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Catalytic Activity of Iron-containing Polymers in Hydroxylation of Benzene with Hydrogen Peroxide

N. I. Rudakova, M. V. Klyuev, Yu. G. Erykalov, and D. N. Ramazanov

Ivanovo State University, ul. Ermaka 39, Ivanovo, 153025 Russia
e-mail: klyuev@ivanovo.ac.ru

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Abstract—Hydroxylation of benzene with hydrogen peroxide in aqueous acetonitrile at 50°C was studied. The KU-2-8 and KU-1 cation exchangers, and also specially synthesized cation exchangers and phenol–formaldehyde resins derived from pyrocatechol and resorcinol, all modified with Fe(III) cations, were used as catalysts. The macrocomplex KU-2-8/Fe^{3+} showed the highest catalytic activity and ensured 32% yield of phenol in 15 min. The formation of phenol depends in a complex fashion on the initial concentration of hydrogen peroxide, content of Fe(III) ions in the polymer, and reaction time.

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The presently used procedures for production of phenol from benzenesulfonic acid, chlorobenzene, and cumene are multistep and power-consuming; furthermore, they involve formation of by-products requiring utilization [1].

Therefore, much researchers' attention is given today to the development of one-step methods of phenol synthesis, based on direct oxidation of benzene with oxygen or substances acting as oxygen donors (N_2O, H_2O_2, etc.); from the viewpoint of ecology, H_2O_2 is preferable. In particular, high yield of phenols (up to 80%) was attained in [2] in hydroxylation of benzene with hydrogen peroxide:

$$C_6H_6 + H_2O_2 \longrightarrow C_6H_5OH + H_2O.$$

The reaction occurs under mild conditions: aqueous phase, 20–80°C, catalysts cetyltrimethylammonium bromide and Fe(II) and Fe(III) cations. Karakhanov et al. [3, 4] used as benzene hydroxylation catalysts macrocomplexes of Fe(III) with polyethers containing a pyrocatechol core. The maximal yield of phenol (aqueous acetonitrile, 50°C, 1 h) was 30%. It was shown that the phenol yield could be increased to 43% by performing the reaction in acetonitrile at 50°C for 2 h under the conditions of homogeneous catalysis with iron(II) sulfate. Under similar conditions, with a 1 : 1 mixture of $Fe_2(SO_4)_3 \cdot 9H_2O$ + CuCl, the yield of phenol reached 48% in 3 h [5].

In this study we examined hydroxylation of benzene in the presence of iron(III) complexes with KU-2-8 (**I**) and KU-1 (**II**) cation exchangers, with sulfonic cation exchangers derived from pyrocatechol (**III**) and resorcinol (**IV**), and also with pyrocatechol–formaldehyde (**V**) and resorcinol–formaldehyde (**VI**) resins. It was found (Table 1) that the KU-2-8 resin absorbed the largest amount of Fe(III) cations [$m(Fe^{3+})$ = 0.068 g of Fe^{3+} per gram of polymer], forming a macrocomplex with Fe(III) via sulfo groups. The presence in polymers **III**–**VI** of phenolic hydroxyls or of hydroxy and sulfo groups simultaneously (polymer **II**) leads to a decrease in the absorption capacity for Fe(III) by a factor of 2–3, to 0.021–0.030 g of Fe^{3+} per gram of the polymer.

Hydroxylation experiments were performed in aqueous acetonitrile at 50°C (Table 1).

The highest yield of phenol was observed in the presence of catalyst **I**/Fe^{3+} (run no. 1, Table 1). The macrocomplex of Fe(III) with polymer **VI** showed no catalytic properties in the hydroxylation. We examined how the phenol yield is influenced by the reaction time, initial concentration of hydrogen peroxide, and mass of the catalyst (**I**/Fe^{3+}). The results are given in Table 2.

The experiment showed that the dependences of the phenol yield on the reaction time, initial concentration (C_0) of H_2O_2, and mass (m) of Fe^{3+} have maxima. These results are consistent with the views, commonly accepted today, that catalytic oxidation of benzene in aqueous solution is a radical ion reaction in which phenol is an intermediate [6]. Table 2 clearly shows that the maximal yield of phenol (P_{max}, %) is attained in different times depending on the ratio of the initial concentration of hydrogen peroxide and mass of Fe^{3+}

Table 1. Hydroxylation of benzene in aqueous acetonitrile at 50°C in the presence of iron-containing polymers

Run no.	Polymer	$m(Fe^{3+})$, g	C_0, M				Time, min	Phenol yield, %	TN × 10^4,[a] mol g^{-1} min^{-1}
			C_6H_6	H_2O_2	CH_3CN	H_2O			
1	**I**	0.067	1.22	1.14	13.90	8.46	15	32.1	106
2	**I**	″	″	″	″	″	30	11.2	18.7
3	**I**	″	″	″	″	″	60	5.5	4.6
4	**II**	0.030	1.28	1.30	15.23	6.35	30	1.6	6.0
5	**II**	″	″	″	″	″	60	3.2	6.0
6	**II**	″	″	″	″	″	90	1.3	1.6
7	**III**	0.024	1.28	1.30	15.23	6.35	90	5.6	8.7
8	**III**	″	″	″	″	″	120	8.6	10.0
9	**III**	″	″	″	″	″	150	11.5	10.7
10	**III**	″	″	″	″	″	180	4.4	3.4
11	**IV**	0.019	1.28	1.30	15.23	6.35	120	6.7	9.8
12	**IV**	″	″	″	″	″	150	9.7	11.4
13	**IV**	″	″	″	″	″	180	3.9	3.8
14	**V**	0.038	1.22	1.56	13.93	8.46	60	2.4	3.5
15	**V**	″	″	″	″	″	90	3.7	3.6

[a] (TN) Turnover number, i.e., amount of phenol (mol) formed in unit time (1 min) per gram of the catalyst.

Table 2. Hydroxylation of benzene in aqueous acetonitrile at 50°C in the presence of catalyst **I**/Fe^{3+}. Initial concentrations, M: C_6H_6 1.22, CH_3CN 13.9, and H_2O 8.46

Run no.	$C_0(H_2O_2)$, M	$m(Fe^{3+})$, g	$C_0(H_2O_2)/m(Fe^{3+})$, mol l^{-1} g^{-1}	Time, min	Phenol yield, %
1	1.56	0.067	23.3	15	12.8
2	″	″	″	30	12.9
3	″	″	″	60	7.8
4	″	″	″	90	7.9
5	1.56	0.043	36.3	15	5.7
6	″	″	″	30	6.7
7	″	″	″	60	9.6
8	″	″	″	90	11.7
9	″	″	″	110	12.6
10	1.56	0.017	91.8	15	1.8
11	″	″	″	30	3.9
12	″	″	″	60	5.7
13	″	″	″	90	13.6
14	1.14	0.067	17.0	15	32.1
15	″	″	″	30	11.2
16	″	″	″	60	5.5
17	1.01	0.038	26.6	15	8.8
18	″	″	″	30	10.8
19	″	″	″	60	12.9
20	″	″	″	90	9.9

on the polymeric support: $f = C_0(H_2O_2)/m(Fe^{3+})$, mol l^{-1} g^{-1}. The maximal yield of phenol, 32.1%, was attained at $f = 17.0$ and reaction time of 15 min. An increase in f to 23.3 and 26.6 led to a decrease in the maximal yield of phenol to 12.9% (at reaction times of 30 and 60 min, respectively). When the reaction was performed for 15 min, a linear correlation between the reciprocal phenol yield $1/P$ and f was observed:

$$1/P = 0.7 \times 10^{-2} \cdot f - 0.081. \quad (1)$$

After a transformation, we obtain

$$P = 12.3/(0.086f - 1). \quad (2)$$

The phenol yields in 15 min, obtained experimentally and calculated by formula (2), are reasonably consistent (Table 3).

Table 3. Comparison of the experimental and calculated yields of phenol (reaction time 15 min)

f, mol l^{-1} g^{-1}	P_{exp}, %	P_{calc}, %
17.0	32.1	26.6
23.3	12.8	12.3
26.6	8.8	9.5
36.3	5.7	5.8
91.8	1.8	1.8

EXPERIMENTAL

Analysis for phenol was performed with a Model 3700 chromatograph (Russia) equipped with a flame ionization detector. A stainless steel column (1 m × 2 mm) was packed with 5% XE-60 on Chezasorb AW (0.20–0.36 mm). The oven temperature was 90°C. The carrier gas was helium (1.8 $l\,h^{-1}$). The error of phenol determination was ±2%.

Hydroxylation of benzene. A three-necked flask was charged with acetonitrile, benzene, and a weighed portion of a catalyst. The mixture was heated to 50°C, and an aqueous solution of hydrogen peroxide was gradually added. Samples of the reaction mixture were taken at definite intervals and quenched by adding a dilute alkali solution to quickly decompose unchanged hydrogen peroxide and convert the phenol into phenolate. The subsequent treatment of the samples consisted in vacuum evaporation of acetonitrile and benzene, acidification of the mixture, and extraction of phenol with diethyl ether. The extract was analyzed by GLC using naphthalene as internal reference.

Preparation of iron-containing catalysts. A flask was charged with 5 g of a polymer and a solution of 2.5 g of $Fe_2(SO_4)_3 \cdot 9H_2O$ in 100 ml of water. The mixture was stirred at room temperature until the concentration of Fe(III) cations in the aqueous solution became constant (usually 1.5–2 h). The polymer was filtered off, washed with distilled water, and dried in air.

To check the stability of the catalysts, a catalyst sample (0.5 g) was placed in a reactor, after which acetonitrile (20 ml), benzene (3 ml), and water (5 ml) were added. The mixture was kept in a thermostat at 50°C with stirring for 1.5 h. The content of Fe(III) cations in solution was monitored. Their absence indicated that the catalysts were stable under the conditions of the experiments.

Cation exchangers **III** and **IV** were prepared by sulfonation of pyrocatechol and resorcinol, followed by condensation of the sulfonic acids with formaldehyde by the procedure in [7]. Polymers **V** and **VI** were prepared by condensation of the corresponding phenols with formaldehyde in accordance with [7].

The concentration of hydrogen peroxide was determined by iodometric titration [8]. Acetonitrile and benzene were purified by procedures suggested in [9]. The other chemicals were of no less than pure grade and were used as received.

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