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Partial Oxidation of Toluene to Benzaldehyde and Benzyl Alcohol by Applying an H_2-O_2 Fuel Cell System

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The cathode of carbon whisker was active for the oxidation of toluene into benzaldehyde and benzyl alcohol during the H_2-O_2 fuel cell reaction under short circuit conditions. Synergism of carbon whisker and active carbon was observed. The increase in the concentration of H_3PO_4 used as an electrolyte improved the selectivity and the oxidation efficiency remarkably.

Benzaldehyde (PhCHO) and benzyl alcohol ($PhCH_2OH$) are important chemicals used in the manufactures of perfumes, dyes, and drugs. The synthesis of these chemicals by catalytic oxidation of toluene with molecular oxygen is of great practical importance. However, the oxidation of toluene cannot avoid the further oxidation into benzoic acid and carbon dioxide. Therefore, a novel catalyst or a new technique for the selective synthesis of PhCHO and $PhCH_2OH$ is strongly required.

We have reported that the oxidation of benzene to phenol or of cyclohexane to cyclohexanol and cyclohexanone can be operated at room temperature using an H_2-O_2 fuel cell system.1,2) The oxidation of toluene applying this technique produced a mixture of cresols, PhCHO, and $PhCH_2OH$.1) Very recently, we have found that the selective oxidation to $PhCH_2OH$ and PhCHO can be realized under appropriate reaction conditions. Therefore, in this report, we describe the technique and the reaction conditions for this selective oxidation.

The reaction system used in this work is demonstrated in Fig. 1. A detailed description of the setup of this reactor has been described elsewhere.3) A silica wool disk impregnated with H_3PO_4(aq) separates the two compartments in Fig. 1. An amount of 1.0 ml of H_3PO_4 (1 M) was added to a silica-wool disk as an electrolyte unless otherwise stated. The carbons used in the electrodes (graphite (Wako), active carbon (Merck),

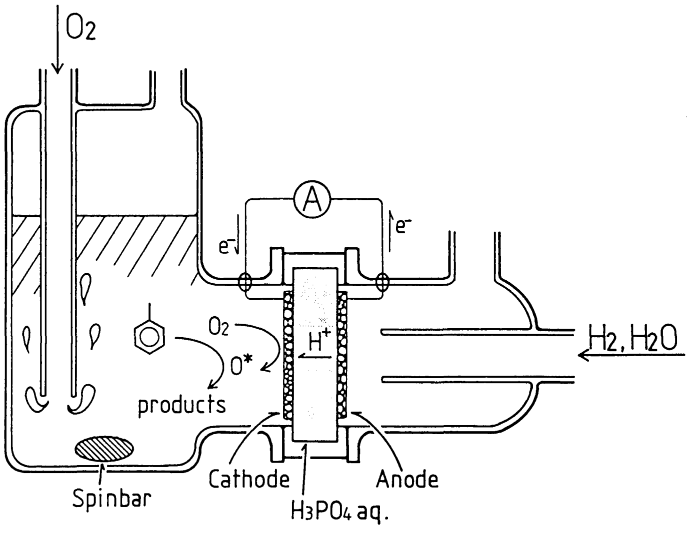

Fig. 1. Schematic diagram of the fuel cell reactor for the partial oxidation of toluene.

carbon black (Tohkai Carbon), and carbon whisker (Asahi Chemical)) were pretreated with an aqueous solution of HNO_3 (6.7 M) at 373 K for 2 h. Impurities dissolved in the solution were filtered and washed out with distilled water. The anode was prepared from the mixture of graphite (50 mg), Pt-black (20 mg) and Teflon powder (5 mg) by the hot-press method.$^{2)}$ The cathode was prepared from the mixture of the carbon (70 mg) and Teflon powder (5 mg). The size of the electrode (round wafer) was 22 mm in diameter and 0.1 mm in thickness. The reaction was started by shorting the circuit and continued for 3 h.

Table 1 shows the results of the oxidation of toluene over the cathode prepared from the four different carbon materials. The graphite, carbon whisker, active carbon and carbon black are abbreviated as Gr, CW, AC, and CB, respectively. The products obtained under the standard reaction conditions were PhCHO, $PhCH_2OH$, cresols(o-,m-,p-cresols), and a trace of phenol, bibenzyl and benzoic acid. The sum of the latter three was less than 3% of the total products. The charge passed (CP), the amount of products, the (cresols)/($PhCHO+PhCH_2OH$) ratio denoted as R/S, and the oxidation efficiency (OE) are listed in Table 1. Here, the OE was defined as,

$$(\mathrm{OE}) = 100\% \times \frac{(\text{Amount of the sum of PhCHO, PHCH}_2\text{OH and cresols})}{(\text{Amount of water produced})}$$

where, the denominator was estimated from the CP by assuming that the current measured was entirely due to the formation of water. The results in Table 1 indicate that the most active cathode for the side-chain oxidation of toluene is the one prepared from CW. On the other hand, the cathode of CB was most active for the ring hydroxylation to cresols. The R/S ratios in Table 1 suggest that CW and Gr are favorable for the side-

Table 1. Oxidation of toluene over the cathodes of various carbons.

Cathode	CP/mF	Products/μmol			R/S	OE/%
		PhCHO	$PhCH_2OH$	cresols		
CW	0.54	22.7	2.9	4.7	0.18	11.3
Gr	0.10	3.2	0.8	1.3	0.33	10.0
AC	0.30	2.5	1.7	5.2	1.23	6.1
CB	0.97	8.7	4.8	21.0	1.56	7.1

Experimental conditions: Temp. = 303 K, Reaction time = 3 h.
In the cathode compartment; $P(O_2)$ = 101 kPa, flow rate = 5 ml(STP)$\cdot$min^{-1}, benzene = 40 ml, in the anode compartment; $P(H_2)$ = 50 kPa, $P(H_2O)$ = 3 kPa, P(Ar) = 48 kPa, total flow rate = 20 ml(STP)$\cdot$min^{-1}.

Table 2. Synergism of AC and CW for the rate of formation of products.

Cathode	AC/CW ratio in mg	CP /mF	Products/μmol			R/S	OE /%
			PhCHO	$PhCH_2OH$	cresols		
(1)	20/50	0.78	28.3	9.3	5.0	0.13	10.9
(2)	35/35	1.17	32.7	15.6	14.8	0.31	10.7
(3)	50/20	1.44	19.5	11.3	25.2	0.82	7.8
(4)	60/10	0.97	8.1	5.3	24.6	1.84	7.8
(5)	35/35[a)]	0.81	32.3	9.9	5.2	0.12	11.7

a) CB/CW ratio for the mixture of CB and CW.
Experimental conditions were same as those of Table 1.

chain oxidation, but AC and CB are suited for the ring-hydroxylation. The cathode of CW showed the highest oxidation efficiency (11.3%) in Table 1. These observations indicate that the CW is the most favorable cathode for the production of PhCHO and $PhCH_2OH$.

The results for the mixture of CW with AC or with CB are shown in Table 2. The comparison of the results in Table 2 with those in Table 1 indicates that the mixtures clearly show a synergism of CW and AC or of CW and CB on the quantities of the products. The addition of AC (or CB) to CW up to 50 wt% (cathode (1),(2), and (5)) enhanced the rate of side-chain oxidation considerably. However, further addition of AC (cathode (3) and (4)) decreased the rate of side-chain oxidation, but enhanced remarkably the rate of cresol formation beyond the rate that was observed for the AC alone(70 mg) in Table 1. These unusual effects of the mixture of the carbons cannot be explained at the moment.

The change in the concentration of H_3PO_4(1 ml) influenced the selectivity to the side-chain oxidation. The results observed for the cathode of CW are shown in Fig. 2. As can be seen in Fig. 2, the

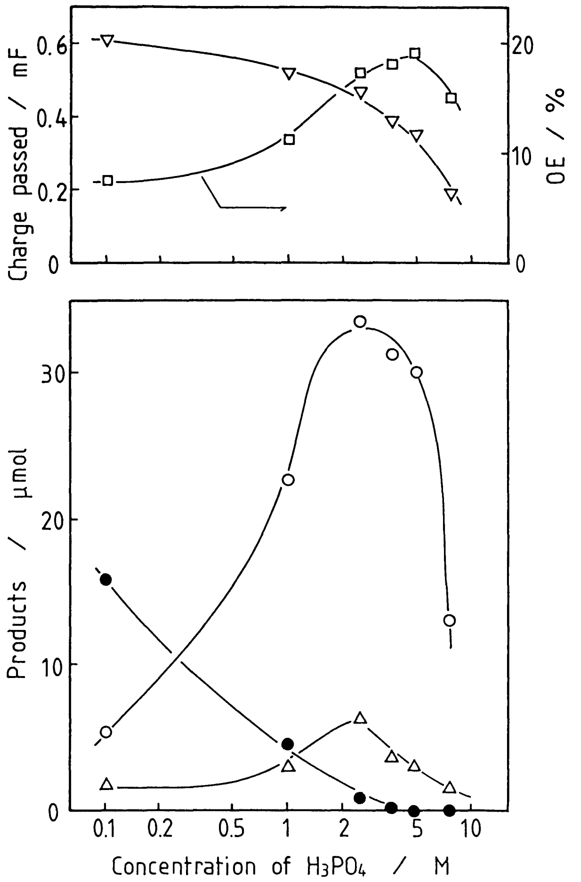

Fig. 2. Effect of H_3PO_4 concentration on the product selectivities, CP and OE: (○), PhCHO; (△), $PhCH_2OH$; (●), cresols; (▽), CP; (□), OE. Cathode was CW. Experimental conditions were same as those of Table 1.

increase in the concentration of H_3PO_4 enhanced the formations of PhCHO and $PhCH_2OH$ remarkably. The rates reached the maxima at the concentration of 2.5 M and decreased with further increase in the concentration. On the other hand, the rate of ring-oxidation decreased with a rise in the concentration of H_3PO_4. No cresol was observed at the concentration > 5 M. The OE for the sum of the formations of PhCHO and $PhCH_2OH$ was improved considerably up to 20% at 4.9 M of H_3PO_4. The results in Fig. 2 indicate that the selective oxidation of toluene into PhCHO and $PhCH_2OH$ is possible at 2 to 5 M of the concentration of H_3PO_4 with an oxidation efficiency greater than 18%. Further investigations are needed to clarify the nature of the active oxygen species (O*) and to elucidate the results in Fig. 2.

References

1) K. Otsuka, I. Yamanaka, and K. Hosokawa, Nature, 354, 697(1990).
2) K. Otsuka and I. Yamanaka, Chem. Lett., 1990, 509.
3) I. Yamanaka and K. Otsuka, J. Electrochem. Soc., 138, 1033(1991).

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