Direct conversion of benzene to phenol in plasma-irradiated aqueous solution

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Phenol is a fundamental chemical and is widely used in chemical industry [1]. Most of phenol is industrially produced by the Cumene process, which requires tree-step reactions with a low production yield. This work focuses on the phenol production using a new chemical process that utilizes active species induced by plasma-liquid interaction. Phenol was produced by adding benzene into water that was irradiated with an atmospheric-pressure air plasma. We optimized the discharge method and the experimental conditions. We measured the optical absorption spectrum of the aqueous solution, and investigated the temporal variations of the concentrations of benzene and phenol.

Figure 1 shows the experimental setup for irradiating a plasma to water. A stainless-steel nozzle electrode was inserted into an alumina tube for electrical isolation. The distance between the tops of the alumina tube and the stainless-steel electrode was 1 mm. Air was bubbled from the nozzle into an NaCl solution (30 ml, 0.1%) at a flow rate of 70 ml/min. A ballast resistor of 50 kΩ was inserted between the nozzle electrode and a dc power supply. A dc voltage was applied between the nozzle electrode and the solution to generate an atmospheric-pressure dc discharge in the bubble. The voltage of the dc power supply was 0.6-1.5 kV, and the current was 13 mA. The duration of the plasma irradiation was 5 min. Immediately after stopping the discharge, benzene with a volume of 62 µl was mixed into the plasma-irradiated water, and the solution was kept in a hermetic glass bottle. The solution pipetted from the hermetic glass bottle was then diluted with an equal volume of water, and we measured the optical absorption spectrum of the solution.

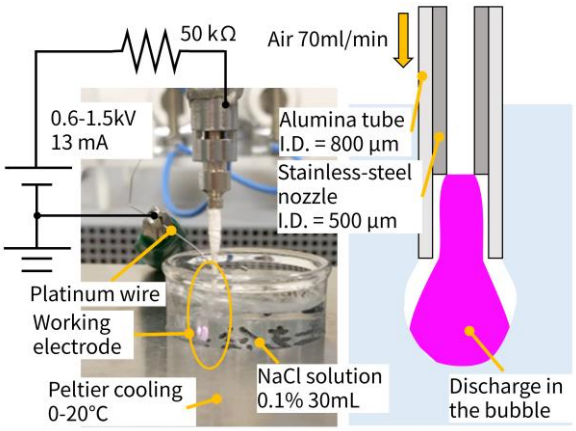

Fig. 1 Photograph of the experimental setup and the details of the working electrode.

Figure 2 shows optical absorption spectrum of the plasma-irradiated water at 7 days after adding benzene. Four absorption peaks observed in the range of 240-260 nm were attributed to benzene, while the absorption in the range of 270-280 nm was attributed to phenol. We fitted the absorption spectrum by adopting the following equation,

$$\begin{pmatrix} \left.\frac{\mathrm{d}A(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda_1} \\ \left.\frac{\mathrm{d}A(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda_2} \end{pmatrix} = \begin{pmatrix} \left.\frac{\mathrm{d}\epsilon_1(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda_1} & \left.\frac{\mathrm{d}\epsilon_2(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda_1} \\ \left.\frac{\mathrm{d}\epsilon_1(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda_2} & \left.\frac{\mathrm{d}\epsilon_2(\lambda)}{\mathrm{d}\lambda}\right|_{\lambda_2} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \end{pmatrix} l,$$

where l is the optical path length, λ is the wavelength (λ_1 = 261 nm, λ_2 = 279 nm), c_1 and c_2 are the concentrations of benzene and phenol, respectively, $A(\lambda)$ is the measured absorption spectrum, and $\epsilon_1(\lambda)$ and $\epsilon_2(\lambda)$ are the absorption coefficient of benzene and phenol, respectively. The absorbance spectra of benzene and phenol obtained by the fitting are shown in figure 2 together with the residue. The concentrations of benzene and phenol were deduced from the absorbance to be 2.5 and 0.27 mM, respectively. In the residue spectrum, the broad peak around 280 nm and the tail at wavelengths longer than 330 nm are attributable to pyrocatechol, hydroquinone, and nitrophenol. Figure 3 shows the temporal variations in the concentrations of benzene and phenol. We observed a relatively steep increase in the phenol concentration in the first few hours. After that, we observed gradual increase for a week. The production yield, which is defined by $-\Delta[\mathrm{Phenol}]/\Delta[\mathrm{Benzene}]$, was 0.013 at 7 days after adding benzene into plasma-irradiated water.

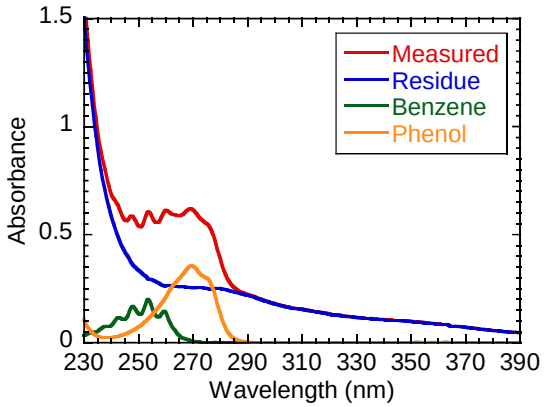

Fig. 2 Absorption spectrum of the plasma-irradiated water at 7 days after adding benzene. The fitted absorbance of benzene and phenol are shown together with the residue.

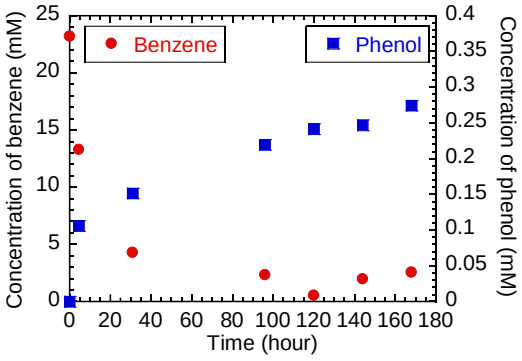

Fig. 3 Concentration of benzene and phenol in the plasma-treated water at various times after adding benzene.

The gradual increase in the phenol concentration shown in figure 3 indicates that the benzene-phenol conversion is driven by long-lived chemical species induced in the plasma-irradiated water. In plasma-irradiated water, $OH^{\cdot}$ and $HO_2^{\cdot}$ are produced from H_2O_2 and NO_2^- via the following reactions [2,3]:

$$\begin{aligned} NO_2^- + H_2O_2 + H^+ &\rightarrow ONOOH + H_2O, \\ ONOOH &\rightleftarrows OH^{\cdot} + NO_2, \\ OH^{\cdot} + H_2O_2 &\rightarrow HO_2^{\cdot} + H_2O, \\ HO_2^{\cdot} + H_2O_2 &\rightarrow O_2 + OH^{\cdot} + H_2O, \\ ONOOH + H_2O_2 &\rightarrow HO_2NO_2 + H_2O, \\ HO_2NO_2 &\rightleftarrows HO_2^{\cdot} + NO_2. \end{aligned}$$

In addition, iron ions were also observed in the plasma-irradiated water, which were thought to be eluted from the stainless-steel electrode. The following reaction, known as the Fenton reaction, is also a possible route for the formation of $OH^{\cdot}$:

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\cdot} + OH^- + Fe^{3+}.$$

It is reported in some papers that benzene is converted to phenol with the help of $OH^{\cdot}$ or $HO_2^{\cdot}$ [4,5]. We speculate that $OH^{\cdot}$ and/or $HO_2^{\cdot}$ produced by the above reactions contribute to the production of phenol in the present experiment.

References

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