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Catalytic Oxygenation of Benzene. Catalyst Design and Its Performance

Atsutaka KUNAI,* Takayuki WANI, Yasushi UEHARA, Fumiaki IWASAKI,
Yasushi KURODA, Sotaro ITO, and Kazuo SASAKI
Department of Applied Chemistry, Faculty of Engineering, Hiroshima University,
Shitami, Saijo-cho, Higashi-Hiroshima 724
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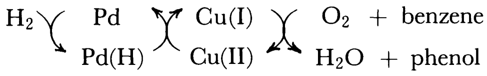
A catalyst system for oxygenation reaction of benzene has been discussed. The catalyst system is composed of Pd and Cu species and operates in neat benzene under ambient conditions by feeding hydrogen and oxygen to the system. By selecting the reaction conditions properly, either phenol or benzoquinone is obtained as the major product.

There is a strong demand in the chemical industry to produce phenol or phenolic compounds in much more efficient ways.[1] Undoubtedly, the most efficient process currently operating in the chemical industry is the "Cumene Process." This process, however, necessitates multi-step operations throughout the whole process and accompanies by-production of equimolar amount of acetone. If benzene is directly converted to phenols without any by-product under moderate conditions, a great benefit will be brought about.

Many reactions are known which lead to phenol from benzene.[1,2] They are, however, too much basic[3-6] to be used for the practical purpose or require severe reaction conditions[7,8] and/or expensive chemical reagents.[7,9] In this paper, we report the nature and the performance of some new solid catalysts developed for the one-step production of phenol.



Scheme 1.

The catalyst system is basically composed of Pd and Cu species and operates in neat benzene under ambient conditions by feeding hydrogen and oxygen gases. The reaction sequence occurring in this system may be expressed as in Scheme 1, where palladium mediates electron transfer from hydrogen to copper(II) ions. The copper(I) ions thus produced activate dioxygen to produce phenol. Furthermore, the main product can be altered at will from phenol to *p*-benzoquinone if the reaction conditions are slightly modified. It should be noted that no effective catalyst has been known so far for the direct conversion of benzene to benzoquinone.

Experimental

Catalyst Preparation. The solid catalysts examined in this study were prepared in three different ways. **Catalyst A:** $PdCl_2$ (0.5 mmol), Cu(II) salt (10 mmol), and silica gel (10 g, Merck No. 9385, 230—400 mesh ASTM) were added to water (30 cm^3) altogether and exposed to ultrasonic wave for 90 min. The resultant mixture was heated to dryness on a steam bath under gentle agitation. **Catalyst B:** $PdCl_2$ was first dissolved in dil HCl (30 cm^3) and Cu(II) salt and silica gel were then added to the solution. The mixture was dried in the same way as described in the catalyst A. **Catalyst C:** A mixture of $PdCl_2$ and silica gel in water was stirred at 60 °C for 2 h to disperse the Pd salt on the silica surface. Copper(II) sulfate was then loaded on it. The mixture was dried in the same manner as described above.

Oxidation of Benzene. Experiments under atmospheric conditions were conducted in an Erlenmeyer flask (50 cm^3) equipped with two gas inlets and one outlet. A mixture of benzene (20 cm^3) and the catalyst (2 g) was taken in the flask and shaken in a thermostated bath at 25 °C at the rate of 140 times/min with 30 mm stroke under atmospheric pressure. The reacting gases were fed to the flask in two different modes. **(1) Simultaneous gas feeding:** During the whole reaction, both hydrogen and oxygen were passed through the flask simultaneously. **(2) Alternate gas feeding:** Gases in the flask were first replaced with hydrogen and shaken for a desired time. Hydrogen was then switched to either air or pure oxygen and the flask was again shaken. This alternate gas feeding was repeated several times in some experiments.

Experiments under pressurized conditions were carried out in a glass-made autoclave equipped with a mechanical stirrer by applying the alternate gas-feeding.

Product Analysis. During the reaction, a small amount of sample was taken up periodically for HPLC analysis. The products were analyzed by using Merck Lichrosorb RP-18 (10×250 mm) as the stationary phase and a solution of acetonitrile-phosphate buffer of pH 3.5 (1 : 3) as the eluent.

Results and Discussion

1. Catalyst Design.

The solid catalyst designed in this study is basically composed of 2 mmol of copper(II) sulfate and a catalytic amount of palladium chloride (0.1 mmol) supported on 2 g of silica. By feeding hydrogen, $PdCl_2$ is reduced to metallic Pd.

As for the role of copper species in the oxidation of benzene, we have already demonstrated that, in aqueous acid solutions, low valent copper ions activate dioxygen to generate hydroxyl radicals (Eqs. 1 and 2), which react with benzene to yield phenolic compound (Eq. 3).[10-13]

$$O_2 + 2Cu^+ + 2H^+ \longrightarrow H_2O_2 + 2Cu^{2+} \qquad (1)$$

Table 1. Catalytic Oxidation of Benzene by Simultaneous Feeding of Hydrogen and Oxygen[a)]

Reaction time/h	0.5	1	2	3	4	5	6	7	8	9
PhOH/μmol	4.7	15	48	77	114	141	167	183	205	229

a) The reaction was carried out using the catalyst C by simultaneous feeding of H_2 and O_2.

Table 2. Effect of Oxidation Time on the Phenol Yield[a)]

Oxidation time/min	5	10	15	20	25	30
PhOH/μmol	18.2	18.6	19.5	19.3	19.6	19.8

a) The reaction was carried out using the catalyst C by alternate feeding of H_2 and O_2. The oxidation started after the catalyst had been treated under H_2 for 90 min.

$$H_2O_2 + Cu^+ + H^+ \longrightarrow \cdot OH + Cu^{2+} + H_2O \qquad (2)$$

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

Since Cu(I) ions are consumed during the reaction, it is necessary to recycle Cu(I) ions by some suitable means in order to set up a continuous reaction system. This may be performed by using hydrogen as the reducing agent when certain metal catalyst is present in the system. Palladium seemed to be the best candidate among such catalysts (Eq. 4).[14)]

$$2\,Cu^{2+} + H_2 \xrightarrow{Pd} 2\,Cu^+ + 2\,H^+ \qquad (4)$$

The overall stoichiometry of the reactions expressed by Eqs. 1—4 can simply be summarized as in Eq. 5 for phenol or in Eq. 6 for benzoquinone. It is interesting to see that the overall reaction of this system resembles in some sense the reactions catalyzed by oxygenase, where dioxygen is activated by some electron-transfer systems to be incorporated in organic substrates. The equations predict that either phenol or benzoquinone will be produced continuously by feeding both hydrogen and oxygen.

$$C_6H_6 + H_2 + O_2 \longrightarrow C_6H_5OH + H_2O \qquad (5)$$

$$C_6H_6 + H_2 + 2\,O_2 \longrightarrow C_6H_4O_2 + 2\,H_2O \qquad (6)$$

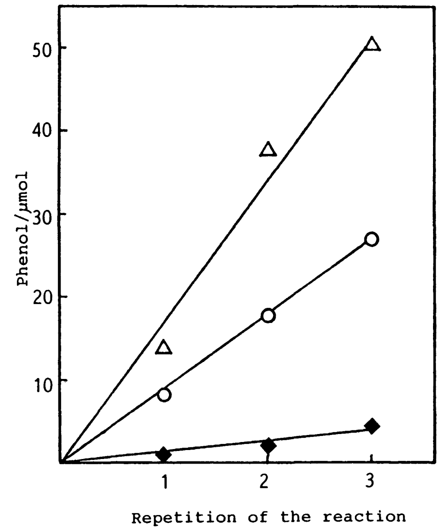


Fig. 1. Effect of reduction time on the phenol yield. The reactions were carried out using catalyst C by applying alternate feeding of H_2 and O_2. Symbols stand for the reduction time of 15 (◆), 30 (○), and 90 (△) min, respectively. Oxidation time was fixed at 5 min.

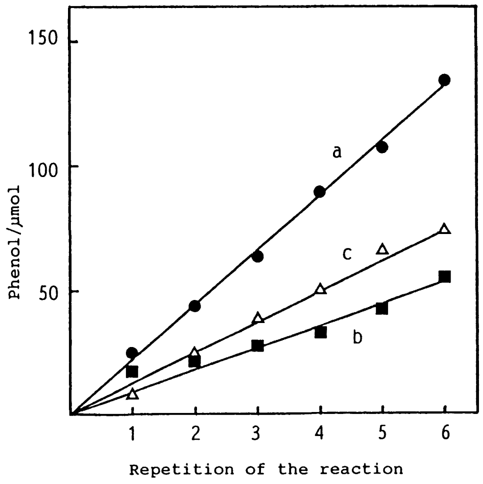


Fig. 2. Effect of preparation methods on the catalyst performance. The reactions were carried out in the same manner as described in Table 3 except that hydrogen reduction (30 min) and air-oxidation (30 min) were applied in each reaction cycle. Symbols stand for the catalysts of type A (●), B (■), and C (△), respectively.

2. Reactions with Catalysts Made from $CuSO_4$. As will be described in the later section, counter ions of copper salts in the catalyst show a definite effect on the reaction pathways. In this section, the nature of the catalyst made from $CuSO_4$ is discussed.

At first, the catalytic oxidation of benzene was conducted by feeding hydrogen and oxygen simultaneously at 25 °C for 9 h. Table 1 shows results obtained with the catalyst C. As is seen in the table, phenol accumulates steadily with increasing reaction time except for the initial period of the reaction, indicating that the catalytic cycle supposed in Scheme 1 is effectively operating. The anomaly appearing in the initial stage may be due to the reduction of Pd(II) to Pd(0).

The simultaneous gas feeding has a definite risk of explosion. We accordingly examined the performance of the alternate gas feeding, where the catalyst may be activated to produce Cu(I) ions in the stage of hydrogen and benzene may be oxidized in the stage of oxygen. The latter method has an additional merit to present separately the behaviors of the catalyst during each stage of hydrogen and oxygen. The results shown in Table 2 were given by using the catalyst C, which was treated with hydrogen for 90 min. The yields of phenol were almost unchanged while the oxidation time was varied from 5 to 30 min,

Table 3. Effect of Catalyst Composition on the Phenol Yield[a)]

Run	Catalyst composition			Additive	Product
	SiO_2/g	$CuSO_4$/mmol	$PdCl_2$/mmol	CH_3COOH/g	Phenol/μmol
1	2	2	0.1	1	83
2	2	2	0.1	0	51
3	2	2	0.2	0	50
4	2	2	0	1	0
5	2	2	0	0	0
6	2	0	0.1	1	3
7	2	0	0.1	0	Trace
8	0	2	0.1	1	Trace
9	0	2	0.1	0	Trace
10	2	2	b)	0	4
11	c)	2	0.1	0	5

a) The reactions were performed using the catalysts corresponding to type A by applying alternate feeding of H_2 for 2 h and air for 1 h. In Runs 8 and 9, powdery mixture of $CuSO_4$ and $PdCl_2$ were used without support. b) H_2PtCl_6 (0.1 mmol) was used instead of $PdCl_2$. c) Alumina (2 g) was used instead of silica.

indicating that the time for 5 min must be enough to complete the oxidation.

In order to see the behavior of catalyst activation under hydrogen atmosphere, the time of hydrogen treatment was varied while the oxidation time was fixed at 5 min. The same process was repeated up to 3 times for each reaction. Results obtained were plotted in Fig. 1, which indicated that the catalyst activation with hydrogen was rather a slower step and the activation was still insufficient even after 90 min.

It should be noted that the preparation method of the catalysts affects the catalyst performance appreciably. This is shown in Fig. 2, where hydrogen and air were fed alternately by a period of every 30 min and the hydrogen/air cycle was repeated 6 times. Lines a, b, and c in the figure stand for results obtained with the catalysts A, B, and C, respectively. Undoubtedly, the catalyst A gave the best result among the three catalysts tested. The rate of phenol production with the catalyst A amounted to 22 μmol per cycle, compared with the corresponding rates of the catalysts B and C (9 μmol and 13 μmol, respectively).

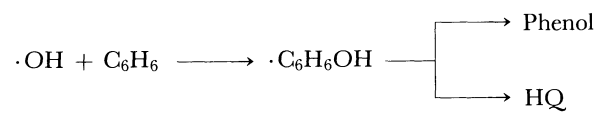
The catalyst A was prepared by using ultrasonic wave for dispersing Pd salt on the silica surface instead of mechanical stirring which was employed for the catalyst C. The different performance appearing in the figure may be attributed to the size and distribution of the catalyst components, particularly of Pd. Superiority of using ultrasonic wave is doubtless.

In contrast, the performance of the catalyst B was the worst among the three. In order to ensure the complete dissolution of $PdCl_2$, this catalyst was prepared by dissolving $PdCl_2$ with a small amount of dil HCl. The worst performance is probably caused by excess chloride ions left in the catalyst.

Results in Table 3 prove that each catalyst component fills its own role in the catalytic cycle. In experiments for this table, the catalysts corresponding to type A were first activated with hydrogen for 2 h and then used for air-oxidation of benzene for 1 h. It is clearly indicated that, as far as the alternate gas feeding is concerned, the best performance is obtained only when Pd and Cu species are both loaded on the silica surface (Runs 1 to 3).[15)]

When $PdCl_2$ was replaced by H_2PtCl_6 (Run 10), phenol was certainly produced, but the yield was low. The catalyst composed of Pd alone produced only a trace amount of phenol (Runs 6 and 7). The absence of silica support seriously decreased the catalyst activity (Runs 8 and 9). When alumina was used instead of silica (Run 11), the yield of phenol decreased markedly, indicating that the supporting material should be hydrophilic and acid-resistant. Silica appears to satisfy these requirements. On the other hand, the inefficiency of alumina catalyst may be attributed to the degradation of alumina surface with sulfuric acid liberated during the reduction of Cu(II) salt.[16)]

3. Effect of Counter Ion in Cu Salts. Previous studies have shown that phenol and hydroquinone are formed competitively from the same intermediate, hydroxycyclohexadienyl radical (Eq. 7).[13)] The product selectivity was quite sensitive to the pH value of aqueous solution.[12)] Phenol predominated in solutions of lower pH, but the relative yield of hydroquinone to phenol (HQ/P) increased markedly with the increase in pH. At about pH=3.5, the HQ/P ratio became 2.5.



$$\cdot OH + C_6H_6 \longrightarrow \cdot C_6H_6OH \longrightarrow \begin{cases} \text{Phenol} \\ \text{HQ} \end{cases} \qquad (7)$$

In the present case, the solution phase is neat benzene and the acidity control in it seems difficult. There is, however, a possibility of controlling the acidity over the surface of the solid catalyst used here.

Table 4. Oxidation of Benzene with Catalysts Made from Various Cu Salts[a)]

Cu salt of	PhOH/μmol	BQ/μmol	Cu salt of	PhOH/μmol	BQ/μmol
SO_4^{2-}	51	5.2	PO_4^{3-}[b)]	40	0.1
Cl^-	0	0	AcO^-	0.4	0
NO_3^-	32	2.2	AcO^-[c)]	34	7.3
ClO_4^-	64	1.0			

a) The reaction was carried out in the same manner as Table 3. b) Phosphoric acid (0.85g) was also loaded onto the support. c) Acetic acid (2 g) was dissolved into benzene.

Table 5. Effect of Oxygen Pressure on the Product Selectivity[a)]

Cu salt	AcOH/vol%	Ratio of BQ/PhOH (Total products/μmol)			
		air, 1 atm	O_2, 1 atm	O_2, 3 atm[b)]	O_2, 6 atm[b)]
$Cu(OAc)_2$	2.5	—	0.79 (47.1)	1.50 (29.6)	—
	5.0	0.16 (24.6)	0.63 (44.2)	1.53 (57.6)	1.39 (29.6)
	10.0	0.20 (41.0)	0.61 (62.6)	0.84 (45.8)	—
	20.0	—	0.45 (43.4)	—	—
$CuSO_4$	0	0.10 (56.2)	0.11 (37.0)	0.12 (70.6)	—
	10.0	0.01 (31.2)	0.15 (39.0)	—	—

a) The reactions were carried out in the same manner as Table 3. b) Hydrogen reduction was also done under the same pressure.

During the stage of catalyst activation with hydrogen, copper(II) salt, CuX_2, is reduced to CuX and liberates free acid, HX (Eq. 8). Accordingly, we can expect that the acid strength of HX affects the fate of the intermediate species.

$$2\,CuX_2 + H_2 \longrightarrow 2\,CuX + 2\,HX \tag{8}$$

This point was examined using several copper(II) salts as listed in Table 4. Reactions were conducted with the catalysts of type A in the same manner as noted on the margin of Table 3.

For salts of strong acid, sulfate, nitrate, and perchlorate, the reaction proceeded to produce 30—50 μmol of phenol. In contrast, no reaction was observed in the case of chloride. This is because initial activation of $PdCl_2$ to Pd(0) did not occur as was confirmed by visual observation.

In the case of acetate salt, when no particular treatment was applied, hydrogen reduction of Cu(II) to Cu(I) ions was extremely slow leading to a very low yield of phenol. For accelerating the reaction, addition of free acid was found to be effective. In fact when a small amount of acetic acid was added deliberately to benzene, the reaction proceeded at a reasonable rate. The yield of benzoquinone was still minor.

It is interesting to see that, however, the relative yield of *p*-benzoquinone vs. phenol (Q/P) increases in the following order: $ClO_4^- < NO_3^- < SO_4^{2-} < AcO^-$: the sequence being in accordance with the decreasing acid strength of their corresponding free acids.

In the case of phosphate salt, the yield of quinone is exceptionally low. In this case, phosphoric acid was used and impregnated onto the silica support during the process of catalyst preparation, because the phosphate salt was hardly soluble in water. Regarding this, it should be noted that the silica surface modified with phosphoric acid exhibits a strong acidity. In fact, the Hammett's H_0 function of the modified surface is said to be comparable with that of sulfuric acid.[17)]

4. Alteration of Product Selectivity. In the foregoing section, it has been indicated that the control of surface acidity permitted alteration of the product selectivity: Q/P varies from 0.02 in perchlorate case to 0.21 in acetate case. This tendency may be amplified by increasing oxygen concentration, since benzoquinone comes from the adduct of hydroxycyclohexadienyl radical with dioxygen.[11)] This point was investigated with the use of the acetate catalyst made by procedure A. Results are summarized in Table 5.

The data of the acetate catalyst indicate that the product ratio is sensitive to the oxygen pressure in the surrounding gas. As far as the oxygen source was ordinary air, the product ratio, Q/P, was only 0.21 even in the highest case. At 5% level of acetic acid added deliberately, the value increased from 0.16 to 1.53 corresponding to the change of oxygen pressure from 0.2 (air) to 3 atm, respectively. At 6 atm, the value tended to saturate. An addition of acetic acid was necessary for accelerating the reaction rate. As the data indicated, however, excess addition of it seemed to affect the Q/P ratio negatively.

In Table 5, are also shown the data for the sulfate catalyst for comparison. The Q/P ratio, in this case, never exceeded 0.15 even if pressurized oxygen was supplied. This clearly indicates that oxygen effect saturates below 1 atm when Cu salt is of a strong acid. In other words, the choice of counter ion is quite important for the effective performance of the dioxygenation reaction of benzene. The effect of counter ion is in agreement with our previous observation, where we have found that the pressure effect is pH dependent and saturates at low level at lower pH.[12)]

Seemingly complicated effects of oxygen pressure, acid concentration, and counter ion in Cu salt are a reflection of multivariable nature of the reaction system. The highest value attained here, ca. $Q/P=1.5$, seems rather low, but we believe that the value will be improved by further modification of the reaction conditions.

The catalyst system described above has several advantages. Firstly, the reaction can be performed under very mild conditions and hence the total selectivity of oxygenated products, phenol and benzoquinone, is quite high. No other product is detected in the reaction mixture. Secondly, the catalyst preparation is simple and the catalysts having the same activity are always obtained. Thirdly, benzene can directly react with catalysts without any use of solvents. This fact leads to an additional advantage, i.e. the extremely simple isolation of the reaction products. Finally, either phenol or benzoquinone can be selectively obtained at will by a slight modification of the reaction conditions. With the use of the copper perchlorate catalyst, phenol is almost exclusively produced regardless of other conditions. Air is sufficient as the oxygen source. On the other hand, benzoquinone is obtained as the major product when the copper acetate system is employed in combination with the use of slightly pressurized oxygen.

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15) Somewhat different aspect appears when the mode of gas feeding is simultaneous. This point will be discussed in the succeeding paper.

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