Gas Phase Oxidation of Benzene to Phenol under the Simultaneous Feeding of Hydrogen and Oxygen. III. Catalyst Prepared from Cu(II) Phosphate[11)]

Tomoyuki Kitano, Toshihiro Nakai, Masahiro Nitta,† Miki Mori, Sotaro Ito, and Kazuo Sasaki*,#
Department of Applied Chemistry, Hiroshima University, Higashi-Hiroshima 724
† Kure Research Laboratory, Babcock Hitachi K. K., Takara-machi, Kure 737

(Received January 24, 1994)

The performance of silica supported Pd–Cu composite catalyst developed previously for direct oxidation of benzene to phenol has been improved by changing the copper ion source from Cu(II) sulfate to Cu(II) phosphate and by additional impregnation of phosphoric acid. The reaction proceeds under the simultaneous feeding of benzene, hydrogen and oxygen at 200 °C with a rate of phenol production ca. 0.4 $\mathrm{mmol\,h^{-1}\,(g\text{-}cat)^{-1}}$, which is ten times greater than that we have reported previously with a catalyst prepared from Cu(II) sulfate. With this catalyst, complete oxidation to carbon dioxide is also retarded to increase the selectivity of phenol. The improvement of catalytic activity arises apparently from the diminution of the yield of water and is ascribed to the presence of a thin liquid film over the silica surface.

Direct conversion of benzene to phenol in a single step reaction has long been desired in chemical industry. Many works[1—4)] were devoted to this purpose and progress has been reviewed by us.[5,6)] We have been working on the same problem throughout the past decade to develop a new process which utilizes *in situ* produced hydrogen peroxide as the oxidizing reagent. A binary catalyst composed of metallic palladium and a Cu-salt supported on the silica surface was found suitable for this reaction system. Actually, both hydrogen and oxygen are fed simultaneously over the catalyst to produce hydrogen peroxide. The reaction mechanism we proposed[7,13,14)] has been supported by a later work of Okunowski et al.[15)] The reaction can be performed in either liquid phase[7—9)] or gas phase.[10—12)]

For the case of a gaseous reaction, we have shown that the use of catalyst prepared from Cu(II) sulfate, with which we have usually been concerned in the past, yields phenol at a rate ca. 0.05 $\mathrm{mmol\,h^{-1}\,(g\text{-}cat)^{-1}}$ with the phenol selectivity of more than 90%. As we have mentioned,[11)] however, a serious drawback associated with this reaction is that too much hydrogen is wasted in the water forming side reaction. For raising the rate of phenol production to an practical value, an important problem is how to suppress the water forming reaction.

In this paper, we will report the performance and characteristics of the catalyst prepared from Cu(II) phosphate in place of sulfate. By changing the copper ion source from sulfate to phosphate, the yield of phenol increased by almost one order of magnitude in comparison with the sulfate catalyst. The improvement in the phenol yield of course causes the reduction of the water yield. Another advantage of the phosphate catalyst is the retardation of another side reaction yielding carbon dioxide. Even at 300 °C, at which CO_2 predominated if the catalyst was of the sulfate, the yield of carbon dioxide is negligibly low.

Experimental

The reactor used was a vertically held Pyrex tube (20 mm in diameter and 350 mm in length) which was divided into two parts by a sintered glass plate. The catalyst, normally 2 g, was placed on it. The central part of the reactor was surrounded by an electric heater to maintain the catalyst at a desired temperature. Reactant gas mixture was introduced from the top to the bottom so as to make a downward plug flow through the catalyst layer. At the lower end of the tube, a small glass tube containing ethanol was located to trap soluble products, out of which the 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. Since benzene is also captured in the trap to vary the liquid volume, the use of a certain internal standard was necessary to determine the amount of water. Acetone was used for this purpose. 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 carbon dioxide before releasing it into the atmosphere.

Products detected were phenol, water, and carbon dioxide. A trace amount of *p*-benzoquinone was frequently detected, but neither biphenyl nor any ring cleavage product from benzene was detected, other than CO_2.

Catalysts used here were prepared in a dual process. Pd was first loaded on the silica surface by ion exchange from an aqueous ammonia solution of $[Pd(NH_3)_4]Cl_2$. The ion exchanged product was reduced in a hydrogen stream at 300 °C for 4 h to make Pd metallic. The copper salt was then deposited on it from an appropriate aqueous solution. Since Cu(II) phosphate has a limited solubility, the addition of some acid was necessary for facilitating the dissolution of the phosphate salt. Phosphoric acid was used for this purpose. In most cases, 30 mmol of phosphoric acid (3 mmol per g-SiO_2) was put into 100 ml of distilled water, to which 10 g of palladized silica gel and a desired amount of copper salt was added. It should be mentioned that, because of its nonvolatile nature, all the phosphoric acid is transferred and remains on the silica surface to play an important role during

---

#Present address: Hiroshima Area Study Center, The University of the Air, 1-1-89 Higashi-Senda, Hiroshima 730.

the reaction. Further details of the experimental procedure are described in Ref. 11.

Results and Discussion

In the previous paper,[11)] we have reported the performance of the Pd–Cu composite catalysts in the gas phase reaction over a temperature range from 140 to 250 °C. Products obtained are almost exclusively phenol and water. Carbon dioxide is also produced but, except under certain reaction conditions, its yield is very low. As a result, a high selectivity of more than 90% is readily achieved for phenol from benzene. On the other hand, since both hydrogen and oxygen are used simultaneously, the production of water is unavoidable and most of hydrogen supplied is consumed by it. It often happens that 90% or more of the hydrogen fed is converted to water by passing through the reactor. Undoubtedly, a predominant formation of water results in a poor yield of phenol, since the two products are competing with each other at the step where OH radical is involved. We therefore tried to seek some possibility of changing the selectivity to favor phenol. In this connection, it is worth recalling the fact that a definite effect of counter anion appears in the liquid phase reaction.[12)] We therefore changed the copper source from sulfate to phosphate and, by doing this, a drastic improvement of catalytic activity was observed.

In the following, results obtained with the phosphate catalyst will be described by comparing to those obtained with the sulfate catalyst. Curve A at the top of Fig. 1 illustrates the performance of the catalyst made from copper(II) phosphate with the aid of phosphoric acid. The production rate from the line slope is 320 μmol h^{-1} (g-cat)$^{-1}$. A remarkable increase in the catalyst activity is seen particularly when it is compared with curve D at the bottom, which stands for the catalyst prepared from copper(II) sulfate: the rate being 40 μmol h^{-1} (g-cat)$^{-1}$. As has been described in the experimental section, the phosphate catalysts contains phosphoric acid, which was added to the depositing solution, and accordingly we have to make clear whether the improving effect comes from copper(II) phosphate or from phosphoric acid. Curves B and C will give some additional information about this. Even the catalyst made from copper(II) sulfate exhibits a better performance when phosphoric acid is impregnated (curve B) than the one made from copper(II) phosphate in which sulfuric acid is impregnated (curve C). Although some ambiguity still remains for the question raised above, it seems probable that the presence of phosphoric acid itself has a specific effect for improving the catalyst performance.

It is interesting to find that the characteristic change in catalyst activity which appeared in the phenol production (Fig. 1) does not appear in the water forming reaction. As is seen in Fig. 2, the production of water is almost unaffected by the nature of catalysts and the one-pass conversion of hydrogen into water is 84% in average. It is also worth noting that the production of carbon dioxide resembles the tendency of Fig. 1 and is affected by the nature of catalysts: The higher the phenol yield is, the lower is the yield of carbon dioxide.

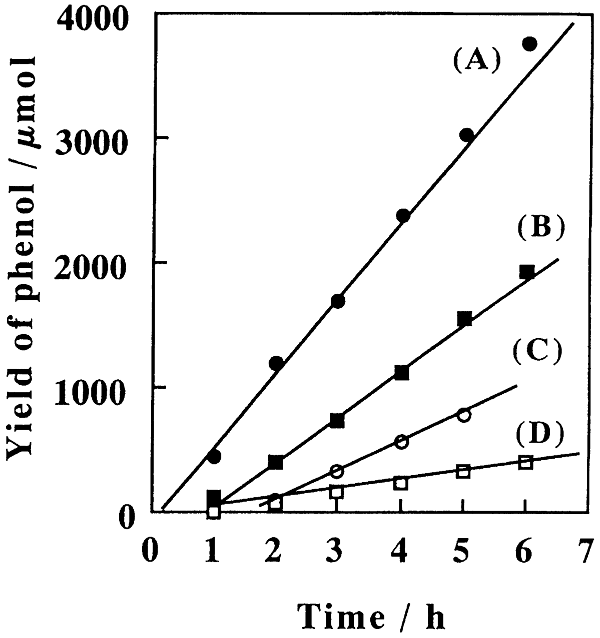

Fig. 1. Yield of phenol with several different catalysts. Reaction conditions: Catalyst: (500 μmol Cu+5 μmol Pd) per g-SiO$_2$, 2 g, Temperature: 200 °C, Molar composition of feed gas: H_2 (0.05)+O_2 (0.05)+ Benzene (0.4)+N_2 (0.6), Feed rate: 90 cm^3 min^{-1}, A: Cu(II) phosphate with 3 mmol phosphoric acid, B: Cu(II) sulfate with 3 mmol phosphoric acid, C: Cu(II) phosphate with 4.5 mmol sulfuric acid, D: Cu(II) sulfate with 4.5 mmol sulfuric acid.

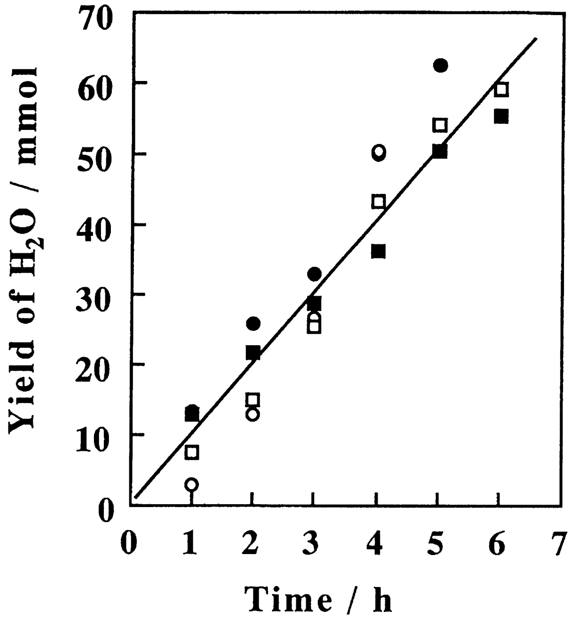

Fig. 2. Yield of water in the experiments of Fig. 1. Symbols are the same as in Fig. 1.

The remarkable difference appearing in Figs. 1 and 2 strongly suggests that the two reactions leading to phenol and water are occurring spatially independently of each other on the catalyst surface. We assume that the water forming reaction is restricted to the palladium sites and the oxidation of benzene to the copper sites. This point is mentioned again in the later section and will be discussed in a succeeding paper which deals with the reaction mechanism.

Effect of the Amount of Phosphoric Acid. This effect has been studied by changing the amount of phosphoric acid added to the depositing solution of Cu(II) phosphate. Results are shown in Fig. 3. Because of the limited solubility of the latter salt, the amount of phosphoric acid to be added was at least 2 mmol $(\text{g-SiO}_2)^{-1}$. At 1.5 mmol, the dissolution was incomplete and a part of the copper salt remained in the crucible without loading on the silica surface. Figure 3 indicates clearly that increasing the amount of phosphoric acid decreases the yield of both phenol and water over the whole range studied although the dissolution is complete. In other words, although the improvement of the catalyst activity due to the use of phosphoric acid is rather drastic, use of an excess amount of it only makes the performance worse.

In order to explain these somewhat contradictory results, we tentatively assume that phosphoric acid forms a thin liquid film over the catalyst surface. Phenomenologically, the yield increase of phenol is a result of the diminution of the yield of water. The diminution may be achieved either by decreasing the catalyst activity of Pd sites or by enhancing the rate of electron transfer between adsorbed hydrogen and bivalent copper ion. The presence of a thin liquid film of phosphoric acid is thought to contribute to both the two mechanisms. When Pd particles are covered by the liquid film, the supply rate of hydrogen to the Pd surface will be retarded to decrease the catalyst activity effectively. The thicker the film is, the slower the diffusion rate of reactants through the film that will be expected. This may be rationalized by the fact that the combustion to carbon dioxide is retarded even at 300 °C. On the other hand, copper ions will dissolve into the liquid film so as to move freely. This will facilitate the chance of contact with immobilized Pd particles to enhance the rate of electron transfer. We rather believe the latter reason to be more important. Although sulfuric acid is also non volatile, it is thought to be released from the silica support in the form of mist when exposed to a gas stream.

Effect of Catalyst Composition. The effect of the amount of metal species on the silica support has been studied. Figure 4 illustrates the effect of Pd content on the yield of products. In this case, the copper ion content was fixed at 500 μmol and the amount of phosphoric acid was 3 mmol per g silica. As is seen, the highest activity for phenol production is already achieved at 5 μmol Pd per g silica. In contrast, the rate of water production still increases at higher Pd contents. Variation in the molar ratio between phenol and water produced due to different reaction conditions will be described in a later section (see Table 1).

A similar study with regard to the copper ion content is shown in Fig. 5. In this case, the palladium was fixed at 5 μmol per gram. The catalyst activity first increases with increasing Cu content up to ca. 300 μmol per g silica but decreases with further increase of the Cu content. The decrease at higher Cu contents was

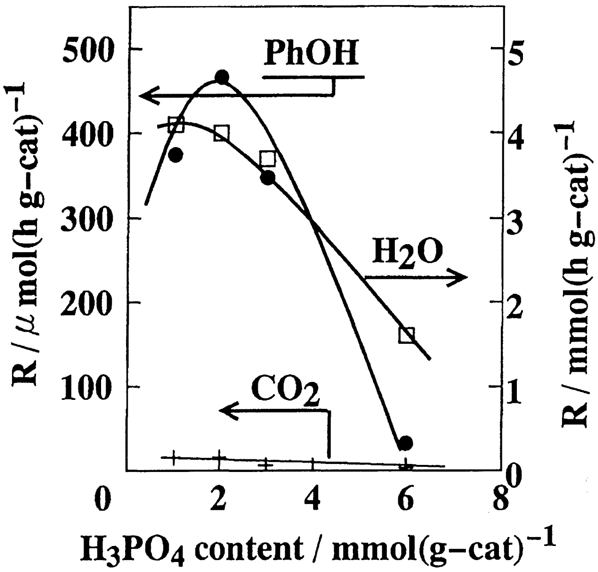

Fig. 3. Effect of the amount of phosphoric acid impregnated in the silica support. Reaction conditions are the same as in Fig. 1.

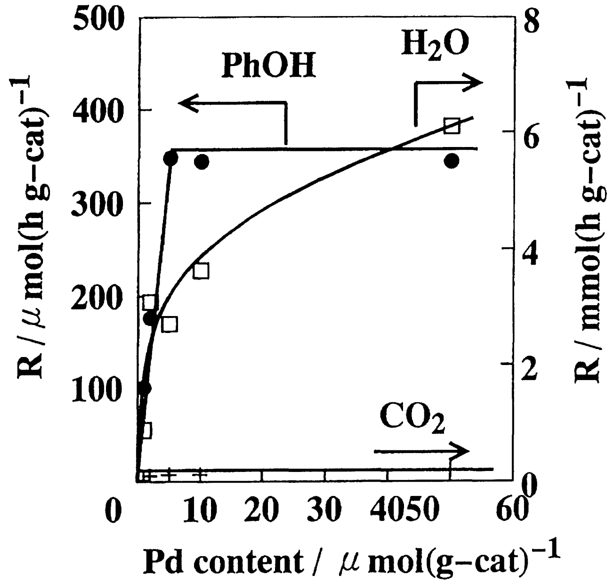

Fig. 4. Effect of Pd content in catalysts. Copper ion content: 500 μmol per g-SiO_2. Other conditions are the same as in Fig. 1.

Table 1. Change in One-Pass Conversion of Benzene and Hydrogen Due to Different Affecting Factors Values are in %.

	(I) Flow rate					(III) Pd-content (x=500)					
	$cm^3\,min^{-1}$					μmol Pd per g-silica					
	45	60	90	120	180	1	2	5	10	50	70
c_b	0.4	0.5	0.8	0.3	0.3	0.2	0.4	0.8	0.8	0.7	0.1
c_p	3.4	3.7	6.3	2.1	2.6	1.7	3.3	5.5	6.3	6.1	0.8
c_w	85	46	67	14	14	16	51	49	66	84	49
c_p/c_w	.04	.08	.09	.15	.19	.10	.08	.11	.10	.06	.01
	(II) Temperature					(IV) Cu-content (y=5)					
	°C					µmol Cu per g-silica					
	140	165	200	245	300	100	175	250	300	500	700
c_b	0.3	0.4	0.8	1.0	0.5	0.2	0.5	0.6	0.9	0.7	0.6
c_p	1.6	2.8	4.9	7.2	2.8	1.5	3.6	4.4	7.0	5.7	4.9
c_w	32	42	51	98	125	30	59	48	63	55	47
c_p/c_w	.05	.07	.10	.08	.02	.05	.06	.09	.11	.11	.10

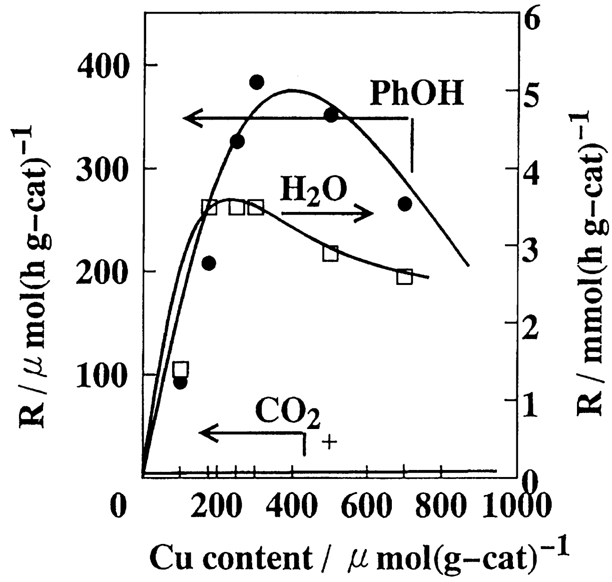

Fig. 5. Effect of copper ion content in catalysts. Pd content: 5 µmol per g-SiO_2.

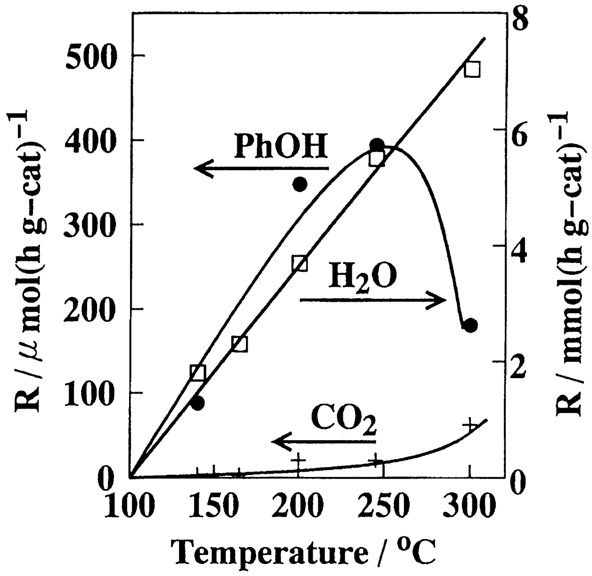

Fig. 6. Temperature dependence of the reaction rates. Catalyst: (5 µmol Pd+500µmol Cu) per g-SiO_2, 2 g. Other conditions are the same as in Fig. 1.

not observed in the previous study (Fig. 2, Ref. 11). This may be ascribed to the difference in the process of catalyst preparation. Since the phosphate catalyst was prepared in two steps, some of the copper salt, particularly at higher concentrations, would have deposited over the Pd particles to bury them underneath.

Effect of Temperature. The effect has been studied over the range between 140 to 300 °C and is illustrated in Fig. 6. The maximum yield of phenol is obtained at temperature about 250 °C and then decreases with increasing temperature. The same behavior was also observed in the sulfate case. On the other hand, the yield of water never decreases but increases steadily indicating that the reaction yielding water and that yielding phenol are independent of each other. In case of sulfate catalyst, the decrease in phenol yield at higher temperatures was ascribed to the enhancement of the complete oxidation to carbon dioxide. In the phosphate case, however, the yield of carbon dioxide is still very low even at 300 °C (see Fig. 6). We may ascribe the reason in the latter case to the dehydration of phosphoric acid at elevated temperatures so as to decrease the catalyst activity. In fact, the phosphate catalysts always coagulated to form hard masses after use at 300 °C. Accordingly the catalyst activity at 300 °C falls with a higher rate than at 200 °C. An irreversible reaction between silica and phosphoric acid must also be accounted for particularly at elevated temperatures. This point has been left for further study, however.

Effect of Partial Pressure. The effect of the partial pressure of each of reactants on the reaction rate has been studied by keeping the partial pressures of other components at fixed values. The fixed values were

0.05 for hydrogen and oxygen and 0.4 for benzene. In order to keep the total pressure constant, nitrogen was used as the inert component, which assures the safety from explosion.

As is expected, the rate of phenol production first increases approximately linearly and then becomes constant for all three reactants. The limiting values of partial pressure, at which the rate increase ceases, were graphically estimated to be 0.1 for both hydrogen and oxygen and 0.2 for benzene, respectively. Accordingly, as a tentative standard, we may guess the feed gas composition (in mole fraction) to be 0.1 : 0.1 : 0.2 for hydrogen, oxygen, and benzene, respectively. The remaining 0.6 is for nitrogen. Elimination or reduction of nitrogen might be possible but no such experiment was attempted.

In this connection, we may add some comments on the safety problem of this reaction. The reaction can be operated without any trouble if the partial pressures of hydrogen and oxygen do not exceed 0.15 simultaneously. If both of these are 0.2, combustion takes place, though we have never had an explosion. In order to assure safety, the continuous monitoring of the temperature inside the catalyst layer is very useful.

Flow Rate. A fact, which could not be observed with the sulfate catalyst, was found regarding the effect of flow rate. In the sulfate case, the highest flow rate was limited to 180 $cm^3\,min^{-1}$, beyond this value the reaction became uncontrollable externally because of the accumulation of reaction heat. In contrast, no such heat accumulated in the phosphate system, and the reaction proceeded steadily even at the flow rate of 270 $cm^3\,min^{-1}$, which was the instrumental limit in our measuring devices. Owing to this difference, the behavior at shorter residence time, which was not detected in the previous paper (Fig. 8, Ref. 11), is available and an ascending part appears at the left half of Fig. 7, where the rate of phenol production is plotted against the average residence time (corresponding values of flow rate are indicated at the upper margin). The rate of water formation seems to have a maximum also at τ=3 s, but the further decrease is small. The increase at the left indicates that some slow process is involved before producing the key intermediate(s): H_2O_2 or OH radical.

The descending tendency at the right should be ascribed firstly to the saturating tendency of the phenol yield at longer residence time: If the yield is saturated the rate must be inversely proportional to the residence time. Note that almost 90% of hydrogen is consumed before leaving the reactor under certain conditions (see below).

One-Pass Conversion. Conversion of starting materials is an important index to evaluate the process performance. In the present case, three values should be taken into account. For the practical purpose, the percentage conversion of benzene into phenol, which is denoted by c_b in Table 1, is of course of a primary importance, although no particular attention has been paid to it in this work. Besides that, however, we have to pay attention on the values of hydrogen into water. As we have mentioned previously,[11] if the reaction conditions are not selected properly, most of hydrogen is wasted by forming water. To raise the rate and conversion of benzene to phenol has practically the equivalent meaning of reducing the yield of water. We shall denote the percentage conversion of hydrogen into water by c_w. For the convenience, we shall further define the apparent percentage conversion of hydrogen into phenol, c_p, on the base of the following balance equation between the feed and product gas compositions.

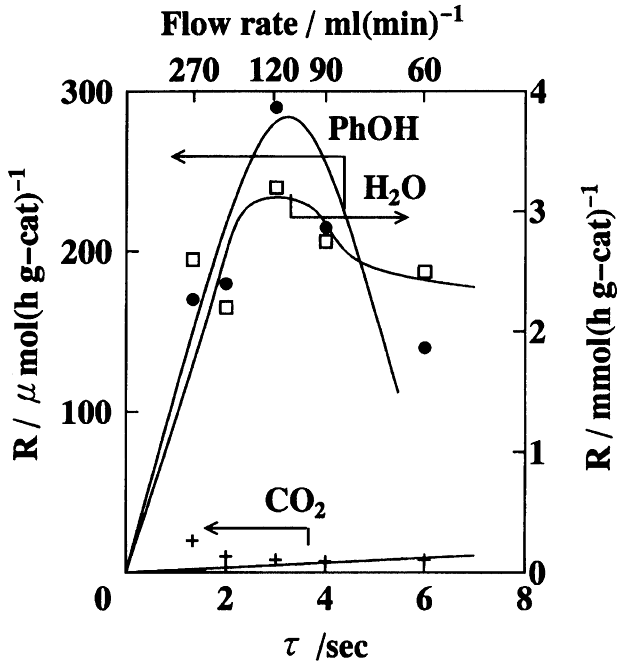

Fig. 7. Production rate of phenol and water as a function of average residence time. Catalyst: Same as in Fig. 6. Temperature: 200 °C. Feed gas: $H_2 : O_2$: benzene=0.05 : 0.05 : 0.4.

$$\begin{aligned} &mC_6H_6 + nH_2 + nO_2 \\ &\quad \rightarrow xC_6H_5OH + yH_2O \\ &\qquad + (\frac{2n-x-2y}{2})H_2 + (\frac{2n-x-y}{2})O_2. \end{aligned}$$

Then c's are given by $c_p=x/n$, $c_b=x/m$, and $c_w=y/n$.

The fractional ratio c_p/c_w gives a measure of hydrogen utilization. Logically, the value of c_w must not exceed unity but actually this is not so in some cases because additional water is released from the catalyst, besides the reaction product. Two reasons account for this additional water: 1) some due to dehydration of phosphoric acid to form pyrophosphoric acid during reaction and 2) some due to incomplete drying of catalyst during its preparation. Discrimination of additional water brought about by these two reasons from that produced by reaction is rather a difficult task and some ambiguity remains in the rate of water formation and thus in c_w values. Statistical judgment through many repeated measurements was necessary. The conversion of benzene into carbon dioxide is not important, since its yield is practically negligible.

For all the experiments described above, the conversion data were calculated. Some are listed in Table 1 to confirm some general tendencies in relation to the reaction conditions. The data in Table 1 are categorized into four groups regarding four different factors: flow rate, temperature, and Pd and Cu contents, respectively. According to this table, the increase in flow rate decreases c_w, but increases c_p/c_w remarkably, indicating that a higher flow rate is advantageous. The increase in Pd content in the catalyst increases both c_p and c_w almost similarly up to 10 μmol per gram silica but c_p ceases the increase while c_w grows further at higher Pd contents indicating that higher Pd content favors water. On the contrary, the effect of copper ion content behaves rather differently and the ratio c_p/c_w increases clearly though not drastically with increasing copper content. On the whole, we may conclude that the Pd sites favor the water-forming reaction and the copper sites the phenol production. In any case, the use of catalysts with higher Pd contents is by no means recommended. This means that the catalyst is very efficient and the turnover number per hour regarding Pd atoms in 0.05% catalyst amounts to 300.

Although the use of the phosphate catalyst has a definite advantage over the sulfate catalyst, it is still a problem that much hydrogen is wasted in the water-forming reaction. The ratio c_p/c_w is theoretically 0.5 and the best value in Table 1 is 0.19. The increase of this value should be reflected in the rate of phenol production and thus the one pass conversion of benzene into phenol.

The authors are grateful to Japan Polyurethane Ind., Co., Ltd. for financial assistance.

References

1) T. Jintoku, H. Taniguchi, and Y. Fujiwara, *Chem. Lett.*, **1987**, 186.

2) R. Morooka, N. Kitajima, and H. Fukui, "Symposium on Oxidation Reactions," Nagoya, 1988, Ext. Abstr., 2, 92.

3) K. Kimura and R. Machida, *J. Chem. Soc., Chem. Commun.*, **1984**, 499.

4) M. Iwamoto, J. Hirata, and K. Matsukami, *J. Phys. Chem.*, **87**, 903 (1983).

5) A. Kunai and K. Sasaki, *Kagaku to Kogyo* (*Chemistry and Industry*), **1989**, 131.

6) K. Sasaki, Y. Kuroda, and T. Kitano, *Hyoumen* (*Surface*), **1993**, 331.

7) S. Ito, T. Yamasaki, H. Okada, S. Okino, and K. Sasaki, *J. Chem. Soc., Perkin Trans. 2*, **1988**, 285.

8) T. Kitano, Y. Kuroda, A. Itoh, L-F. Jiang, A. Kunai, and K. Sasaki, *J. Chem. Soc., Perkin Trans. 2*, **1990**, 1991.

9) A. Kunai, M. Hamada, T. Kitano, S. Ito, and K. Sasaki, *Bull. Chem. Soc. Jpn.*, **64**, 3089 (1991).

10) T. Kitano, T. Ohnishi, J-F. Jiang, Y. Kuroda, and K. Sasaki, *Catal. Lett.*, **1991**, 11.

11) T. Kitano, Y. Kuroda, M. Mori, S. Ito, K. Sasaki, and M. Nitta, *J. Chem. Soc., Perkin Trans. 2*, **1993**, 981.

12) A. Kunai, T. Wani, Y. Uehara, F. Iwasaki, Y. Kuroda, and K. Sasaki, *Bull. Chem. Soc. Jpn.*, **64**, 2613 (1991).

13) A. Kunai, S. Hata, S. Ito, and K. Sasaki, *J. Am. Chem. Soc.*, **108**, 6012 (1986).

14) A. Kunai, S. Hata, S. Ito, and K. Sasaki, *J. Org. Chem.*, **51**, 3471 (1986).

15) J. K. Okunowski, H. E. van Dam, and H. van Bekkum, *Recl. Trav. Chem. Pays Bas*, **109**, 103 (1990).