Pd/SiO$_2$ CATALYST FOR OXIDATION OF BENZENE TO PHENOL

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Catalytic hydroxylation of *benzene* Pd based catalysts for *phenol production* Direct conversion of benzene to *phenol*

Usefulness of silica supported palladium catalysts applied for the hydroxylation reaction of benzene under ambient conditions has been demonstrated. Two types of catalyst, Pd alone and CuPd composite catalysts both being supported on silica, were found to behave in remarkably different ways which are dependent also on the mode of reactant gas feeding. The Pd single component catalyst is powerful when hydrogen and oxygen are simultaneously present in the reacting system and produces phenol almost exclusively. On the other hand, the composite catalyst can be used irrespective of the mode of gas feeding. If quinones are desired, the use of the composite catalyst is recommended but if phenol is desired the Pd single component catalyst seems to be advantageous.

In a series of foregoing papers [1–4], we have reported that the Cu$^{+/2+}$ redox couple in combination with palladium supported on silica is an effective catalyst for the aerial oxidation fo benzene to phenol. The principal of the reactions is as follows. Cu(I) species, which may either be fixed on the silica support or be dissolved in the solution phase, reduces oxygen to form finally hydroxyl radical, the key reactant in the oxidation process [5,6]. Cu(II) species accumulated during the oxidation process is reactivated by hydrogen reduction, for which palladium works as an efficient catalyst. We have also shown [7] that two gaseous reactants, oxygen and hydrogen, can be supplied either alternately or simultaneously.

In this paper we should like to report further development of our study.

2. Experiments

Catalysts: Palladium chloride and copper(II) sulfate were deposited on the surface of powdery silica gel by evaporation from their aqueous solutions. Further details of catalyst preparation are described in the previous papers. The catalysts here used are denoted as *x*Cu-*y*Pd, where *x* and *y* stand for micro moles of metal species per one gram of silica support.

Reaction: A given amount of benzene (20 ml in experiments related to fig. 1 and 100 ml for others) is taken in a 100 ml Erlenmeyer flask with a desired amount of catalyst (2, normally). Reaction was started by feeding the reacting gas stream (either hydrogen or oxygen or both) through the gas space over agitated benzene. The flask was thermostatted at 25 ° C throughout the experiment. Product analysis was made with the use of HPLC.

3. Results and discussion

Figure 1 shows results of some preliminary studies of alternate gas feeding. For curves A and B, hydrogen was first supplied for two hours and oxygen followed it for one hour and the cycle was repeated three times. Under this feeding condition, it is undoubted that the performance of the composite catalyst (1000 Cu-50 Pd, Curve A) is much better than that of the single component catalyst (50 Pd, Curve B). However, the situation becomes different when the reactant gases are alternated more frequently. Point C was obtained after three repetitions of a (10 min H_2-10 min O_2) cycle using the same catalyst as that of Curve B (50 Pd).

It is interesting that, with the composite catalyst (Curve A), phenol accumulates mainly during the stage of oxygen as is expected from the reaction

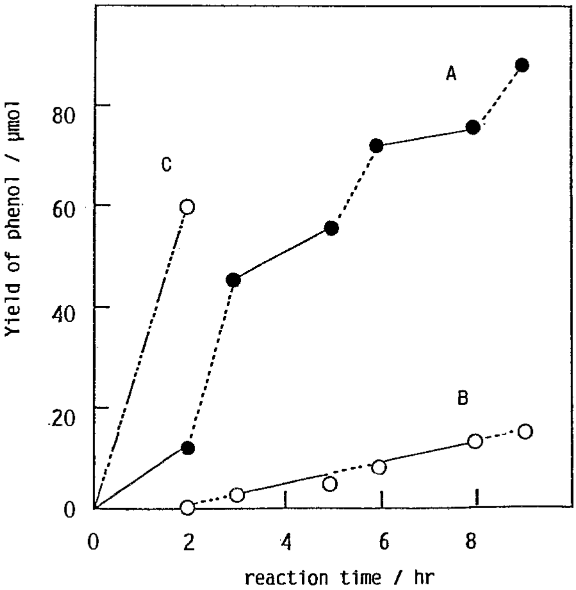

Fig. 1. Yield of phenol(micro mol in 20 ml of benzene) under the condition of alternate gas feeding. Feed rate: 7.5 ml min^{-1} for both H_2 and O_2. Curve A: Cu-Pd composite catalyst (1 g). Curves B and C: Pd single component catalyst (1 g). Period of full and dashed lines stand for hydrogen and oxygen stages, respectively.

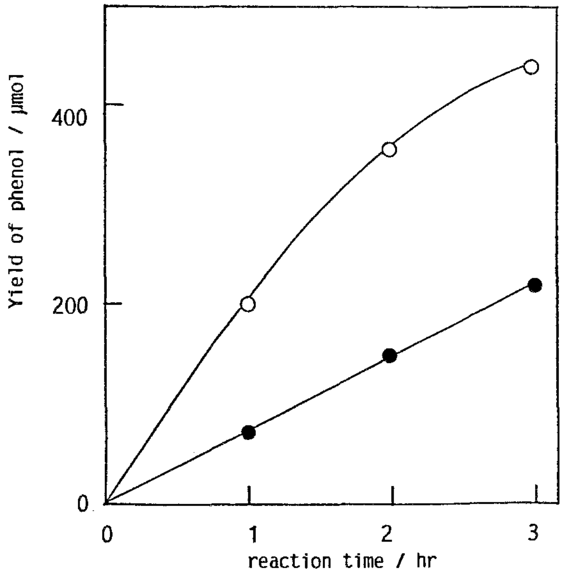

Fig. 2. Yield of phenol (micro mol in 100 ml of benzene) under the simultaneous gas feeding. Feed rate: 7.5 ml min^{-1} for both H_2 and O_2. Upper curve: Pd single component catalyst. Lower curve: Cu-Pd composite catalyst.

mechanism described before. On the other hand, with the single component catalyst (Curve B), the yield of phenol seems to increase almost steadily irrespective of the feeding gas. In addition, it was confirmed separately that if nitrogen was shortly introduced between the two gas streams in order to avoid transient mixing, the phenol yield was drastically suppressed. These suggest strongly that on the Pd alone catalyst, simultaneous presence of both hydrogen and oxygen is an essential requirement for converting benzene to phenol; the presence of copper salt being unnecessary. If the two gases are supplied separately , on the other hand, no effective reaction is expected. Palladium will produce hydrogen peroxide when adsorbed hydrogen atoms have a chance to meet oxygen as some patents indicate [8]. The palladium catalyzed synthesis of hydrogen peroxide was also reported by Pospelova et al. [9].

We thus studied the performance of the Pd single component catalyst a little more in detail under the condition of simultaneous gas feeding. First of all, the performance is compared with that of Cu-Pd composite catalyst in fig. 2. Undoubtedly, the performance of the Pd-alone catalyst is much superior when the two gases are supplied simultaneously.

We have next studied the effect of the loading ratio of Pd on the silica support and results obtained are shown in fig. 3. The figure indicates that optimum composition is somewhere around 60 micro mol per one gram of silica. The effect of catalyst dose (grams of catalyst per a given volume of benzene) was also studied (see table 1). When these are graphically plotted, the phenol yield

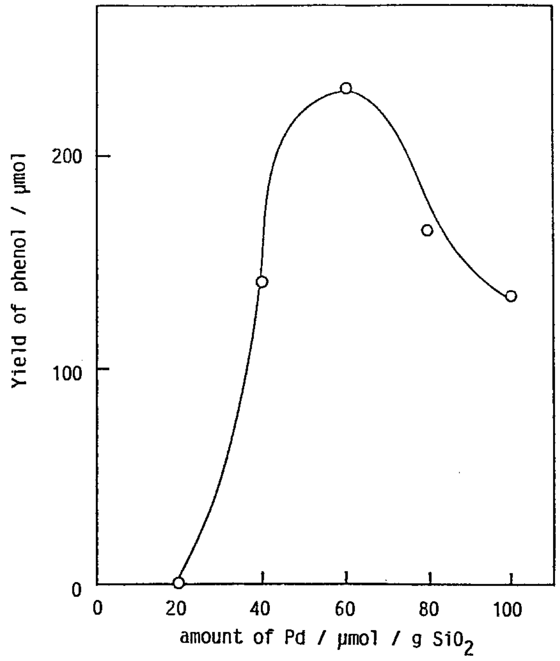

Fig. 3. Yield of phenol (micro mol in 100 ml of benzene) as a function of the amount of Pd(micro mol/g SiO_2). Feeding mode: simultaneous, 7.5 ml min^{-1}

increases linearly up to 3 gram of catalyst per 100 ml of benzene and, after that, the curve declines with increasing amount of catalyst. This is because paladium has dual functions as the catalyst; one in forming hydrogen peroxide and the other in decomposing it.

We have shown that quinones (hydroquinone and benzoquinone) are produced beside phenol and the selectivity between them can be altered by controlling the

Table 1
Product distribution [a]

Catalyst [b]	Product (µmol/100 ml benzene)			Selectivity	Turnover freq. (hr^{-1})
	Phenol	Benzo-quin.	Hydro-quin	Quinones in total products	
1000 Cu-50 Pd [b]	220.3	47.5	1.8	0.2	–
50 Pd [b]	423.1	10.8	3.8	0.030	1.4
60 Pd, 1g [c]	232.9	4.4	–	0.019	2.0
60 Pd, 2g [c]	384.2	2.4	4.5	0.018	1.7
60 Pd, 3g [c]	578.9	1.8	3.5	0.009	1.6
60 Pd, 5g [c]	713.9	1.7	3.3	0.007	1.2

[a] Both hydrogen and air were fed at a rate of 7.5 ml/min for each of them.
[b] Values correspond to 3 hr data in fig. 2. The catalyst used was 2 g.
[c] The reaction was continued for 2 hrs.

reaction conditions [5,6]. The present result is also the case. Table 1 shows some typical examples of the product distribution. Although the ratio (quinones over total products) varies rather widely, there are some general tendencies i.e., 1) the ratio is always greater with copper containing catalysts and, 2) the ratio increases with increasing oxygen partial pressure in the feed gas and with increasing content of copper in the catalyst. Some of the data in table 1 demonstrate that the attainment of phenol selectivity of at least 95% can be realized [10] if we use the Pd-alone catalyst under appropriate reaction conditions. The turnover frequency (hr^{-1}) is also listed at the last column.

We have now seen that the presence or absence of copper salt in the catalyst results in a drastic change of catalytic performance. Roughly speaking, the Cu-Pd composite catalyst favors reactions occurring under the condition of separate gas feeding, while the Pd-alone catalyst favors those of simultaneous gas feeding. The choice will depend on the strategy of the process design.

In fact, the use of Pd-Cu composite catalyst has basically two advantages over the Pd single component catalyst. First of all, dangerous explosion associated with the simultaneous use of hydrogen and oxygen is eliminated. The second advantage is that the selectivity between singly and doubly hydroxylated products (phenol and hydroquinone in case of benzene) can be altered by changing acidity and oxygen pressure in the reaction environment. In particular, the Cu-Pd composite catalyst is probably the only catalyst so far reported which converts benzene directly to hydroquinone (or benzoquinone).

On the other hand, Pd catalyst is advantageous if the safety operation is assured because of its simplicity of the process design. Because there is no need of catalyst reactivation a much higher production rate can be expressed.

The reaction mechanisms operating on the two catalysts are thought to be much the same, particularly after forming hydrogen peroxide. The latter will be decomposed by either Cu(I) ion or Pd metal to produce the OH radical which readily adds to the benzene nucleus [11]. Therefore, the difference in mechanism must appear in the process of producing hydrogen peroxide. In case of the copper containing catalyst, there is no doubt that dioxygen is first activated by receiving the electron from Cu(I) species: Cu(I) ions act as the electron sink. On the other hand, in case of Pd catalyst, atomic hydrogen adsorbed on the Pd surface directly reacts with oxygen to form the peroxide.

Reference

[1] A. Kunai, K. Ishihata, S. Ito and K. Sasaki, Chem. Lett. (1988) 1967.
[2] A. Kunai, T. Wani, Y. Uehara, Y. Kuroda, S. Ito and K. Sasaki, Chem. Express 4 (1989) 201.
[3] A. Kunai, F. Iwasaki, T. Wani, Y. Kuroda, S. Ito and K. Sasaki, ibid. 4 (1989) 261.
[4] A. Kunai, T. Wani, Y. Uehara, F. Iwasaki, Y. Kuroda, S. Ito and K. Sasaki. Bull. Chem. Soc. Jpn. 62 (1989) 2613.
[5] S. Ito, T. Yamasaki, H. Okada, S. Okino and K. Sasaki, J. Chem. Soc., Perkin Trans. II (1988) 285.

[6] S. Ito, A. Kunai, H. Okada and K. Sasaki, J. Org. Chem. 53 (1988) 296.
[7] K. Sasaki, S. Ito and A. Kunai, 1st World Congress on New Developments in Selective Oxidation, Rimini (Italy), Sept. 1989.
[8] US Patent, 4,009,252(1977) , 4,279,883(1981).
[9] T.A. Pospelova, N.I. Kobozev and E.N. Eremin, Russ. J Phys. Chem. 35 (1961) 143.
[10] There are a very few amount of several by-products including catechol though not listed in the table .
[11] L.M. Dorfman and G.E. Adams, Reactivity of the hydroxyl radical in aqueous solutions, Report No. NSRDS-NBS-6, U.S. Gov. Print. Office, Washington D.C., 1973.