Effects of Salt, Acid and Base on the Decomposition of 2-Chlorophenol in Supercritical Water

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The effect of salt, acid and base as additives on the decomposition of 2-chlorophenol (2CP) in supercritical water was investigated. Four additives were selected, NaCl as a salt, HCl and H_2SO_4 as acids, and KOH as a base. The addition of salts and acids had a little effect on the decomposition of 2CP in supercritical water (SCW), but that of bases showed a significant effect to enhance the decomposition rate.

Many studies have been reported on supercritical water oxidation (SCWO), a promising technology for the treatment of hazardous organic compounds.[1–3] In a conventional SCWO process, organic compounds, air, water and sodium hydroxide (NaOH) together in a mixture are introduced into the reactor.[4] However, most studies on SCWO have been conducted under the condition without the addition of NaOH, and therefore it is not known whether the addition of NaOH affects the decomposition of organic compounds in SCWO. We firstly investigated the effect of NaOH on the decomposition of 2CP in SCW without oxidant before investigating the effect of NaOH at SCWO conditions, and we have already certified that the addition of NaOH promoted the decomposition of 2CP in SCW.[5] Also, the addition of NaOH was reported to promote the decomposition of chlorinated organic compounds such as halotoluenes,[6] allyl chloride[7] and polychlorinated biphenyls[8] in subcritical water, and trichloroacetic acid[9] and chlorofluorocarbons[10] in SCW. The added NaOH in our experiments would dissociate into sodium ion and hydroxide ion in water, but these ions might be instable in SCW because of their poor solubility. Therefore, the dissociated sodium ion and hydroxide ion would affect the decomposition of 2CP in SCW. We are interested which ion accelerates the decomposition of 2CP, which can give us many knowledge of reaction mechanism in SCW. For this purpose, four additives are selected: NaCl as a salt, HCl and H_2SO_4 as acids, and KOH as a base.

Experiments were performed in a plug-flow reactor. Two preheaters and a reactor were made of coiled tubes of 1.59-mm OD × 0.25-mm thickness SUS-316 stainless steel with 4-m or 35-cm in length. Two feed lines were installed for aqueous feed streams containing 2CP and additives. Oxygen dissolved in the solutions was purged with helium gas prior to feeding. Two high-pressure pumps were used to pressurize the feed streams that were preheated by flowing through the preheater tubes. The experiments were conducted at a temperature of 440 °C and a pressure of 26 MPa. The initial 2CP concentration was 3.89×10^{-3} mol/L and each additive concentration was 600% of the molar concentration of 2CP. The reactor residence time ranged from 0.13 to 0.51 s. Collected liquid samples were adjusted to about pH 2 prior to the analyses. The concentration of unreacted 2CP in the liquid samples was determined by reverse-phase, high performance liquid chromatography using a UV detector (HP-1100 series, Nova-Pack C-18 3.9 × 150 mm column). Intermediates in the liquid sample were identified using a Hewlett-Packard 6890 gas chromatograph with a model 5973 mass selective detector (GC/MS, HP-5, 30 m × 0.25 mm × 0.25 μm film thickness column).

Figure 1 shows the relevant results in terms of the 2CP conversion as a function of residence time for four additives. In addition, the results of the decomposition of 2CP with NaOH addition obtained from our other experiments were presented in Figure 1 to compare with the effect of KOH on the 2CP decomposition. Some data under the condition of the addition of salt and acids could not be obtained because the reactor clogging happened when the flow rate was slow. These results suggested that the addition of NaCl, HCl and H_2SO_4 led to the reactor clogging because salts generated by reaction or corrosion of the reactor were almost insoluble in SCW and precipitated in the reactor. On the other hand, the reactor clogging did not happen under the condition of NaOH or KOH addition, which is because the addition of NaOH or KOH does not cause a severe corrosion and production of salts. Under this operating condition, the concentration of KOH was 0.0233mol/L, which was very low in comparison with the solubility of KOH (7.11 mol/L at 450 °C and 27.6MPa).[11] As shown in Figure 1, the addition of KOH largely accelerated the decomposition of 2CP in SCW like the addition of NaOH, but the addition of HCl, H_2SO_4 and NaCl did not increase the decomposition of 2CP. These results show that the addition of an alkali is more effective for the decomposition of 2CP in SCW than that of salts and acids. Also, it is suggested that hydroxide ion has a greater influence on the decomposition of 2CP than sodium ion and potassium ion. We already explained that the addition of NaOH promoted the decomposition of 2CP by the acceleration of both radical reaction and ionic reaction, and especially ionic reaction was

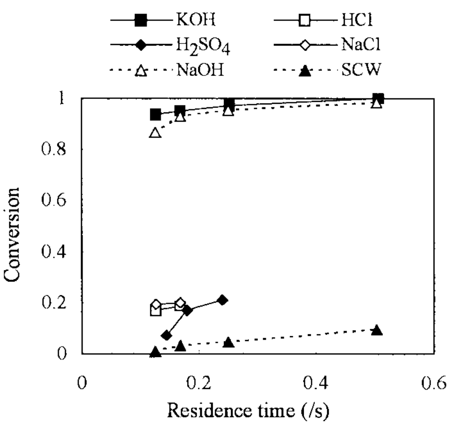

Figure 1. Conversions of 2CP with addition of KOH, HCl, H_2SO_4, or NaCl in SCW (conditions : at 440 °C and 26 MPa).

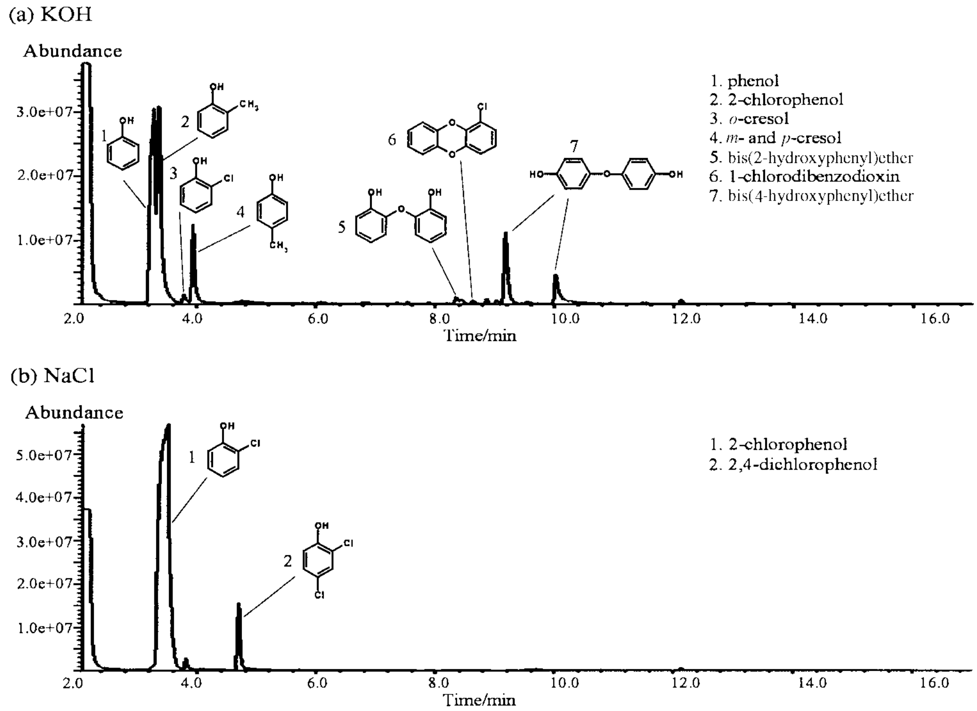

Figure 2. GC–MS charts for 2CP decomposition products with addition of KOH (a) and NaCl (b) at 440°C, 26 MPa and 0.17 s residence time.

largely promoted in which hydroxide ion reacted as a nucleophilic reagent in SCW.[5]

Intermediates in the liquid sample were identified. Figures 2 (a) and (b) show examples of GC–MS chart of the effluents under the condition of KOH and NaCl addition. The chemical structures given in Figure 2 are the results of the computer matches of the mass spectra. Under the condition of KOH addition, phenol, *o*-cresol, *p*- and *m*-cresol, bis(2-hydroxyphenyl)ether, bis(4-hydroxyphenyl)ether and 1-chlorodibenzodioxin were detected as intermediates, which were almost the same as those obtained by the addition of NaOH. Therefore, the reaction mechanism on the decomposition of 2CP by KOH addition in SCW is probably the same as that by NaOH addition. On the other hand, 2,4-dichlorophenol was identified as a main product under the condition of the salt and acids addition and Figure 2 (b) shows the representative GC–MS chart of a sample obtained by NaCl addition. 2,4-Dichlorophenol was detected as one of the intermediates at 2CP SCWO, which was generated by radical reaction.[12,13] Therefore, it is considered that the addition of HCl, H_2SO_4 and NaCl has an influence on the decomposition of 2CP not by ionic reaction but by radical reaction in SCW. In contrast, the addition of KOH or NaOH promotes ionic reaction of organic compounds as well as radical reaction in SCW, leading to much more accelerated decomposition rates of 2CP.

References and Notes

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