

Byproduct Shape Selectivity in Supercritical Water Oxidation of 2-Chlorophenol Effected by CuO/ZSM-5

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Reduction of trace polycyclic aromatic hydrocarbon (PAH) byproducts in supercritical water oxidation (SCWO) of 2-chlorophenol (2CP) effected by CuO/ZSM-5 has been investigated in the present work. In the channels of ZSM-5, due to a restricted environment, formation of undesired PAH byproducts in the SCWO of 2CP was significantly suppressed. Only trace light-PAHs with a molecular size less than 6 Å were formed in the SCWO of 2CP. Carcinogenic PAHs (heavy-PAHs) were not found. Structures of CuO and Cu₂O in the channels of ZSM-5 that involved in the catalytic SCWO of 2CP were studied by X-ray photoelectron spectroscopy (XPS). The Cu₂O-to-CuO ratio was approximately 0.15. Existence of the Cu(I) and Cu(II) was also confirmed by the preedge X-ray absorption near edge structural (XANES) spectroscopy. The copper oxides with a square-plane structure were observed by electron paramagnetic resonance (EPR) spectra. Furthermore, the extended X-ray absorption fine structural (EXAFS) spectra suggest that the copper oxides in the channels of ZSM-5 may form Cu₃O₂ clusters with Cu–Cu and Cu–O bond distances of 2.79 and 1.91 Å, respectively. The Cu₃O₂ clusters were oxidized to Cu₃O₄ by H₂O₂ in supercritical water.

Introduction

Polycyclic aromatic hydrocarbons with two or more fused benzene rings are frequently found in the processes of pyrolysis or incomplete combustion and carbonization of organic materials.^{1–3} Many PAHs are toxic and suspected carcinogens and/or mutagens.¹ From an environmental viewpoint, complete destruction and removal of hazardous compounds with a minimal release of toxic byproducts are essential in the most waste disposal processes.^{1,2}

At supercritical water oxidation conditions ($T > 647.3$ K, $P > 22.1$ MPa), water is relatively nonpolar because of the diminished hydrogen bonding.^{4–6} Thus, organic species, oxygen, and water form a single homogeneous 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.^{4,5} 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.^{5,6} Most toxic organic compounds can be rapidly oxidized to CO₂ and H₂O in a very short residence time in supercritical water.^{7–10} The destruction and removal

efficiency (DRE) may be achieved in seconds or minutes in the SCWO process.^{11–13} By contrast, solubility of inorganic salts decreases abruptly in supercritical water.^{4–6}

2-Chlorophenol, widely used in paper, pulp, pesticide, and herbicide industries, is a priority pollutant.^{7,14} 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.^{7,14} Due to the disadvantages of high-temperature and high-pressure operational conditions in the SCWO process, oxidation catalysts such as Cr₂O₃, MnO₂/CeO, CuO/ZnO, and ZnCl₂ have been widely studied in the catalytic SCWO process but only limited in the laboratory-scale research.^{15–18}

Because of the unique pore systems, zeolites have excellent shape selectivities in catalytic reactions.^{19–22} ZSM-5 (Zeolite Socony Mobil-5) has a three-dimensional (3D) channel structure. The straight channels have an elliptical cross section of 5.7–5.8 Å by 5.1–5.2 Å. These channels are interconnected by zigzag channels with a nearly circular cross section and a diameter of 5.4 Å.^{19–21}

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Because of the restricted environment in the channels of zeolite ZSM-5, formation of high-molecular-weight PAH byproducts may be very limited. However, reduction of undesired byproducts in the waste thermal treatment process effected in the zeolite channels has not been extensively studied.^{19–22} It should be noted that maximum DRE as well as a minimum of toxic byproducts formed in the disposal process of hazardous wastes are of increasing interest and importance. Therefore, the main objective of the present work was to investigate the shape selectivity of toxic trace PAH byproducts formed in the SCWO of 2CP (catalyzed by CuO) in the channels of ZSM-5. The nature of the oxidation active species in ZSM-5 was also determined by EXAFS, XANES, XPS, and EPR spectroscopies.

Experimental Section

The SCWO experiments of 2CP were conducted in a high-pressure quartz-lined batch reactor (volume = 20 mL). The system pressure was controlled by a back-pressure regulator (Tescom, P_{\max} = 408 atm) and a pressure regulator (Tescom, P_{in} = 250 atm; P_{out} = 7 atm). A safety rupture disk rated at 400 atm was installed. The experiments of 2CP oxidation in supercritical water with Li^+ cations (0.02 N) were conducted at 673–773 K with the reaction residence times between 0.5 and 5 min. 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 mole ratio = 0.95–2.0) in the SCWO experiments. Zeolite ZSM-5 with a Si/Al ratio of about 60 was ion exchanged in a 0.01 N $\text{Cu}(\text{CH}_3\text{COO})_2$ aqueous solution for 24 h. The Cu/ZSM-5 samples were calcined at 823 K for at least 6 h. About 0.15 g of catalysts (3 wt % CuO/ZSM-5) was used in the SCWO of 2CP.

Polycyclic aromatic hydrocarbon byproducts (extracted with a dichloromethane (Merck, purity > 99%) solvent) formed in 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). An HP Ultra 2 capillary column (50 m \times 0.32 mm \times 0.17 μm) was heated 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 (Mix 610-M (>99%, Supelco) and PNA-550JM (>99%, ChemService)) and samples. Analyses of PAH byproducts in the SCWO of 2CP were also conducted by HPLC (spectra system, SP) with a 3D UV detector (model UV-3000). PAHs were separated by a Spherisorb S5 PAH 5 μm column (150 mm \times 4.6 mm) with a mixed acetonitrile/water mobile phase.

X-ray photoelectron spectra of the CuO/ZSM-5 catalysts used in the SCWO experiments were measured on a Fison ESCA 210 (VG Scientific) spectrometer with a Mg K α X-ray (1253.6 eV) excitation source. The electron line intensities were estimated using a linear background.²³ The binding energy (E_b) of the Cu 2P $_{3/2}$ line was calibrated with that of O 1s (530.8 and 532.5 eV) and C 1s (284.4 eV) lines. The standard deviation of the binding energy (E_b) measurement was ± 0.3 eV typically.

The EPR spectra of the catalysts were recorded on a Bruker model EMX-10 EPR spectrometer with a maximum microwave power of 200 mW at 298 K. About 30–60 mg of catalyst samples was placed in the quartz tube (5 mm o.d.). The magnetic field was modulated at 100 kHz. Diphenylpicrylhydrazyl (DPPH) was used for determination of the absolute g -factor ($g = 2.0037$). All EPR spectra were normalized to the same frequency, sample weight, and spectrometer gain. The operational parameters used in these EPR experiments were the following: 3300 G center field; 6000 G sweep width; 9.784 GHz microwave frequency with 20 mW microwave power; 1.60 G modulation field amplitude; 7.10×10^4 receiver gain.

The EXAFS spectra were collected at a bending-magnet double-crystal monochromator (DCM) X-ray beamline at the Synchrotron Radiation Research Center (SRRC) of Taiwan. The electron storage ring was operated with an energy of 1.3 GeV and a current

Table 1. Trace PAH Byproducts Formed in the SCWO of 2CP with or without CuO/ZSM-5 at 673 K for 1 min^a

	min size ^b (Å)	amt ($\mu\text{g/g}$ of 2CP)	
		no catal	CuO/ZSM-5
naphthalene	5.85	27.5	6.6
acenaphthylene	8.15	7.3	0.5
acenaphthene	8.15	2.9	N.D.
fluorene	5.85	3.4	1.3
phenanthrene	9.10	4.2	0.6
anthracene	5.85	3.9	1.8
fluoranthene	9.45	1.5	0.2
pyrene	9.10	1.2	N.D.
benz[a]anthracene	9.10	1.7	0.1
chrysene	9.10	0.2	N.D.
benzo[b]fluoranthene	9.10	0.3	N.D.
benzo[k]fluoranthene	9.10	N. D.	N.D.
benzo[a]pyrene	9.10	0.4	N.D.
indeno[1,2,3- <i>cd</i>]pyrene	9.45	0.2	N.D.
dibenz[a,h]anthracene	9.45	N. D.	N.D.
benzo[ghi]perylene	9.45	N. D.	N.D.

^a N.D. denotes "not detectable". ^b The Lennard-Jones minimum kinetic diameter.^{19–21}

of 100–200 mA. A Si(111) DCM was used for providing highly monochromatized photon beams with energies of 1–9 keV and an energy resolution of 1.9×10^{-4} . Data were collected in fluorescence mode with a Lytle detector²⁴ in the region of the Cu K edge (8978.9 eV) at room temperature. The absorption spectra were collected using ion chambers that were filled with helium gas. The photon energy was calibrated by characteristic preedge peaks in the absorption spectrum of a copper foil. The raw absorption data in the region of 50–200 eV below the edge position were fit to a straight line using the least-squares algorithms. The fitted preedge background curves were extrapolated throughout all data ranges and subtracted and normalized to minimize the effect of sample thickness. The near-edge structure in an absorption spectrum covers the range between the threshold and the point at which the EXAFS begins.^{24–26} The XANES extend to an energy of the order of 50 eV above the edge. The k^2 -weighted and EXAFS spectra were Fourier transformed to R space over the range between 2.5 and 10.8 Å⁻¹. The EXAFS data were analyzed using the UWXAFS 3.0 and FEFF 7.0 programs.^{25,26}

Results and Discussion

Most organic wastes can be rapidly oxidized to CO_2 and H_2O in supercritical water.^{7–12} To obtain detectable quantities of incomplete combustion compounds or byproducts in the SCWO reactions, we have intentionally conducted the experiments at temperatures somewhat lower than 773 K or with insufficient oxygen (O/C < 1.0) so that the undesired byproducts from the oxidation of 2CP could be detected. Note that operational temperatures for commercial applications of the SCWO technology would be typically 773–923 K to achieve a maximum DRE as well as minimum of undesired PAHs formed.^{27–29}

Because of the restricted environment in the channels of zeolites, formation of high-molecular-weight PAHs was very limited. As shown in Table 1, concentrations of carcinogenic PAH byproducts such as benz[a]anthracene (BaA), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), and dibenz[a,h]anthracene (DBA) formed in the SCWO of 2CP effected by CuO/ZSM-5 at 673 K were not found (under detection limits). Yield of

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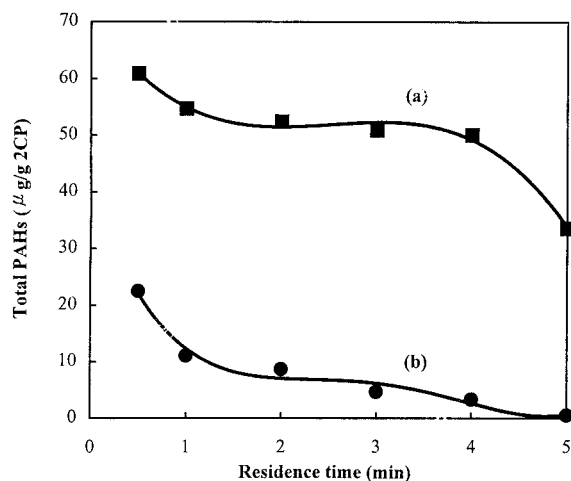


Figure 1. Total PAHs formed in the SCWO of 2CP (a) without a catalyst and (b) catalyzed by CuO/ZSM-5 at 673 K for 1–5 min.

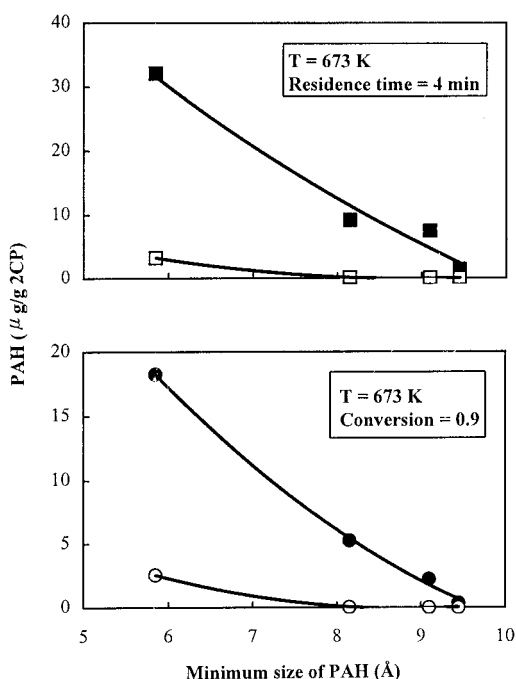


Figure 2. Size distribution of PAHs formed in the SCWO of 2CP without a catalyst (expressed in solid symbols) and effected by CuO/ZSM-5 at 673 K (expressed in open symbols). ("Minimum size" denotes the Lennard-Jones minimum kinetic diameter¹⁹.)

most other PAH byproducts decreased with increasing molecular sizes. The residence time dependence for formation of total PAH byproducts in the SCWO processes is shown in Figure 1. It is very clear that, in the presence of the CuO/ZSM-5 catalyst, the yield of total PAHs was reduced by at least five times. The effect of molecular sizes of PAHs formed in the SCWO of 2CP with CuO/ZSM-5 is also shown in Figure 2. As expected, mainly low-molecular-weight PAHs (or light-PAHs) such as naphthalene (Nap) ($5.75 \mu\text{g/g}$ of 2CP), fluorene (Flu) ($0.73 \mu\text{g/g}$ of 2CP), and anthracene (Ant) ($1.47 \mu\text{g/g}$ of 2CP) were formed in the SCWO of 2CP. Due to limited spacing in the channels of ZSM-5, heavy-PAHs including BaP, BbF, chrysene (CHR), DBA, and benzo[ghi]perylene (BghiP) were not found in the SCWO of 2CP. The unique PAHs shape selectivities for oxidation of 2CP in supercritical water in ZSM-5 are shown in Scheme 1. 2-Chlorophenol is tightly fitted in the channels of ZSM-5. In a separate

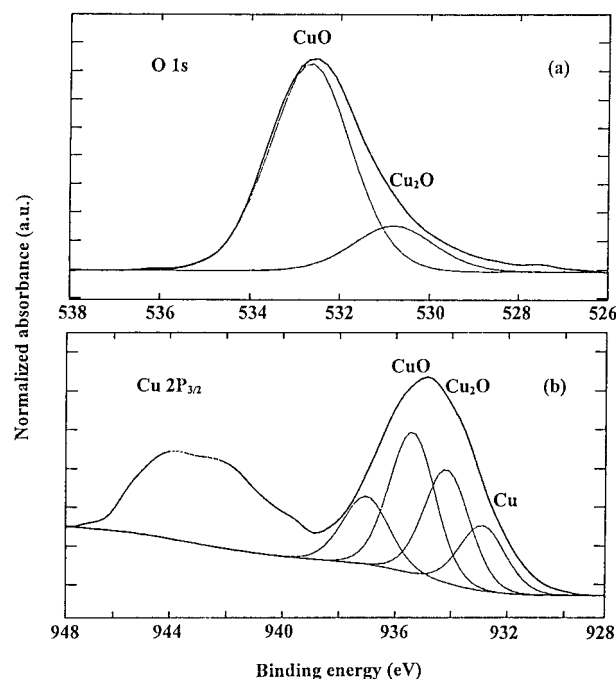
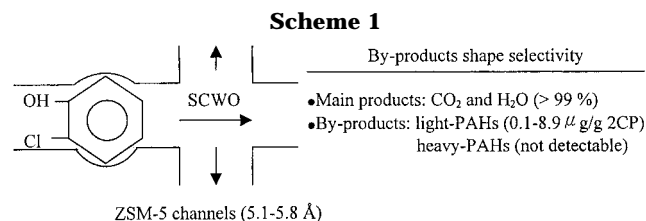


Figure 3. XPS spectra of (a) O 1s and (b) Cu 2P_{3/2} of the CuO/ZSM-5 catalyst used in the SCWO of 2CP at 673 K.



experiment, by using FTIR spectroscopy, we have found that the benzene molecules in the channels of ZSM-5 distorted the zeolite channel structures.³⁰ Benzene molecules in the channels still have a high symmetry of D_{6h} .

Formation of toxic PAHs in the SCWO of 2CP may be via the carbonization or ring-condensation mechanism.^{1–3} It may be not necessary to completely break down the aromatic ring of 2CP to ethyl or propyl species to form heavier PAHs. Note that reactions of ring opening in which products are ultimately oxidized to CO₂ and H₂O are predominant in the overall reaction network.

To more thoroughly examine the nature of the copper species of the catalysts effected in the SCWO of 2CP, XPS spectra of the catalyst were measured and calculated. The copper O 1s spectrum of the catalyst in Figure 3a indicates that the copper species in ZSM-5 has two oxidation states (Cu₂O and CuO). The relative amount of Cu₂O-to-CuO of the catalyst was about 0.15. In addition, Figure 3b also shows that the copper (Cu 2P_{3/2}) species exhibit mainly three oxidation states such as Cu, Cu(I) (Cu₂O), and Cu(II) (CuO). A very small amount of metallic Cu was also found in the used catalyst. The Cu(II) species in the CuO/ZSM-5 catalyst was reduced to Cu(I) in the SCWO process. The Cu(I) species were reoxidized by the oxidant (H₂O₂) in supercritical water.

To further confirm the structure of the active copper species in ZSM-5, X-ray absorption spectroscopic studies were conducted. The XANES spectroscopy provides information of electronic configuration, stereochemistry, and the oxidation states of the copper atom being investigated.

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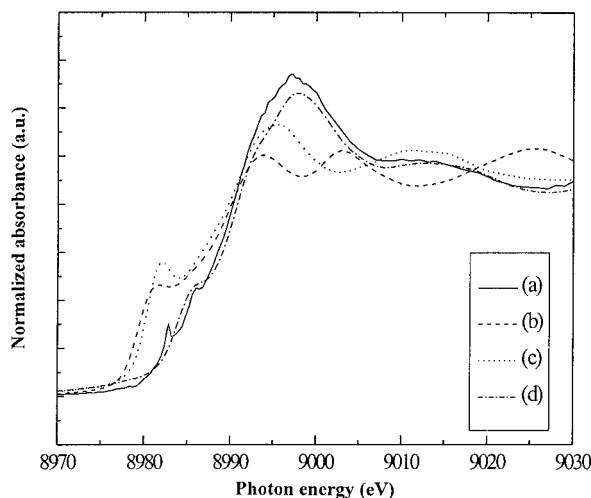


Figure 4. XANES spectra of (a) CuO/ZSM-5 catalyst used in the SCWO of 2CP at 673 K, (b) copper foil, (c) Cu₂O, and (d) CuO.

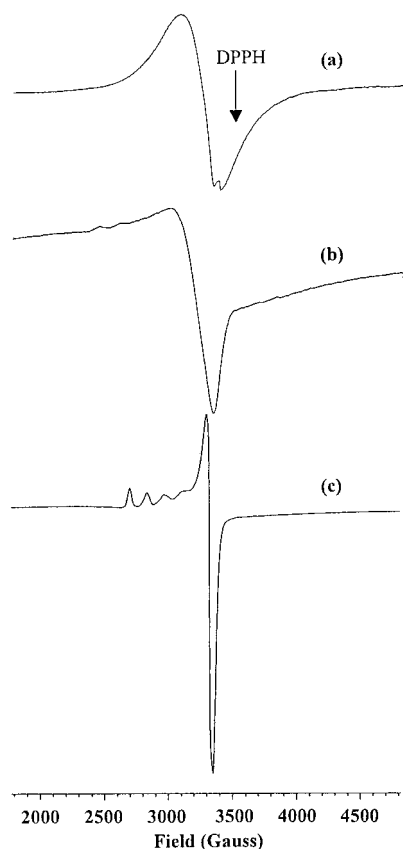


Figure 5. EPR spectra of CuO/ZSM-5 catalysts used in the SCWO of 2CP at 673 K measured at (a) 463 K (b) 298 K, and (c) 77 K ($\nu_{\text{EPR}} = 9.784$ GHz, field (G) = 3475 or $g_{\text{DPPH}} = 2.0037$).

The XANES spectra of the CuO/ZSM-5 catalyst used in the SCWO of 2CP at 673 K compared with CuO, Cu₂O, and Cu are shown in Figure 4. The preedge XANES spectrum of CuO/ZSM-5 exhibits a very weak absorbance feature for the 1s to 3d transition which is forbidden by the selection rule in the case of perfect octahedral symmetry. The sharp feature at 8983–8985 eV, due to the dipole-allowed 1s to 4p_{xy} electron transition, indicates the existence of Cu(I). The intensity of the 1s to 4p_{xy} transition is proportional to the population of Cu(I) in ZSM-5. A shoulder at 8986–8989 eV and an intense feature at 8995–8997 eV are attributed to the 1s to 4p_{xy}

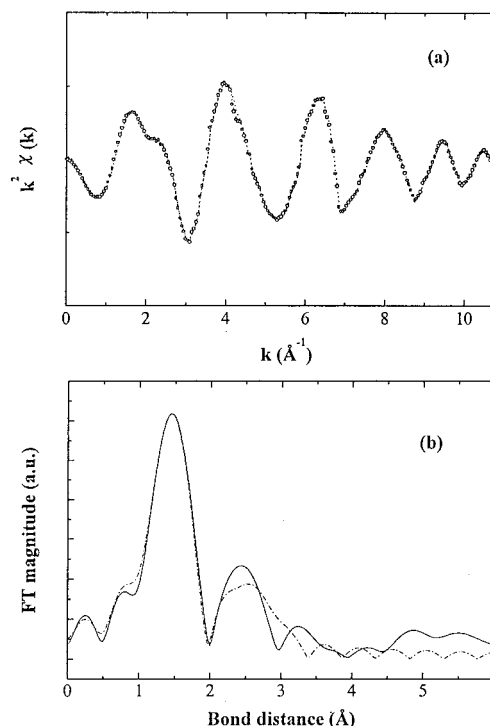
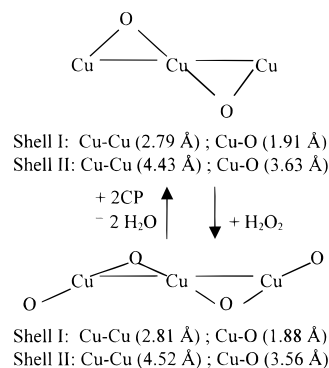


Figure 6. (a) Cu K-edge EXAFS oscillation $k^2\chi(k)$ and (b) Fourier transform (FT) of the CuO/ZSM-5 catalyst used in the SCWO of 2CP at 673 K. The best fittings of the EXAFS spectra are expressed by the dotted lines.

Scheme 2 Postulated Structure of the Copper Oxide Clusters Involved in the SCWO of 2CP in the Channels of ZSM-5



transition that indicates the existence of Cu(II) species in the channels of ZSM-5. The upshift of the edge energy and a very weak 1s to 3d forbidden transition near the preedge also confirm the observations. The XANES spectra work particularly well in distinguishing between Cu(I) and Cu(II) coexisting in ZSM-5 in the SCWO of 2CP.

In addition, coordination and valence states of the paramagnetic Cu(II) species in ZSM-5 were also studied by EPR spectroscopy. The EPR spectra of the CuO/ZSM-5 catalyst measured at 77, 298, and 463 K are shown in Figure 5. Since the minimum g -factor of the catalyst is 2.11 (g_{DPPH} factor = 2.0037 at 298 K), it is likely that the Cu(II) species has a square-planar structure in the channels of ZSM-5 (Scheme 2). Square-planar structures of CuO in ZSM-5 were also observed by Kucherov, Tanabe, and Larsen et al.^{31–33} Figure 5a shows that the EPR spectrum of the CuO/ZSM-5 catalyst at 463 K is broad and structureless. On the contrary, at 77 K the spectrum

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Table 2. Fine Structural Parameters of CuO in ZSM-5 Analyzed by EXAFS Spectroscopy

	shell	CN ^a	R (Å) ^b	$\Delta\sigma^2$ (Å ²) ^c
Cu ₃ O ₂ Cluster				
Cu–O	1st	2.3	1.91	0.005
	2nd	1.9	3.63	0.009
Cu–Cu	1st	4.6	2.79	0.016
	2nd	5.7	4.43	0.019
Cu ₃ O ₄ Cluster				
Cu–O	1st	2.5	1.88	0.007
	2nd	2.0	3.56	0.011
Cu–Cu	1st	4.5	2.81	0.012
	2nd	5.6	4.52	0.017

^a CN: coordination number. ^b R: bond distance. ^c σ : Debye–Waller factor.

(Figure 5c) exhibits a sharp signal and characteristic structure of Cu(II) complexes where the hyperfine coupling between the 3d unpaired electron and the copper ($I = 3/2$) nuclear spin is well resolved. Furthermore, the broad EPR spectrum observed in Figure 5c suggests that the copper oxide species may be mobile in the channels of ZSM-5. At 77 K, the appearance of the parallel edges in the EPR spectra is observed in Figure 5b, which indicates a reduced mobility of copper species in ZSM-5 at low temperatures.

Generally, EXAFS spectroscopy can provide information on the atomic arrangement of catalysts in terms of bond distance, number and kind of near neighbors, and thermal and static disorders. The EXAFS spectra were recorded and analyzed in the k range between 2.5 and 10.8 Å⁻¹ (Figure 6a). Over 99% reliability of the EXAFS data fitting for Cu species in zeolite was obtained. The standard deviation calculated from the averaged spectra was also determined. In all EXAFS data analyzed, the Debye–Waller factors ($\Delta\sigma^2$) were less than 0.02 Å. The EXAFS spectra of the CuO/ZSM-5 catalyst are shown in Figure 6. The structural parameters obtained from the best fit

to the EXAFS data are summarized in Table 2. Interactions of the copper species with the ≡Si–O–Al≡ sites on ZSM-5 seem to be insignificant. Due to the restricted environment in the channels of ZSM-5, it is possible that copper oxide species may be formed as clusters in ZSM-5. The postulated structure of the copper oxide clusters involved in the SCWO of 2CP in the channels of ZSM-5 is Cu₃O₂ (Scheme 2). Bond distances of Cu–O and Cu–Cu species are 1.91 and 2.79 Å, respectively, in the clusters. The coordination number (CN) of the Cu–O species is 2.5. The Cu₃O₂ clusters were oxidized by H₂O₂ to form Cu₃O₄ clusters in which the bond distances of Cu–Cu and Cu–O are 2.81 and 1.88 Å, respectively. Furthermore, chlorine-bonded CuO species in the channels of ZSM-5 were not observed by EXAFS spectroscopy. Thus, one may eliminate the possibility that Cu was involved in the abstraction of Cl from 2CP in the SCWO process.

Conclusions

An enhancement in oxidation and reduction in the formation of trace PAHs in the SCWO of 2CP effected by CuO/ZSM-5 catalysts was found experimentally. In the highly restricted environment of ZSM-5 channels, the formation of PAH byproducts was extremely limited in the SCWO of 2CP at 673 K (O/C = 0.95). Only trace light-PAHs with a molecule size less than 6 Å were formed in the SCWO of 2CP. Carcinogenic PAHs (heavy-PAHs) were not found. The existence of Cu₃O₂ clusters with Cu–O and Cu–Cu bond distances of 1.91 and 2.79 Å, respectively, in the channels of ZSM-5 was also observed by EXAFS spectroscopy. The Cu₃O₂ clusters were oxidized to Cu₃O₄ by H₂O₂ in supercritical water.

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