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Effects of background-gas composition on phenol decomposition by pulsed-discharge plasma above a water surface
水上パルス放電によるフェノール分解におけるバックグラウンドガスの影響

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By-products from phenol by the exposure of pulsed-discharge plasma above a phenol aqueous solution are investigated, and the effects of background-gas composition on phenol decomposition by the pulsed plasma exposure above a water surface are examined. When Ar is used as a background gas, catechol, hydroquinone and 4-hydroxy-2-cyclohexene-1-on are produced. When O_2 is used as a background gas, CO_2, CO, catechol, hydroquinone, formic acid, maleic acid, succinic acid and 4,6-dihydroxy-2,4 -hexadienoic acid are produced. When Ar-O_2 mixture is used as a background gas, by-products, produced in O_2, are produced, and the quantities of the products tend to be proportional to the mixture ratio of O_2.

1. Introduction

Water pollution by persistent organic pollutants and volatile chlorinated organic compounds is serious problem. Species, having high oxidation potential, such as OH, H_2O_2 and ozone, can be produced when pulsed-discharge plasma is generated above or in water, and those species have potential to decompose the pollution, water treatment techniques using a pulsed discharge have attracted attention. In this work, we minutely investigate the by-products of phenol decomposed by pulsed-discharge plasma generated above a phenol aqueous solution when Ar, O_2 and Ar-O_2 mixture are used as a background gas, and deduce decomposition processes of phenol from the by-products. Further, we investigate effects of background gas composition on phenol decomposition.

2. Experimental apparatus and procedure

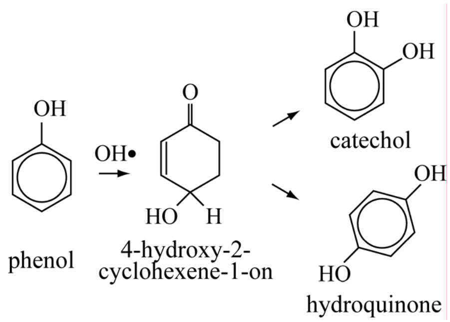
A needle electrode and a water bath electrode, made of stainless steel, are placed in a cylindrical discharge chamber made of acrylic resin, having 140 mm in inner diameter and 100 mm in height. The needle electrode is 1.5 mm in diameter and 19 mm in length, and the water bath electrode, which is earthed, is 119 mm in inner diameter and 12 mm in depth, having 0.13 L in capacity. 70 g of phenol aqueous solution with a concentration of 3000 ppm is poured into the water bath, and the distance between the needle electrode and the surface of the phenol aqueous solution is fixed at 4 mm. Ar and O_2, the purities of which are 99.99% and 99.5 %, respectively, are used as a background gas, and it is fed into the discharge chamber at a constant flow rate of 1 L/min. The mixture ratios of the background gas are Ar:O_2=100:0, 95:5, 90:10, 50:50 and 10:90.

Liquid samples are taken before and after the plasma exposure, and there are analyzed by a Gas Chromatograph Mass Spectrometer (Shimadzu, GCMS-QP2010 Plus, column: DB-17ms). Further, off-gas from the discharge chamber is analyzed by a Fourier Transform Infrared Spectrophotometer (Shimadzu, FTIR-8900).

3. Results and Discussion

In a previous work [1], it is found that catechol, hydroquinone and 4-hydroxy-2-cyclohexene-1-on are produced from phenol when Ar is used as a background gas, and that formic acid, maleic acid, succinic acid, 4,6-dihydroxy-2,4-hexadienoic acid, catechol and hydroquinone are produced from phenol when O_2 is used as a background gas. Also, CO_2 and CO are found in the off-gas from the discharge chamber only when O_2 is used as a background gas.

Figure 1 shows the decomposition process of phenol when Ar is used as a background gas. No ozone production is observed, so that OH radicals generated in the plasma can initiate the decomposition of phenol. Also, 4-hydroxy -2-cyclohexene-1-on is detected in this work, it is likely that phenol is converted into 4-hydroxy-2-cyclohexene-1-on at first by the reaction with OH radical, and that 4-hydroxy-2-cyclohexene-1-on is converted into catechol and hydroquinone. Since catechol and



gas.

Fig. 1. Decomposition process of phenol when Ar is used as a background gas.

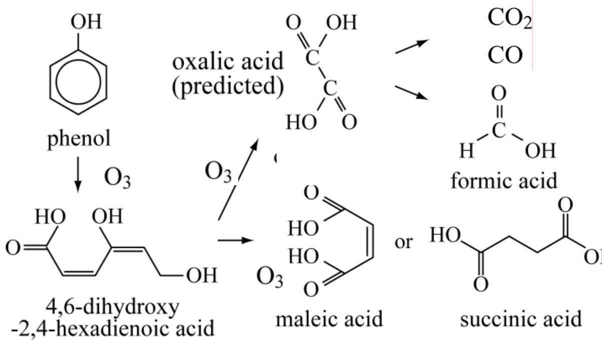


Fig. 2. Decomposition process of phenol when O_2 is used as a background gas

hydroquinone can be produced through another process, which is not clarified, because catechol and hydroquinone are detected when Ar-O_2 mixture gas is used as a background gas, at which no 4-hydroxy-2-cyclohexene-1-on is produced. Figure 2 shows the decomposition process of phenol when pure O_2 is used as a background gas. Since ozone is produced when O_2 is used as a background gas, phenol is probably decomposed into 4,6-dihydroxy-2,4-hexadienoic acid by 1,3-dipolar addition reaction with ozone. Further, 4,6-dihydroxy-2,4-hexadienoic acid is decomposed into two fragments, which contain two and four carbon atoms, namely, maleic acid or succinic acid and oxalic acid, by 1,3-dipolar addition reaction with ozone. Oxalic acid is not detected in this work, but formic acid, CO_2 and CO are produced by decomposition of oxalic acid as shown in reactions (1) and (2)[2,3]. Therefore, oxalic acid can be produced by phenol decomposition.

$$HOOCCOOH \rightarrow HCOOH + CO_2 \quad (1)$$

$$HOOCCOOH \rightarrow CO_2 + CO + H_2O \quad (2)$$

Figure 3 shows the concentration of ozone and by-products as functions of mixture ratio of Ar-O_2. Ozone and by-products produced by cleavage of benzene ring in figure 3 (a) decrease with the decrease of O_2 mixture ratio. In Ar, ozone and by-products show in figure 3 (a) are not produced, so that it is considered that 1,3-dipolar addition reaction with ozone can cleave a benzene ring of phenol, but OH radical cannot cleave the benzene ring. By-products in figure 3 (b) decreases significantly by the mixture of O_2 into Ar, so that the decomposition process of phenol can be dramatically changed by the mixture O_2 into background gas.

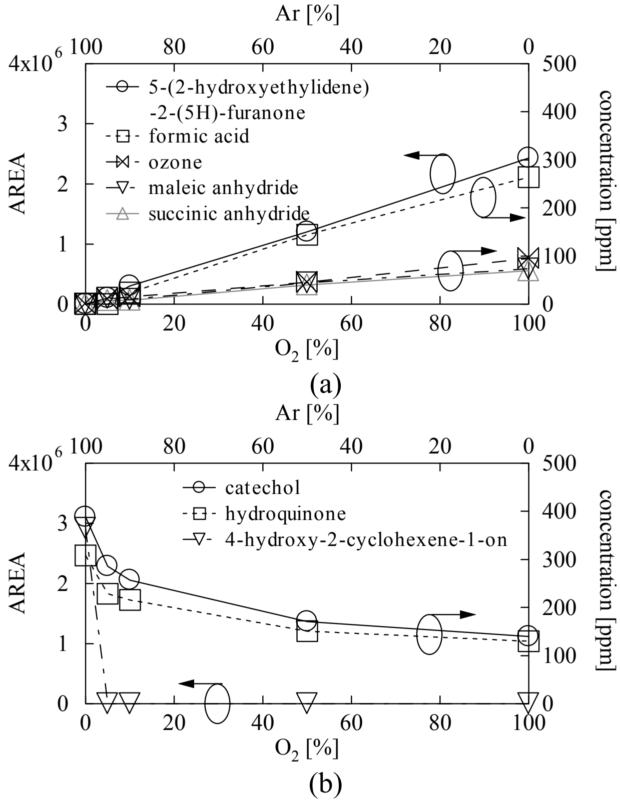


Fig. 3. Concentration of O_3 and by-products as functions of mixture ratio of Ar-O_2

4. Conclusions

We have investigated the decomposition process of phenol by exposure of pulsed-discharge plasma above a phenol aqueous solution, and effects of background gas composition on phenol decomposition. In Ar, 4-hydroxy-2-cyclohexene-1-on can be produced by OH radical. Further, 4-hydroxy-2-cyclohexene-1-on can be converted into catechol and hydroquinone. In O_2, phenol is probably decomposed into 4,6-dihydroxy-2,4-hexadienoic acid by 1,3-dipolar addition reaction with O_3, and 4,6-dihydroxy-2,4-hexadienoic acid can be decomposed into oxalic acid, maleic acid and succinic acid by O_3, and oxalic acid is probably decomposed into formic acid, CO_2 and CO.

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