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Stoichiometric Oxidation of Benzene to Phenol with Copper(II) Salts

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Phenol is readily produced by some stoichiometric reactions of benzene with certain copper(II) salts. The main part of the reaction using copper(II) sulfate is estimated to be expressed by the following equation:

$$\text{Benzene} + 2\text{CuSO}_4 + \text{H}_2\text{O} = \text{Phenol} + \text{Cu}_2\text{SO}_4 + \text{H}_2\text{SO}_4.$$

This reaction was carried out in a flow system at 300 °C, where a vapor mixture of benzene and water flowed through a packed bed of copper(II) sulfate supported on silica gel. The products were mainly phenol and CO_2 with a trace amount of biphenyl. The phenol yield became appreciable at temperatures higher than 250 °C, and reached a maximum at ca. 300 °C. At higher temperatures, the CO_2 yield increased along with the consumption of phenol. The percentage yield of phenol based on copper(II) salt was 86% at the highest. Although copper(II) phosphate was similarly useful, it required a higher reaction temperature (ca. 500 °C).

Throughout the past 10 years we have worked to develop the one-step oxidation of benzene to phenol in both liquid and gas phases. Three different processes have been found to be worthy of practical application. The electrochemical process using the Cu^+/Cu^{2+} redox couple was found to be very attractive, particularly when the target product is *p*-benzoquinone.[1—3] In the liquid-phase catalytic reaction, the use of a Pd catalyst supported on some suitable solid surface is quite useful if chloride ion is in the reaction system.[4,5] When the process was operated in the gas phase, the use of a Pd–Cu composite catalyst supported on the surface of silica provided a very good catalytic performance.[6,7]

The proposed catalytic systems[4—7] necessitate the simultaneous feeding of hydrogen and oxygen to produce phenol from benzene, and is risky to be entirely free from detonation, although the actual reaction system seems to be quite safe. We thus attempted to find another reaction system which is free from detonation. A patent claimed by Mitsui-Toatsu Co.,[8] which insists that phenol is catalytically produced when water and benzene are supplied to a packed bed of copper(II) phosphate, prompted us to utilize water as the oxygen source.

Experimental

Reagents. Copper(II) sulfate was impregnated from an aqueous solution on commercial silica gel (Silica gel 60, Merck) for chromatographic use. Although copper(II) phosphate reagent was also prepared similarly, in order to facilitate its dissolution, phosphoric acid was added to the impregnating solution. The phosphoric acid remains on the silica surface because it is nonvolatile. Benzene, H_2SO_4, and oxygen were certified standards, and were used without further purification. Hereafter, the catalysts are denoted as xCuSO$_4$ (or $Cu_3(PO_4)_2$)/SiO_2, where x stands for the number of micromoles of copper(II) salt per gram of silica support.

Procedure. Experiments were carried out using a flow reactor made of a vertically held Pyrex glass tube (19 mm in diameter, 345 mm in length) having a sintered glass plate at the middle, on which copper containing silica powder was placed. The reactor tube was heated to a desired temperature by a small electric furnace. Liquid reactants, benzene and water were dropped from the top of the reactor tube and vaporized before entering the silica layer. During the early stage of experiments, nitrogen was also supplied together with a liquid reactant. At the bottom of reactor, a small glass tube containing ethanol was placed in order to trap soluble products, of which aromatics were analyzed by HPLC. Trap ethanol was renewed at every sampling at 1 h intervals. The exhaust gas was passed through an aqueous solution of $Ba(OH)_2$ to capture CO_2 before releasing it into the atmosphere. Further details concerning the experiments have been described elsewhere.[4,6]

Results and Discussion

Under conditions without feeding oxygen, the detected products were mainly phenol and carbon dioxide. In contrast to the other hydroxylation of benzene in a catalytic gas-phase reaction over Cu–Pd/SiO_2[6,7] and in a liquid-phase reaction with Fenton's reagent,[9]

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very small amounts of biphenyl and quinones were detected in this case. No ring-cleavage product other than CO_2 was found. Figure 1 shows the accumulation of products and the rate of phenol production as a typical example. The yield of CO_2 has been multiplied by 1/6 to show the moles of benzene consumed. Although the reaction still continued even after 5 h from initiation, the rate of phenol formation decreased quickly and ca. 50% of the total yield of phenol was produced within the first 1 h. This phenomenon can be explained by the consumption of copper(II) salt. Since all of the external reagents were supplied steadily, the time-dependent variable should only be the activity of the copper(II) salt. In addition, the accumulation of phenol increased according to the first-order rate equation regarding the amount of copper(II) salt (see Ref. 7 and also Fig. 3 below). From these results it is concluded that the present hydroxylation of benzene with copper(II) sulfate is a stoichiometric reaction.$^{14)}$

The color of silica-bearing copper(II) salt on its surface was pale sky-blue, but became light brown after the reaction. When the latter was put into distilled water and exposed to ultrasonic waves, a brown-colored gel-like material was readily separated from silica and floated over the water surface. Having been separated and dried, the colored flocculate was subjected to both elemental analysis and infrared spectroscopy. Neither a copper species nor a carbonaceous material was detected; however, signals of silica alone appeared in the infrared spectra. After separating the flocculate, water was again evaporated, and the resulting pale sky-blue product was used to test the recovery of the oxidizing ability. The ability recovered completely, and the phenol yield was even improved, compared to that of the first run. It is interesting to note that the silica surface neither became brown color after the second use nor released flocculate upon meeting with water. Probably, some surface modification of commercial silica accounted for the flocculate.

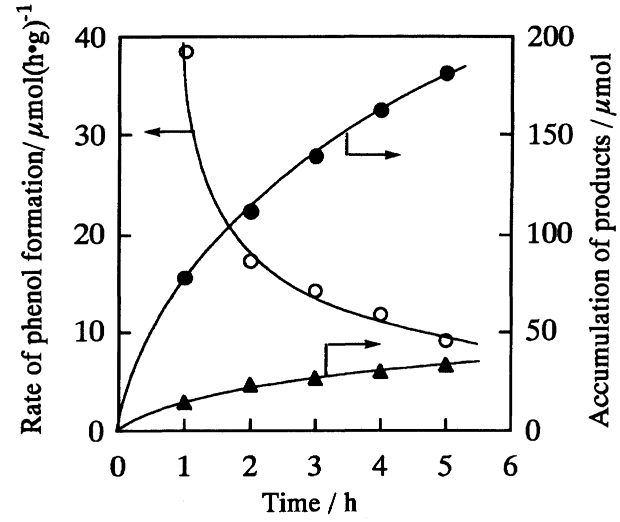

Fig. 1. Oxidation of benzene. ○ and ●, phenol; ▲, CO_2. Moles of CO_2 are multiplied by 1/6. Reagent: 200 $CuSO_4/SiO_2$. Weight of reagent: 2 g. Gas reactant: benzene, 34; H_2O, 114; N_2, 74 mmol h^{-1}. Temperature: 573 K.

The yields of the products were measured as a function of the reaction temperature, as shown in Fig. 2. The yield of phenol indicated a maximum at about 300 °C, and decreased at higher temperatures, probably due to a further degradative oxidation of phenol. On the other hand, the yield of CO_2 steadily increased with increasing temperature. The results for copper(II) phosphate,$^{8)}$ which has been claimed in patent literature, is also indicated for a comparison. Although they regarded copper(II) phosphate as a catalyst, we believe that its role is merely that of an oxidant. The results given in Fig. 2 clearly indicate that a similar yield of phenol can be achieved at definitely lower temperatures. However, the production of CO_2 seems to be somewhat enhanced.

The effect of the surface concentration of copper(II) sulfate over the silica surface is illustrated in Fig. 3, in which the production rate increases monotonously with increasing concentration of copper(II) sulfate, and seems to reach saturation. At the lower concentration range of less than 200 μmol (g-SiO_2)$^{-1}$, the rate increase can be approximated as being a linear function of the copper concentration. However, it should be noted that when crystalline copper(II) sulfate was used without loading on the silica support, but merely placed

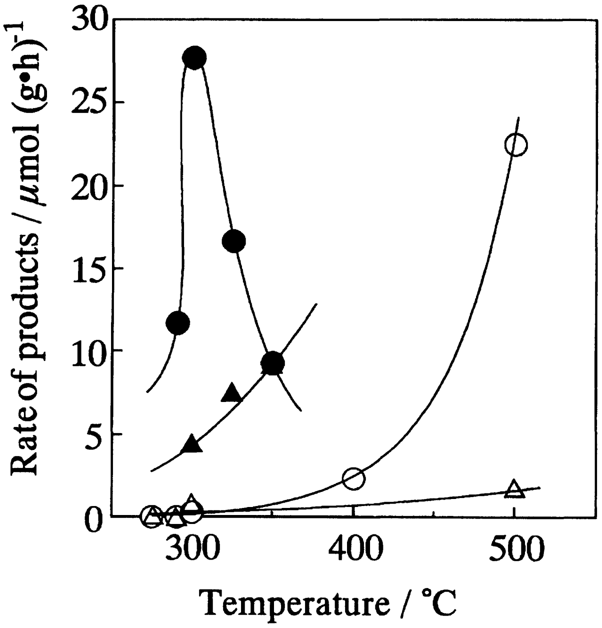

Fig. 2. Temperature dependence of reaction with (●, ▲) 200 $CuSO_4/SiO_2$ and (○, △) 200 $Cu_3(PO_4)_2/SiO_2$. ●, ○; phenol. ▲, △; CO_2. Moles of CO_2 are multiplied by 1/6. Wight of reagent: 2 g. Gas reactant: benzene, 34; H_2O, 114; N_2, 74 mmol h^{-1}. Reaction time: 3 h.

Table 1. Effect of Reactant Composition on the Yield of Product[a)]

Entry	Reactant composition	Yield/10^{-6} mol			Conv.[b)]
	(N_2 : O_2 : H_2O : benzene)	PhOH	CO_2[c)]	Total	%
1	0.29 : 0.06 : 0.05 : 0.05	34	142	174	0.18
2	0.35 : 0 : 0.05 : 0.05	102±6	24±1	126±7	0.12
3	0 : 0 : 0.5 : 0.5	154±18	3±0	157±18	0.05

a) Reaction time, 3 h. b) Conversion of benzene. c) Values are multiplied by 1/6 to show moles of benzene reacted.

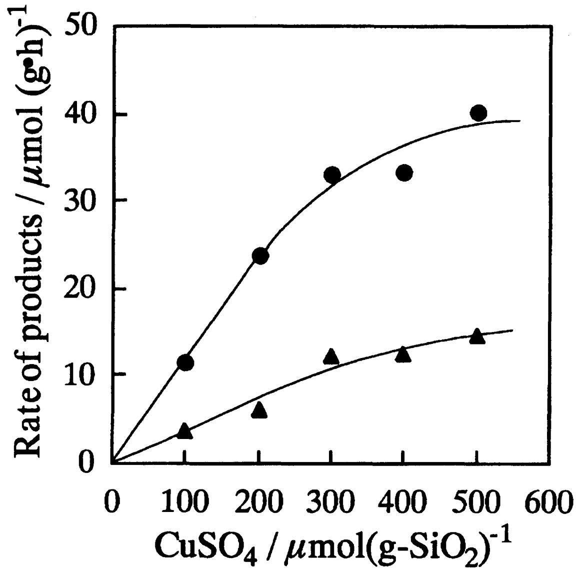

Fig. 3. Effect of surface concentration of $CuSO_4$ over SiO_2 support. ●; phenol ▲; CO_2. Moles of CO_2 are multiplied by 1/6. Weight of reagent: 2 g. Gas reactant: benzene, 34; H_2O, 114; N_2, 74 mmol h^{-1}. Reaction time: 3 h. Temperature: 573 K.

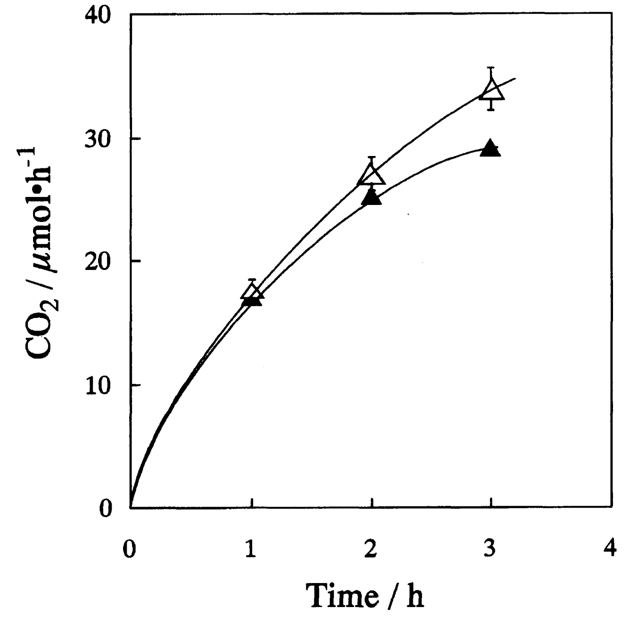

Fig. 4. Evolution of CO_2 from benzene (▲) and phenol (△). Reagent: 200 $CuSO_4/SiO_2$. Weight of reagent: 2 g. Gas reactant: benzene (phenol), 34 (0.04); H_2O, 114; N_2, 74 mmol h^{-1}. Temperature: 573 K.

between two layers of silica powder, scarcely any product was detected. This may be attributed to the matter of the surface area.

Figure 2 indicates that the yield of phenol decreased at higher temperatures, exceeding 300 °C, while that of CO_2 increased monotonously. The question as to whether CO_2 is produced solely from phenol as the secondary product, or is produced directly from benzene, remains unsolved. In order to confirm this point, the CO_2 production from phenol was studied separately. In this case, 120 μmol of phenol, which corresponds to the total yield of phenol during the reaction of benzene for 3 h, was supplied to the reactor in the form of a dilute aqueous solution. As can be seen in Fig. 4, the production curve of CO_2 from phenol almost coincides with that from benzene. Taking into account that the feed rate of benzene and phenol were 34 and 0.04 mmol per hour, respectively, the rate from phenol is much faster than that from benzene by a factor of 1000. As a consequence, it can be concluded that the source of CO_2 is almost exclusively phenol, and that the direct path from benzene to CO_2 can be ignored.

The results obtained with three different compositions of reactants are listed in Table 1. In each composition, measurements were repeated 4 to 5 times, and only the mean values are shown in this table. The values for the CO_2 yield were multiplied by 1/6 in order to show the moles of benzene consumed. The last column shows the percentage conversion of benzene.

Regarding this table, several important findings can be pointed out. Firstly, when oxygen was contained in the reactant mixture, the yield of phenol was drastically suppressed and, instead, the yield of CO_2 increased while the total yield of CO_2 and phenol was slightly increased. The latter fact also supports that CO_2 is

Table 2. Loss of SO_4 from Silica Support during the Reaction[a)]

Reaction temp	Method of determination			
°C	Turbidimetry	pH	I.C.[b)]	E.A.[c)]
300	31.2	44.5	32.6	71.0
350	65.6	—[d)]	—[d)]	—[d)]

a) Values are indicated in %. b) Ion chromatography. c) Element analysis of sulfur. d) Not measured.

Table 3. Loss of Cu^{2+} from Silica Support during the Reaction

	Amount of $Cu^{2+}/10^{-6}$ mol		Loss of Cu^{2+}	Yield of phenol
	Before	After	10^{-6} mol	10^{-6} mol
Reaction[a)]	319±9	264±17	55±14	109
Blank[b)]	310	310	0	

a) Copper reagent, 200 $CuSO_4$/g-SiO_2 (2 g); reaction gas, benzene : H_2O : N_2=0.15 : 0.51 : 0.34; reaction gas rate, 222 mmol h^{-1}; temperature, 300 °C; time, 3 h. b) Blank experiment was done under the same reaction conditions as above except that an equimolar mixture of H_2O and N_2 was supplied. No benzene was supplied.

produced via phenol. Secondly, in the experiment of Entry 3, a certain amount of phenol was detected, even in the absence of N_2 and O_2. It follows that the oxygen incorporated into the phenol molecule came from water. Thirdly, only in the case of Entry 1, where oxygen was supplied continuously, did the rates of the production of both phenol and CO_2 not decrease, and their yields increased linearly with the reaction time, as shown in Fig. 5, suggesting that bivalent copper ions are regenerated by oxygen. This also suggests that there is a possibility of designing a continuous process by controlling the oxygen content appropriately. It is also remarkable that quinones are produced at an appreciable rate due to the presence of oxygen. Quinones are the products characteristic to a system involving both copper ion and dioxygen simultaneously.[10,11)]

In order to confirm the stoichiometry of the reaction, an analysis of silica-supported Cu-reagents before and after the reaction was carried out. A determination of sulfate ion was made in several ways, including the turbidimetry of $BaSO_4$, ion chromatography, pH measurements as well as the elemental analysis of sulfur. The obtained results are summarized in Table 2. Among them, the change in the pH was determined with trap water both before and after the reaction, by assuming that the pH change is solely caused by released H_2SO_4. Except for the elemental analysis, which resulted an erroneously large loss, the data are in fairly good agreement. Obviously, sulfate ions are released from the silica surface during the reaction. Similarly, copper ion was analyzed by spectrophotometry using 2,9-dimethyl-4,7-diphenyl-1,10-phenanthrolinedisulfonic acid.[12)] As can be seen in Table 3, copper ion is also released from silica, though its amount is much less compared with that of the sulfate ion. After the reaction for 3 h, 375×10^{-6} mol, which amounts to 49% of the original value, of sulfate ion was lost from the silica support, while the loss of copper was 115×10^{-6} mol (15%).

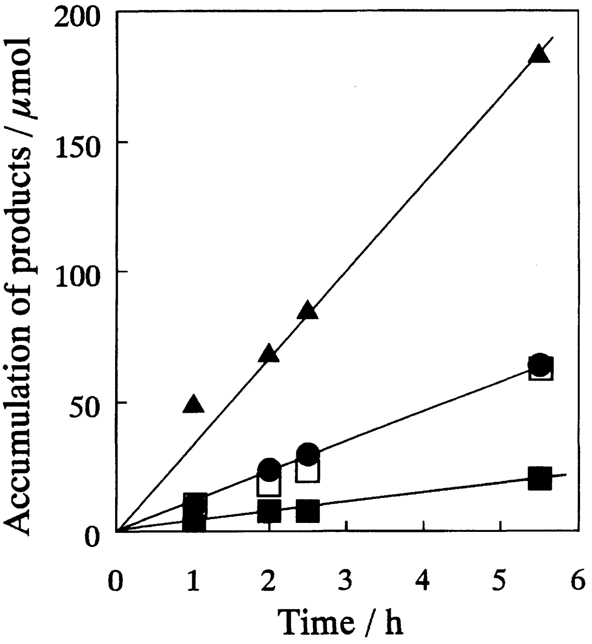

Fig. 5. Effect of O_2 supply. ●, phenol; □, benzoquinone; ■, hydroquinone; ▲, CO_2. Moles of CO_2 are multiplied by 1/6. Reagent: 200 $CuSO_4/SiO_2$. Weight of reagent: 2 g. Gas reactant: benzene, 34; H_2O, 114; O_2, 13; N_2, 61 mmol h^{-1}. Temperature: 573 K.

In connection with this, a surface analysis using XPS as well as scanning electron microscopy (SEM) assembled in an X-ray microanalyzer were also carried out with silica samples for detecting the chemical change of $CuSO_4$ during the reaction. An X-ray microanalysis and an SEM observation indicated that both copper and sulfur were not uniformly dispersed over the silica surface, but formed localized patches having sizes of up to 700 nm. The size and shape of the patches of sulfur coincided with those of copper, indicating that most of the sulfate ions were not free, but bound to copper ions. Regarding the sample before use, XPS spectra exhibited a peak at a binding energy of 936 eV, which was assigned to $CuSO_4$.[13)] For used samples, the peak split at 936 and 933 eV, the latter being assignable to either Cu(I) or metallic copper.[13)] Although the principal photoelectron spectrum did not result in a clear-cut assignment, the presence of both metallic and monovalent states of copper was indicated in the Auger electron spectrum, which comprised an intense peak at 913 eV with a weak shoulder at 918 eV, corresponding to monovalent and metallic states, respectively. These facts, together with those of chemical analysis, suggest that the greatest part of reaction can be expressed by the following reaction:

$$2CuSO_4 + \text{Benzene} + H_2O = \text{Phenol} + H_2SO_4 + Cu_2SO_4, \quad (1)$$

rather than

$$CuSO_4 + \text{Benzene} + H_2O = \text{Phenol} + H_2SO_4 + Cu^0. \quad (2)$$

Actually, both reactions would take place simultaneously, since metallic copper was estimated in the used copper reagent from the Auger electron spectrum. Metallic copper might be formed through the disproportionation of monovalent salts: $Cu_2SO_4 = CuSO_4 + Cu^0$. The percentage yield of phenol is 43% at highest on the basis of Eq. 2, which becomes 86% if Eq. 1 is considered.

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14) According to Fig. 1, total moles of CO_2 produced after 5 h of the reaction amounts to 190 μmol which requires 950 μmol of Cu^{2+} ion if the latter species is the only oxidant and the reaction obeys the following equation.

$$C_6H_6 + 12H_2O + 30Cu^{2+} \rightarrow 6CO_2 + 30H^+ + 30Cu^+$$

This is of course not the case since the amount of Cu^{2+} used is only 400 μmol. We believe that a trace amount of oxygen in the reaction system plays a definite role in the CO_2 producing reaction, probably at the stages after forming phenol.