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HYDROXYLATION OF BENZENE BY HYDROGEN PEROXIDE CATALYZED BY AN Fe^{3+}-CATECHOL CATALYST SUPPORTED ON SILICA GEL

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A silica gel-supported Fe^{3+}-catechol catalyst was found to be active to convert benzene to phenol in moderate yields.

Enzymatic aromatic hydroxylation has recently attracted much attention due not only to its important role in biology but also potential applicability to organic syntheses. However, there are still only a few reports of synthetically useful catalysts for aromatic hydroxylation modeled after iron-containing enzymes, horse-radish peroxidase and cytochrome P-450.$^{1)}$ Quite recently, we have reported the use of Fe^{3+}-lipophilic catechol catalysts for H_2O_2-oxidation of benzene to phenol in benzene-H_2O two phase system.$^{2)}$ The disadvantage of this process, however, is the difficulty in work-up owing to the disturbance of the two phase interface by tarry products. One of the most reasonable improvement for this disadvantage would involve the development of heterogeneous catalysts. Accordingly, we have prepared a silica gel-adsorbed Fe^{3+}-catechol catalyst and have examined its synthetic utility as catalyst for the hydroxylation of benzene to phenol. We report the results of that work here.

A silica gel-adsorbed Fe^{3+}-catechol complex was prepared by mixing $Fe_2(SO_4)_3$ and catechol into a stirred suspension of silica gel in H_2O.$^{3)}$ The excess H_2O was evaporated at 60-80°C at 15 mmHg. The resultant silica gel catalyst was dried further in a vacuum oven at 50°C for 2 h. No careful control of drying conditions was required to obtain effective catalysts. The color of the catalysts varies from gray to black with increasing loadings of Fe^{3+} and catechol.

The hydroxylation of benzene with H_2O_2 was conducted in the presence of the silica gel catalyst.$^{4)}$ Neither silica gel-Fe^{3+} nor silica gel-catechol combination alone was sufficient to catalyze the reaction. In the standard procedure, aqueous H_2O_2 (35 %, 3.25 mmol) was added all at once to a stirred suspension of the catalyst (10 g) in 20 ml of benzene under nitrogen. After 2.5 h, filtration to remove the used silica gel gave a clean solution, which was examined by HPLC. The results thus obtained are summarized in Table I.

Table I includes the data of the effects of altering the Fe^{3+}-catechol loading on silica gel (runs 1-4), the molar ratio of $Fe^{3+}$to catechol (runs 5-7), and the used amount of silica gel (runs 8-14). It is apparent from runs 8-14 that the quantity of silica gel was important and the yield reached the maximum when 10 g of silica gel was employed. In this case, 0.2 mmol of Fe^{3+} and catechol had been

Table I. Yield of phenol from hydroxylation of benzene under N_2

Run	Fe^{3+},mmol	Catechol,mmol	H_2O_2,mmol	Silica gel,g	Yield,%[a)]
1	0.1	0.1	3.25	10	25
2	0.2	0.2	3.25	10	44.1[b)]
3	0.4	0.4	3.25	10	12
4	0.8	0.8	3.25	10	5
5	0.2	0.1	3.25	10	34.7
6	0.2	0.4	3.25	10	33.8
7	0.2	0.6	3.25	10	36.6
8	0.2	0.2	3.25	0	2.3 (0.37)[c)]
9	0.2	0.2	3.25	0.5	4.2
10	0.2	0.2	3.25	1	4.8
11	0.2	0.2	3.25	2.5	31.8
12	0.2	0.2	3.25	5	31.0
13	0.2	0.2	3.25	10	44.0 (7.2)[c)]
14	0.2	0.2	3.25	15	15.1
15	0.15	0.15	1.3	10	60.1 (5.0)[c)]

a) Based on H_2O_2. b) 28.8 % under air. c) Turnover number for Fe^{3+}.

loaded. The comparison of runs 1-4 shows that the loading of too much or too little Fe^{3+}-catechol complex resulted in decreased catalytic efficiency. However, the changing amount of catechol seems less important (runs 5-7). Thus, the maximum catalytic efficiency is obtained, when 0.2 mmol of Fe^{3+} and catechol are loaded on 10 g of silica gel. Detailed studies to elucidate these observations are now in progress.

In conclusion, we have described the successful use of the silica gel-adsorbed hydroxylation catalyst which is as effective as the previously reported lipophilic catechol-Fe^{3+} catalyst. The present system is cheap to prepare and convenient to handle.[5)] Furthermore, the work-up procedure is particularly easy, the used silica gel-supported catalyst or its decomposition products being removed by simple filtration, giving the clean solution with no appreciable by-product. Obviously, this catalytic system should be useful from the practical point of view.

References

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2) K. Hotta, S. Tamagaki, Y. Suzuki, and W. Tagaki, Chem. Lett., 1981, 789; G.A. Hamilton et al., J. Am. Chem. Soc., 88, 5266 (1966).
3) Wakogel C-300 purchased from Wako Pure Chemical Industry, LTD., Tokyo.
4) Other inorganic materials such as Na_2SO_4, celite, zeolite, and aluminas were not effective as supports. Both the porosity and acidity of silica gel is considered to be responsible for the catalyst activation.
5) The recovered catalyst was inactive and could not be reused, although silica gel itself could be easily recovered for reloading of $Fe^{3+}$and catechol.

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