Oxidation of 2-Chlorophenol Effected by Na^+ and CuO/Zeolites in Supercritical Water

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Supercritical water oxidation (SCWO) of 2-chlorophenol (2CP) is very effected in the presence of 0.02 M Na^+ that reduces the formation of by-products (higher chlorinated phenols). The undesired by-products in the SCWO of 2CP catalyzed by CuO in zeolites Y, ZSM-5, and ZSM-48 is also reduced extensively. Chlorine-bonded CuO species in the channels of ZSM-5 are not observed by EXAFS (extended X-ray adsorption fine structure) spectroscopy.

Complete destruction and removal of hazardous compounds with a minimal release of toxic by-products are essential in the most waste disposal processes.[1-5] At supercritical water oxidation conditions (T_c=647 K, P_c=218 atm), organic species, O_2, and H_2O form a single homogenous phase.[6] Thus, organic compounds can be oxidized to CO_2, and H_2O in seconds or minutes in supercritical water.[1-9] On the contrary, solubility of inorganic salts decreases abruptly in the supercritical water. Thus, abstraction of Cl of 2CP by Na^+ in the supercritical water was investigated. Reduction of undesired by-products (higher chlorinated phenols and polycyclic aromatic hydrocarbons (PAHs)) in the SCWO of 2CP catalyzed by CuO/zeolites was also studied.

The SCWO experiments of 2CP were conducted in a high-pressure quartz-lined batch and an isothermal, isobaric fixed-bed flow reactors, approximated operationally as a plug-flow behavior. Hydrogen peroxide (Merck, 30 wt.%) was used as the oxidant (O/C ratio = 1-2) in the SCWO experiments. The amount of catalysts used in the SCWO of 2CP was about 0.15-0.20 g. By-products of the SCWO of 2CP was determined quantitatively by GC/MS (hp 5890A/5972) and 3-D HPLC (SP UV-3000). The EXAFS spectra were collected at double-crystal monochromator (DCM) soft X-ray beamline at the Taiwan Synchrotron Radiation Research Center (SRRC) with a positron beam energy of 1.5 GeV and stored current between 100 and 200 mA. Data were collected with a Si (111) DCM in fluorescence absorption mode in the region of the Cu K edge (8979 eV) at room temperature. The monochromator was calibrated at the Cu K edge by recording spectrum of copper foil. The EXAFS data were analyzed using the UWXAFS and FEFFIT programs.[10]

The presence of a single phase and high temperature allows the supercritical water oxidation proceed rapidly by an elimination of the potential interface mass transport limitations. Table 1 shows that a highly enhanced oxidation of 2CP (2500 mg/L) is effected in the presence of 0.02 M Na^+ ($Na_2C_2O_4$) in supercritical water. Supercritical water, as compared to liquid water, exhibits an abrupt decrease in dielectric constant and inorganic solubility at temperatures above 673 K.[1,6] Perturbation of the 2CP's ring by the Na^+ ions that enhance the oxidation of 2CP in supercritical water is thought to involve the intermediate species **I**:

Table 1. Supercritical water oxidation of 2CP at 673 K in the presence of 0.02 M Na^+ and/or CuO/zeolite catalysts

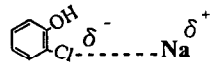
Catalysts	Zeolite pore opening / Å	Na^+ conc. / M	S/D[a] / %
None	—	0	42.6
None	—	0.02	92.4
CuO/Y	7.4	0	81.5
CuO/Y	7.4	0.02	99.1
CuO/ZSM-5	5.1 × 5.8	0	85.5
CuO/ZSM-5	5.1 × 5.8	0.02	99.6
CuO/ZSM-48	5.3 × 5.7	0	88.8
CuO/ZSM-48	5.3 × 5.7	0.02	99.7

[a] "S/D" is defined as the selectivity to decomposition (%) = (amount of 2CP decomposed completely) / (amount of 2CP reacted).

Table 2. Trace by-product shape selectivity for SCWO of 2CP at 673 K effected by Na^+ or CuO/zeolite catalysts

By-products	L-J[a] Size / Å	Formation of by-product (μ g/g 2CP) None	0.02 M Na^+	CuO/ Y	CuO/ ZSM-5	CuO/ ZSM-48
Phenol	5.85	1370	345.7	443.6	165.6	75.45
2,4-DCP	6.84	2590	256.5	31.12	20.45	8.568
2,4,6-TCP	7.75	7056	385.2	43.05	N.D.	1.587
2,3,4,6-TCP	7.75	2101	N.D.	5.240	N.D.	N.D.
PCP	7.75	159.0	N.D.	N.D.	N.D.	N.D.
Naphthalene	5.85	25.56	5.117	17.54	6.362	3.437
Acenaphthylene	8.15	6.648	1.934	4.235	N.D.	N.D.
Acenaphthene	8.15	2.491	0.448	2.129	N.D.	N.D.
Fluorene	5.85	3.337	0.201	1.633	1.020	1.236
Phenanthrene	9.10	4.044	0.329	0.336	0.116	N.D.
Anthracene	5.85	3.175	N.D.	1.664	1.553	N.D.
Fluoranthene	9.45	1.223	N.D.	N.D.	N.D.	N.D.
Pyrene	9.10	0.835	N.D.	N.D.	N.D.	N.D.

N.D. denotes "not detectable". 2,4-DCP: 2,4-dichlorophenol; 2,4,6-TCP: 2,4,6-trichlorophenol; 2,3,4,6-TCP: 2,3,4,6-tetrachlorophenol; PCP: pentachlorophenol.
[a] "L-J size" is the Lennard-Jones minimum kinetic diameter.[11-15]



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Note that in Table 2, formation of higher chlorinated phenols are substantially decreased in the presence of Na^+. The abstraction of Cl of 2CP by Na^+ may occur in the early stage of oxidation of 2CP in supercritical water.

Oxidation of 2CP in supercritical water is also very effective in the presence of oxidation active center CuO in the zeolites Y, ZSM-5, and ZSM-48. The structure data of CuO in ZSM-5, used in the SCWO of 2CP were analyzed by EXAFS spectroscopy. Table 3 shows that Cu-O and Cu-Cu are the main species in ZSM-5. Chlorine-bonded CuO species in the channels of ZSM-5 are not observed. Thus, one may eliminate the possibility that Cu does not involve in Cl abstraction from 2CP in the supercritical water oxidation.

Table 3. Structural parameters of the CuO/ZSM-5 catalyst analyzed by EXAFS

Atomic pair	CN	Bond length / Å	$\Delta\sigma^2$ / Å^2
Cu-O (shell I)	2.3	1.87	0.007
Cu-Cu (shell I)	4.1	2.79	0.002
Cu-O (shell II)	1.9	3.58	0.003
Cu-Cu (shell II)	5.6	4.53	0.002

CN: Coordination number; σ : Debye-Waller factor.

Zeolites, generally, have a shape selectivity in catalytic reactions due to their unique pore systems.[11-13] In Table 2, due to the trace by-product selectivity for oxidation of 2CP in supercritical water catalyzed by CuO/zeolites, ring condensation (PAHs) and Cl-reinsertion (higher chlorinated phenols) are considerably reduced. As expected, in the two-dimensional channel of ZSM-48, a further suppression of the formation of undesired by-products is observed. Note that reactions of ring-opening of 2CP, in which products are ultimately oxidized to CO_2 and H_2O, are predominant in the overall reaction network. Because of the restricted environment in the channels of ZSM-5 and ZSM-48, formation of heavier PAHs is almost not possible.

In conclusion, an enhancement of oxidation reaction and reduction of formation of toxic by-products in the SCWO of 2CP are effective in the presence of Na^+ and/or CuO/zeolite catalysts. Trace by-product shape selectivity of CuO in the zeolite channel of Y, ZSM-5, and ZSM-48 in the SCWO is noted. In the more restricted environment of ZSM-48 channels, formation of the undesired by-products (higher chlorinated phenol and PAHs) are extremely reduced in the SCWO of 2CP at 673 K.

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