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Abstract

Full Text

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CATALYTIC DEMETHYLATION OF ISOMERIC CRESOLS TO PHENOL UNDER THE ACTION OF WATER VAPOR

The conversion of alkylphenols into phenol is of practical importance because of the high chemical value of phenol. The study of this reaction has been described in many works (^1), which may be divided into three groups: 1) thermal dealkylation in the presence of water and hydrogen at 600–800° and atmospheric pressure; 2) homogeneous hydrogenolysis under an initial hydrogen pressure of 100–300 atm and at a temperature of about 500°; 3) catalytic dealkylation in the presence of hydrogen. In the works of M. G. Gonikberg and Li Guan-nyan (^2,3), who used the second method, it was shown that at 490° and an initial hydrogen pressure of 200 atm the yield of phenol is 29, 12.7, and 21.3 wt.% based on the *o*-, *m*-, and *p*-cresols introduced into the reaction. The yield of catalyzate, respectively, is 81.6, 85.6, and 76.6 wt.%. In parallel, a dehydroxylation reaction proceeds with the formation of 10–20% benzene and toluene. Work in our laboratory has established that dealkylation of benzene homologs (^4) and pyridine (^5) is readily carried out in the presence of water on mixed Ni–clay catalysts. In the present work, under the same conditions, the demethylation reaction of isomeric cresols was studied. Table 1 gives some results of the study of the transformations of *m*-cresol in the presence of a large excess of water on three Ni–clay catalysts of different composition. In processing the experimental data (see below), three reactions possible under these conditions were taken into account:

During the conversion of organic substances with water, CO and CO_2 are formed; in most of our experiments with cresols, CO is formed in the predominant amount, taking which into account equations (1) and (2) were compiled. It may be assumed that reaction (3) is the limiting result of the condensation processes of cresols, the first products of which may be anthracene, phenanthrene, and other polynuclear aromatic hydrocarbons and their derivatives. The number of hydrogen molecules evolved in these processes, calculated per one molecule of the initial cresol, n, may vary from 1 to 3. In the calculations we took $n = 2.5$.

$$C_6H_4(CH_3)OH + H_2O = C_6H_5OH + CO + 2H_2 \quad (1)$$

$$C_6H_4(CH_3)OH + 6H_2O = 7CO + 10H_2 \quad (2)$$

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$$C_6H_4(CH_3)OH = 7C + H_2O + 3H_2 \quad (3)$$

For *m*-cresol, the optimum result, with respect to the depth and selectivity of the demethylation reaction of cresol to phenol, was obtained in experiment No. 7 on a catalyst containing ~22% Ni, in the presence of which, at a space velocity of 5 and 410°, 24 mol.% (21.8 wt.%) phenol is formed from the *m*-cresol introduced into the reaction, and 83.5% from that which reacted. When the space velocity is decreased by half (experiment No. 6), by a corresponding increase in the amount of catalyst, the degree of participation of cresol in side reactions sharply increases—the yield of phenol based on reacted cresol decreases to 34.5 mol.%. The total amount of cresol converted by reactions (1) and (2)—30.4% in experiment No. 6 and 26.3% in experiment No. 7; 19.7 in experiment No. 28 and 25.33% in experiment No. 35—depends little on the space velocity. It may be assumed that in the reaction of cleavage of the aromatic ring, it is mainly the phenol formed by ···

Table 1

Conversion of *m*-cresol with water over Ni–alumina catalysts. Rate of cresol feed in experiments Nos. 6, 7, 16, 19 = 0.1 ml/min; in experiments Nos. 20, 21, 28 = 0.05 ml/min; in experiment No. 35 = 0.194 ml/min

Experiment No.	Temperature, °C	Volumetric feed rate of cresol, h^{-1}	Amount of catalyst, ml; catalyst No.	Feed rate of vapor–gas mixture (n.t.p.), H_2O / C_7H_8O, mol	Gas composition, h^{-1}	Gas composition, CO_2, %	Gas composition, CO, %	Gas composition, H_2, %	Gas composition, CH_4, %	Phenol content in the catalyzate, mol. %	Amount of converted C_7H_8O, mol. %: to phenol	Amount of converted C_7H_8O, mol. by reaction (1)	In (mol. %) of converted cresol: Unreacted cresol, mol. %	In (mol. %) of converted cresol: products of reaction (2)	In (mol. %) of converted cresol: products of reaction (3)
6	409	0.62	9.7; 2	36:1	74.0	8.05	22.3	68.5	1.2	22.1	15.6	14.8	54.8	34.5	32.8	32.8
7	410	1.25	4.8; 2	36:1	25.1	7.0	24.3	67.2	1.5	25.1	23.8	2.54	71.5	83.5	8.7	7.9
16	426	0.6	10; 3	36:1	14.3	12.3	16.4	69	2.3	8.2	7.8	1.97	87.9	65.5	16.1	19
19	470	1.2	5; 3	36:1	13.7	12.3	16.4	69	2.3	13.2	12	4.5	79.35	56	21	24

Experiment No.	Temperature, °C	Volume feed rate of cresol, h^{-1}	Amount of catalyst, ml; catalyst No.	H_2O / C_7H_8O, mol	Feed rate of vapor-gas mixture (n.t.p.), l/h^{-1}	Gas composition, CO_2, %	Gas composition, CO, %	Gas composition, H_2, %	Gas composition, CH_4, %	Phenol content in the catalyzate, mol. %	Amount of converted C_7H_8O, mol. %: to phenol	Amount of converted C_7H_8O, mol. % by reaction (1)	Unreacted cresol, mol. %	In (mol. %) of converted cresol: products of reaction (2)	In (mol. %) of converted cresol: products of reaction (3)
20	464	0.6	5; 2	72:1	64	12.8	14.3	73	—	19.1	6.5	20.6	26.7	8.55	36.3	55.2
21	464	0.6	5; 2	72:1	14.3	10.7	16.3	73	—	31.5	29	1.81	63.1	78.5	4.92	16.3
28	439	1.2	2.5; 1	410:1	45.2	10	9.4	76	4.6	15.2	5.06	14.1	28.6	7.04	49.2	7.3
35*	443	2.32	5.0; 1	30:1	57.6	13.35	14.1	66.2	6.43	23.9	22.7	3.33	67.3	67.5	10.2	43.35

* 9% of the reacted cresol was converted into benzene and toluene.

reaction (1). The rate of reaction (3) increases considerably with increasing contact time (cf. experiments Nos. 6 and 7, 28 and 35).

Raising the temperature by 50° in the range 410–480° lowers the relative degree of the demethylation reaction, and the selectivity of the catalyst action falls more sharply at a higher nickel content (cf. experiments Nos. 6 and 20, 16 and 19). Partial poisoning of the catalyst by carbonaceous deposits substantially increases its activity and selectivity with respect to reaction (1). Experiment No. 21 was carried out on a portion of catalyst used in experiment No. 20; between the experiments the catalyst was removed from the reaction tube and cooled. Its selectivity thereby increased from 8.55 to 78.5%, and the conversion of cresol to phenol in experiment No. 21 was 31.5%, as against 19.1% in experiment No. 20. The reaction of cresol dehydroxylation in the presence of water becomes noticeable only on a catalyst with a high Ni content: in the reaction products in experiment No. 35 there are about 10 mol. % benzene and toluene, calculated on the reacted cresol.

Table 2 compares the results of experiments carried out with *m*-, *p*-, and *o*-cresols. The reactivity of *o*- and *p*-cresols differs sharply from the behavior of *m*-cresol under the same conditions. The selectivity of the demethylation reaction decreases from 67.5% for *m*-cresol to 13.9 and 21.1% for *p*- and *o*-cresols, mainly

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because of the strong increase in the rate of condensation processes (reaction (3)). The rate of complete cleavage (reaction (2)) also increases approximately twofold for *p*- and fourfold

for *o*-cresols, compared with the rate of ring cleavage for *m*-cresol. The conditions under which *m*-cresol is demethylated with good yields are completely unsuitable for the *p*- and *o*-isomers. Lowering the temperature from 440 to 415° considerably increases the yields of phenol from *o*- and *p*-cresols.

Table 2

Transformations of *m*-, *o*-, and *p*-cresols with the participation of water on the catalyst Ni/Al_2O_3 = 1 : 1 (No. 1) (catalyst volume 5 ml; feed rate of cresols 0.194 ml/min, water 0.9 ml/min)

Experiment No.	T-ra, °C	Feed rate of gas, ml/min (n.t.p.)	Gas composition, vol. % CO_2	Gas composition, vol. % CO	Gas composition, vol. % H_2	Gas composition, vol. % CH_4	Gas composition, vol. % C_2H_4 and C_3H_6	Gas composition, vol. % C_5H_8	Phenol content in catalyst, %	Amount of converted C_7H_8O, mol. % to phenol	Amount of converted C_7H_8O, mol. % by reaction (2)	Amount of converted C_7H_8O, mol. % by reaction (3)	Amount of unreacted cresol, mol. %	Amount per converted cresol, mol. % phenol	Amount per converted cresol, mol. % product of reaction (2)	Amount per converted cresol, mol. % product of reaction (3)
m-Cresol	35	443	57.6	13.35	14.1	66.2	6.43	Not det.	23.9	22	3.33	4.37	67.3	67.5	10.2	13.35	
p-Cresol	37	441	58.1	4.62	16.6	75.8	1.25	Not det.	11.2	6.6	7.65	33	52.5	13.9	16.2	70	
	38	413	31.4	4.3	15	79	1.1	Same	0.1	7.9	1.2	11.9	79	37.6	5.8	56.5	
o-Cresol	41	442	97	7	11	74	—	5.3	2.7	26.2	13.3	12.7	36.4	37	21.1	20.3	57
	42	415	70.5	7.2	10.3	72	—	5.0	5.65	23.1	17.3	2.34	21.6	57.5	40	7.9	52.1

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Experimental Part

The experiments were carried out on an automated catalytic flow-type unit described previously ([6]), with inserted reactors ([7]). Catalysts of composition $Ni/Al_2O_3 = 1 : 1$ (No. 1); $1 : 2$ (No. 2) and $1 : 4$ (No. 3) were prepared by the method of N. D. Zelinsky ([8]). The cresol : water ratio varied in different experiments from 30 to 70 and, thus, the partial pressure of cresol was 10–25 mm Hg. For analysis of the liquid and gaseous reaction products, methods of gas–liquid ([9]) and adsorption chromatography were used. The application of the gas–liquid chromatography method for quantitative analysis of phenol mixtures was studied in detail by Yanak ([10]), Sokol ([11]), Bergman ([12]), and others. In the present work we carried out analysis of the catalyst on a column 2 m long and 4.5 mm in diameter, packed with a charge of diatomaceous brick (grain size 0.25–0.5 mm). Methylphenylpolysiloxane in an amount of 30 wt.% was deposited on the brick as the stationary phase. Packing the column required 7 g of methylphenylpolysiloxane. Nitrogen was used as the carrier gas. About 20 mg of the mixture being analyzed was taken for analysis and was introduced into the column by means of a syringe through a rubber cap at the top of the column. Detection was carried out by means of a thermal-conductivity cell consisting of two parallel glass tubes with platinum filaments stretched along their axes, 0.04 mm in diameter and with a resistance of 14 Ω each. Detector signals were recorded on an EPP-09. To carry out detection at room temperature, a method of preliminary conversion of the vapors of substances after their separation in the chromatographic column ([12], [13]) to hydrogen was used. On the chromatographic column employed, not only phenol and its homologs but also aromatic hydrocarbons were clearly separated, with the exception of the *m*- and *p*-isomers for both classes of substances. A preliminary check on artificial mixtures showed that the absolute error of analysis in the overwhelming majority of experiments did not exceed 0.5–1%. Chromatograms of the analyses of experiments No. 21 and 41 are presented in Figs. 1 and 2.

Analysis of the gaseous products was carried out on a VTI apparatus (CO_2, CO, and H_2) and on a chromatographic column 6 m long, filled with aluminum oxide, in a stream of CO_2, with development of the components in an azotometer with a 40% KOH solution (hydrocarbons C_1—C_4). The results were processed from the analytical data using the following equations:

$$m = \gamma \cdot 100 + m_2 + m_3; \qquad V_{CO}/22400 = \Phi\gamma + 7m_2;$$

$$V_{H_2}/22400 = 2\Phi\gamma + nm_3 + 10m_2 - (B + T)\gamma,$$

where m is the amount of cresol (g-mol.) passed in 1 min.; γ is a multiplier for recalculating the results of chromatographic analysis of the liquid catalyzate; V_{CO} and V_{H_2} are the volumes of CO and H_2 (ml) evolved in 1 min.;

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Fig. 1. Chromatogram of the catalyzate from experiment No. 21: 1 –phenol, 2 –*m*-cresol

Fig. 2. Chromatogram of the catalyzate from experiment No. 41: 1 –phenol, 2 –*o*-cresol

m_2 and m_3 are the amounts of cresol (g-mol.) converted according to reactions (2) and (3) in 1 min.; Φ is the percentage of phenol in the catalyzate; (B + T) is the percentage of benzene and toluene in the catalyzate. For convenience of calculation, the composition of the gaseous products was reduced to a two-component system ($CO + H_2$) by equivalent replacement of the remaining components by CO and H_2.

Thus it has been shown that isomeric cresols, in the presence of a large excess of water vapor over Ni-alumina catalysts of various composition in the temperature range 410-470°, undergo demethylation to phenol. The optimum among the results obtained for *m*-cresol–phenol yield of 24 mol.% based on the amount passed and 83.5% based on decomposed cresol–was obtained at 410° over a catalyst $Ni/Al_2O_3 = 1 : 2$, at a volumetric rate of cresol passage equal to $1 : 25$. The behavior of *o*- and *p*-cresols under the selected reaction conditions differs sharply from that of *m*-cresol: the side reaction of condensation, with formation of resinous and carbonaceous substances, as well as the reaction of cleavage of the benzene ring, proceeds at a significantly higher rate.

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