Liquid-phase Oxidation of Benzene under Ambient Conditions

Tomoyuki Kitano, Yasushi Kuroda, Akikazu Itoh, Jian Li-Fen, Atsutaka Kunai and Kazuo Sasaki *
Department of Applied Chemistry, Hiroshima University, Higashi-Hiroshima, 724 Japan

Oxidation of benzene on silica-supported palladium catalysts has been studied under ambient conditions. Products are phenol and three quinones/quinols (benzoquinone, hydroquinone and catechol), with some minor products produced in negligible amount. Two types of catalyst, Pd alone and Cu–Pd composite catalysts, both being supported on silica gel, were found to behave in remarkably different ways. The palladium catalyst is effective only when hydrogen and oxygen are both present in the reaction system simultaneously and produces phenol almost exclusively [the highest yield of phenol being 200 μmol g^{-1} cat. h^{-1} in benzene (100 cm^3) and the selectivity $>90\%$]. On the other hand, the selectivity shifts towards quinones when the Cu–Pd composite catalyst is used (selectivity for quinones: 28%). The effects of various factors, such as temperature, feeding mode of reaction gases and catalyst composition including moisture content are discussed.

We have already demonstrated[1–4] that a Cu–Pd composite catalyst supported on the surface of silica is very effective for the oxidation of benzene. Products were mainly phenol and hydroquinone. The working principle of the catalyst is[5–7] based on the formation of hydrogen peroxide in the reaction of oxygen with Cu^I ion according to eqn. (1).

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

The hydrogen peroxide formed is further reduced to OH radical [eqn. (2)], the key reactant in the reaction.

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

When benzene is present in the surrounding medium, $OH^\bullet$ radical attacks it to produce phenol in a single-batch reaction. For the utilization of this reaction mechanism and to set up a continuous phenol-producing process, we have to regenerate Cu^I ions from Cu^{II}. Hydrogen reduction with the use of silica-supported palladium catalysts was found to fit this demand.[3,4] Copper salts may either be fixed on the silica surface or be dissolved in the reaction solution. In our latest paper,[2] in which the reaction was carried out in benzene itself instead of in aqueous solution, we have shown that, for producing phenol selectively, the use of a copper species as a catalyst component is not always necessary. In fact, when hydrogen and oxygen are simultaneously present on the Pd surface, the reaction does occur, even giving superior performance to that in the Cu-containing system under some conditions.

This paper reports full information on the reaction with benzene. A similar reaction in organic solvents will be reported in due course.

Experimental

Catalyst Preparation.—Catalysts were prepared by deposition of $PdCl_2$ and $CuSO_4$ from an aqueous solution of the desired composition on the surface of powdery silica (Merck No. 9385, 230–400 Mesh ASTM). In experiments related to Fig. 5, a calculated amount of sulphuric acid was added to the mother solution. In order to attain homogeneous deposition, we used ultrasonic irradiation during the evaporation–deposition process. After being dried, the product was put into stirred benzene and subjected to reduction with hydrogen for 45 min at room temperature. By this treatment, the catalyst became black; $PdCl_2$ is believed to be converted into metallic Pd and $CuSO_4$ into Cu_2SO_4. No effort was made, however, to determine the exact oxidation state of the metal species. The mixture was filtered and the residue was used directly for the reaction.

Oxidation of Benzene.—Reaction was carried out in a small glass flask fitted with a gas inlet and outlet. Ordinarily, catalyst (2 g) and benzene (100 cm^3) were placed in the flask and stirred with a magnetic stirrer. The reactant gas (or gas mixture) was bubbled into the benzene. As will be described, the two reactant gases (H_2 and O_2) were supplied either separately or simultaneously.

Product Analysis.—An Hitachi HPLC unit with a Merck Lichrosorb HP-18 column (10 × 250 mm) was used for product analysis. The eluant used was a mixed solution of a phosphate buffer (pH 3.5) and acetonitrile in the volume ratio 3:1. UV detection at 270, 240 and 290 nm wavelength was employed for phenol, benzoquinone and hydroquinone, respectively. Determination of catechol was performed at 270 nm.

Reproducibility.—Experiments were repeated at least twice for a single measurement. As far as previously prepared catalysts are concerned, the reproducibility of measurements was quite good and the data scattering in duplicate measurements was within the error-limit circles in each Fig. When, however, a larger scattering appeared, it is indicated by error bars.

Results and Discussion

Fig. 1 shows some basic features of the reaction. Curves with empty circles correspond to experiments with the Cu–Pd catalyst and those with full circles to the Pd catalyst. The lower two curves were obtained by feeding hydrogen and oxygen alternately, while the upper two were obtained by feeding the two gases simultaneously. Fig. 1 shows that: (1) under the alternate feeding of reactant gases, phenol accumulates mainly during the stage(s) when oxygen is bubbled through the mixture, as is expected from the reaction mechanism [see curve (*c*)]. In contrast, phenol is not produced when the catalyst is Pd alone [curve (*d*)]. The very little production shown for curve (*d*) is the result of transient mixing of the two gases during the short period(s) of gas alteration. In fact, if the frequency of alternate gas feeding is increased, the yield of phenol increases appreciably.[2] On the other hand, if we insert nitrogen between the hydrogen and oxygen stages the yield decreases remarkably;

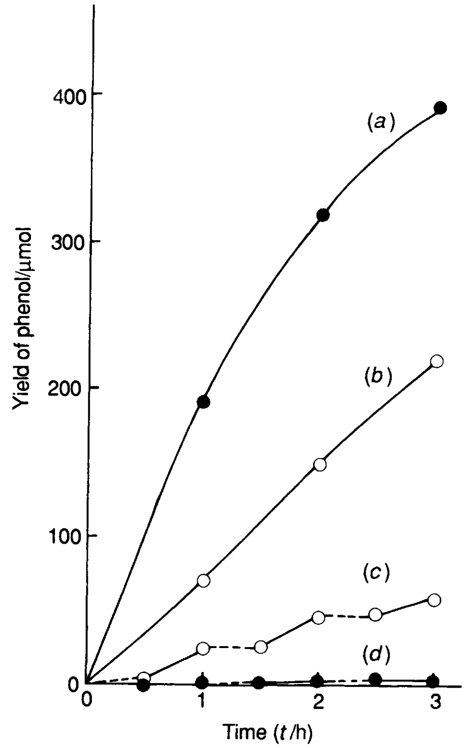

Fig. 1. Basic features of the phenol-producing reaction at 25 °C. Catalyst (2 g): $CuSO_4$ (0.1 mmol) and $PdCl_2$ (0.05 mmol) per 1 g of SiO_2 [curves (*a*) and (*d*)]. $PdCl_2$ (0.05 mmol) g^{-1} SiO_2 [curves (*b*) and (*c*)]. Gas glow rate: 7.5 cm^3 min^{-1} for both H_2 and O_2. Mode of gas supply: simultaneous [curves (*a*) and (*b*)], alternate [curves (*c*) and (*d*)]. Regions expressed by broken and full lines indicate periods of hydrogen and oxygen flow, respectively.

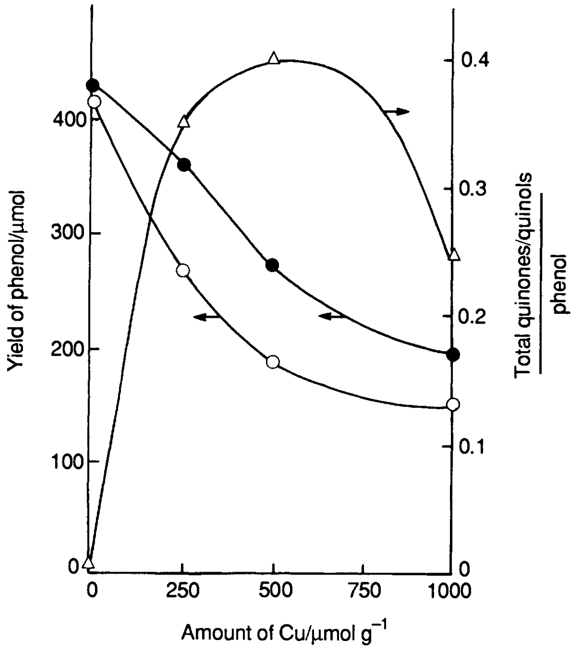

Fig. 2. Effect of copper content in the composite catalyst. Catalyst: [$PdCl_2$ (0.05 mmol) + $CuSO_4$ (*x* mmol) g^{-1} SiO_2] × 2 g. Reaction: simultaneous feeding of an equimolar mixture of H_2 and O_2 for 2 h.

and (2) under the conditions of simultaneous gas feeding, phenol is produced on the Pd catalyst, and the rate of production on the latter catalyst is even higher than that on the composite catalyst. The latter fact is, of course, related to the fact that hydrogen peroxide is produced when hydrogen reacts with oxygen on a palladium catalyst, as has been reported by several authors.[8,9] The reaction mechanism operating on the Pd catalyst seems to be much the same as that operating on the composite catalyst. The difference between the two catalysts is that Pd activates hydrogen, causing it to dissociate into atoms, while Cu^I activates dioxygen by transferring one electron to one oxygen molecule.[5–7] In spite of this difference, both the catalysts give the same product, hydrogen peroxide. The rate and the mechanism of the decomposition of hydrogen peroxide may also be different for the two catalysts. We cannot say much about this point, however. For the composite catalyst, it is quite likely that the decomposition occurs mainly by the electron-transfer reaction of eqn. (2). On the other hand, for the Pd catalyst, we merely estimate the intermediate formation of $OH^{\bullet}$ radical from the detection of hydroxylated products. It is still uncertain whether palladium changes its valence state or merely catalyses the hydrogen transfer in the decomposition of hydrogen peroxide, though we believe the latter mechanism to be more plausible.

Fig. 2 shows the effect of the copper content in the composite catalyst. Under the present conditions, hydroquinone, benzoquinone and a very small amount of catechol are also produced at levels indicated by the difference between the two descending curves of Fig. 2. The two curves refer to the yield of phenol and the total yield sum, respectively, and a bell-shaped curve for the molar ratio of total quinones to phenol. In the case of simultaneous gas feeding, the presence of copper in the catalyst affects the reaction badly. Copper probably promotes the wasteful decomposition of hydrogen peroxide into water. As a result, if we aim at the selective production of phenol, the use of the Pd single-component catalyst is advantageous in every respect, *e.g.*, high productivity and high selectivity. This does not mean, however, that the Pd single-component catalyst is always superior. Fig. 2 shows that there is a definite tendency for the presence of copper to increase the relative yield of quinones. It should be noted that when the reaction is carried out in weakly acidic, aqueous solutions the selectivity for *p*-benzoquinone is 0.7–0.8 or even more when copper species are present in the system.[10] Except for anodic oxidation,[11] no direct process for the production of benzoquinone from benzene has been reported before. Furthermore, the alternate gas feeding is useful only with the composite catalyst. This is important since the alternate gas feeding is of course preferable from the standpoint of safe operation of the reaction.

The effect of the palladium content in the catalyst was next studied and the results obtained are shown in Fig. 3. The maximum efficiency appears at a composition of *ca.* 50 µmol of Pd per gram of silica. A higher content of Pd will probably increase the rate of decomposition of hydrogen peroxide in a wasteful manner, and will result in a lower productivity of phenol.

During the course of the present study, we found that the moisture content in the catalyst (or in benzene) affected the catalyst efficiency in a remarkable manner. This is shown in Fig. 4. In this experiment, a known amount of water was added to nominally dry catalyst as prepared, to the extent of *ca.* 0.1 g of water per gram of catalyst, and the simultaneous gas feeding was continued for 2 h. Product analysis was performed every 30 min after commencement of the reaction. With a nominally dry catalyst (curve 1), the yield of phenol after 1 h of reaction was 20 µmol in contrast to the 180 µmol observed with a catalyst moistened by water (0.5 g) in every 1 g (curve 5) of the silica support. It is interesting to note that catalysts of lower water content (curves 1 and 2) showed an *increase* in their catalytic activity during the progress of the reaction; however, in contrast, those of higher water content (curves 4 and 5)

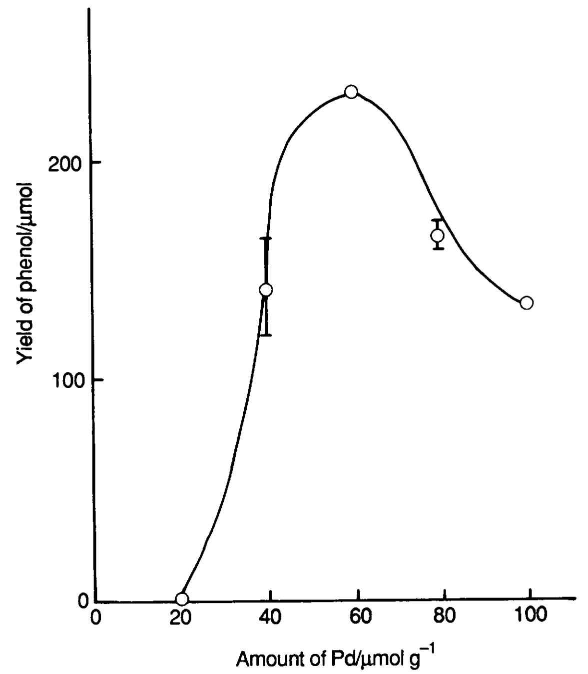

Fig. 3. Effect of Pd content in the Pd catalyst. Reaction: simultaneous feeding (7.5 cm^3 min^{-1} for H_2 and O_2) for 2 h at 25 °C.

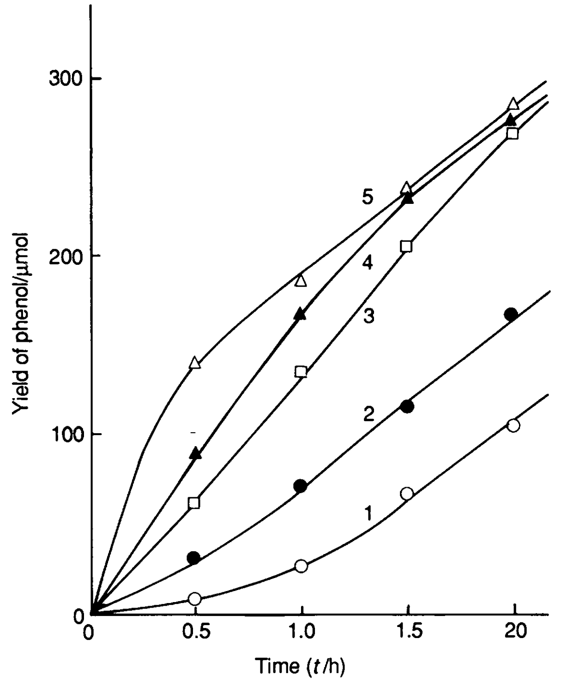

Fig. 4. Effect of water content in the catalyst. Catalyst: $PdCl_2$ (0.05 mmol) g^{-1} SiO_2 × 2 g. Reaction: as for Fig. 3. 1, as prepared; 2, 1 + water (0.05 g); 3, 1 + water (0.1 g); 4, 1 + water (0.2 g); 5, 1 + water (0.5 g). Catalyst as prepared was found to contain water (*ca.* 0.1 g per 1 g of silica support).

showed a *decrease* in activity. Curve 3 lies between the two cases and shows an S-shaped curve. These curves indicate that the best performance is associated with a properly moistened catalyst. The best water content appears to be somewhere around 0.5 g per 1 g of the silica support. Unfortunately, however, water is unavoidably produced during the reaction and steadily accumulates, leading to the gradual deterioration

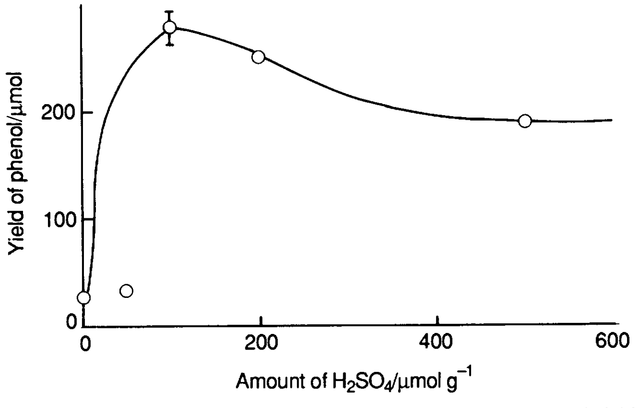

Fig. 5. Effect of acid (H_2SO_4) content in the catalyst on the phenol yield. Catalyst: $PdCl_2$ (0.1 mmol) g^{-1} SiO_2 × 1 g. Reaction: as for Fig. 3. Catalyst prepared was first reduced under hydrogen for 1 h at 100 °C. The hydrogen chloride liberated was removed by heating of the catalyst at 300 °C in a H_2 stream. A calculated amount of aq. H_2SO_4 was added to the product so as to have a given composition.

of catalytic activity. The gradual loss of activity shown in Fig. 9 and curve (*a*) in Fig. 1 are typical of this effect. When the silica support is heavily moistened, it becomes pasty and, in some extreme cases, muddy spots deposit on the glass surface. It is a fundamental problem to control the moisture level in the reaction system.

Besides this, the activity of catalyst is also affected by the surface acidity; addition of some sulphuric acid to the silica support definitely improves the catalytic activity. This is shown in Fig. 5. In our previous paper,[1] we reported that the counterion in copper salts in the composite catalyst affects the nature of the reaction appreciably. For instance, when the salt was the acetate, the main product changed from phenol to benzoquinone. In order to obtain high phenol selectively, it seemed desirable to maintain the surface acidity properly. Walling[12] stated that too high an acidity of the reaction medium results in undesirable degradation of the hydroxycyclohexadienyl radical, the key intermediate of the reaction. The descending yield at higher acid concentrations shown in Fig. 5 may be related to such an effect.

In order to investigate the effect of the reactant gas composition, a series of experiments was carried out, the results of which are shown in Fig. 6. As is clearly seen, the best performance is obtained with an equimolar gas composition in accordance with the expected formation of hydrogen peroxide.

The effect of reaction temperature is illustrated in Fig. 7. The best result is obtained at 50 °C and above that the productivity decreases drastically. The left-hand part of the curve may indicate the existence of a finite activation energy. The energy formally determined is *ca.* 5.3 kcal mol^{-1} * and is believed to be associated with gas diffusion onto the solid catalyst through the interfacial layer. On the other hand, the reason why the curve declines at temperatures above 50 °C is not clear. The solubility decrease of the reacting gases may be partly responsible, although the fall between 70–80 °C may reflect the volatile nature of benzene.

All the experiments described above were carried out using catalyst (1 or 2 g) in benzene (100 cm^3). The percentage conversion based on the amount of hydrogen supplied to the reactor flask was 2.8% in the highest case. Accordingly, we attempted to raise the conversion by increasing the amount of catalyst to be used. Fig. 8 indicates results obtained for a fixed amount of benzene (100 cm^3). As is seen, the yield of phenol

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* 1 cal = 4.184 J.

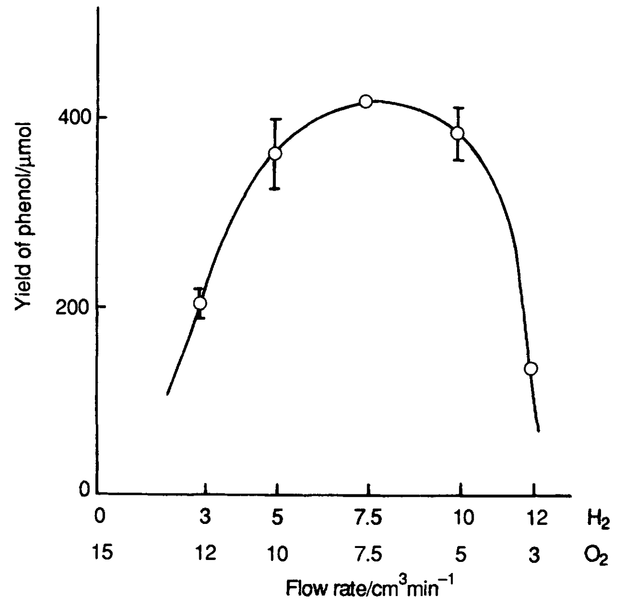

Fig. 6. Effect of gas composition. Catalyst: $PdCl_2$ (0.05 mmol) g^{-1} SiO_2 treated with water (0.5 g) × 2 g.

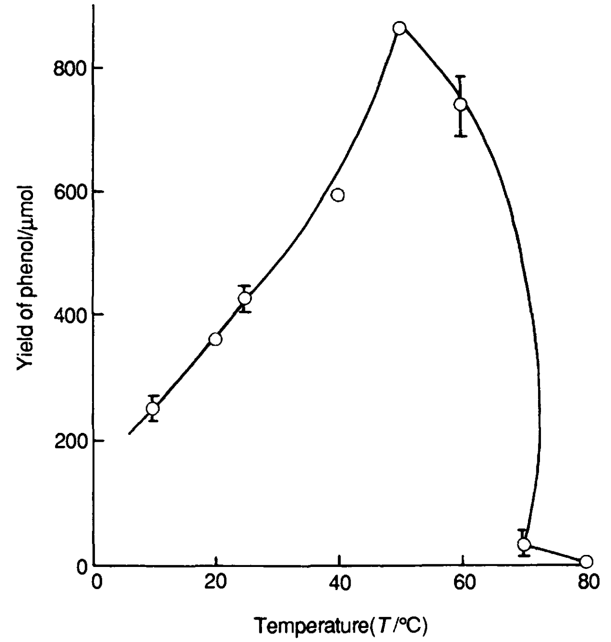

Fig. 7. Effect of temperature. Catalyst: as for Fig. 6.

increases proportionately with increasing amount of catalyst. The deviation from the straight line appearing at the final (5 g) point seems not to be intrinsic but is merely caused from insufficient mixing of the solution which will result in a localized dispersion of catalyst particles.

The results of a prolonged experiment are shown in Fig. 9. Owing to loss of activity of the catalyst, the rate of phenol production decreases gradually in the initial 3 h of the reaction but, after that, it remains constant until after 15 h, at which time the experiment was stopped. The curve can be divided roughly into three parts and the corresponding rates of phenol production are 143, 60 and 22 µmol g^{-1} silica h^{-1}. Stabilization of the high initial catalyst activity was a major problem. Besides the heavy moistening, the loss of activity of the catalyst is caused by the mechanical collapse of silica particles. Further study on the supporting materials is thus required.

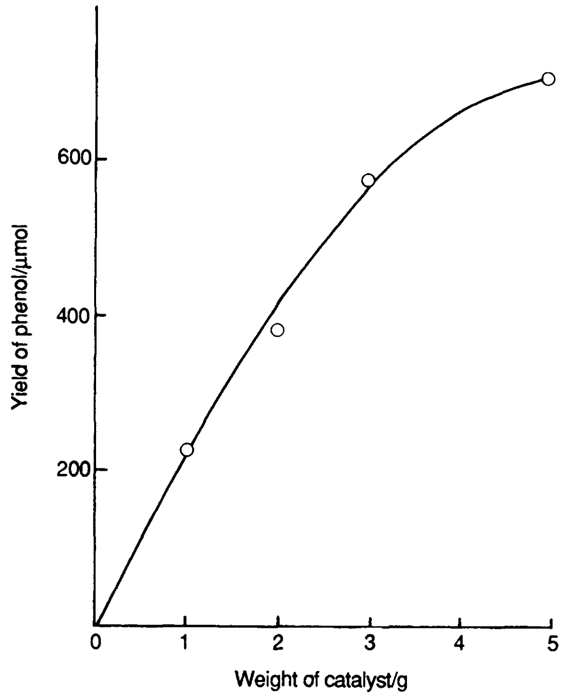

Fig. 8. Yield of phenol against the amount of catalyst. Catalyst: $PdCl_2$ (0.06 mmol) g^{-1} SiO_2. Reaction: as for Fig. 3.

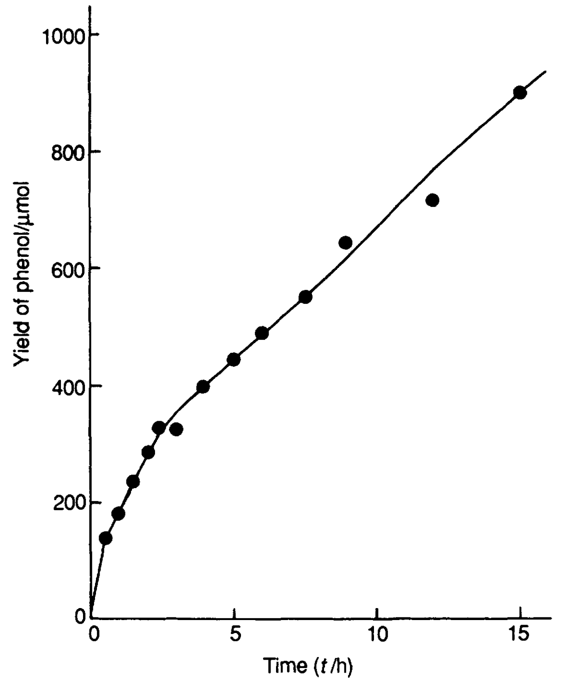

Fig. 9. Change in catalytic activity with progress of the reaction. Catalyst: as for Fig. 6. Reaction: as for Fig. 3.

As has been stated, the product selectivity inclines towards quinones when copper is present in the reacting system. In such a system, the yield of catechol, which is believed to be a secondary product derived from phenol, is negligible. In the case of the Pd catalyst, on the other hand, the selectivity for quinones is minimized and that for phenol increases. As a result, the appearance of catechol becomes rather conspicuous. Some typical examples of product distributions are listed in Table 1 together with the turnover frequency (turnover number per

Table 1. Some examples of product distribution.

Entry	Flow rate/ cm^3 min^{-1}		T/°C	Products (μmol g^{-1} h^{-1})				Turnover[a] frequency/h^{-1}
	H_2	O_2		PhOH	BQ	HQ	CA	
1	7.5	7.5	25	105.8	0.1	0.9	0	2.1
2	1.5	1.5	25	53.5	0	0.9	1.8	1.1
3	15.0	15.0	25	97.2	0.3	0.9	2.4	2.0
4	7.5	7.5	50	192.1	0.3	1.7	*b*	3.8

[a] Turnover number per hour based on palladium. [b] Not determined.

hour), which has been calculated on the basis of the amount of palladium present.

Conclusions

It has been demonstrated that phenol is produced efficiently in a single-batch reaction using palladized silica catalyst. The selectivity for phenol readily exceeds 90%. The highest rate of phenol production observed is *ca.* 200 μmol h^{-1} per 1 g of catalyst. The problem to be solved is how to minimize the loss of activity of the catalyst, which is mainly caused by moistening of the silica support with water generated *in situ*.

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