SUPERCritical WATER OXidATION OF 2-CHLOROPHENOL
EFFECTED BY Li⁺ AND CuO/ZEOlITES

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ABSTRACT

Catalytic oxidation of 2-chlorophenol (2CP) in supercritical water was investigated. Experimentally, conversion of 2CP in supercritical water oxidation (SCWO) process is effectively enhanced in the presence of Li⁺ that also reduces the formation of higher chlorinated phenols and PAHs. The global reaction rate of SCWO of 2CP in the presence of Li⁺ is expressed as: $92.5 \exp \left(-10.5/RT\right) \left[2CP\right]^{0.95} \left[O_2\right]^{0.56} \left[H_2O\right]^{0.45}$. The undesired by-products in the SCWO of 2CP are also extensively reduced in the channels of zeolite catalysts. By EXAFS spectroscopy, Cu-O and Cu-Cu are identified as the main oxidation active species in the zeolite channels. Cl-bonded CuO species in zeolite Y are not observed.

Key words: SCWO, 2-chlorophenol, shape selectivity, EXAFS, PAHs

1 INTRODUCTION

At supercritical water oxidation conditions ($T_C > 647$ K, $P_C > 218$ atm), organic species, oxygen, and water form a single homogenous phase. The presence of a single phase and high temperatures in supercritical water allows the oxidation to proceed rapidly by an elimination of the potential interface mass transport limitations (1,2). Indeed, properties of supercritical water such as the complete miscibility in all proportions with oxygen, negligible surface tension, high
diffusivity, low viscosity, and low solubility of inorganic salts, are very unique especially in
disposal of toxic compounds (1,2). Hazardous organic compounds can be completely oxidized to
CO₂ and H₂O in a very short residence time in the supercritical water (3-9). The desired
destruction and removal efficiency (DRE) may be achieved in seconds or minutes in the SCWO
process (10-16). On the contrary, solubility of inorganic salts decreases abruptly in the
supercritical water (1,2).

2-Chlorophenol, widely used in paper, pulp, pesticide, and herbicide industries, is a
priority pollutant (6,7). 2CP is very toxic and poorly biodegradable. 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 (2,7-9). Due to a high-
temperature and high-pressure reaction condition for the SCWO process, oxidation catalysts have
been explored in the laboratory-scale studies (9-15). Because of the unique pore systems,
zeolites have excellent shape selectivities in catalytic reactions (17-20). Zeolites Y and ZSM-5
have a three-dimensional channel structures with pore sizes of 7.4 Å and 5.1 × 5.8 Å,
respectively (17-19). Zeolite ZSM-48 has a two-dimensional channel structure with a pore
opening of 5.3 × 5.6 Å (20). Since the restricted environment in the channels of zeolites Y,
ZSM-5, or ZSM-48, formation of high-molecular weight by-products would be very limited.

Maximum DRE as well as minimum of undesired by-products formed 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 by products such as polycyclic aromatic hydrocarbons (PAHs), dioxins, and furans
(21-23). Therefore, the main objectives of the present work were to investigate the oxidation
kinetics of 2CP in supercritical water in the presence of Li⁺ ions. Reduction of by products
(higher chlorinated phenols and polycyclic aromatic hydrocarbons) in the SCWO of 2CP
catalyzed by CuO in the channels of zeolites Y, ZSM-5, and ZSM-48 was also investigated. The
oxidation active centers (CuO) in zeolite channels were determined by EXAFS (extended x-ray
absorption fine structure) spectroscopy.

2 EXPERIMENTAL

The SCWO experiments of 2CP were conducted in a high-pressure quartz-lined batch (volume =
20 mL) and an isothermal, isobaric fixed-bed flow reactors (volume = 14.9 mL), approximated
operationally as a plug-flow behavior. The system pressure was controlled by a back-pressure regulator (Tescom, P\text{max} = 408 \text{ atm}) and a pressure regulator (Tescom, P\text{in} = 238 \text{ atm}, P\text{out} = 7 \text{ atm}). A safety rupture disk rated at 400 \text{ atm} was installed. The experiments of 2CP oxidation in supercritical water were conducted at 673-773 K with the reaction residence times between 1 and 10 minutes. Concentrations of 2CP in the SCWO experiments were 189-1500 mg/L.

Hydrogen peroxide (Merck, 30 wt.%) was used as the oxidant (O/C ratio = 1-2) in the SCWO experiments. Li,C,O, was added in the SCWO of 2CP as the Li⁺ source. Condensation by-products (extracted with a dichloromethane (Merck, Purity > 99%) solvent) of the SCWO of 2CP (Merck, Purity > 98%) was determined quantitatively by gas chromatography (Hewlett-Packard 5890A) with a mass selective detector (HP 5972) and an automatic sampler (HP-7673A). A HP Ultra 2 capillary column (50 m x 0.32 mm x 0.17 µm) was heated up programmably 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 and samples. Condensation by-products which were identified by searching and fitting the GC/MS library for compounds with similar mass spectra at a reliability over 90%. Analyses of by-products 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 x 4.6 mm) with a mixed acetonitrile/water mobile phase. Chlorinated phenols were analyzed by an Envirosep-PP column (125 mm x 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.

The EXAFS spectra were collected at beamline B-11B at the Taiwan Synchrotron Radiation Research Center (SRRC). Beamline B-11B is a bending-magnet double crystal monochromator (DCM) x-ray beamline which provides highly monochromatized photon beams with energies from 1 to 9 keV and resolving power (E / ΔE) of up to 7000. Data were collected in fluorescence mode with a Lytle detector in the region of the Cu K edge (8979 eV) at room temperature. The absorption spectra were collected using ion chambers that were filled with helium gas. The photon energy was calibrated at the Cu K edge by recording spectrum of copper foil. Standard deviation calculated from the averaged spectra was used as estimate of the statistical noise for the evaluation of the error associated with each structural parameter (24-28). The EXAFS data were analyzed using the UWXAFS 3.0 and FETT 7.0 programs (24).
3 RESULTS AND DISCUSSION

Implications of reaction rate law to design of a scale-up supercritical water oxidation reactor are essential, and are used to determine if further development of this technology would be warranted. Indeed, development and rational design, control, optimization, analysis and evaluation of the SCWO processes requires a knowledge of governing reaction kinetics (29-31). The global kinetic parameters for oxidation of 2CP in supercritical water at 673-773 K are shown in Table 1. The preliminary reaction rate of the oxidation of 2CP in supercritical water can be expressed as: $116 \exp \left(-\frac{12.8}{RT}\right) [2\text{CP}]^{0.79} [\text{O}_2]^{0.85} [\text{H}_2\text{O}]^{0.40}$. For comparison, Table 1 also summarizes the reported data for oxidation of chlorophenols in supercritical water. Since the major kinetic parameters for SCWO of chlorophenols are, to some extents, in the same orders, a similar oxidation reaction pathway may be expected.

Table 1. Global kinetic parameters for oxidation of chlorophenols in supercritical water.

<table>
<thead>
<tr>
<th></th>
<th>A</th>
<th>$E_a$</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Chlorophenol</td>
<td>100.0</td>
<td>11.0</td>
<td>0.88</td>
<td>0.41</td>
<td>0.34</td>
<td>(4)</td>
</tr>
<tr>
<td>2-Chlorophenol</td>
<td>116.0</td>
<td>12.8</td>
<td>0.79</td>
<td>0.85</td>
<td>0.40</td>
<td>this work</td>
</tr>
<tr>
<td>2-Chlorophenol/Li$^+$</td>
<td>92.5</td>
<td>10.5</td>
<td>0.95</td>
<td>0.56</td>
<td>0.45</td>
<td>this work</td>
</tr>
<tr>
<td>$p$-Chlorophenol</td>
<td>N.A.</td>
<td>N.A.</td>
<td>1-2</td>
<td>0</td>
<td>0</td>
<td>(10)</td>
</tr>
<tr>
<td>$p$-Chlorophenol/Cu$^{2+}$</td>
<td>N.A.</td>
<td>N.A.</td>
<td>1-2</td>
<td>0</td>
<td>0</td>
<td>(10)</td>
</tr>
<tr>
<td>$p$-Chlorophenol/MnCl$_2$</td>
<td>N.A.</td>
<td>N.A.</td>
<td>1-2</td>
<td>0</td>
<td>0</td>
<td>(10)</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>90.0</td>
<td>28.5</td>
<td>1.00</td>
<td>0</td>
<td>0</td>
<td>(3)</td>
</tr>
<tr>
<td>2,4-Dichlorophenol</td>
<td>72.9</td>
<td>13.6</td>
<td>0.97</td>
<td>1.16</td>
<td>0</td>
<td>(9)</td>
</tr>
</tbody>
</table>

The reaction rate is expressed as: $A \exp\left(-\frac{E_a}{RT}\right) [2\text{CP}]^a [\text{O}_2]^b [\text{H}_2\text{O}]^c$ and $E_a$ is in kcal/mol.

"N.A." denotes "not available".
Supercritical water, as compared to liquid water, exhibits an abrupt decrease in dielectric constant \( (\varepsilon) \) and solubility of inorganics at temperatures above 673 K \((1,2)\). Table 2 shows that a highly enhanced oxidation of 2CP is effected in the presence of \( \text{Li}^+ \) in supercritical water. The reaction rate for the SCWO of 2CP with \( \text{Li}^+ \) is described as: \( 92.5 \exp (-10.5/RT) [2\text{CP}]^{0.95} [\text{O}_2]^{0.56} [\text{H}_2\text{O}]^{0.45} \).

Due to the extremely low solubility of metal salts in supercritical water, abstraction of Cl of 2CP by \( \text{Li}^+ \) may occur in the early stage of oxidation of 2CP in supercritical water. In order to obtain detectable quantities of incomplete combustion compounds or by-products in the SCWO reactions, we have intentionally conducted the experiments at temperatures somewhat lower than 773 K so that the condensation by-products from the oxidation of the 2CP could be detected. Note that operational temperatures for the commercial applications of SCWO technology would be typically 773-923 K \((29-31)\). As shown in Figure 1, formation of by-products (higher chlorinated phenols) is substantially decreased in the presence of \( \text{Li}^+ \).

<table>
<thead>
<tr>
<th>Temp. (K)</th>
<th>Catalysts</th>
<th>( \text{Li}^+ ) conc. (M)</th>
<th>Conversion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>673</td>
<td>None</td>
<td>0</td>
<td>42.6</td>
</tr>
<tr>
<td>673</td>
<td>None</td>
<td>0.02</td>
<td>93.3</td>
</tr>
<tr>
<td>673</td>
<td>\text{CuO/Y}</td>
<td>0</td>
<td>84.4</td>
</tr>
<tr>
<td>673</td>
<td>\text{CuO/Y}</td>
<td>0.02</td>
<td>99.9*</td>
</tr>
<tr>
<td>673</td>
<td>\text{CuO/ZSM-5}</td>
<td>0</td>
<td>85.5</td>
</tr>
<tr>
<td>673</td>
<td>\text{CuO/ZSM 5}</td>
<td>0.02</td>
<td>99.9*</td>
</tr>
<tr>
<td>673</td>
<td>\text{CuO/ZSM-48}</td>
<td>0</td>
<td>89.1</td>
</tr>
<tr>
<td>673</td>
<td>\text{CuO/ZSM 48}</td>
<td>0.02</td>
<td>99.9*</td>
</tr>
<tr>
<td>773</td>
<td>None</td>
<td>0.02</td>
<td>88.5</td>
</tr>
</tbody>
</table>

Table 2. Catalytic oxidation of 2CP in the presence of 0.02 M \( \text{Li}^+ \) and/or CuO/zeolite catalysts in supercritical water.
Oxidation of 2CP in supercritical water is also enhanced by CuO in the channels of zeolites Y, ZSM-5, or ZSM-48. The unique product (by-product) selectivity for oxidation of 2CP in supercritical water effected by CuO/zeolite catalysts is shown in Figure 1. In the absence of CuO/zeolite catalysts, 2,4-Dichlorophenol (2,4-DCP) and 2,4,6-trichlorophenol (2,4,6-TCP) are the major high-chlorinated phenols formed in the SCWO of 2CP at 673 K. These by-products may be formed directly from Cl-reinsertion or condensation. Due to the product shape selectivity for zeolites Y, ZSM-5, and ZSM-48 in the SCWO of 2CP, large molecules such as 2,3,4,6-tetrachlorophenol (2,3,4,6-TCP) and pentachlorophenol (PCP) are not formed in the tight-fit environments of zeolite channels. Note that reactions of ring-opening, in which products are ultimately oxidized to CO₂ and H₂O, are predominant in the overall reaction network.

Table 3. PAHs formed in the SCWO of 2CP at 673 K in the presence of Li⁺ or CuO/zeolite catalysts.

<table>
<thead>
<tr>
<th>By-products</th>
<th>Minimum size a(Å)</th>
<th>None</th>
<th>0.02 M Li⁺</th>
<th>CuO/ Y</th>
<th>CuO/ ZSM-5</th>
<th>CuO/ ZSM-48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalene</td>
<td>5.85</td>
<td>25.56</td>
<td>6.32</td>
<td>17.54</td>
<td>6.36</td>
<td>3.44</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>8.15</td>
<td>6.65</td>
<td>1.43</td>
<td>4.24</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>8.15</td>
<td>2.50</td>
<td>0.53</td>
<td>2.13</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Fluorene</td>
<td>5.85</td>
<td>3.34</td>
<td>N.D.</td>
<td>1.63</td>
<td>1.02</td>
<td>1.24</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>9.10</td>
<td>4.04</td>
<td>0.26</td>
<td>0.34</td>
<td>0.12</td>
<td>N.D.</td>
</tr>
<tr>
<td>Anthracene</td>
<td>5.85</td>
<td>3.18</td>
<td>N.D.</td>
<td>1.66</td>
<td>1.56</td>
<td>N.D.</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>9.45</td>
<td>1.22</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Pyrene</td>
<td>9.10</td>
<td>0.84</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Chrysene</td>
<td>9.10</td>
<td>0.25</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>9.10</td>
<td>0.51</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

N.D. denotes "not detectable".

a The Lennard-Jones minimum kinetic diameter (17,20).
Fig. 1. By-product distribution of the SCWO of 2CP (a) in the absence of Li⁺ (b) in the presence of 0.02 M Li⁺ and by-product selectivities effected by zeolite (c) CuO/Y, (d) CuO/ZSM-5, and (e) CuO/ZSM-48 catalysts in the SCWO of 2CP.
Because of the restricted environment in the channel of zeolites, formation of high molecular weight PAHs is almost not possible. In Table 3, mainly lower molecular weight PAHs such as naphthalene, fluorene, and anthracene are formed in the SCWO of 2CP. Carcinogenic PAHs including Benzo[a]pyrene (BaP) and Chrysene (CHR) are not found in the SCWO of 2CP effected by CuO/zeolite catalysts. As expected, in the two-dimensional channel of ZSM-48, a further suppression of the formation of undesired by-products (ring-condensation (PAHs) and Cl-reinsertion (higher chlorinated phenols)) is observed. Because of the highly restricted environment in the channels of ZSM-48, formation of heavier PAHs in the catalytic oxidation process is not possible.

The structural data of the active CuO species, for instance in the zeolite Y, analyzed by EXAFS spectroscopies are shown in Figure 2. An over 99% reliability of EXAFS data fitting (dotted line) for CuO/Y catalyst is represented in Figure 2. It is clear that Cu-O (1.87 Å) and Cu-Cu (2.79 Å) are the main oxidation active sites in the zeolite channels for the SCWO of 2CP. Furthermore, the structure parameters obtained from the best fit to the EXAFS data are also represented in Table 4. The Cu-O (I) with a coordination number (CN) of 2.3 has a Cu-O bond length averaged 1.87 Å. In all EXAFS data analyses, the Debye-Waller factors (Δσ²) are less than 0.01 (Δσ < 0.1 Å in general). It should be noted that chlorine-bonded CuO species in the channels of zeolite Y are not observed.

<table>
<thead>
<tr>
<th>Atom pair</th>
<th>CN</th>
<th>Bond length (Å)</th>
<th>Δσ² (Å²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-O (shell I)</td>
<td>2.3</td>
<td>1.87</td>
<td>0.008</td>
</tr>
<tr>
<td>Cu-Cu (shell I)</td>
<td>4.2</td>
<td>2.79</td>
<td>0.003</td>
</tr>
<tr>
<td>Cu-O (shell II)</td>
<td>2.0</td>
<td>3.58</td>
<td>0.004</td>
</tr>
<tr>
<td>Cu-Cu (shell II)</td>
<td>5.5</td>
<td>4.53</td>
<td>0.002</td>
</tr>
</tbody>
</table>

Table 4. Structural parameters of CuO/Y catalyst analyzed by EXAFS.
Fig. 2. Fourier transform (FT) of the Cu K-edge EXAFS of zeolite (a) CuO/Y (with Li⁺) (b) CuO/Y catalysts in the SCWO of 2CP. The experimental data are the solid line and the best fit is the dotted line.
4 CONCLUSIONS

The global reaction rate of the supercritical water oxidation of 2CP in the presence of Li⁺ is expressed as: 92.5 \exp(-10.5/RT) \ [2CP]^{0.95} \ [O_2]^{0.56} \ [H_2O]^{0.45}. An enhancement of oxidation conversion and reduction of formation of toxic by-products such as PAHs and high-chlorinated phenols in the SCWO of 2CP are effected in the presence of Li⁺. By-product shape selectivities of CuO in the channels of zeolites Y, ZSM-5, and ZSM-48 for the SCWO of 2CP are also observed. In the more restricted environment of ZSM-48 channels, formation of toxic by-products (higher chlorinated phenol and PAHs) is extremely reduced in the SCWO of 2CP at 673 K. Main oxidation active species in the channels of zeolite Y are Cu-O (1.87 Å) and Cu-Cu (2.79 Å) that are identified by EXAFS spectroscopy. Chlorinated-bonded CuO species in the channel of zeolite Y are not observed.

5 ACKNOWLEDGEMENTS

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6 REFERENCES


