

Interaction of 2-Methyl Phenol by Methanol in the Presence of Palladium-Containing Dealuminum Mordenite

Muradov M.M.

Sumgait State University, Azerbaijan Republic, AZ5008 Sumgait, 43 quarter, Tel: +994 51 740 85 92,

Abstract—The catalytic properties of palladium-containing dealuminized mordenite in the alkylation reaction of 2-methyl phenol by methanol have been investigated. The basic and side products of catalytic process have been determined, the conditions allowing to synthesize the mixtures of 2,6- and 2,4-dimethyl phenols with the best technological indices have been revealed.

Keywords— 2-methyl phenol, methanol, alkylation, mordenite catalyst, 2,6-dimethyl phenol, 2,4-dimethyl phenol, activity, yield .

2,6- and 2,4-isomers among dimethyl phenols find more wide application. On the basis of 2,6-dimethyl phenol the new thermoplastic material – polyphenylene oxide is prepared. These stable construction plastics produced in General-Electric Plastics (USA) and in other countries found a successful application in automobile and machine-building [1]. In addition, the polyphenylene oxide has good dielectrical characteristics and stable to action of acids, alkalies and overheated steam. It is a key component of noryl. 2,4-dimethyl phenol finds application in medicine, animal husbandry and in the synthesis of pesticides.

These isomers of xylenol are mainly prepared by alkylation of 2- and 4-methyl phenols by methanol over various catalysts [2-5]. There are known the works [6-7] on preparation of 2,6-xylenols from phenol and methanol. However, a preparation of the mixture of 2,6- and 2,4-dimethyl phenol by alkylation of more accessible 2-methyl phenol with methyl alcohol, in our opinion, is more interesting for economic reasons.

The catalytic interaction of 2-methyl phenol by methanol is carried out in a reactor with fixed bed of the catalyst. The products were condensed in refrigerator – separator. The analysis of liquid reaction products was carried out by chromatographically and spectral methods.

The preliminary investigations of influence of composition of the mordenite catalysts on their activity showed that the most high yields of xylenols are observed in a case of Pd, H-mordenites ($x = 18-25$). In this connection it has been studied the influence of palladium

concentration on yield of xylenols and on degree of the cresols conversion. The obtained results are presented in Fig.1. The investigation was carried out in the following conditions: temperature – 360°C, volume feeding rate of raw material – 0,5 h⁻¹, molar ratio of o-cresol: methanol – 1:1.

It is seen that in increase of concentration from 0,1 to 1.0 mass % a yield of 2,6-xyleneol is rather increased, and a yield of 2,4-xyleneol and conversion of o-cresol is decreased. A further increase of the palladium concentration up to 5 mass % leads to a fall of the catalyst activity. At low concentrations of modifier (0,1 – 0,5 mass %), in spite of the best indices of the process, the catalysts work instable. The analogous regularities were observed in a case of methylation of o- and m-cresols. Therefore, as an optimal catalyst it was chosen the sample containing 1.0 mass % palladium, on which the influence of temperature, volume feeding rate of raw material, molar ratio of the initial components on yield of reaction products and conversion of isomer cresols were in detail investigated.

In Table the results of investigation of the alkylation reaction of o-cresol by methanol at various temperatures and volume feeding rates of the liquid raw material are presented. As it is seen, at low temperatures the main reaction products are o-methylanisole and 2,6-xyleneol. With temperature rise a yield of 2,6-xyleneol increases and a quantity of o-methylanisole is decreased. The reaction temperature growth increases also a yield of 2,4-xyleneol and 2,4,6-trimethylphenol. In the ranges of temperatures 300 – 360°C a formation of 2,6-xyleneol occurs advantageously due to isomerization of forming o-methylanisole. This has been established in contacting o-methylanisole with Pd,H-mordenite catalyst in the conditions of alkylation of o-cresol by methanol. It is seen from Fig.2 that at temperatures 300 – 320°C as a result of isomerization of o-methylanisole a yield of 2,6-xyleneol is 90.1 – 95.4%, at ether conversion – 40.5-73.4 %. The temperature rise to 360°C decreases a yield of 2,6-xyleneol to 69.2-81.1% and increases a content of 2,4-xyleneol and trimethylphenols in catalyzates.

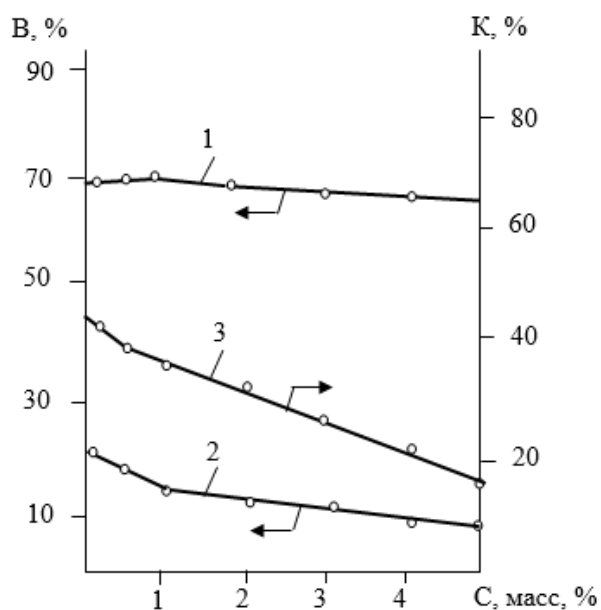


Fig.1: Influence of the palladium concentration (C) in H-mordenite on yield (Y) of 2.6- (1) and 2.4- (2) xylenols and conversion (C) of o-cresols (3).

Conditions: Temperature – 380 °C, volume feeding rate of raw material – 0.5 h⁻¹, molar ratio of o-cresol: methanol = 1:1.

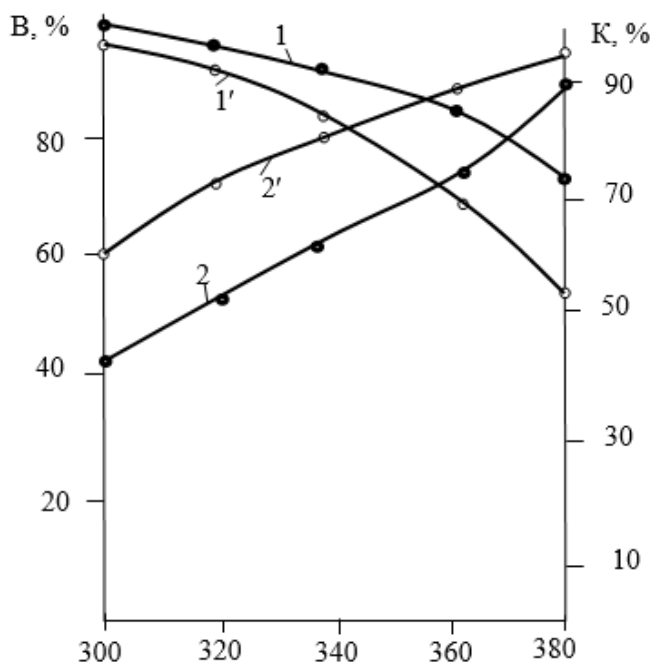


Fig.2: Influence of temperature on yield of 2.6-xylenol (1.1) per reacted o-methyl-anisole and on ether conversion (2.2).

●- volume feeding rate of raw material – 1.0 h⁻¹.
 ○- volume feeding rate of raw material – 0.5 h⁻¹.

It follows from Fig.2 that an increase of the volume feeding rate of o-methylanisole from 0.5 to 1.0 h⁻¹ favors

more selective ether conversion in 2.6-xylenol. Consequently, at low temperatures the O-alkylation of o-cresol by methanol with the subsequent conversion of the prepared o-methylanisole and formation of advantageously 2.6-xylenol prevails. In this, a share of C-alkylation is insignificant. With temperature rise (≥ 360 °C) C-alkylation rate of o-cresol in 4- and 6-positions is increased, although a definite quantity of 2.6-isomers is formed by intramolecular conversion of o-methylanisole. As it is seen from Table, a further temperature increase essentially influences on isomer composition of the xylenol in favour of 2.4-isomer, although an ultimate yield of 2.6- and 2.4-xylenol remains almost unchanged (78-88.8 %). It should be noted that in isomerization of o-methylanisole in the prepared catalyzates only traces of 2.4-xylenol have been detected.

An influence of the volume feeding rate of raw material on alkylation reaction of o-cresol by methanol is as follows: at low volume feeding rate of raw material (0.3 h⁻¹) a yield of 2.6- and 2.4-xylenols are respectively 64.6 and 16.6 %. With increase of the volume feeding rate of raw material a yield of 2.6-xylenol grows to 76.4-77.6 % and a yield of 2.4-xylenol decreases to 3.6 %. With temperature rise and decrease of the volume feeding rate of raw material the degrees of conversions of cresol and methanol grow.

A molar ratio of components of the raw material also influences on reaction parameters (Fig. 3). At molar ratio o-cresol:methanol = 2:1 a yield of 2.6-xylenol per reacted o-cresol is the highest and is 79.5 %.

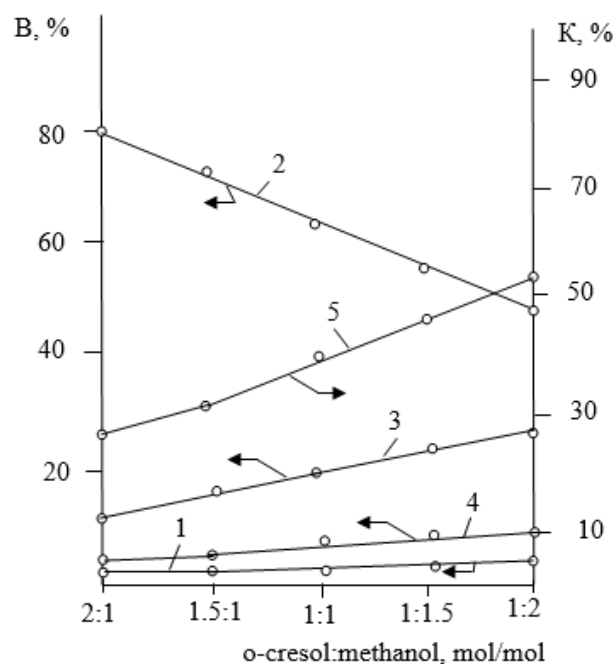


Fig.3: Influence of molar ratio of components of the raw material on yield (Y) of main reaction products and on conversion © of o-cresol.

Conditions: Temperature – 380 °C, volume feeding rate of raw material – 0.5 h⁻¹.

1 – o-methylanisole; 2 – 2.6-xylenol; 3 – 2.4-xylenol; 4 – 2.4.6-trimethylphenol; 5 – o-cresol.

An increase of partial pressure of methanol in raw material (1:2 mol) decreases a yield of 2.6-xylenol to 48.7, in this case, a yield of 2.4-xylenol (26.5 %), 2.4.6-trimethylphenol (10.5 %) and polymethylphenols (5.0 %) grow. Such changes of the composition of di- and polymethylphenols in a case of increase of concentration of alkylating agent confirm our opinion about prevalence of methylation of o-cresol to nucleus at temperatures ≥ 360°C. In the investigated conditions, along with indicated conversions, the disproportionation reaction and isomerization of o-cresol proceed on the catalyst. However, a degree of these conversions is insignificant, which shows the small quantities of the prepared phenols and m- and p-cresols.

The obtained data show the high activity of Pd, H-mordenite in the heterogeneous alkylation reaction of o-cresol by methanol allowing to prepare 2.6- and 2.4-xylenols with good yields and can be recommended for practical application.

REFERENCES

- [1] Gunchak S, Vorobey S, Ishbayeva A. New polymers-polyphenyl oxide // Eurasian Chemical Market, 2009, №2 (50), p. 8-13.
- [2] Korenev D.K., Zavarotniy V.A. Catalytic synthesis of isomers of alkyl phenols // Techn.oil and gas, 2005, №2, p. 21-28.
- [3] Kharlampovich G.D., Churkin Yu.V. Phenols. M.: Khimiya 1990, 386 p.
- [4] Magerramov A.D., Bayramov M.R. Chemistry of alkenyl phenols. B.: Nurlar, 2015, 399 p.
- [5] Patent №726867 USA. Alkylation process with use of zeolite VZM-8 / Jan Deng-Jang, Johanson Zames/ publ. in RZhKhim 08-10-19H85II.
- [6] Agayev A.A., Tagiyev D.B., Mutallimova K.M. Preparation of 2.6-xylenol by catalytic alkylation of phenol and (or) o-cresol by methanol (Coll. of scient.works. Monomers for thermostable polymers. Tula, 1991, p. 187-189).
- [7] Patent №59-320003 Japan. Method of preparation of methylation products of phenol /Khaara Nabuesi, Yasima Takzaki/ publ. in RZhKhim, 1988, 12H161.

Table.1: Influence of temperature and volume feeding rate of raw material on yield of the reaction products
 Molar ratio of o-cresol:methanol = 1:1

T, °C	v, h ⁻¹	Yield, %		Conversion, %		Yield of reaction products per reacted o-cresol, %						
		alkylate	water	o-cresol	methanol	o-methyl-anisole	phenol	m-, p-cresol	2.6-xylenol	2.4-xylenol	2.3:3.4-xylenols	2.4.6-trimethyl-phenol
300	0,5	95.8	4.0	16.2	35.2	58.2	-	-	39.8	-	-	-
320	0.5	93.6	4.4	22.8	40.8	35.3	2.0	-	58.5	3.0	-	0.9
340	0.5	92.0	6.0	29.4	50.4	21.7	1.4	-	68.4	6.4	-	1.5
360	0.3	90.3	6.8	38.9	59.4	3.9	3.8	1.9	64.6	16.6	1.9	4.4
360	0.5	91.2	6.4	34.8	53.9	6.6	2.3	0.7	70.1	13.2	1.3	4.7
360	0.7	91.9	6.2	33.0	51.3	8.4	3.2	-	77.6	6.4	0.5	3.6
360	0.9	92.5	5.8	28.7	48.7	15.6	1.7	-	76.4	3.6	-	1.4
380	0.5	89.0	8.2	40.2	67.0	2.8	3.7	1.5	64.8	17.5	2.2	6.0
400	0.5	85.6	10.4	43.6	79.1	-	6.1	2.9	56.3	21.6	3.1	7.1