Gas Phase Oxidation of Benzene to Phenol Using Pd–Cu Composite Catalysts. Part 2. Performance of $CuSO_4$-based Catalysts†

Tomoyuki Kitano,[a] Yasushi Kuroda,[a] Miki Mori,[a] Sotaro Ito,[a] Kazuo Sasaki *,[a]
and Masahiro Nitta[b]
[a] *Department of Applied Chemistry, Hiroshima University, Higashi-Hiroshima, 724 Japan*
[b] *Kure Research Laboratory, Babcock Hitachi Co. Ltd., Takara-machi, Kure, 737 Japan*

Gas phase oxidation of benzene to phenol has been studied using Pd–Cu composite catalysts which were prepared mainly by impregnating the respective metal salts on silica gel. If one of the two metal species is absent from the catalyst, no catalytic activity is observed. Good performance is obtained with catalysts having 5–10 × 10^{-6} mol Pd and 5–10 × 10^{-3} mol $CuSO_4$ per gram silica over the temperature range 140–250 °C. When Pd is loaded by means of ion exchange instead of impregnation, the performance is nearly doubled. The reaction rate is rather high and the use of a higher gas flow rate is also advantageous. The water content of the catalyst affects the performance appreciably, and an external supply of steam improves the performance by a factor of almost two. A rate of phenol production of 0.7 × 10^{-4} mol (h g-cat)$^{-1}$ with more than 90% selectivity is readily achieved. How to suppress the predominant formation of water is the remaining task to be studied.

Phenol is an important starting material having widespread applications in industrial chemical processes. Among many processes utilized in practice, the so-called Cumene process is widely employed because of its excellent process performance and design. The production of acetone, which is inherent to the process is, however, likely to become a serious drawback of the process in the future. Direct conversion of benzene into phenol without any by-product is desirable and many previous efforts have been made.[1–5] Fujiwara[1] reported that the coordinated complex of palladium with *o*-phenanthroline is an efficient catalyst. Moro-oka[2] uses an oxo-binuclear iron complex, while Kimura[3] works with macrocyclic polyamines. In some system, nitrous oxide[4] is used as the oxidant. In comparison to these rather sophisticated catalysts and reagents used by other workers, our reaction system is composed of a very simple traditional catalyst and reagents. The catalyst is basically Cu^I ion, which is either fixed on some suitable support or in some cases dissolved in solution. Cu^I ion activates dioxygen by electron transfer to produce OH radical in cooperation with a proton. Pd serves as the auxiliary catalyst, which regenerates Cu^I from Cu^{II} ions with the aid of suitable reducing agents such as hydrogen. The oxidant is simple dioxygen. The role of the copper redox couple can be compared with that of enzyme monooxygenases in biological systems.

The usefulness of our system has already been demonstrated in some liquid phase oxidation reactions.[6–9] Here, we report the reaction in the gas phase, which seems to be more practical for industrial applications. Since this work is the first study regarding the gas phase reaction, experiments were carried out to collect basic parameters affecting the reaction and also to discover the best conditions for preparing the catalyst. The catalyst used here is restricted to that prepared from $CuSO_4$. Different performances associated with other catalysts, prepared in different ways will be reported separately.

Experimental

Catalyst.—The catalyst was prepared by depositing both $PdCl_2$ and $CuSO_4$ simultaneously from an aqueous solution onto a given amount of silica gel (Merck Kieselgel 60). For further details of the catalyst preparation, ref. 6 should be referred to, where the specific effect of Cl^- ion contained in catalysts is also discussed. Catalysts are denoted in this paper as xCu–yPd, where x and y stand for the number of micromoles of metal species per gram of the silica support. In one batch, 10 g of catalyst was prepared and portioned for several measurements. For a given reaction, the catalyst was sustainable for more than 30 h reaction without any loss of activity. When, however, the reaction was interrupted after a given time, 3–5 h, a remarkable loss of activity appeared in successive measurements, for some unknown reason. Accordingly, each individual measurement was done with fresh catalyst.

In some experiments, catalysts prepared by an ion exchange technique were used for which readers should refer to our previous paper.[7]

Reactor.—The reactor used is shown schematically in Fig. 1. All parts of it were made of Pyrex glass. The catalyst, normally 2 g, was placed over the sintered glass plate located half way up the vertically held tube reactor, which was surrounded by an electric furnace. In order to preheat the reactant gas mixture before it entered the catalyst zone, the catalyst bed was covered by a thick layer (*ca.* 4 cm in depth) of silica gel. The temperature was monitored inside the catalyst bed and the reading was fed back to a regulator to control the variation within ± 10 °C.

In contrast to the previous report,[10] all of the reactants were introduced from the top of the reactor tube to form a downward plug flow through the catalyst layer. Benzene (and water on occasion) was supplied by means of a micro feeder, and both hydrogen and oxygen, as well as nitrogen, were supplied through three independent flow regulators. At the lower end of the tube, a small glass tube containing ethanol was placed to trap soluble products, of which aromatics were analysed by HPLC. The trapping liquid used was ethanol which enabled us to detect and analyse water, another important reaction product, by gas chromatography (GC). In the ethanol trap, an appreciable amount of benzene is captured so that the liquid volume increases with increasing reaction time, although some of it may be vaporized. In order to minimize these effects, a given amount of acetone as the internal standard for determining the amount of water was added to each sample

---

† Part 1: ref. 10.

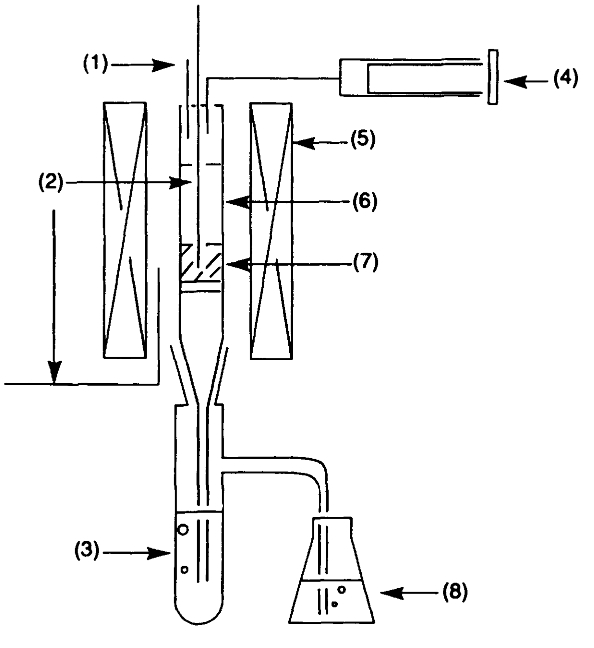

Fig. 1 Schematic view of the reactor: (1) Gas inlet; (2) Thermocouple; (3) Ethanol trap; (4) Micro feeder; (5) Electric furnace; (6) Silica layer for pre-heating; (7) Catalyst layer: (8) $Ba(OH)_2$ trap

Table 1 Effect of temperature on yield, under different reaction modes (μmol/h g-SiO_2)[a]

		Alternate gas feeding[b]		Simultaneous gas feeding[c]		
Run	T/°C	PhOH	BQ	PhOH	BQ	CO_2
1	80[d]	0 (23.6)	0 (3.9)	0 (34.2)	0 (14.1)	
2	80[e]	0 (tr.)	0 (0)			
3	140	0 (tr.)	0 (0)	18.2 (18.2)	0 (2.0)	
4	140[f]	4.1 (tr.)	2.6 (tr.)			
5	200	0 (0)	0 (0)	44.2 (7.5)	0 (1.0)	
6	200			23.4 (tr.)	0 (tr.)	tr.
7	250			24.5 (0)	0 (tr.)	1.1
8	300			2.2 (0)	0 (0.3)	594.0

[a] Values in parentheses stand for the yield of products remained in the catalyst layer. Catalyst: 500$CuSO_4$–50Pd/SiO_2 (2 g). [b] An equimolar gas mixture of (H_2 + Bz + N_2) was first supplied for 30 min to activate catalyst, and then another gas mixture (O_2 + Bz + N_2) was supplied for another 30 min. [c] Total flow rate: 40 cm^3 min^{-1} for runs 1–4, 90 cm^3 min^{-1} for 6–8., partial pressure (atm): $P(H_2):P(O_2):P(Bz):P(N_2)$ = 0.13:0.13:0.5:0.25 for 1–5; 0.05:0.05:0.4:0.5 for 6–8; reaction time: 3 h. [d] 0.5 g water per g catalyst was added before the reaction. [e] The catalyst was dried at 200 °C for 1 h under N_2 before the reaction. [f] Water vapour was supplied in the reactant gas at a liquid flow rate 4 cm^3 h^{-1}.

before GC analysis. Trap ethanol was renewed at every sampling. The exhaust gas was passed through an aqueous solution of $Ba(OH)_2$ to capture CO_2 before releasing it into the atmosphere.

By-products.—Since hydrogen and oxygen are used simultaneously in our reaction system, water is unavoidably formed. Even if the reaction proceeds ideally an equal amount of water to phenol should be produced. In addition, when the complete oxidation of benzene takes place, CO_2 is also expected in the products. We thus attempted total analysis of the products. A trace amount of *p*-benzoquinone was frequently detected, but neither biphenyl nor any ring cleavage product from benzene other than CO_2 were observed.

Reproducibility.—The yields of phenol in repeated measurements under the same reaction conditions were normally reproducible within an error range of ± 10% around the mean value. We occasionally encountered, however, a very low yield, less than one half of the normal value, when catalysts of different batches were used. This happens, probably, because the relative distribution of Pd and Cu species on the silica surface is beyond the external control during the deposition process. In fact, XPS analysis indicated that both Pd and Cl species are distributed quite uniformly on the silica surface but copper is localized appreciably in the form of patches.* Data in the following illustrations are mostly the mean value of two or more repeated measurements.

Results

Effect of Temperature and Moisture.—In the previous communication,[10] we have reported that the composite catalyst is effective regardless of the mode of gas supply, *i.e.* both alternate and simultaneous feedings of hydrogen and oxygen are equally effective for phenol production. Later experiments, however, indicated that this conclusion needs some correction. In Table 1 are listed several results regarding the effect of temperature. It should be noted that phenol is adsorbed readily on the silica surface and an appreciable amount of it always stays in the catalyst bed. Values in parentheses stand for this 'hold up' determined after finishing the reaction.

As can be seen, when the temperature was low enough, 80 °C (run 1), phenolic products are obtained in almost equal amounts, regardless of the mode of gas supply, in agreement with the previous paper. When, however, the temperature was raised to 140 °C (run 3) or 200 °C (run 5), no product was obtained when gas was supplied alternately.

The latter result occurs because there is a large effect of moisture around the catalyst. In fact, even in the case of alternate feeding at elevated temperatures (run 4) a definite amount of product was obtained when water vapour was added to the reactant gases. In contrast, when the catalyst, which normally contains water (*ca.* 10% in weight), was dried before use no phenol was produced even at 80 °C (run 2). These results indicate that the presence of a sufficient amount of water in the catalyst is necessary for the present reaction to occur. The primary reason for this is that water acts as the proton source, one of the necessary reactants for producing hydrogen peroxide which is the active species in our reaction system. Secondly, the hygroscopic nature of the silica surface may also be important, although the detailed mechanism is unknown. It should be noted that even in case of the reaction in acetic acid, we found[8] that addition of a small amount of water improved the reactivity significantly.

The enhancing effect of temperature on the rate of phenol production seems to be appreciable only in the range less than 200 °C. At higher temperatures, the rate decreases with increasing temperature, probably owing to degradative further oxidation of phenol. Table 1 also indicates that the production of CO_2 starts at about 250 °C and is predominant at 300 °C. On the whole, we may conclude that the practical reaction should be carried out at temperatures in the range 140–250 °C, and the hydrogen and oxygen should be supplied simultaneously.

Catalyst Composition and Preparation.—Using $PdCl_2$ and $CuSO_4$ the effect of catalyst composition per gram silica on the yield of phenol has been studied from several aspects, and some of the results obtained were reported in the previous communication.[10] It should be noted, however, that the reactor mode employed in the previous paper was of the back mix type *i.e.* gas flowed in the upward direction so as to agitate the catalyst layer. On the other hand, the gas flow in the present experiments was made in the opposite direction so as to flow

---

* Surface characterization of our catalyst will be reported separately.

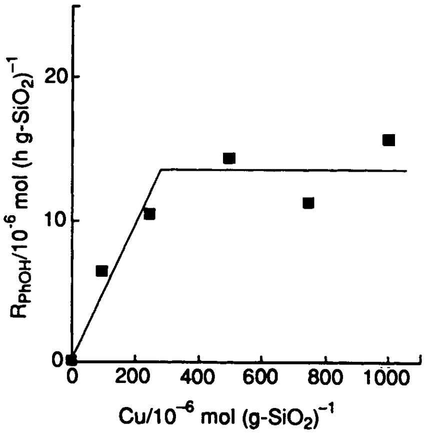

Fig. 2 Effect of copper content in the catalyst. Catalyst: xCu–5Pd (2 g); Temperature, 200 °C; Partial pressures (atm): $P(O_2):P(H_2):P(Bz):P(N_2) = 0.50:0.05:0.4:0.5$; Total flow rate: 90 cm^3 min^{-1}.

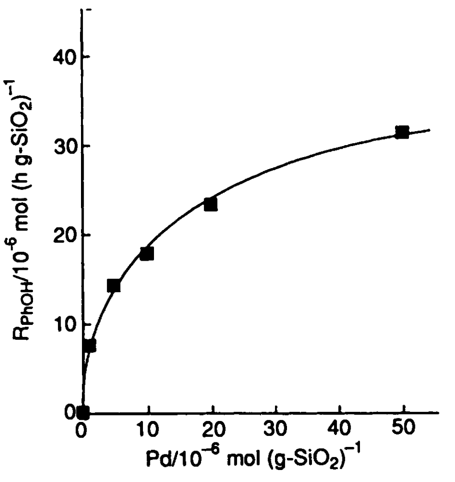

Fig. 3 Effect of palladium content in the catalyst. Catalyst: 500Cu–yPd (2 g); other conditions were the same as Fig. 2

through the still-standing catalyst bed (plug flow). This change in the reactor mode caused some obvious changes. The reactivity seems to be somewhat decreased in the case of plug flow, and the dependence on the reaction conditions is also affected as will be described. Regarding catalyst composition, it may be worth mentioning that the specific effect of chloride ion, which appeared in liquid phase reactions,[6,7] was not found in the gas phase. This is reasonable since chloride ion is retained in the catalyst as prepared in the form of HCl which is volatile at elevated temperatures.

When the palladium content y was fixed at 5×10^{-6} mol per gram silica (*ca.* 0.05% in weight) and the copper content x was varied, the yield of phenol first increased with increasing copper content, up to 300×10^{-6} mol Cu per gram silica and then became constant (Fig. 2). This means that one Pd atom can activate *ca.* 60 Cu ions ($x/y = 300/5$) on average. This value seems a little smaller than the previous observation, where the value is *ca.* 100 (estimated from Fig. 3 in ref. 10). As a tentative explanation, we assume that, in the back mix-type reactor, inter particle contact (collision) enhances the electron transfer between Pd and Cu ion. A remarkable fact is that the single component Pd catalyst exhibits no catalytic activity, indicating that the low valent copper species is the key reactant. This is in contrast to some reactions occurring in acetic acid, where a high catalytic activity was found with some copper-free Pd catalysts. The latter point is quite sensitive to the presence of Cl$^-$ ion and was discussed in refs. 6 and 7.

When, on the other hand, palladium content is varied and that of copper is fixed (500×10^{-6} mol Cu per gram silica), Fig. 3 is obtained. Although the phenol yield increases with increasing amount of Pd, the increase is not linear but logarithmic with regard to the amount of Pd, showing that use of too much Pd is insignificant and not recommended. The turnover number per hour with respect to Pd decreases with increasing amount of Pd, the value being 10 at $y = 1$, compared with 35 found in the back mix-type reactor.

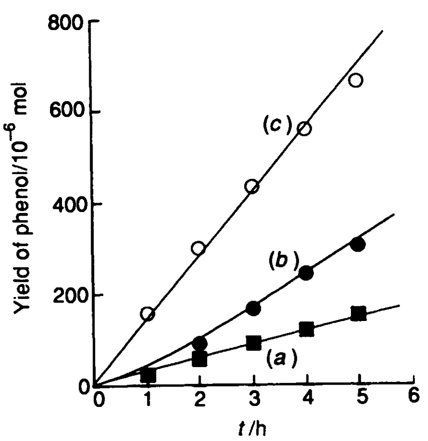

Fig. 4 Performance of differently prepared catalysts. Catalyst: 500Cu–50Pd (2 g). Inert gas was either H_2O (empty marks) or N_2 (full marks). Square symbols (*a*) correspond to catalysts prepared by impregnation and circles (*b*, *c*) by ion exchange. Other conditions were the same as Fig. 2.

The reason why the catalytic activity does not increase proportionally to the Pd content may be worth noting. The main reason should be ascribed to the fact that the active sites, on which oxygen is activated by receiving an electron, are not of Pd but of Cu^I. In the present reaction system, Pd is merely an auxiliary catalyst which mediates electron transfer from hydrogen atoms to Cu^{II} ions and, as we have described above, the electron transfer to Cu^{II} ion is performed quite efficiently: one Pd atom can activate 60 Cu ions on average. Accordingly, when the Cu content is fixed at a constant value ($x = 500$ in the case of Fig. 3), the increase in Pd content does not result in a linear increase in phenol production.

The rate of water production was scattered over the range $1\text{–}3 \times 10^{-3}$ mol (h g-cat)$^{-1}$ and was almost independent of the catalyst composition. This rather large scattering was caused, probably, because some bound water was liberated from the silica support by heat, in addition to the reaction product. Similarly, the rate of CO_2 production was almost independent of the catalyst composition, having values of $5\text{–}9 \times 10^{-6}$ mol (h g-cat)$^{-1}$.

All catalysts hitherto used were prepared by impregnating both the Pd and Cu salts simultaneously from one solution. When the fixation of Pd is done by an ion exchange technique, and the impregnation of Cu salt is done subsequently, a definite improvement of catalyst activity appears (Fig. 4). In this figure, curves (*a*) and (*b*) represent the accumulation of phenol observed during a 5 h reaction with impregnated and ion-exchanged catalysts, respectively. The reactivity of catalysts prepared by ion exchange is roughly twice as high as the impregnated catalysts. This may be related to the difference in either the degree of dispersion of Pd or the relative distribution of Pd to Cu on the silica surface. Attempts at surface characterization are in progress.

Composition of Reactant Gas.—By keeping the total flow rate constant, the effect of the reactant concentration was studied for each of the components, H_2, O_2, and benzene, respectively. When hydrogen was tested, for instance, flow rates of the other components were fixed, and the variation in hydrogen rate was compensated for with nitrogen. Results obtained are illustrated

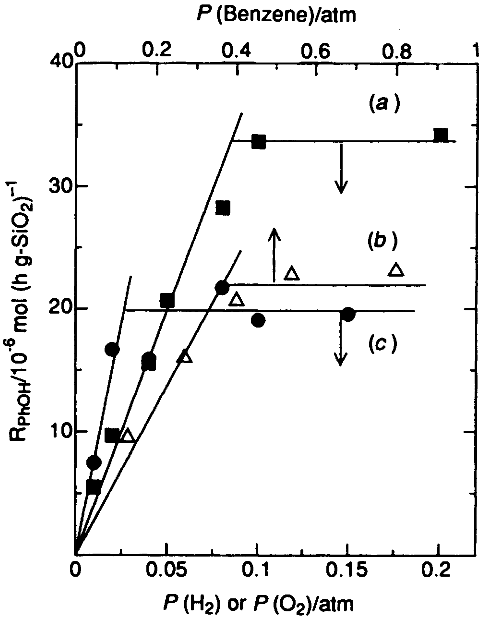

Fig. 5 Effect of partial pressure of reactant gases. Partial pressure: $P(N_2)$ = balance; (*a*) variable $P(H_2)$ at fixed $P(O_2) = 0.05$ and $P(Bz) = 0.4$; (*b*) variable $P(Bz)$ at fixed both $P(H_2)$ and $P(O_2) = 0.05$; (*c*) variable $P(O_2)$ at fixed $P(H_2) = 0.05$ and $P(Bz) = 0.4$. Catalyst: 500Cu–50Pd (2 g); Temperature: 200 °C; Total flow rate: 90 cm^3 min^{-1}.

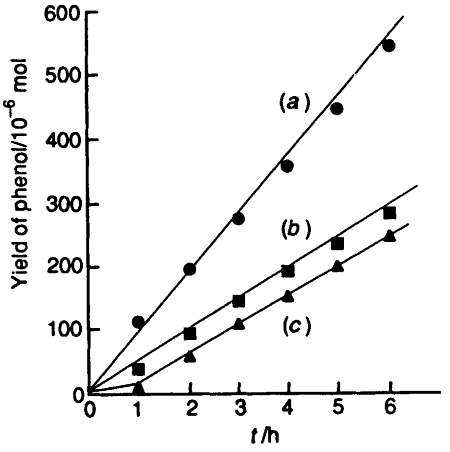

Fig. 6 Effect of water vapour. Inert gas was H_2O (*a*) and N_2 (*b*, *c*). Catalysts (*a*, *c*) were dried with N_2 at 200 °C for 1 h before starting the reaction. Partial pressures (atm): $P(H_2)$:$P(O_2)$:$P(Bz)$:P(Inert gas) = 0.05:0.05:0.4:0.5. Other conditions were the same as Fig. 5.

in Fig. 5, where the abscissa is expressed in terms of partial pressure, and the value regarding benzene is indicated in the upper margin. All curves in Fig. 5 rise almost linearly at lower pressures, indicating that the reaction is first order with respect to each reactant, and then reach a plateau. The phenol yield at the plateau is larger in curve (*a*) for hydrogen than those for oxygen [curve (*b*)] and benzene [curve (*c*)], in which the plateau values are more or less the same. It is interesting that curve (*a*) reaches saturation at a point where $P(H_2)/P(O_2)$ is equal to 2. This may be further evidence for the necessity of water on the catalyst surface. Accordingly, we have studied the effect of water a little more systematically in Figs. 6 and 7. Curve (*b*) in Fig. 6 represents a result obtained with catalyst prepared in the normal way, which contains water, *ca.* 10% in weight. Curve (*c*) was obtained with the same catalyst, but it had been dried at 300 °C in a stream of nitrogen for 1 h. This treatment causes the initial activity to drop significantly, but it is regained quickly after 1 h use, because water is produced as the reaction proceeds. In contrast, when nitrogen is replaced by steam, the rate of phenol production increases nearly two times.

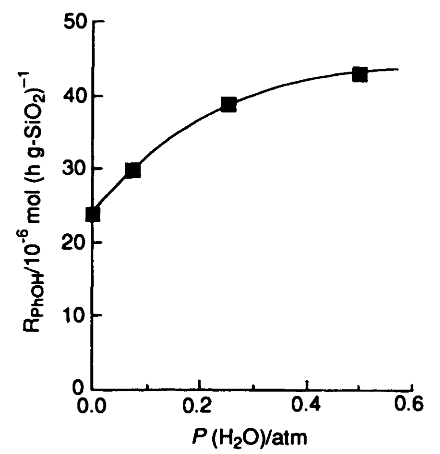

Fig. 7 Effect of partial pressure of H_2O. Reaction conditions were the same as Fig. 6.

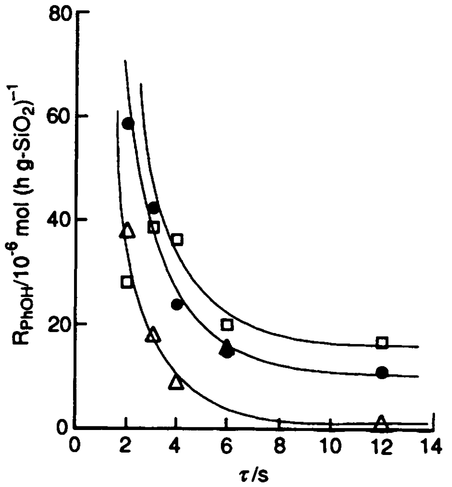

Fig. 8 Rate of phenol production as a function of apparent residence time. Partial pressures (atm): $P(Bz) = 0.4$, $P(N_2) = 0.45$. Symbols specify the partial pressure ratio $P(H_2)/P(O_2)$ by keeping $P(H_2 + O_2) = 0.15$: △, 1/2; ●, 1; □, 2. Total flow rate: 30–180 cm^3 min^{-1}. Other conditions were the same as Fig. 5.

The rate increase as a function of the partial pressure of steam is shown in Fig. 7. The same effect of steam was also tested with the ion-exchanged catalyst and the result obtained is shown by curve (*c*) in Fig. 4. The corresponding phenol rate is 71 × 10^{-6} mol (h g-cat)$^{-1}$.

Flow Rate and Residence Time.—At the earlier stage of this experiment, we wrongly believed that the rate of the reaction would be rather slow and suspected the involvement of some diffusion-limited step in the whole process. This was not true, as will be described below. At that time, we underestimated the rate of water production and did not attempt any determination. Now it is not doubted that water is produced at a much higher rate than phenol, and hydrogen supplied is almost completely converted to it at the exit of the reactor.

In this connection, we studied the effect of flow rate on the phenol yield. Here, the amount of catalyst was fixed and only the gas flow rate was varied over the range 30–180 cm^3 min^{-1} to investigate the effect of residence time. The yield of phenol increased linearly with increasing flow rate, and when it is plotted against the residence time, Fig. 8 is obtained. This figure indicates that the rate of reaction is fast enough, and shortening of the residence time will increase the specific rate of phenol production. Of course, a high supply rate of hydrogen raises the average hydrogen partial pressure over the catalyst bed and increases the phenol yield.

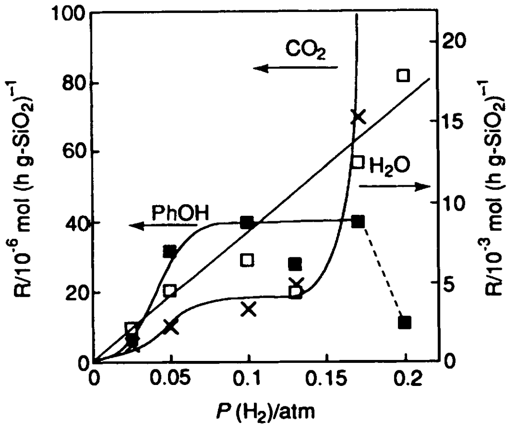

Fig. 9 Production rate as a function of hydrogen partial pressure. Partial pressure: P(Bz) = 0.4, $P(N_2)$ = balance, $P(H_2)$ was kept equal to $P(O_2)$. Symbols specify the three main products: ■, phenol; □, H_2O; ×, CO_2. Other conditions were the same as Fig. 5.

Table 2 Percentage conversion of benzene and hydrogen as a function of hydrogen partial pressure [a]

	Conversion (%)		
$P(H_2)$/atm	PhOH [b]	CO_2 [b]	H_2O [c]
0.025	0.01 (4.9)	0.002 (5.4)	78.0 (2.1)
0.05	0.07 (31.3)	0.004 (10.4)	80.9 (6.4)
0.1	0.09 (39.4)	0.014 (15.1)	58.2 (6.4)
0.13	0.08 (35.2)	0.014 (36.8)	65.9 (9.6)
0.17	0.09 (39.4)	0.027 (69.7)	66.6 (12.5)
0.2	0.02 (10.5)	0.413 (10.90)	81.4 (17.9)

[a] Catalyst: 500$CuSO_4$–50Pd/SiO_2 (2 g); total flow rate: 90 cm^3 min^{-1}; temperature: 200 °C. Partial pressure of oxygen was kept equal to hydrogen, and P(Bz) was fixed at 0.4. The rest was balanced with nitrogen. Values in parentheses stand for the production rate [μmol (h g-cat)^{1}]. [b] Conversion is based on benzene. [c] Conversion is based on hydrogen.

Reactions to Yield Water and CO_2.—In the foregoing section, we showed that the yields of both water and CO_2 were insensitive to the catalyst composition. A definite effect was found, however, when the partial pressures of hydrogen and oxygen were varied. Results obtained for a series of experiments are shown in Fig. 9, in which the rate of formation of the three main products are plotted as a function of the partial pressure of hydrogen. In contrast to Fig. 5, partial pressures of hydrogen and oxygen were kept equal to each other. The graph shows that the rate of phenol production rises only in the lower pressure range and becomes constant at a value of *ca.* 40×10^{6} mol (h g-cat)^{1}. A notable fact is that the rate abruptly decreases at $P(H_2)$ = 2, and instead, a tremendous amount of CO_2 is produced. At this point, the combustion of benzene becomes predominant making temperature control difficult. A similar effect appears when the total flow rate of the reactant gas exceeds 200 cm^3 min^{1}, even if $P(H_2)$ and $P(O_2)$ are small enough, *e.g.* $P(H_2)$ = 0.05. The rate of water formation is almost 100 times greater than that of phenol and increases linearly with increasing pressure. On the other hand, the production of CO_2 is very small in the lower pressure region but increases sharply. The use of high partial pressures of hydrogen and oxygen is, of course, undesirable for safety reasons.

Using the data in Fig. 9, the percentage conversions of benzene into phenol and CO_2, and hydrogen into water are summarized in Table 2, in which production rates are also listed in parentheses.

Discussion

Based on the data in Table 2, together with other results described above, several points are worth noting. Firstly, the rate of phenol production can be expected to exceed 1×10^{4} mol (h g-cat)^{1} which corresponds to 100 kg (h ton)^{1}. This seems to be attractive, though not sufficient. Probably, a tenfold increase in the production rate will be required in order to produce a practical process. Secondly, the selectivity of the reaction leading to CO_2 is less than 10%, and thus the selectivity for phenol is more than 90%. This may also be an acceptable value. One-pass conversion of benzene to phenol is only 0.09% at most in Table 2. This value will increase with the increase in the production rate of phenol. Use of ion-exchanged catalyst, use of steam in place of nitrogen, and reduction of the supply rate of benzene will assist in this purpose. These are, however, not thought to provide an essential answer.

According to our view, the most important problem of the present system is how to suppress the undesirable production of water. If the water production is reduced to one tenth of the present value, most of the hydrogen supplied will remain unchanged, so as to improve the phenol production rate greatly. This will be achieved only by the improvement of the catalyst activity. Work along this line is in progress.

References

1 T. Jintoku, H. Taniguchi and Y. Fujiwara, *Chem. Lett.*, 1987, 186.
2 R. Moro-oka, N. Kitajima and H. Fukui, Extended Abstract 21 Symposium on Oxidation Reactions, 1988, 92, Nagoya.
3 K. Kimura and R. Machida, *J. Chem. Soc., Chem. Commun.*, 1984, 499.
4 M. Iwamoto, J. Hirata and K. Matsukami, *J. Phys. Chem.*, 1983, **87**, 903.
5 T. Kitano, Y. Kuroda, A. Itoh, L.-F. Jiang, A. Kunai and K. Sasaki, *J. Chem. Soc., Perkin Trans. 2*, 1990, 1991.
6 Y. Kuroda, M. Mori, A. Itoh, T. Kitano, F. Yamaguchi, K. Sasaki and M. Nitta, *J. Mol. Catal.*, 1992, **73**, 237.
7 A. Itoh, Y. Kuroda, T. Kitano, Z.-H. Guo, A. Kunai and K. Sasaki, *J. Mol. Catal.*, 1991, 215.
8 Y. Kuroda, A. Kunai, M. Hamada, T. Kitano, S. Ito and K. Sasaki, *Bull. Chem. Soc. Jpn.*, 1991, 3089.
9 A. Kunai, T. Kitano, Y. Kuroda, L.-F. Jiang and K. Sasaki, *Catal. Lett.*, 1990, 139.
10 T. Kitano, T. Wani, T. Ohnishi, L.-F. Jiang, Y. Kuroda, A. Kunai and K. Sasaki, *Catal. Lett.*, 1991, 11.

Paper 2/06070A
Received 16*th November* 1992
Accepted 8*th February* 1993