Oxidation of Benzene to Benzoquinone during Electrolysis of Water over the Carbon Fiber-Anode

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Direct oxidation of benzene to benzoquinone was performed by the electrolysis of water over the porous anodes. The porous anodes made from carbon materials, especially vapor-grown-carbon-fiber, and PTFE were active for the formation of benzoquinone. Graphite structure of carbon is essential for the electro-oxygenation of benzene with H_2O

The study on a new system for the direct functionalization of C-H bond of benzene is one of the most attractive subjects in the current chemistry. Several electrolysis systems for the hydroxylation of benzene mediated by redox mediators such as Fe^{3+}/Fe^{2+} and Cu^{2+}/Cu^{+} over a cathode have been reprted.[1] While, direct electrolysis system for oxidation of benzene over an anode was only one using the β-PbO_2 anode.[2] Benzoquinone (BQ) was selectively produced by the electrolysis of the solutions of benzene, H_2SO_4 and H_2O over the β-PbO_2 anode. However, Pb is environmentally hazardous compound. If an environmentally safety anode materials would be used for oxygenation of benzene, it might bring a considerable progress in the fields of electrorganic synthesis for oxygenates, especially the direct oxygenation of aromatic rings.

In this study, a two-compartments electrolysis cell assembled as [benzene(l) | porous anode | silica wool membrane holding H_3PO_4 aq. | Pt-Gr cathode | H_2O(g), He] was used for the oxidation at 298 K. The porous electrodes were made from powders of electrode material and PTFE by the hot-press method. Products in benzene phase were analyzed by HPLC and GC. The advantage of this electrolysis system compared with conventional ones is that the separation procedure of electrolyte and solvent from the reaction mixture is not necessary.

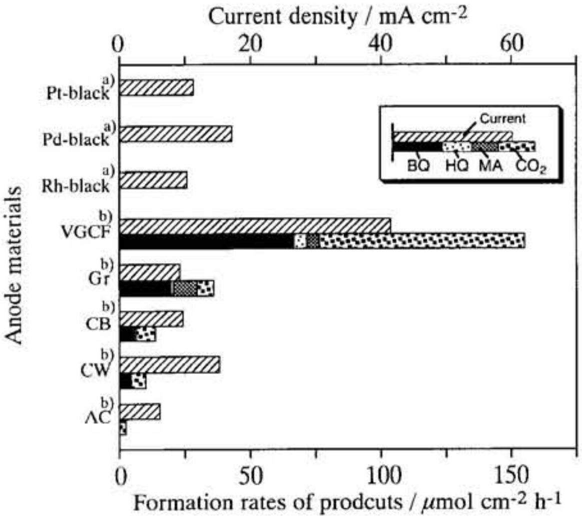

Figure 1. Oxidation of benzene over various anodes during H_2O electrolysis at 298 K. Reaction time 2 h, H_3PO_4 1 mol/l, benzene 40 ml. Anode potential (Ag|AgCl); a) 1.5 V, b) 2.0 V. BQ benzoquinone, HQ hydroquinone, MA mareic acid.

Figure 1 shows the catalytic activities of various anodes for the partial oxidation of benzene during H_2O electrolysis at anode potentials of 1.5 or 2.1 V (Ag | AgCl). The anodes of Pt-black and Pd-black were active for the oxidation of alkenes to epoxides and ketones[3] but these precious metals were not active for the oxidation of benzene at all. In contrast to the precious metals, some carbon anodes were active for the oxidation of benzene during H_2O electrolysis. The most active anode for the oxidation was the Vapor Grown Carbon Fiber (VGCF) produced by Showa Denko Co. among the anodes tested in this work. This VGCF has graphite structure. Major product were BQ (75% selectivity) and CO_2 (14%). Minor products were hydroquinone (HQ, 7%), maleic acid (MA, < 4%) and no evolution of O_2 into the gas phase. When the electrolysis of H_2O over VGCF anode was carried out with CH_2Cl_2 instead of benzene in the anode compartment, no oxygenates were formed. This result proved that oxygenates were produced not from VGCF but from benzene. Graphite powder (Gr), carbon black (CB) and carbon whisker (CW) also showed the formation of BQ. The graphite structure is also contained a certain extent in CB and CW. These results suggest that the graphite structure of carbon is one of the key factors for the active anode in the oxidation of benzene to BQ.

Figure 2 shows the formation rate of the products in the

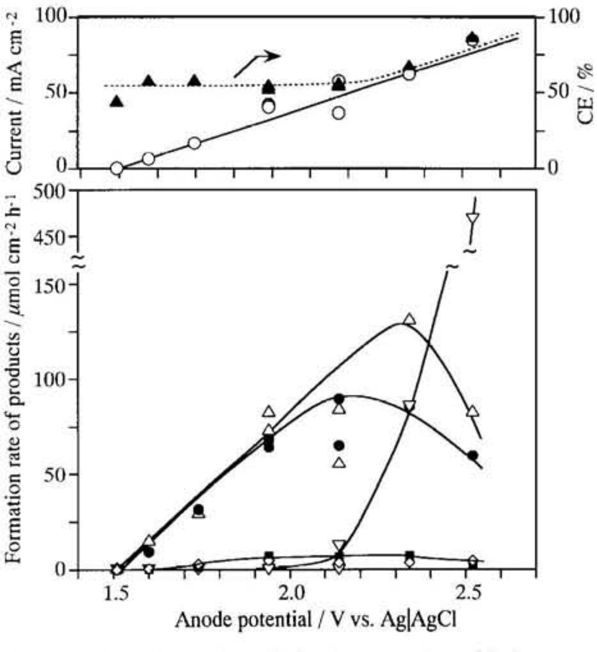

Figure 2. Effects of applied voltage on the oxidation of benzene over the VGCF anode at 298 K. Reaction time 2 h, H_3PO_4 1 mol/l, benzene 40 ml. BQ ●, HQ ■, MA ◇, CO_2 △, O_2 ▽, current ○, current efficiency ($BQ+HQ+MA+CO_2+O_2$) ▲.

oxidation of benzene as functions of anode potential. When the anode potential was increased above 1.50 V, the current flowed and the formations of BQ, HQ, MA and CO_2 were observed but no evolution of O_2. The current and the formation rates of BQ, HQ and CO_2 increased with increasing the anode potential. The maximum formation rate of BQ was obtained at 2.14 V and that of CO_2 was at 2.34 V. In contrast, the formation of O_2 was observed at anode potentials of 2.14 V. The amount of O_2 formation increased sharply with increasing the anode potential > 2.2 V. The decrease in the yields of the oxidation products of benzene above 2.2 V may be due to the formation of O_2. Active oxygen species must desorb as O_2 to the gas phase before they oxidize benzene. These observations indicate that a suitable anode potential for the formation of BQ was 2.1~2.2 V under the conditions in this work. If the oxidation of benzene proceeded through the reactions of Eqs. 1-3, the current efficiency for the formation of BQ was estimated to be 28% and that for the sum of BQ, HQ and CO_2 was 60% at 2.14 V.

$$C_6H_6 + 2\,H_2O \rightarrow C_6H_4O_2 + 6\,H^+ + 6\,e^- \quad (1)$$

$$C_6H_6 + 12\,H_2O \rightarrow 6\,CO_2 + 30\,H^+ + 30\,e^- \quad (2)$$

$$C_6H_6 + 2\,H_2O \rightarrow C_6H_6O_2 + 4\,H^+ + 4\,e^- \quad (3)$$

While, the current efficiency for the formation of H_2 observed at the cathode was more than 96% based on Eq. 4.

$$2\,H^+ + 2\,e^- \rightarrow H_2 \quad (4)$$

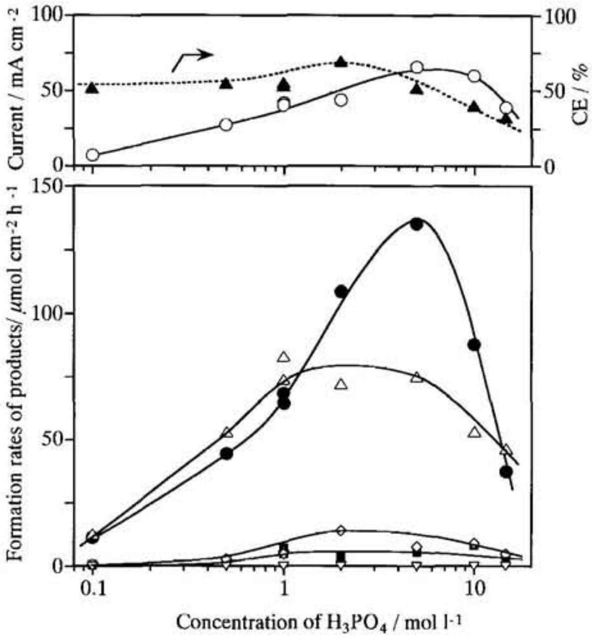

Figure 3. Effects of concentration of H_3PO_4 in the diaphragm on the oxidation of benzene over the VGCF anode at 1.5 V (Ag|AgCl). T = 298 K, reaction time 2 h, benzene 40 ml. BQ ●, HQ ■, MA ◇, CO_2 △, O_2 ▽, current ○, current efficiency (BQ+HQ+MA+CO_2+O_2) ▲.

These results suggest that some unknown products are formed at the anode or the electrochemical reactions Eqs. 1-3 are not correct. At the moment, it is not clear why the current efficiency at the anode estimated from the equations of the products was so low.

Effects of the concentrations of H_3PO_4 aq. (0.1~14.7 mol/l) in silica wool disk on the oxidation of benzene were studied (Figure 3). The current increased with increasing the concentrations of H_3PO_4. The maxima in the current and the formation rate of BQ were obtained at 5 mol/l The current efficiency for the formation of BQ was roughly constant, ca. 30%, at 0.1 ~ 5 mol/l. The formation rate of CO_2 was almost constant at 1~5 mol/l. The maximum selectivity of 88% to BQ was obtained at 5 mol/l. A marked decrease in the current efficiency was observed at > 5 mol/l. Unidentified side reactions occur over the anode at the high concentrations of H_3PO_4. Thus, the optimum concentration of H_3PO_4 for the formation of BQ was 5 mol/l.

Over the β-PbO_2 anode, HO• was proposed as the active oxygen species for the oxidation of benzene to BQ.[2] The active oxygen species over the VGCF anode can not oxidize cyclohexane and 1-hexene. This fact proposed that HO• is not likely to the active oxygen species of the VGCF anode.

The methoxylation and the acetoxylation of toluene, and the oxidation of toluene to benzaldehyde mediated by Ce(IV/III) over the carbon anode using the conventional electrolysis cell have been reported.[4] However, the direct oxidation of benzene at the carbon anode using a conventional electrolysis cell did not succeed in previous reports. In this study, we used porous electrodes for the oxidation. The electrochemical reaction is expected to proceed at the three-boundary interface of benzene (organic phase), anode (porous solid), and H_3PO_4 solution (aqueous phase). This three-boundary interface may be important for the formation of active oxygen species and the oxidation of benzene. Detail studies are necessary to clarify the nature of the active oxygen species and the reaction mechanism of the BQ formation over the porous anode of carbons containing the graphite structure, especially VGCF.

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