.

Toluene, o-, m-, p-xylenes and trimethylbenzenes are used as a transmethylating agent for these kinds of researches and catalytic properties of zeolite containing catalysts have been determined.

In this proceeding, the results of the investigation of the transmethylation reaction of phenol with tetramethylbenzene in the presence of palladium pentasil are presented.

2. EXPERIMENTALS

The experiments have been operated at floating reactor which has a catalyst with a static layer and the products have been analysed in Chrome – 5 device by gas – liquid chromatography method. 15% of Apiezon M has been taken as a liquid phase and it has been absorbed on chromosorb W, then it has been filled in a column with a dimension of 3.6m x 4mm. The analysis has been operated in the temperature interval of 80 - 180°C by increasing the temperature with 8°C/minute and helium with a usage of 60 ml/minute has been used as a carrier gas. 18% (by mass) dimenthylphthalate which is absorbed on chromotone H has been used in order to separate the isomer mixture of cresol. Dimenthylphthalate has been synthesized on the basis of menthol and phthalic anhydride by accelerated method. The relative error for the analysis was 3.2%. The spectral analyses of the products have been done in UR-20 device.

1% (by mass) HZSM (x=60) has been used as catalyst and activation of it has been done in hydrogen medium before the reaction.

All three isomers of tetramethylbenzene (1,2,3,4-tetramethylbenzene, 1,2,3,5-tetramethylbenzene and 1,2,4,5-tetramethylbenzene) have been used as transmethylating agent and their activities in the synthesis of cresols have been determined.

3. RESULTS

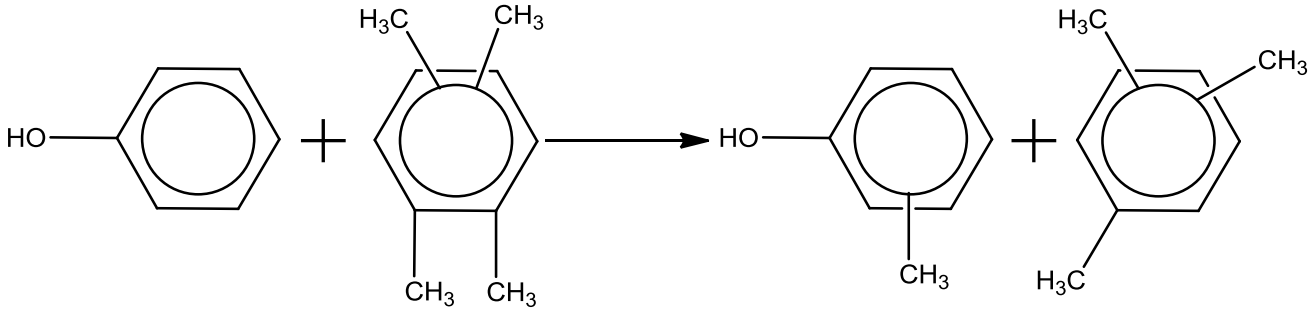
The comparative analysis of the interaction of phenol with tetramethylbenzenes are given in the table. The yield of the cresols according to converted phenol (selectivity) and the yield according to initial phenol have been taken as comparative criteria.

Table – 1: The results of the interaction of phenol with tetramethybenzenes
T=425°C, P=1.0MPa, v=0.5hour^{-1}, mole ratio of phenol to tetramethybenzene = 1:1

Indicator	Composition of the feedstock		
	Phenol-1,2,3,4-tetramethylbenzene	Phenol-1,2,3,5-tetramethylbenzene	Phenol-1,2,4,5-tetramethylbenzene
Conversion of phenol, %	30.0	44.5	34.0
Conversion of tetramethylbenzene , %	31.5	46.5	38.5
Yield of the cresols according to converted phenol, %	72.0	80.0	78.5
Isomer content of the produced cresol, % by mass			
o-cresol	62.5	48.0	50.0
m-cresol	25.0	29.0	22.5
p-cresol	12.5	23.0	27.5

The yields of the product, gas and coke were 96.0-99.5%, 0.2-1.4% and lower than 2.5% respectively. The gas is mainly composed of hydrogen and methane. In some cases, C_3-C_4 hydrocarbons can also be found. Unconverted phenol and tetramethylbenzene, as well as trimethyl- and dimethylbenzenes, isomers of cresol and xylenol and the compounds with high boiling points are found when the chemical content of the product is investigated.

The main products of the reaction are the isomer mixture of cresol and trimethylbenzenes and they are formed according to the general scheme which is shown below.



Most probably, the formation of the xylenol is due to either the systematic disproportion of two methyl group from tetramethybenzene to phenol molecule or produced cresol and dimethylbenzene isomers are formed as well.

As can be seen from the table, the most powerful transmethylating agent is 1,2,3,5-tetramethylbenzene. The conversion of phenol and the conversion degree of tetramethylbenzene have been 44.5% and 46.5% respectively. In this case, the selectivity of the reaction according to the produced cresol has been 80%, the concentration of m- and p- cresol mixture in cresol isomer has been 52.0% and the concentration of 3-methylphenol in diisomer has been 55.8%. The lowest result has been observed with 1,2,3,4-tetramethylbenzene. The concentration of 2-methylphenol in produced tricresol mixture has been 62.5%, however the mass proportion of 3-methylphenol in diisomer has been high enough (66.7%).

When 1,2,4,5-tetramethylbenzene is used as transmethylating agent, moderate results have are recorded in comparison to the other isomers. According to the tricresol, the selectivity of the reaction has been 78.5% and the conversion of phenol has been 34.0%. The concentration of 3-methylphenol in dicresol has been 45.0% and the proportion of o-isomer in tricresol has been 50.0%. As it is obvious, the structure of tetramethylbenzene has a sufficient influence on the selectivity of the reaction, its yield and isomer content according to the cresol mixture. The analysis of the results reveals that the interaction of 1,2,3,5 tetramethylbenzene with phenol produces a cresol with high technological criteria. That is why the transmethylation reaction of phenol with this isomer has been widely studied.

The influence of temperature (T), pressure (P) and special overloading (v) on main indicators of the reaction is given in Figure 1-3.

The conversion of the feedstock components doubles as a result of the increase of the temperature from 400°C to 475°C, however the selectivity for desired product decreases from 88.0% to 72% (Fig.1). The increase in the pressure from 0.25MPa to 1.0MPa has the same effect on conversion and selectivity. The only difference is that there are no any sharp conversion and selectivity differences (Fig.3).

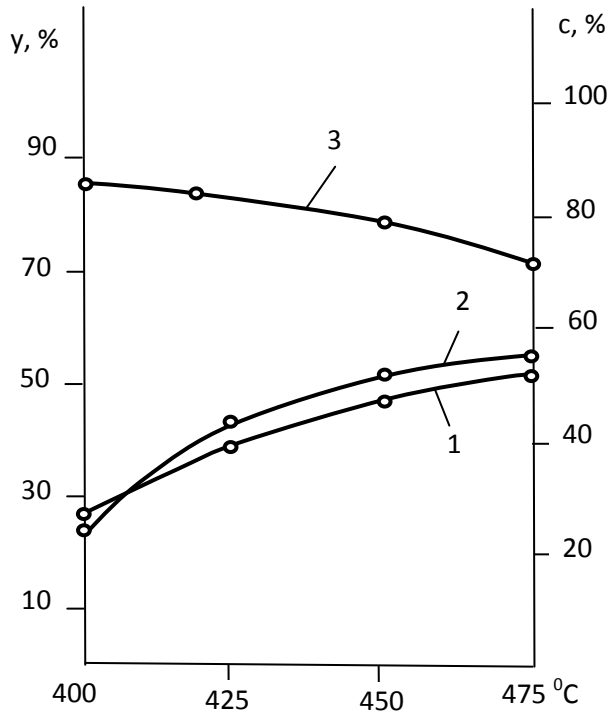


Fig-1: The influence of temperature on transmethylation reaction of phenol with 1,2,3,5 tetramethylbenzene.
Catalyst – Pd-ZSM-5, P-0.75 MPa, υ-0.75 hour^{-1}, ν=1:1.
1. Conversion of phenol, %.
2. Conversion of 1,2,3,5-tetramethylbenzene, %.
3. The yield of cresol according to converted phenol, %

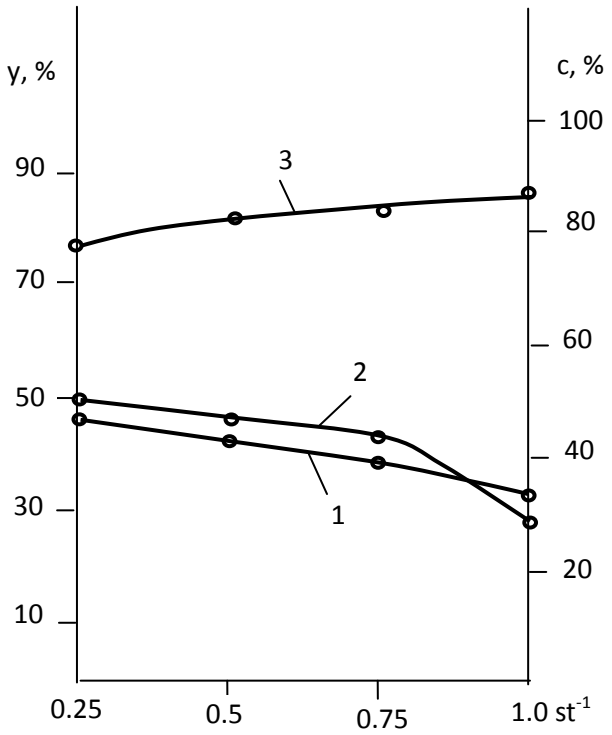


Fig-2: The influence of special overloading on transmethylation reaction of phenol with 1,2,3,5 tetramethylbenzene.
Catalyst – Pd-ZSM-5, P-0.75 MPa, T-425 0C, ν=1:1.
1. Conversion of phenol, %.
2. Conversion of 1,2,3,5-tetramethylbenzene, %.
3. The yield of cresol according to converted phenol, %

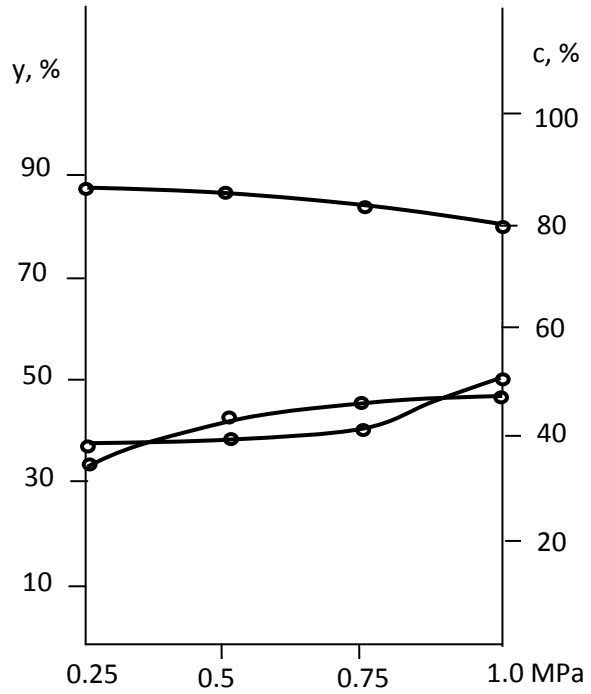


Fig-3: The influence of pressure on transmethylation reaction of phenol with 1,2,3,5 tetramethylbenzene. Catalyst– Pd-ZSM-5, T-425 0C, υ-0.75 hour^{-1},ν=1:1.
1. Conversion of phenol, %.
2. Conversion of 1,2,3,5-tetramethylbenzene, %.
3. The yield of cresol according to converted phenol, %

The increase in the special overloading from 0.25 hour^{-1} to 1.0 hour^{-1} decreases the conversion of phenol and 1,2,3,5-tetramethylbenzene from 48% to 37.5% and from 50.5% to 26.5% respectively, whereas it increases the selectivity of the reaction from 73.0% to 84.5% according to tricresol mixture.

As a result of the spectral analysis, it has been determined that the compounds with high boiling point belong to oxygen containing diphenylalkanes. These compounds are formed on the surface of catalyst and they may be the intermediates during the formation of cresols. The positive effect of pressure for the yield of cresols and absence of anisole in product can prove it. However, these compounds can be the source for the formation of coke in some cases. The results of the research indicates that the tetramethylbenzenes are absorbed on Lewis acid centers and undergo disproportion reactions during the transmethylation of phenol. In the catalytic process, the isomerization reaction of methylphenols and the dimethylation reaction of tetramethylbenzenes are observed.

4. CONCLUSIONS

So, the practical importance of the interaction of phenol with 1,2,3,5-tetramethylbenzene which has more fickle methyl group has been indicated and new and selective (83%) catalytic production method of tricresol mixture has been proposed. The mass proportion of isomers (o-, m-, p-) in cresol mixture under defined conditions (T=425°C, P=0.75MPa, -0.75 hour^{-1}) is like following: 0.44:0.35:0.21

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