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Heterogeneous Catalysts for the Continuous Oxidation of Benzene to Phenols

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The catalytic oxidation of benzene in the presence of air and reducing gases has been examined. All the catalysts studied, active carbon, several forms of platinum, zeolite of Cu form, and Pd/silica, were found to be effective for reducing Cu(II) to Cu(I) and thereby producing phenols. Among these, Pd/silica showed the best performance and is capable for practical use.

In a series of papers,$^{1-9)}$ we have demonstrated that phenols are readily produced from benzene in aqueous acid solutions containing monovalent copper ions. The reaction sequence to lead to phenol and hydroquinone has been confirmed by the ^{18}O-tracer study$^{5,6)}$ and several other experiments.$^{7-9)}$ The essential point of this reaction is in the use of monovalent copper ions which convert oxygen molecule to hydrogen peroxide. The latter is further converted to OH radical by the aid of Cu(I) ions as shown by Eqs. 1 and 2. Because of the highly reactive nature of OH radical, benzene is readily converted to phenol (Eq. 3).

$$2Cu^+ + O_2 + 2H^+ \longrightarrow 2Cu^{2+} + H_2O_2 \qquad (1)$$
$$Cu^+ + H_2O_2 + H^+ \longrightarrow Cu^{2+} + \cdot OH + H_2O \qquad (2)$$
$$C_6H_6 + \cdot OH + Cu^{2+} \longrightarrow C_6H_5OH + H^+ + Cu^+ \qquad (3)$$

Although this reaction is promising to be applied as a new industrial process, there is a problem regarding the regeneration of monovalent copper ions from divalent ones. One answer is the application of the electrochemical method which has been studied extensively in our group in recent years$^{2,3,9)}$ and was proved to be useful for the reactions occurring in aqueous solutions. Electrochemical method has, however, a serious limitation. Even if we permit the expensive cost of electricity, the method cannot be applied for a reaction occurring in non-conducting solvents which are desirable for many of aromatic compounds.$^{10)}$ We have, therefore, sought another possibility, i.e., the use of reducing chemicals.

The reducing chemicals should be cheap and must not bring about unnecessary complication in the reaction. Practically, either hydrogen or carbon monoxide seems advantageous. Since both the gases supply electron and proton (Eqs. 4 and 5), the regeneration of Cu(I) species will proceed.

$$2Cu^{2+} + H_2 \longrightarrow 2Cu^+ + 2H^+ \qquad (4)$$
$$2Cu^{2+} + H_2O + CO \longrightarrow 2Cu^+ + 2H^+ + CO_2 \qquad (5)$$

As a whole, the overall reaction of phenol production is expressed by Eq. 6, which suggests that phenol will be continuously produced as far as a certain reducing gas is supplied to the reaction system.

$$C_6H_6 + H_2(\text{or } CO) + O_2 \xrightarrow{\text{cat.}} C_6H_5OH + H_2O(\text{or } CO_2) \quad (6)$$

In order to proceed the above reaction with an appreciable rate under ambient conditions, the use of heterogeneous catalyst which accelerates the step of (4) or (5) seems to be essential.11) The present study started from this view. All the reactions described below were carried out at ordinary temperature and pressure.

At the preliminary stage of this study, we have confirmed that, with all of the solid catalysts listed in Table 1, Cu(II) ions in solution phase are successfully reduced to their monovalent state with streaming hydrogen at room temperature. With both active carbon and platinized platinum, it was also confirmed that carbon monoxide can be used instead of hydrogen. In the case of platinized platinum, however, it was found that 95% of Cu(II) ions were deposited as metallic copper on the platinum surface and only 5% of those were converted to monovalent state. In order to avoid metal deposition, it was necessary to add a small amount of acetonitrile (ca. 10%). Addition of chloride ion of appropriate concentration (>5mM) was also effective to stabilize monovalent copper ions.12)

The oxidation of benzene was thus carried out on the base of the above findings. Each of the solid catalyst and benzene were put into aqueous acidic solution containing copper(II) sulfate and both air and reducing gas were bubbled simultaneously for 1 h. We summarize the results in Table 1.

The use of platinum catalysts gave always favorable results (runs 1 to 5), where three types of catalysts, i.e., platinized Pt-wire, platinized Zeolon (900-Na), and platinum-black powder, were chosen. The defect of these catalysts is that the rate of phenol production decreases with the duration of reaction time (see curves **a** and **b** in Fig. 1). This may be attributed to the surface blocking by the product phenols. As a consequence, in the case of Pt/Zeolon catalyst, a heat treatment at 500 °C was found to be effective for regaining the catalytic activity (curve **c** in Fig. 1).

In Table 1, are also shown data with a Y type of zeolite (run 6), which has been ion-exchanged with copper(II) ions and baked before use. This catalyst contrasts with others in the point that copper species is supported in the zeolite pore but none of noble metal is added. This catalyst, though its performance was attractive, degradated during the reaction in strong acid solutions making the repetitive use impossible.

When active carbon is used as the catalyst, the phenol yield seems exceptionally low (run 7). This, however, does not mean that active carbon is useless. In fact, an appreciable amount of phenol was recovered when the carbon once used was subjected to continuous extraction with ether indicating that most part of phenol produced was adsorbed on the carbon surface. Since carbon is an attractive material in many respects, a more detailed study will be worth an effort.

It is worth noting that phenol is definitely produced in all cases, though the copper salt initially taken in the solution is in divalent state. This is the unequivocal proof of that the catalytic redox cycle of Cu(I)/Cu(II) is efficiently operating by virtue of the reducing gas.

Table 1. Continuous Oxidation of Benzene in the Presence of Heterogeneous Catalysts at Room Temperature[a]

Run	Solid catalyst	Amount	Additives	Reducing gas	Phenol/μmol
1	Platinized Pt-wire	3.0 cm^2	5% AN, 5 mM Cl^-	H_2	3.69
2			5% AN, 5 mM Cl^-	H_2	15.6 [b]
3			10% AN, 10 mM Cl^-	CO	6.24
4	Pt-black[c]	30 mg	10% AN	H_2	6.45
5	Platinized Zeolon[d]	10 mg/1 g	10% AN	H_2	4.41
6	Zeolite(Y),Cu-form[e]	5 g	10% AN	H_2	0.82
7	Active carbon	1.5 g	10% AN	CO	0.79

a) All the reactions were carried out in 0.05 M H_2SO_4 (10 cm^3) containing 0.1 mmol of $CuSO_4$, catalyst, and 1 g of benzene for 1 h, during which reducing gas and air were bubbled simultaneously at ordinary temperature and pressure. b) Mechanical stirring was applied in this case. c) Pt-black powder was prepared chemically and used without any support. d) Chloroplatinic acid was adsorbed on the Zeolon-900-Na surface and then reduced with formalin. e) Zeolite(Y) was equilibrated with a 0.1 M $CuSO_4$ + 0.05 M H_2SO_4 solution and reduced in a hydrogen gas stream at 250 °C.

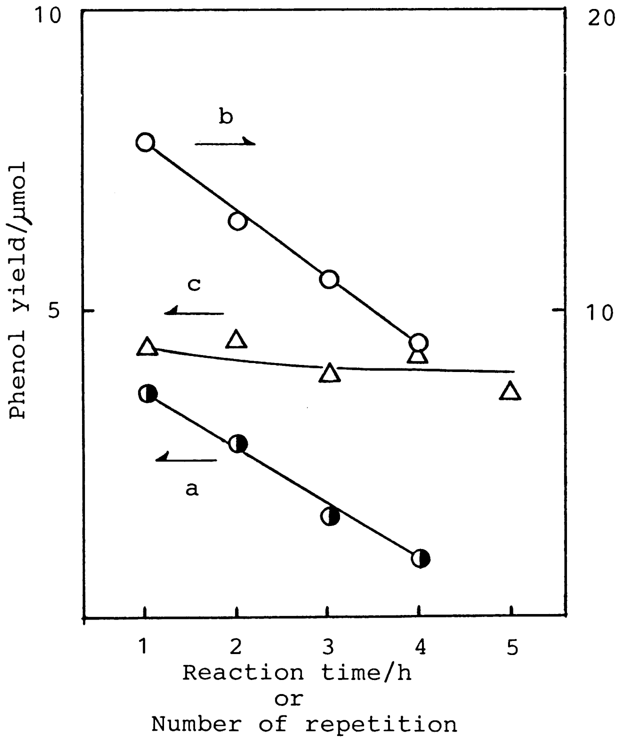

Fig. 1. Change in catalyst activity with reaction time (a,b) or with number of repetitive use (c).

Reaction conditions are the same as those described in Table 1.

Curve (a) corresponds to run 1 (without stirring) and (b) to run 2 (with stirring).

Curve (c) corresponds to run 5. Prior to reuse, the catalyst was washed with water and baked at 500 °C.

A remarkable improvement was achieved when palladized silica-gel was used as the catalyst. We summarize the results in Table 2. For preparing this catalyst, $PdCl_2$ was dispersed onto the silica-gel surface (Merck 9385) of 230-400 mesh and then reduced under hydrogen atmosphere before use. In contrast to the foregoing experiments where both H_2 and air were fed simultaneously, alternate feeding of these two gases was employed in this experiment. The alternate gas feeding will be useful in the practical cases. The relative time of catalyst activation to oxidation of benzene can be varied at will. Here, we tentatively employed 30 min for both the activation and oxidation.13) Under the conditions of Table 2, the amount of phenol produced in an hour (single reaction cycle) attained to approximately 45 micro-mol and the rate was unchanged for the successive repetitions of the reaction cycle.

The present study proves the effectiveness of the combined use of heterogeneous catalyst with copper(I)/(II) couple. Undoubtedly, the production rate of phenol depends on working conditions such as the nature of the heterogeneous catalyst, mode of gas feeding, reactor design and so on. Further exploitation of more suitable system is now in progress.

Table 2. Production of Phenols Using Palladized Silica Catalyst at Room Temperature[a)]

Number of repetition[b)]	1	2	3
Phenol/μmol	44.3	44.3	44.0
Hydroquinone/μmol	17.0	10.1	9.7

a) The solid catalyst used consisted of Pd (5 mg) and silica-gel (1 g). The reaction was carried out with stirring in 0.05 M H_2SO_4 (25 cm^3) containing 10% of acetonitrile, 1 mmol of $CuSO_4$, 1 g of Pd/silica catalyst, and 1 g of benzene. b) In each cycle, the solution was first exposed to H_2 for 30 min and then exposed to air for 30 min.

References

1) K.Sasaki, S.Ito, S.Saheki, Y.Kinoshita, T.Yamasaki, and J.Harada, Chem. Lett., 1983, 37.
2) K.Sasaki, S.Ito, T.Kinoshita, and J.Harada, Chem. Lett., 1983, 445.
3) T.Kinoshita, J.Harada, S.Ito, and K.Sasaki, Angew. Chem. Suppl., 1983, 599.
4) S.Ito and K.Sasaki, Yuki Gosei Kagaku Kyokaishi, 41, 839 (1983).
5) A.Kunai, S.Hata, S.Ito, and K.Sasaki, J. Org. Chem., 51, 3471 (1986).
6) A.Kunai, S.Hata, S.Ito, and K.Sasaki, J. Am. Chem. Soc., 108, 6012 (1986).
7) S.Ito, A.Kunai, H.Okada, and K.Sasaki, J. Org. Chem., 53, 296 (1988).
8) S.Ito, T.Yamasaki, H.Okada, S.Okino, and K.Sasaki, J. Chem. Soc., Perkin Trans. 2, 1988, 285.
9) S.Ito, H.Okada, R.Katayama, A.Kunai, and K.Sasaki, J. Electrochem. Soc., in press.
10) We have already confirmed that this catalyst system is usable in several non-conducting organic solvents. The use of such organic solvents is useful for hydroxylating hydrophobic aromatic compounds. Details will follow successively.
11) J.Halpern, Ann. Rev. Phys. Chem., 16, 103 (1965).
12) Use of higher concentration of Cl^- (or acetonitrile), however, lowers the efficiency of oxidation.
13) The duration time of H_2-reduction and air-oxidation should be reexamined for obtaining highest yield.

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