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CATALYSIS

Catalytic Alkylation of Cresols with Propanol-1

D. B. Tagiev, N. A. Agaeva, and M. K. Nazarova

Sumgait State University, Sumgait, Republic of Azerbaijan
e-mail: irapon.sdu@mail.ru

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Abstract—Study of the reaction of alkylation of ortho-, meta-, and para-cresols with propanol-1 in the presence of ferrite cobalt and manganese catalysts is reported. The effect of the catalyst composition and reaction conditions on the yield and isomeric composition of the resulting propyl derivatives of cresol was examined and the main and side conversions occurring in the catalysis were determined.

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Propyl derivatives of cresol are valuable half-products in manufacture of antioxidants, stabilizers, medicinal preparations, and vitamins [1, 2]. These derivatives are produced by alkylation of cresols with propene or propanol in the presence of various catalysts [3, 4]; however, these catalytic systems have low activity and selectivity in syntheses of propyl derivatives of *ortho*-, *meta*-, and *para*-cresols.

Our communication presents results of a study of the reaction of alkylation of of *ortho*-, *meta*-, and *para*-cresols with propanol-1 in the presence of ferrite cobalt and manganese catalysts.

Cobalt- and manganese-ferrite catalysts were synthesized by joint deposition of nitrate salts of iron(III) and cobalt(II) and(or) manganese onto γ-Al_2O_3, followed by drying and calcination. The atomic ratio between a divalent metal and iron, M : Fe, is 1 : (2–2.3). The preliminarily found optimal content of MFe_2O_4 in the catalyst is 22 wt %. Improvement of the high-temperature method for synthesis of ferrite catalyst makes it possible to obtain chemically homogeneous and finely porous ferrite particles having good catalytic properties.

Experiments were performed on a flow-through laboratory installation in a flow of hydrogen. The volume of the fixed bed of a ferrite catalyst in the reactor was 10 cm^3. Liquid and gaseous reaction products were analyzed by gas-liquid chromatography on a Khrom-5 instrument. As the liquid phase was used Apiezon M deposited in an amount of 12 wt % on Chromaton N. Isomeric propyl-cresols were also separated by fractional distillation of the reaction mixture at 0.010 MPa.

We synthesized five mixtures of ferrite catalysts $Co_xMn_{1-x}Fe_2O_4{\cdot}\gamma Al_2O_3$ (x = 0.3, 0.6, 0.9, 1.0) and studied their catalytic properties in the reaction of alkylation of *ortho*-, *meta*-, and *para*-cresols with propanol-1. It can be seen in the figure that an increase in the fraction of cobalt in a mixture with manganese makes higher the conversion of all the three isomers of cresol in the alkylation reaction and improves the formation selectivity of the main propyl isomers of cresol: 2-propyl-6-methylphenol (**1**) in the case of *ortho*-cresol, 2-propyl-5-methylphenol (**2**) in alkylation of *meta*-cresol, and 2-propyl-4-methylphenol (**3**) in the interaction with *para*-cresol with propanol-1.

As regards the formation selectivity of the above propyl derivatives of cresol, *ortho*-cresol surpasses the other isomers, whereas the highest conversion of cresol is observed for *meta*-cresol. Interestingly, the yield and formation selectivity of the target products of the reaction of alkylation of *ortho*-, *meta*-, and *para*-cresols with propanol are at a maximum at x = 0.9. In addition, the cobalt-ferrite catalyst largely surpasses in activity that of the manganese-ferrite type in the reaction of propylation of cresols. For example, the formation selectivities of

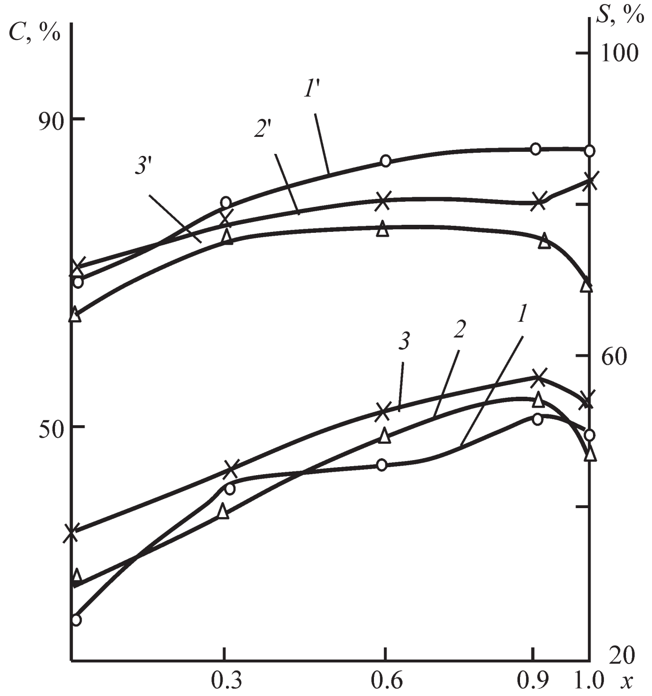
1 in the presence of manganese- and cobalt-ferrite catalysts are, respectively, 69.7 and 85.0%. The yields of compound **2** in terms of the reacted meta-cresol for these catalysts are, respectively, 63.5 and 67.5%. In the case of alkylation of *para*-cresol with propanol-1, the formation selectivity of **3** over the cobalt-ferrite catalyst is 83.0%, and that in the presence of the manganese-ferrite catalyst is 70.0%.

The table lists the results obtained in the reaction of alkylation of *ortho*-, *meta*-, and *para*-cresols with propanol-1 in the presence of a manganese-containing cobalt-ferrite catalyst (x = 0.1). In this case, low temperatures preferably promote the O-alkylation, whereas an increase in temperature enhances the propylation of cresols into a ring. Analysis of the data obtained shows that alkylation of cresols with propanol-1 occurs by the parallel-consecutive mechanism, namely, simultaneous O-alkylation and propylation in the cresol molecule are observed.

In the case of alkylation of *ortho*-cresol with propanol-1, the main reaction products are *n*-propyl ether of 2-methylphenol, (**1**), and *n*-propyl ether of compound **1**. At high temperatures (360°C), 2,4-dipropyl-6-methylphenol is also formed in a noticeable amount. Alkylation of 3-methylphenol with propanol-1 mostly yields product **2**, propyl ether **3**, methylphenol, propyl ether **2**, and 2,6-dipropyl-3-methylphenol. At low temperatures (300°C) an alternating parallel-consecutive mechanism is more noticeable. At higher temperatures (≥330°C), predominance of the carbon-propylation is observed.

The main products formed in the reaction of alkylation of *para*-cresol with propanol-1 are compound **3**, propyl ether of 4-methylphenol, propyl ether **3**, and 2,6-dipropyl-4-methylphenol. It can be seen that cresol undergoes in this reaction depper conversion than other cresol isomers, with the result that the concentration of dipropylcresol and, in particular, 2,6-dipropyl-4-methylphenol in the reaction mixture increases. In all cases, an increase in the partial pressure of the alcohol in the raw material makes lower the yield of target products **1**–**3** in terms of the reacted cresol and enhances the conversion of al the three isomers of cresol.

The concentration of high-boiling propyl derivatives of cresol and alcohol gasification products in the catalyzates grows.



Effect of the atomic fraction x of a divalent metal (Co, Mn) in the ferrite catalyst $Co_xMn_{1-x}Fe_2O_4$ γ-Al_2O_3 on the conversion C of (*1*) *ortho*-, (*2*) *meta*-, and (*3*) *para*-cresols and also on the formation selectivity S of (*1'*–*3'*) main products formed in the reaction of alkylation of cresols with propanol-1. (*1'*) 2-Propyl-6-methylphenol, (*2'*) 2-propyl-5-methylphenol, and (*3'*) 2-propyl-4-methylphenol.

The resulting propyl ethers of 2-methylphenol and products **1**–**3** undergo under mild conditions a partial intramolecular migration of propyl groups into a ring (Scheme 1).

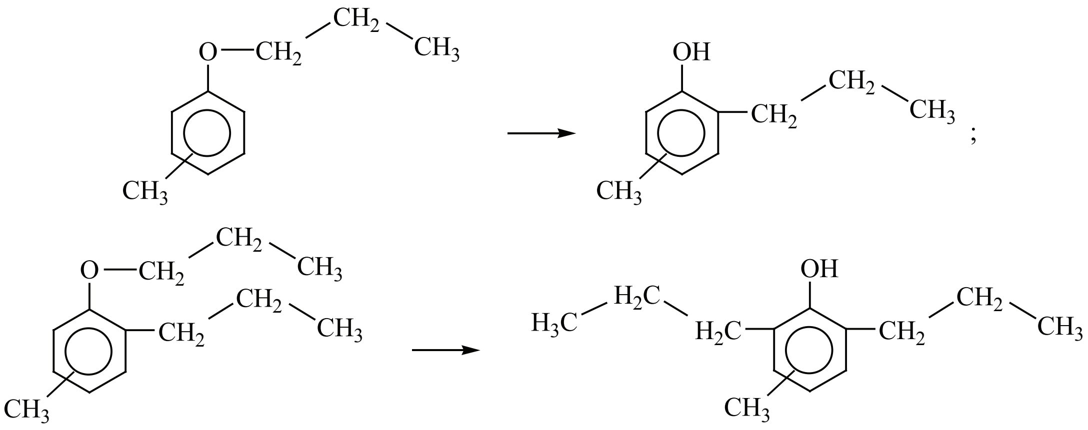
Under the catalyzate conditions, there presumably occurs a rearrangement of propyl groups (Scheme 2).

An increase in the temperature of alkylation of cresols with propanol-1 (>360°C) enhances a number of side reactions, specifically, the dealkylation and isomerization of propyl derivatives of cresol. The concentrations of xylenol, ethylphenol, and a variety of isomeric propyl cresols in the catalyzates obtained grows.

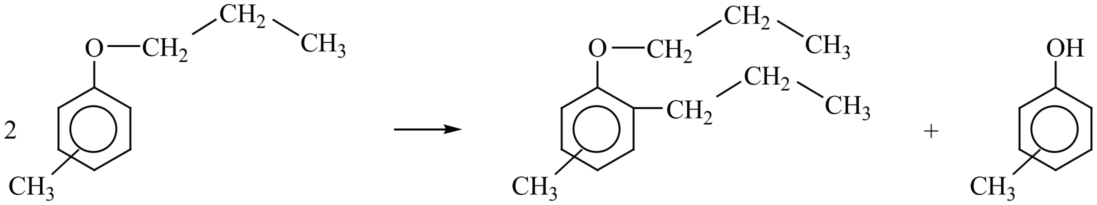
The absence of arenes, diaryl ethers, and high-boiling alkylphenols in the reaction products indicates that the reaction of dehydration of cresol with the subsequent auto-hydrocracking of the resulting aromatic ethers does not occur.

Interestingly, the gaseous reaction products contain no propylene, and only trace amounts of this alkene

Scheme 1.



Scheme 2.



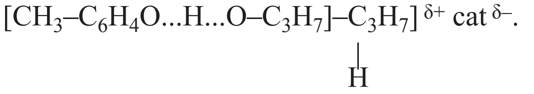
Alkylation of cresols with propanol-1 in the presence of $Co_xMn_{1-x}Fe_2O_4$ γ-Al_2O_3 ($x = 0.9$). Reaction conditions: $\nu = 0.8$ h^{-1}

Run conditions		Conversion of cresol, %	Yield in terms of the reacted cresol, %			
T, °C	$HOC_6H_4CH_3$: n-C_3H_7OH, mol/mol		propyl ether of 1-methylphenol	**1**	propyl ether (**1**)	2,4-dipropyl-6-methylphenol
			ortho-Cresol–propanol-1			
300	1 : 1	35.0	30.0	48.0	18.0	2.5
330	1 : 1	52.0	3.0	85.5	8.0	3.0
360	1 : 1	61.5	1.0	76.0	7.0	10.0
330	1 : 2	60.0	2.5	81.0	4.0	5.6
			meta-Cresol–propanol-1			
			propyl ether of 3-methylphenol	**2**	propyl ether (**2**)	2,6-dipropyl-3-methylphenol
300	1 : 1	39.0	28.0	51.0	14.0	2.0
330	1 : 1	53.0	12.0	73.0	10.0	4.0
360	1 : 1	64.0	3.0	70.0	8.0	14.0
330	1 : 2	59.0	3.6	71.0	6.0	4.5
			para-Cresol–propanol-1			
			propyl ether of 4-methylphenol	**3**	propyl ether (**3**)	2,6-dipropyl-4-methylphenol
300	1 : 1	40.0	34.0	43.0	20.0	1.5
330	1 : 1	57.5	4.0	80.5	8.5	6.5
360	1 : 1	66.0	1.0	72.5	8.0	15.8
330	1 : 2	63.5	5.0	75.0	10.0	7.6

are observed at temperatures $T \leq 330°C$. Presumably, the alkylation of cresols with propanol-1 occurs via the stage of olefin formation. As evidence in favor of this mechanism also serves the absence of macromolecular compounds in the catalyzates obtained. In addition, it was shown that alkylation does not occur in the reaction of *ortho*-cresol with propylene under the conditions specified above over a ferrite catalyst. This can be attributed to the catalytic properties of the ferrite catalyst having an MFe_2O_4 active paste of spinel structure.

The ferrite systems under study possess mixed spinel structures and are bifunctional, i.e., they have basic and oxidative catalytic properties.

The mechanism of the selective *ortho*-alkylation of cresols with propanol-1 differs only slightly from a similar reaction of cresols with methanol and ethanol [5]. The adsorption of cresol on the catalyst surface is accompanied by a charge transfer to the catalyst, weakening of the OH bond, and enhancement of the ortho-orientation effect of the OH group in this state. In this case, the chemisorption leads to formation of the complex



$$[CH_3–C_6H_4O...H...O–C_3H_7]–\underset{\substack{|\\ H}}{C}{}_3H_7]^{\delta+}\ cat^{\delta-}.$$

Otherwise, formation of a wide variety of isomers of propyl derivatives of cresols and undesirable products synthesized on the basis of propylene would be observed.

CONCLUSIONS

(1) The cobalt-ferrite catalyst modified with manganese exhibits a selective ortho-propylating capacity in the reaction of interaction of *ortho*-, *meta*-, and *para*-cresols with propanol-1.

(2) Under the reaction conditions found in the study ($T = 330°C$, $\nu = 0.8$ h–1, $HOC_6H_4CH_3 : C_3H_7OH = 1 : 1$ mol mol^{-1}), the formation selectivity of target propyl derivatives of cresols is 73.0–85.5%, and the conversion of monomethylphenols is 52.0–57.5%.

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