Rate Enhancement by Cations in Supercritical Water Oxidation of 2-Chlorophenol

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Interactions between cations and Cl species in the supercritical water oxidation (SCWO) of 2-chlorophenol (2CP) has been investigated in a high-pressure quartz-lined reactor at 673−773 K. Experimentally, we found that the S/D ratio (defined as the amount of 2CP converted to CO_2 and H_2O/disappearance of 2CP) for SCWO of 2CP was enhanced by cations (such as Li^+, Na^+, K^+, Ca^{2+}, Fe^{2+}, or Fe^{3+}). The S/D ratio increased as the charge density of cations increased ($Fe^{3+} > Fe^{2+} > Li^+ > Ca^{2+} > Na^+ > K^+$). Due to the extremely low solubility of metal salts in the supercritical water, abstraction of Cl in 2CP via an intermediate ($(OH)PhCl^{\delta-}$- - - - -$M^{\delta+}$) was postulated. Formation of these metal chloride (such as KCl, $CaCl_2$, and $FeCl_3$) precipitates in the SCWO of 2CP were identified by X-ray diffraction (XRD) spectroscopy. Since the formation of toxic highly chlorinated phenols and heavy polycyclic aromatic hydrocarbons (PAHs) was notably reduced, abstraction of Cl of 2CP by cations may occur in the early stage of the SCWO process.

Introduction

2-Chlorophenol is a very toxic and poorly biodegradable pollutant (*1*−*3*). Oxidation of 2CP in supercritical water is of practical interest since a wastewater stream containing 2CP over 200 ppm may not be treated effectively by direct biological methods (*2*−*5*). Water above its critical point (647.3 K and 217.6 atm) becomes completely miscible with oxygen and most nonpolar organic compounds, and the oxidation is allowed to proceed rapidly by an elimination of the potential interface mass transport limitations (*3, 6, 7*). Thus, high carbon conversion levels can be obtained with a very short residence time in the SCWO process. The desired destruction and removal efficiency (DRE) may be achieved in seconds or minutes (*8*−*10*). In addition, with increased reaction temperatures, solubility of inorganic salts is decreased dramatically in supercritical water (*11, 12*).

Solubility of metal chlorides has been reported to decrease from its ambient solubility (298 K, 1 atm) of about 10% to 3−120 ppm in supercritical water (773 K, 250 atm), a decrease of 10^4-fold (*13, 14*). Supercritical water, as compared to liquid water, exhibits an abrupt decrease in the static dielectric constant (ϵ) from 79.11 (liquid water, 298 K) to 1.83 (supercritical region, 673 K) (*3, 6, 7*). Ionic dissociation constant (K_w) of supercritical water is less than 10^{-22} mol/kg^2 at 773 K and 247 atm (*6, 7*).

Maximum DRE as well as minimum formation of undesired byproducts in the disposal process of toxic compounds are also of increasing interest. It is also very important from an environmental viewpoint, especially when one considers that incineration of wastes can produce carcinogenic byproducts such as PAHs and chlorinated dioxins or furans (*15, 16*). In a separate experiment, we have found that a highly enhanced oxidation of 2CP was effected in the presence of Na^+ or Li^+ in the supercritical water (*17*). Therefore, the main objectives of the present work were to investigate the abstraction of Cl of 2CP by metal cations with different charge densities in the SCWO of 2CP. In addition, the reduction of trace toxic byproducts (higher chlorinated phenols and PAHs) formed in the SCWO of 2CP with cations was also studied.

Experimental Section

The SCWO experiments of 2CP (Merck, purity >98%) were conducted in a high-pressure quartz-lined batch reactor at 673−773 K with residence times of 0.5−5 min. The system pressure was controlled by a back-pressure regulator (Tescom, $P_{max} = 408$ atm) and a pressure regulator (Tescom, $P_{in} = 238$ atm; $P_{out} = 7$ atm). A safety rupture disk rated at 400 atm was installed. Concentrations of 2CP in the SCWO experiments were between 189 and 1500 mg/L. Hydrogen peroxide (Merck, 30 wt %) was used as the oxidant (O/C ratio = 1.05−1.95) in the SCWO experiments.

High purity oxalates (Merck, purity >99%) were used in the SCWO of 2CP as cations sources (equivalent mole ratios ([M]/[Cl]) were 1.2−1.3) for the abstraction of Cl of 2CP in the SCWO process. The counteranions ($C_2O_4{}^{2-}$) were decomposed in the SCWO process. Salt precipitates formed in the SCWO process were determined by X-ray powder diffraction spectroscopy (RIGAKU model D/MAX III-V).

Trace PAHs (extracted with a dichloromethane (Merck, purity >99%) solvent) formed in the SCWO of 2CP were determined quantitatively by GC/MSD (HP 5890A and 5972). A HP Ultra 2 capillary column was heated programmably up to 563 K to obtain a resolvable separation of PAH species. Masses of primary and secondary ions of PAHs were determined using the scan mode for PAH standards (Mix 610-M (Supelco, purity >99%) and PNA-550JM (Chem Service, purity >99%)) and samples. Analyses of trace byproducts of the SCWO of 2CP were also conducted by HPLC (spectra system, SP) with a 3-D UV detector (model UV-3000). PAHs were separated by a Spherisorb S5 PAH 5 μm column (150 mm × 4.6 mm) with a mixed acetonitrile/water mobile phase. Chlorinated phenols were analyzed by an Envirosep-PP column (125 mm × 3.2 mm) with a mixed methanol/water (both with 1% acetic acid) mobile phase. A variable wavelength program was used in the system software (model PC-1000) to optimize detector sensitivity and selectivity.

Results and Discussion

Figure 1a shows that oxidation of 2CP (represented by S/D ratio) is highly enhanced by cations (such as Li^+, Na^+, K^+, Ca^{2+}, Fe^{2+}, or Fe^{3+}) in supercritical water at 673 K with a residence time of 1 min. The observed high S/D ratios for the SCWO of 2CP with cations would suggest perturbation of the 2CP ring by cations that enhanced the oxidation of 2CP in supercritical water. Possibly the interaction of Cl of 2CP with cations was the major distinguishing factor in increases of S/D ratios for the SCWO of 2CP with cations. The S/D ratio

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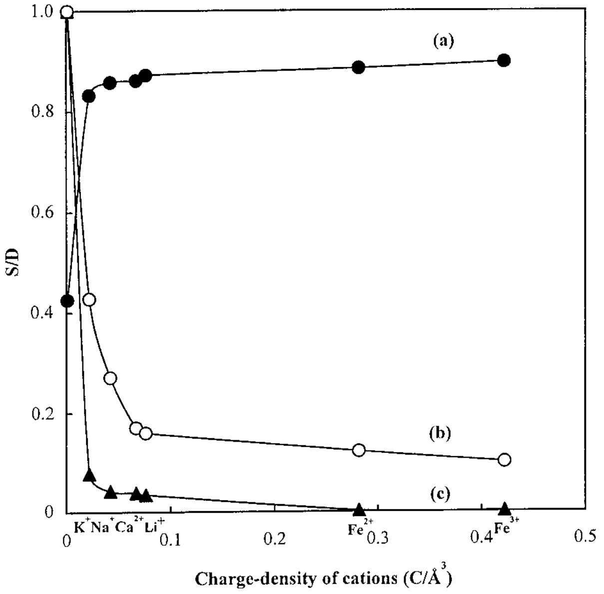


FIGURE 1. Effect of charge-density of cations on (a) the S/D ratio and the relative concentrations (RC) of (b) PAHs and (c) chlorophenols formed in the SCWO of 2CP at 673 K for 1 min. S/D = (amount of 2CP converted to CO_2 and H_2O)/(disappearance of 2CP); RC_{PAHs} = $concn_{PAHs}$ (with cations)/$concn_{PAHs}$ (without cation); $RC_{chlorophenols}$ = $concn_{chlorophenols}$ (with cations)/$concn_{chlorophenols}$ (without cation).

for the SCWO of 2CP is shown as a function of charge-density of cations in Figure 1a. The reaction rates for the SCWO of 2CP with K^+, Ca^{2+}, and Fe^{3+} cations can be expressed as follows: $109 \exp(-11.4/RT)[2CP]^{0.79}[O_2]^{0.41}[H_2O]^{0.44}$, $94.5 \exp(-10.8/RT)[2CP]^{0.85}[O_2]^{0.52}[H_2O]^{0.48}$, and $82 \exp(-9.0/RT)[2CP]^{1.05}[O_2]^{0.55}[H_2O]^{0.58}$, respectively (rate = $A \exp(-E_a/RT)[2CP]^a[O_2]^b[H_2O]^c$ and E_a is in kcal/mol). Because of the rapid decrease in the static dielectric constant of water and the solubility of inorganic salts at high temperatures and pressures in supercritical water, one may expect an increase in the attractive forces between anions and cations (*17*–*19*). Most interestingly, for the higher charge density cation (e.g., Fe^{3+}), the S/D ratio was very high, whereas for the low charge density cations a reduced S/D ratio was found, assuming approximately equal and low solubility in the SCWO process. Due to the extremely low solubility of metal salts in the supercritical water, the metal salt species may be precipitated in the early stage of the SCWO process. The precipitated metal salts identified as, for instance, KCl, $CaCl_2$, and $FeCl_3$ species by X-ray diffraction spectroscopy are evidently shown in Figure 2.

To obtain detectable quantities of incomplete combustion compounds or byproducts in the SCWO experiments, it is necessary to operate at conditions that do not provide a good DRE. We intentionally conducted the SCWO experiments at temperatures somewhat lower than 773 K so that the incomplete combustion products or byproducts in the SCWO of 2CP could be detected. As expected in Table 1, formation of trace byproducts (higher chlorinated phenols) in the SCWO of 2CP was substantially decreased in the presence of cations (for instance, K^+, Ca^{2+}, or Fe^{3+}). Abstraction of chlorine species from 2CP by a metal cation may be an important step regarding the formation of the trace byproducts. Table 1 indicates that increasing the charge density of the cations in SCWO of 2CP may suppress the reinsertion of Cl species into 2CP that forms highly chlorinated phenols. 2,4-Dichlorophenol (2,4-DCP), 2,4,5-trichlorophenol (2,4,5-TCP), and 2,4,6-trichlorophenol (2,4,6-TCP) were the major high chlorinated phenols formed in the SCWO of 2CP at 673 K. These trace byproducts may be formed directly from Cl reinsertion. Large molecules such as 2,3,4,6-tetrachlorophenol (2,3,4,6-TeCP) and pentachlorophenol (PCP) were not formed in the presence of metal cations in the SCWO of 2CP. Although the mechanism of the formation of higher chlorinated phenols during SCWO of 2CP is not well-known, the fact that an extraction of Cl species from 2CP is significantly effected in supercritical water oxidation condition with higher charge density cations (see Figure 1). Most importantly, due to the suppressed formation of higher chlorinated phenol byproducts (Table 1), it is apparent that abstraction of Cl of 2CP by cations may occur in the early stage of oxidation of 2CP in supercritical water.

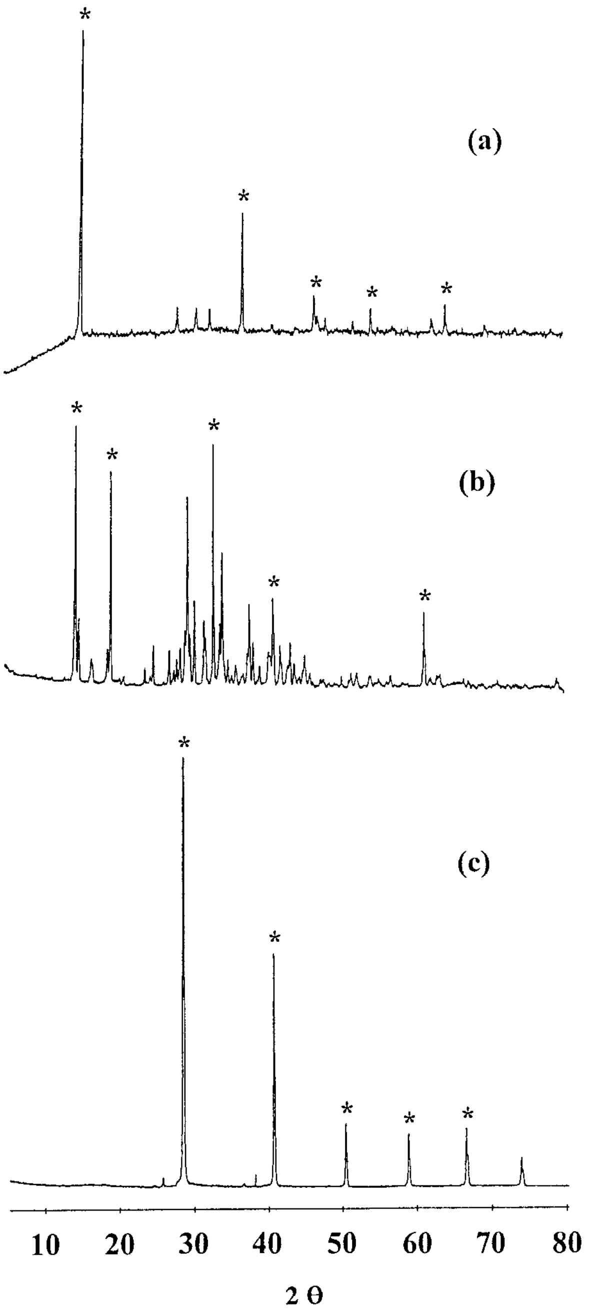


FIGURE 2. X-ray diffraction patterns of (a) $FeCl_3$, (b) $CaCl_2$, and (c) KCl precipitates in the SCWO of 2CP with cations. An asterisk (*) denotes the XRD characteristic peaks of each metal chloride.

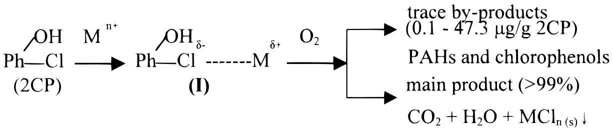
The reduction of highly chlorinated phenols byproducts as well as the enhancement of the S/D ratio for SCWO of 2CP with K^+, Ca^{2+}, or Fe^{3+} cations may be due to at least two possibilities: (a) The solubility of KCl, $CaCl_2$, and $FeCl_3$ abruptly decreased, and extremely fast formation of metal chloride precipitates occurred in supercritical water. (b) The

TABLE 1. Formation of Trace Byproducts in the SCWO of 2CP with Metal Cations (0.02 N) at 673 K for 1 min

	concentration of byproducts (μg/g 2CP)			
	none	K^+	Ca^{2+}	Fe^{3+}
Chlorophenols				
2,4-dichlorophenol	2590	239.1	134.2	48.9
2,4.5-trichlorophenol	5740	184.7	73.5	27.5
2,4.6-trichlorophenol	7060	202.6	95.5	36.7
2,3,4,6-tetrachlorophenol	2100	47.3	5.4	ND[a]
pentachlorophenol	160	ND	ND	ND
PAHs				
naphthalene	25.6	10.4	7.9	3.6
acenaphthylene	6.7	5.1	2.6	0.9
acenaphthene	2.5	1.9	1.0	0.4
fluorene	3.3	1.0	1.2	0.1
phenanthrene	4.0	1.2	0.7	ND
anthracene	3.2	1.4	0.2	ND
fluoranthene	1.2	0.2	ND	ND
pyrene	0.8	ND	ND	ND
benz[*a*]anthracene	1.8	0.1	ND	ND
chrysene	0.3	0.1	ND	ND
benzo[*b*]fluoranthene	0.2	0.1	ND	ND
benzo[*k*]fluoranthene	ND	ND	ND	ND
benzo[*a*]pyrene	0.5	ND	ND	ND
indeno[1,2,3-*cd*]pyrene	0.2	ND	ND	ND
dibenz[a,*h*]anthracene	ND	ND	ND	ND
benzo[*ghi*]perylene	ND	ND	ND	ND

[a] ND denotes not detectable.

SCHEME 1[a]



[a] M^{n+} denotes K^+, Ca^{2+}, or Fe^{3+} cation. Note that >99% of Cl was abstracted by cations and formed metal chloride precipitates in SCWO of 2CP.

electron-withdrawing effect of cations was involved in which an intermediate species **(I)** was postulated. A possible reaction pathway for SCWO of 2CP with K^+, Ca^{2+}, or Fe^{3+} cations at 673 K is shown in Scheme 1.

Frenklach indicated that the formation of PAHs increases with an increase of Cl/H ratio in the combustion of chlorinated hydrocarbons (*20*). Chlorine atoms may accelerate the abstraction of aromatic H from PAH molecules that are activated for further mass growth of PAHs to form eventually soot (*20*). Experimentally, because of the abstraction of Cl by cations that reduced the availability of free Cl species in the SCWO of 2CP, the formation of PAHs was considerably reduced (see Figure 1b). In Table 1, only trace low molecular weight PAHs such as naphthalene (Nap), fluorene (Flu), and anthracene (Ant) were observed in the SCWO of 2CP with cations. In the presence of high charge-density cations such as Ca^{2+} and Fe^{3+}, carcinogenic PAHs including benzo[*a*]pyrene (BaP), indeno[1,2,3-*cd*]pyrene (IND), dibenz[*a,h*]anthracene (DBA), and benzo[*ghi*]perylene (BghiP) were essentially not found in the SCWO of 2CP. Note that reactions of the ring opening of 2CP in which products were ultimately oxidized to CO_2 and H_2O (see Scheme 1) were predominant in the overall reaction network.

In conclusion, we found that the S/D ratio for SCWO of 2CP was enhanced by cations experimentally. The S/D ratio increased as the charge density of cations increased. Due to the extremely low solubility of metal salts in the supercritical water, abstraction of Cl in 2CP via an intermediate ((OH)-$PhCl^{\delta-}$- - - - -$M^{\delta+}$) was postulated. Formation of these metal chloride precipitates in the SCWO of 2CP was identified by XRD spectroscopy. Since the formation of toxic highly chlorinated phenols and heavy PAHs was notably reduced, abstraction of Cl of 2CP by cations may occur in the early stage of the SCWO process.

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