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BRIEF COMMUNICATIONS

Catalytic Activity of a Mordenite Catalyst in Alkylation of Xylenols with Methanol

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Abstract—The catalytic activity of a palladium-containing mordenite catalyst in alkylation of 2,6-, 2,4-, 2,5-, 2,3-, 3,4-, and 3,5-xylenols with methanol was studied. The main and by-products of catalysis and the activity of the catalyst in synthesis of individual trimethylphenols were determined.

Methyl derivatives of phenol are consumed in considerable amounts because of their being the most important half-products of small- and medium-tonnage chemistry. However, the last decade exhibited not only an absolute increase in the amount of their manufacture, but also, and to a greater extent, an expansion of their assortment [1].

Catalytic alkylation of phenols with methanol, which is employed with success in manufacture of *ortho*-cresol and 2,6-xylenol [2–4] or recommended for use in synthesis of other isomers of mono- and dimethyl derivatives of phenol, virtually has not been systematically studied in synthesis of individual trimethylphenols.

The aim of this study was to examine the catalytic activity of a mordenite catalyst in alkylation of isomeric xylenols with methanol.

EXPERIMENTAL

Experiments on alkylation were performed in a laboratory reactor under stationary conditions with a fixed catalyst bed of volume 10 cm^3. Synthetic mordenites ($SiO_2 : Al_2O_3$ molar ratio $x = 25$), containing Pd-H-mordenite, served as catalysts. The mordenites were obtained by treating a Na-mordenite ($x = 10$) with a 1 N NH_4Cl solution, with the subsequent washing and drying. Palladium was introduced in an amount of 1.0 wt % into grains of a mixture of a zeolite and γ-aluminum oxide with an aqueous solution of $[Pd(NH_3)_4]Cl_2$. Before delivering the raw material, the catalysts were calcined at 450°C in a flow of dry air (1 h, 1000 h^{-1}) and then kept for 1 h in a flow of hydrogen (1000 h^{-1}) at 410°C and a pressure of 0.1 MPa. The products formed were condensed in a refrigerator-separator and analyzed by gas-liquid chromatography on a Khrom-5 chromatograph with a column (3.6 m × 4 mm) packed with dimenthylphthalate (18 wt %) on Chromocorb W and catharometer as detector. Dimenthylphthalate was synthesized using an accelerated procedure from menthol and phthalic anhydride.

To reveal the role of noncatalytic transformations, preliminary experiments were performed under the reaction conditions, but without a catalyst. In this case, more than 98% of methanol and 100% of isomeric xylenols (virtually all the isomers) were recovered in an unreacted state, which indicated that there was no reaction in the after-catalyst space [6]. In addition, it was established that isomeric xylenols are isomerized and disproportioned over the Pd-H-mordenite catalyst under the conditions studied (350°, 0.8 h^{-1}) to only a slight extent, because a study of transformations of 2,6-, 2,4-, 2,5-, and 3,5-xylenols in the presence of Pd-H-mordenite without methanol demonstrated that their conversion does not exceed 3.2%.

Analysis of the results obtained in alkylation of isomeric xylenols with methanol shows that this reaction occurs by the concurrent-consecutive mechanism. In this case, the alkylation of isomeric xylenols at the carbon atom of the benzene ring is far ahead of the methylation at the hydroxy group of a particular xylenol. Formation of trimethylphenols via intramolecular conversion of the resulting methyl esters of the respective xylenols is unlikely at the given temperature. According to the previously obtained data [5, 7], such a scheme of formation of methyl homologues of phenol in the presence of mordenite and other zeolite catalysts is accompanied by a low selectivity with respect to the target isomers.

It can be seen from the table that trimethylphenols are formed rather selectively with respect to some of the isomers. For example, 2,4,6-trimethylphenol is

Alkylation of xylenols with methanol in the presence of a Pd-containing mordenite (T = 350°C, v = 0.8 h^{-1}, xylenol : methanol molar ratio 2 : 1)

Xylenol–methanol	Conversion of xylenol, %	Yield of trimethylphenol in terms of a xylenol taken, %	Yield of reaction products in terms of reacted xylenol, %							
			dimethylanisole	2,4,6-trimethylphenol	2,3,6-trimethylphenol	2,4,5-trimethylphenol	2,3,4-trimethylphenol	2,3,5-trimethylphenol	3,4,5-trimethylphenol	tetramethylphenols
Xylenol:										
2,6-	35	28	2	80	8	–	–	–	–	8
2,4-	48	35	0.5	73	–	13	–	–	–	11
2,5-	40	32	–	–	79	3	–	–	–	13
2,3-	51	41	–	–	80	–	5	5	–	7
3,4-	53	45	–	–	–	40	45	–	1	10
3,5-	58	40	1	–	–	–	–	70	6	17

the main reaction product in methylation of 2,4- and 2,6-xylenols, mainly 2,4,6-trimethylphenol is formed in methylation of 2,5- and 2,3-xylenols, and predominant formation of 2,3,6-trimethylphenol is observed in the catalytic system constituted by 3,5-xylenol and methanol. In contrast to other xylenols, the 3,4-isometer is methylated less selectively on the mordenite catalyst. Methylation of 3,4-xylenol yields two isomers, 2,4,5- and 2,3,4-trimethylphenols in a virtually equimolar ratio. However, the total yield of these isomers in terms of reacted 3,4-xylenol is rather high (95%), and the conversion of 3,4-xylenol in a single pass is practically important (53%).

It can also be seen in the table that the Pd-containing mordenite exhibits a sufficiently high selectivity in methylation of isomeric xylenols. The highest selectivity of the reaction with respect to the target trimethylphenols is observed in the case of methylation of 2,6- and 2,3-xylenols (80%), and the lowest (70%), in the case of a 3,5-xylenol. It should be noted that the yield of trimethylphenols in terms of reacted methanol is also high (74–88%).

In addition to the main isomers listed above, other trimethylphenols are also formed under the reaction conditions, but in a considerably lower yield. The concentration of the main trimethylphenol in the mixture of its isomers varies rather widely (47–82%).

The composition of the tetramethylphenols obtained is not complex and depends on the starting xylenol only slightly. The 2,3,5,6-isomer predominates in the tetramethylphenol fraction obtained in the case of 3,5-xylenol, and mostly 2,3,4,6-tetramethylphenol is formed in other cases.

A comparison of the yields of the main reaction products (trimethylphenols) in terms of a xylenol taken demonstrated that, on the whole, the catalytic activity of the Pd-containing mordenite decreases in the following order: 3,4-xylenol > 2,3-xylenol > 3,5-xylenol > 2,4-xylenol > 2.5-xylenol > 2.6-xylenol.

Under the conditions of catalysis, methanol is transformed only slightly: it undergoes dehydration, dehydrogenation, decarbonylation, and decomposition. Methyl ether, CO, CO_2, and trace amounts of formaldehyde and ethylene were found in the gaseous reaction products.

CONCLUSIONS

(1) A sufficiently high catalytic activity of a Pd-containing zeolite catalyst in synthesis of individual trimethylphenols and their mixtures from xylene isomers and methanol was demonstrated.

(2) It was shown that, under the conditions studied, the conversion of xylenols is 35–57% and the yield of the main trimethylphenol in terms of a reacted xylenol, 70–80%.

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