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Phenol Synthesis

Alternating-Current Electrolysis for the Production of Phenol from Benzene**

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Phenol is conventionally produced from benzene by the following three-step process: alkylation of benzene with propylene, oxidation of cumene to cumene hydroperoxide, and decomposition of cumene hydroperoxide to phenol and acetone. Although phenol can also be synthesized by the oxidation of toluene in a two-step process, the phenol yield is low and requires improvement. Thus, the development of methods for a one-step hydroxylation of benzene to phenol is desirable to achieve high economic viability and efficiency. Direct oxidation of benzene to phenol has been widely investigated using various oxidants, such as N_2O,[1–4] H_2O_2,[5–8] O_2,[9] and a mixture of H_2 and O_2.[10] Major issues concerning these processes are deactivation of the catalyst by heavy coke formation during the gas-phase reaction[11] and the separation of phenol from the reaction mixture in the liquid-phase reaction.[12] The use of membrane reactors has also been proposed, using a compact Pd membrane as a barrier permeable only to hydrogen, and at the same time as a catalyst for the formation of active oxygen species;[13] however, the material cost of such a membrane is very high for industrial applications.

An alternative approach is to apply an electrochemical cell to the direct oxidation of benzene to phenol. Otsuka et al. reported the partial oxidation of benzene to phenol by an active oxygen species, O*, generated at the cathode in a phosphoric acid fuel cell:[14]

$$\text{Cathode}: \; O_2 + 2\,H^+ + 2\,e^- \rightarrow O^* + H_2O \qquad (1)$$

$$C_6H_6 + O^* \rightarrow C_6H_5OH \qquad (2)$$

We have also recently reported the partial oxidation of benzene to phenol by an active oxygen species, O*′, generated at the anode in a solid acid electrochemical cell:[15]

$$\text{Anode}: H_2O \rightarrow O^{*\prime} + 2\,H^+ + 2\,e^- \qquad (3)$$

$$C_6H_6 + O^{*\prime} \rightarrow C_6H_5OH \qquad (4)$$

A common goal for both of these processes is to achieve one-step phenol production with high selectivity at atmospheric pressure and low temperatures. This has motivated us to use an alternating current (AC) rather than a direct current (DC) as a power source, because phenol can be formed during both the positive and negative parts of the period. Furthermore, the nature of the active oxygen species is considered to be influenced by the AC frequency; therefore, AC electrolysis can be used to control the electrode reaction not only by the voltage but also the frequency. This provides an advance in the method for phenol production. As a result, the quantity of the phenol product was 1.3–2 times higher for the present study than for the previous study. At the same time, the phenol yield based on current consumption did not decrease. The resultant phenol production should differ from that obtained using a DC supply. The advantage of AC electrolysis over DC electrolysis has been reported for the purification of organic pollutants[16,17] and for the synthesis of chemicals.[18,19]

Based on these observations and assumptions, it is expected that the electrochemical synthesis of phenol could be improved by optimizing the AC frequency for Reactions (1), (2), (3), and (4). The goals of the present work are to: 1) characterize both the anode and cathode reactions under DC with respect to the current efficiency for phenol production and the selectivity toward phenol; 2) clarify the reaction mechanism by various means, including electrochemical, kinetic, and spectroscopic techniques; and 3) enhance the phenol production using AC with optimal frequency.

The solid acid electrolyte used in this study was $Sn_{0.9}In_{0.1}P_2O_7$, which exhibits high proton conductivity (ca. $0.1\,S\,cm^{-1}$) between 50 and 300 °C without excess humidification.[20,21] The anode/cathode material employed in this study was developed through trial and error. Vanadium oxide with mixed penta- and tetravalent vanadium (referred to as V_xO_y hereafter) was found to be a good candidate as both the anode and cathode materials for phenol production. Vanadium is one of the most widely used elements in catalysts for the direct hydroxylation of benzene to phenol with hydrogen peroxide.[5–8] Furthermore, the addition of $Sn_{0.9}In_{0.1}P_2O_7$ to V_xO_y was confirmed to effectively increase the number of reaction sites in the entire electrode (Supporting Information, Figure S2), the largest effect of which was achieved with a $Sn_{0.9}In_{0.1}P_2O_7$ content of 20 wt %.

Anodic benzene oxidation was first inspected over the V_xO_y-$Sn_{0.9}In_{0.1}P_2O_7$ electrode in a feed mixture of benzene and H_2O vapor (He balance) at various temperatures. The current increased almost linearly with increasing DC potential, and a similar relationship between the current and potential was observed over the temperature range tested (Figure 1 a). The products in the outlet gas from the anode chamber at each temperature were analyzed. Phenol, CO_2, and O_2 were detected as the predominant products (Figure 1 b–d).[22] The quantitative results for these products

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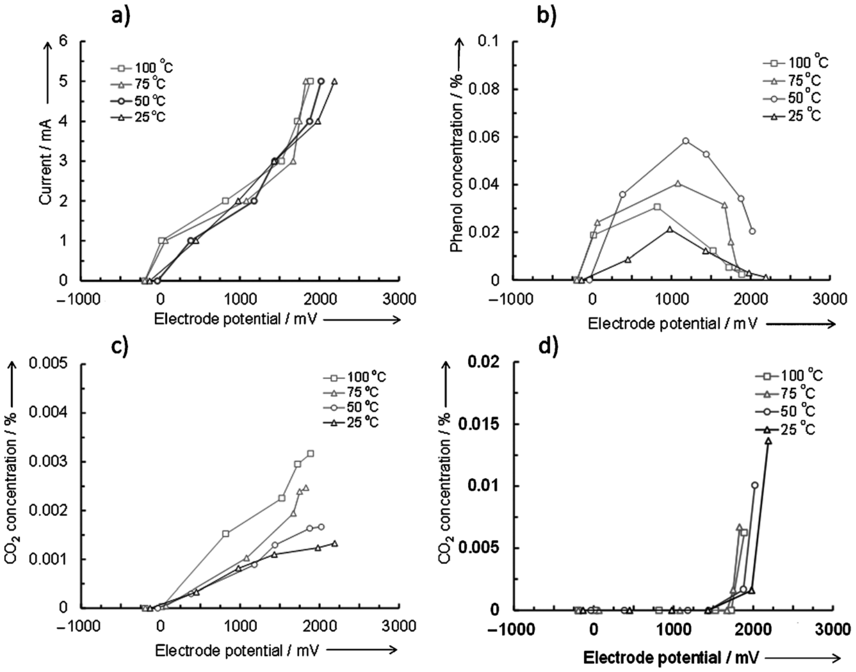

Figure 1. a) Current flow to the electrochemical cell and concentrations of b) phenol, c) CO_2, and d) O_2 measured at various temperatures from 25 to 100 °C as a function of the anode potential.

revealed three significant features: 1) the phenol and CO_2 concentrations immediately increased upon application of potential to the cell; 2) the increase in the phenol concentration deteriorated at high potentials; and 3) the O_2 concentration started to increase when the phenol concentration became zero. These results suggest that benzene is converted directly into phenol and CO_2 at low potentials by Reactions (4) and (5), respectively, and that O_2 is formed at high potentials by Reaction (6).

$$\text{Anode}: \; 1/6\,C_6H_6 + 5/2\,O^{*\prime} \rightarrow CO_2 + 1/2\,H_2O \qquad (5)$$

$$2\,H_2O \rightarrow O_2 + 4\,H^+ + 4\,e^- \qquad (6)$$

Interestingly, although the phenol concentration at each potential was dependent on the temperature, the production of phenol always reached a maximum at potentials of around +1000 mV (Figure 1 b). It is likely that the formation of the active oxygen species is inhibited by excess polarization of the anode, which results in the appearance of Reaction (6). Moreover, the optimal temperature for phenol production was determined to be 50 °C (Figure 1 b). The resultant current efficiency for phenol production and selectivity toward phenol were 59 and 98 %, respectively, when the phenol concentration reached a maximum.

Cathodic benzene oxidation was then verified over the V_xO_y-$Sn_{0.9}In_{0.1}P_2O_7$ electrode in a feed mixture of benzene and O_2 (He balance) at various temperatures. Although the current increased with decreasing DC potential, the temperature dependence was complicated (Figure 2 a); the current at each potential was higher for operation at 125 °C than that for operation at other temperatures, which is probably due to a decrease in the polarization resistance at 125 °C. The products in the outlet gas from the cathode chamber at each temperature were analyzed. Phenol and CO_2 were the major products (Figure 2 b,c),[22] which were considered to be formed via Reactions (2) and (7), respectively.

$$\text{Cathode}: \; 1/6\,C_6H_6 + 5/2\,O^{*} \rightarrow CO_2 + 1/2\,H_2O \qquad (7)$$

It should be noted that the concentrations of both phenol and CO_2 increased with decreasing potential (Figure 2 b,c), which differs from the dependence of the phenol concentration on the potential for anodic benzene oxidation (Figure 1 b). Therefore, there is no effect of the electrode potential on phenol production for cathodic benzene oxidation. Furthermore, the optimal temperature for phenol production was 100 or 125 °C, which is also different from the temperature

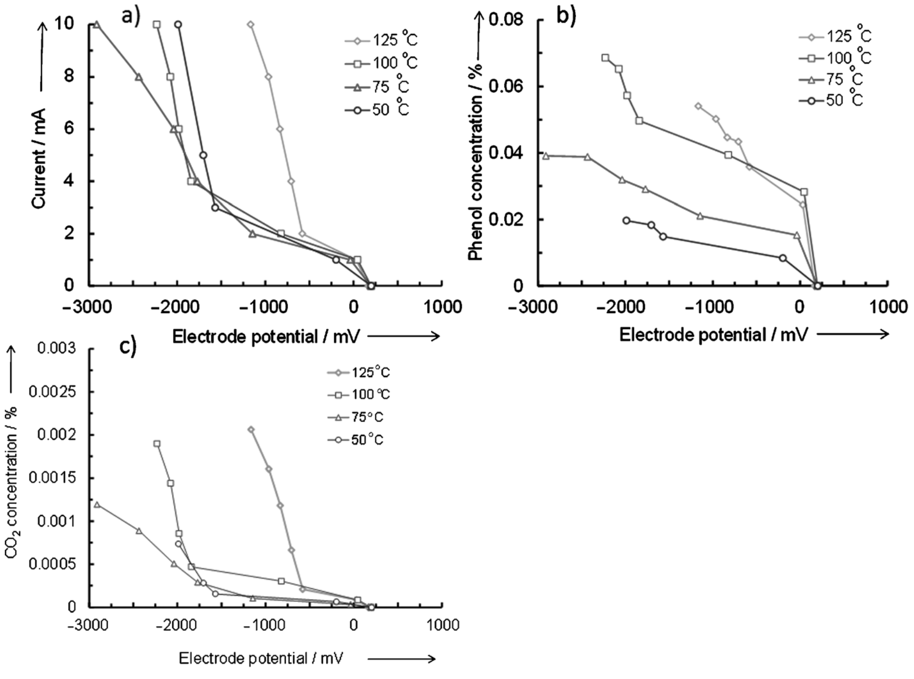

Figure 2. a) Current flow to the electrochemical cell and concentrations of b) phenol and c) CO_2 measured at various temperatures from 50 to 125 °C as a function of the cathode potential.

dependence of the phenol concentration for anodic benzene oxidation (Figure 1b). These findings reflect a significant difference in quality between the anodically and cathodically activated oxygen species. This difference resulted in a lower current efficiency for cathodic phenol production of 14% when the phenol concentration reached a maximum compared to that obtained for anodic phenol production, although the selectivity toward phenol was as high as 97%.

Cyclic voltammetry (CV) measurements indicate the potential dependence of phenol production. CV profiles of the V_xO_y-$Sn_{0.9}In_{0.1}P_2O_7$ anode in the presence and absence of benzene at 50°C were compared. A large anodic peak between +0.8 and +1.3 V was observed during anodic polarization in the presence of benzene, whereas such a peak did not appear in the absence of benzene (Supporting Information, Figure S3a). Therefore, this peak can be attributed to benzene oxidation by the active oxygen species. However, further anodic polarization oxidizes the active oxygen species to atomic or molecular oxygen, which is assumed to be inactive toward the partial oxidation of benzene. The results correspond well with those shown in Figure 1b and d. CV curves measured for the V_xO_y-$Sn_{0.9}In_{0.1}P_2O_7$ cathode in the presence and absence of benzene at 100°C were compared. In the presence of benzene, the onset of benzene oxidation by the active oxygen species occurred at −1.5 V during cathodic polarization, and deterioration of the current was not observed until the negative potential scan was completed (Supporting Information, Figure S3b). This result indicates that benzene oxidation by the active oxygen species over the cathode is not strongly affected by the electrode potential, in contrast to the oxidation reaction over the anode, and this is consistent with the result shown in Figure 2b.

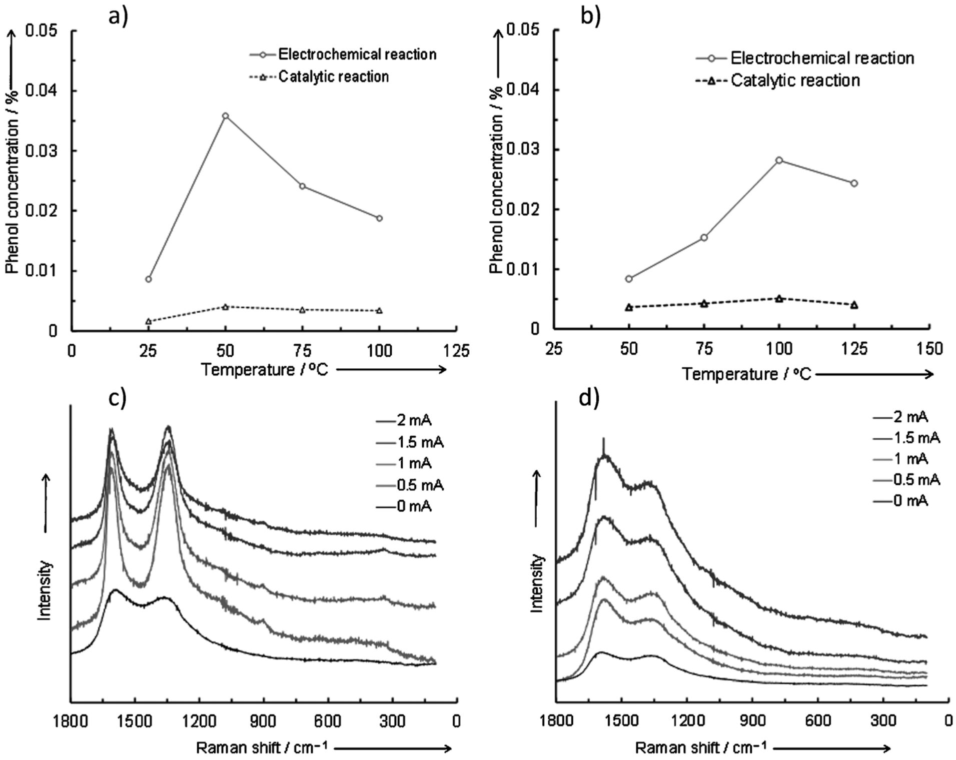

Figure 3. a), b) Phenol concentrations produced by the oxidation of benzene with electrochemically and catalytically activated oxygen species at a) the anode from 25 to 100°C, and b) at the cathode from 50 to 125°C. c), d) Raman spectra of the c) anode and d) cathode surfaces measured at room temperature.

To compare the electrochemical activation of oxygen with the catalytic activation of oxygen, 0.012 vol% O_2 and 0.023 vol% H_2 were added to the anode and cathode gases, respectively, outside the system. These gas concentrations are equivalent to the amounts of oxygen and hydrogen species transferred to the anode and cathode, respectively, when a current of 1 mA is passed through the electrochemical cell. The following reactions for the catalytic activation of oxygen over the V_xO_y-$Sn_{0.9}In_{0.1}P_2O_7$ electrode are proposed:

$$\text{Anode}: \; 1/2\,O_2 \rightarrow O^{*''} \qquad (8)$$

$$\text{Cathode}: \; H_2 + O_2 \rightarrow O^{*'''} + H_2O \qquad (9)$$

The concentrations of phenol produced with O_2 and H_2 at open-circuit voltage were found to be considerably lower than those obtained with application of a 1 mA current (Figure 3a,b). The difference observed between the two oxygen or two hydrogen species is indicative of the higher efficiency for electrochemical activation of oxygen than for catalytic activation.

Further details of the active oxygen species were obtained by measuring Raman spectra from the surface of the V_xO_y-$Sn_{0.9}In_{0.1}P_2O_7$ electrode during application of current to the electrochemical cell. A band appeared around 900 cm^{-1} with the anodic current flow (Figure 3c), which is assigned to the OH bending mode.[23] It is thus reasonable to conclude that the active oxygen species formed by the anodic polarization of H_2O vapor is the $HO^{\bullet}$ radical. Accordingly, the following reaction is possible:

$$\text{Anode}: \; C_6H_6 + HO^{\bullet} \rightarrow C_6H_5OH + H^+ + e^- \qquad (10)$$

However, another possible pathway is the oxidation of benzene to produce a benzene radical cation that could react with a water molecule to form phenol.[24,25] No new band was observed when the cathodic current was applied (Figure 3d), which indicates that the cathodically activated oxygen species is qualitatively distinct from the anodically activated oxygen species, and this is supported by the difference in the catalytic properties of the two active oxygen species (Figure 1 b and Figure 2 b). Identification of the cathodically activated oxygen species still remains unclear at the present time. However, it has been reported that H_2O_2 is formed over a catalytically inert cathode according to a two-electron redox reaction.[26,27] H_2O_2 is used as an oxidant for the direct hydroxylation of benzene to phenol, where H_2O_2 is decomposed to active oxygen species and H_2O vapor.[5–8] Therefore, we speculate that phenol is produced over the cathode according to Reactions (11) and (2).

$$\text{Cathode}: \; H_2O_2 \rightarrow O^* + H_2O \qquad (11)$$

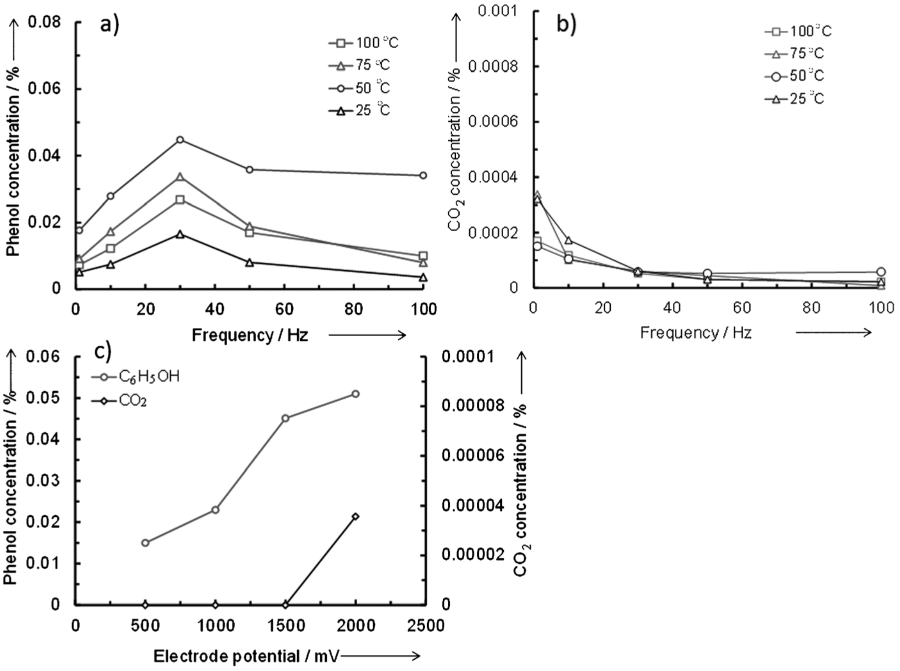

Figure 4. a), b) Concentrations of a) phenol and b) CO_2 measured at an AC peak voltage of 1500 mV at various temperatures from 25 to 100 °C as a function of the frequency. c) Product concentrations observed at 50 °C and 30 Hz as a function of the AC peak voltage.

The observations in this investigation confirm that phenol can be produced by both anodic and cathodic benzene oxidations over the V_xO_y-$Sn_{0.9}In_{0.1}P_2O_7$ electrode, although there is a significant difference in each reaction process. This allows the use of AC electrolysis for phenol production, because one electrode acts as the anode in a half-cycle and as the cathode in the other half-cycle. An AC peak voltage of 1500 mV was applied to the electrode in a feed mixture of benzene, H_2O vapor, and O_2 (He balance) at various frequencies and temperatures between 25 and 100 °C. Note that the peak voltage E [mV] should be treated as:

$$\text{root mean square of } E = E\sqrt{2} \qquad (12)$$

Hence, the actual voltage averaged over time is less than 1500 mV. The concentrations of phenol and CO_2 products were influenced by the frequency in a different manner; the phenol concentration was the highest at 30 Hz (Figure 4 a) and the CO_2 concentration was decreased by an increase in the frequency (Figure 4 b). Thus, the optimal frequency for phenol production was determined to be 30 Hz, where the reaction intermediates would be stabilized by repetition of a series of oxidation and reduction processes. Another important result is that the production of phenol was significant at 50 °C (Figure 4 a), which is similar to the result over the anode during DC electrolysis (Figure 1 b). Accordingly, anodic benzene oxidation is speculated to be dominant in AC electrolysis. These results suggest that AC application in the middle frequency range increases the quantity of $HO^{\bullet}$ radicals or extends the lifetime of the radicals. It is also important to note that the concentration of phenol produced by AC electrolysis remained almost constant for at least 5 h (Supporting Information, Figure S4).

Benzene oxidation was conducted by changing the AC peak voltage at a frequency of 30 Hz and at 50 °C. The phenol concentration increased with the AC peak voltage and reached 0.051 vol % at 2000 mV (Figure 4 c), which is comparable to the results obtained for DC electrolysis (Figure 1 b and Figure 2 b). However, the current passed through the electrochemical cell during AC application is always lower than that for DC application at the same voltage; therefore, the current efficiency for phenol production with the former is expected to be higher than that for the latter. Under AC electrolysis, the CO_2 concentration was almost zero until the AC peak voltage was 1500 mV (Figure 4 c), so that a high selectivity toward phenol of ca. 100 % was accomplished, even at 2000 mV. This demonstrates that AC electrolysis is more efficient and selective toward phenol production than DC electrolysis. However, the phenol yield at present is low owing to the small area of the electrode used, although this could be addressed by scaling up the reactor system.

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