Thermal Degradation of Octachloronaphthalene over As-Prepared Fe_3O_4 Micro/Nanomaterial and Its Hypothesized Mechanism

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Supporting Information

ABSTRACT: Decomposition of octachloronaphthalene (CN-75) featuring fully substituted chlorines was investigated over as-prepared Fe_3O_4 micro/nanomaterial at 300 °C. It conforms to pseudo-first-order kinetics with $k_{\text{obs}} = 0.10 \text{ min}^{-1}$ as comparable to that of hexachlorobenzene and decachlorobiphenyl. Analysis of the products indicates that the degradation of CN-75 proceeds via two competitive hydrodechlorination and oxidation pathways. The onset of hydrodechlorination producing lower chlorinated naphthalenes (CNs) is more favored on α -position than β -position. Higher amounts of CN-73, CN-66/67, CN-52/60, and CN-8/11 isomers were found, while small content difference was detected within the tetrachloronaphthalene and trichloronaphthalene homologues, which might be attributed to lower energy principle and steric effects. The important hydrodechlorination steps, leading to CN-73 $\gg$ CN-74 in two heptachloronaphthalene isomers contrary to that in technical PCN-mixtures, were specified by calculating the charge of natural bond orbitals in CN-75 and the energy of two heptachloronaphthalene radicals. On the basis of the molecular electrostatic potential of CN-75, the nucleophilic O_2^- , and electrophilic O_2^- and O^- , present on the Fe_3O_4 surface, might attack the carbon atom and π electron cloud of naphthalene ring, producing naphthol species with Mars–van Krevelen mechanism, and formic and acetic acids.

INTRODUCTION

Polychlorinated naphthalenes (PCNs) are ubiquitous environmental pollutants that have 75 possible compounds based on the naphthalene ring, featuring 1–8 chlorine atoms. PCNs were proposed for inclusion into Annex A, B, and/or C of the Stockholm Convention (SC) on POPs in 2011.¹ Traditionally, PCNs were widely used as a component in cable insulation, wood preservatives, engine oil additives, electroplate masking compounds, and dye production. They are also present in the formulations of polychlorinated biphenyls (PCBs) due to their structural similarity. Although the production and use of PCNs were prohibited in the United States and Europe in the 1980s, large amounts of PCNs were released in the environment because of their historical widespread use. Moreover, unintentional formation during thermal industrial processes, such as coking and metallurgy, occurs because of impurities present in the raw materials.³ As established, PCNs exert dioxin-like toxicity effects on mammalian liver cell line⁴ and display potential toxicity on embryos⁵ owing to their structural similarity.^{4,6} The toxicity of PCNs is mainly ascribed to

penta-, hexa-, and hepta-chlorinated naphthalenes. Some researchers have proposed the 2,3,7,8-tetrachlorodibenzo-*p*-dioxin relative potency factors (RPFs) of PCN isomers.^{7,8} The annual toxic emissions of PCNs from the coking industry and secondary nonferrous metallurgical facilities was estimated to be comparable to that of dioxin-like polychlorinated biphenyls.^{9,10} The toxic contribution of PCNs in human serum was reported to amount to ~26.8% of the total toxic equivalents of polychlorinated dibenzo-*p*-dioxin, polychlorinated dibenzofuran, polychlorinated biphenyls, and polychlorinated naphthalenes.¹¹ Therefore, the reduction of PCN content is a matter of public concern in the context of environmental protection.

The Review Committee of persistent organic pollutants recommended the Conference of the Parties of SC to consider

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listing and specifying related control measures for PCNs in October 2013.² Numerous methods have been used to convert chlorinated aromatics into less toxic chemicals, as reported in the literature, such as photodegradation and biodegradation.^{12–14} High-temperature incineration is the most widely used up to now, but it has many disadvantages such as high equipment costs, stringent conditions, and improper burning that may lead to the formation of dioxins.¹⁵ Catalytic degradation at lower temperatures involving metal oxides has also attracted much attention for the removal of organic chlorine, owing to the relatively low costs, high catalytic activity, thermal stability, and the ease of preparation of high-surface area materials. However, to our knowledge, studies investigating the decomposition of PCNs by metal oxides are rare in the literature, and the involved degradation mechanism is unclear.

Of the metal oxides, Fe_3O_4 with a reverse spinel structure has been identified as a suitable catalyst because of its unique ferromagnetic property and recycling capability. In particular, micro/nano Fe_3O_4 with a three-dimensional (3D) hierarchical structure has attracted much attention in environmental remediation-related fields.¹⁶ 3D hierarchically micro/nano materials are micro-sized particles composed of nanosized building blocks.^{16,17} The hierarchical structure is highly beneficial toward targeted reactions because of the adequately high specific surface area, as provided by the nanosized building blocks, and reduced aggregation phenomenon, as facilitated by the microstructure. Previous studies demonstrated that as-prepared micro/nano Fe_3O_4 exhibits higher activity toward the degradation of decachlorobiphenyl and hexachlorobenzene—the degradation mechanism reactions were proposed.^{18,19} PCNs are structurally composed of a π -conjugated naphthalene ring, whereas chlorinated benzenes and polychlorinated biphenyl consist of a phenyl ring and two phenyl rings connected by a carbon–carbon bridge, respectively. It is therefore important to investigate the decomposition of PCNs by micro/nano Fe_3O_4 and the associated degradation pathways.

In this study, micro/nano Fe_3O_4 was prepared through a simple and cost-effective ethylene glycol-mediated process according to previous studies.^{16,19} The reactivity of the as-prepared Fe_3O_4 toward model compound CN-75, featuring fully substituted chlorine atoms, was evaluated at 300 °C. To further investigate the degradation process, the degradation products were comprehensively determined by gas chromatography–mass spectrometry (GC/MS), high-performance liquid chromatography/hybrid quadrupole time-of-flight mass spectrometry (HPLC/Q-ToF-MS/MS), and ion chromatography (IC). Possible degradation pathways of CN-75 over the as-prepared Fe_3O_4 were traced based on identification of intermediates, and elucidated by density functional theory, and reactive oxygen species present on the surface of micro/nano Fe_3O_4 detected by O_2 -temperature-programmed desorption (O_2 -TPD).

MATERIALS AND METHODS

Preparation and Characterization of Fe_3O_4 . All chemicals were purchased from Beijing Chemical Co. (Beijing, China) and used without further purification. Micro/nano Fe_3O_4 was prepared by a simple and low-cost ethylene glycol-mediated process according to a procedure described in a previous study.^{16,19} Typically, 1.9 g of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), 4.5 g of PEG-10000, and 2.7 g of urea were added to 180 mL of ethylene glycol (EG), and heated at 230 °C. The

resulting precursor material was calcined in nitrogen flow at 350 °C.

O_2 -TPD experiments were conducted on a Thermo-TPRO 1100. The catalysts were pretreated in He at 300 °C for 30 min prior to analysis and then cooled to ambient temperature. The oxygen adsorption process was performed by treatment with a 5% O_2 in He mixture for 30 min. The temperature was then raised to 800 °C at a rate of 10 °C min^{-1} ; meanwhile, the system was purged with He (50 mL min^{-1}) for 30 min to achieve desorption.

The surface analysis of the Fe_3O_4 catalyst by X-ray photoelectron spectroscopy (XPS) was performed using a ESCALAB 250 instrument using monochromatized Al $K\alpha$ (1486.6 eV) radiation (200 W, 200 eV) as the X-ray source. Typical operating pressures were $\sim 1 \times 10^{-8}$ Torr.

Degradation Studies. The degradation experiments were carried out in sealed glass ampules. Typically, 1.5 or 7.5 μL of hexane solution of CN-75 (990.1 or 4950.5 nmol) and a given amount of micro/nano Fe_3O_4 were mixed. The samples were then heated at 300 °C for an appropriate time. A blank experiment was carried out in the absence of Fe_3O_4 under the same conditions. All experiments were performed in triplicate to ensure repeatability of the results.

Degradation Product Analysis. After the decomposition reaction, the ampule was cooled to room temperature. The ampule was then crushed to extract the sample.

For analysis of PCNs by GC/MS, the samples were extracted with hexane and then treated with anhydrous sodium sulfate. The resulting samples were then analyzed for unreacted CN-75 and newly formed PCNs using an Agilent 6890 gas chromatograph equipped with a DB-SMS capillary column (30 m $\times$ 0.25 mm i.d., 0.25 μm film thickness) and an Agilent 5973N mass selective detector (MSD). The carrier gas through the column was helium ($\geq 99.999\%$), at a flow rate of 1 mL/min. A 1.0- μL aliquot of the diluted sample was injected in splitless mode. Injector was set at 260 °C. Column temperature was initially set at 75 °C for 2 min, gradually increased to 150 °C at 20 °C/min, then increased to 205 °C at 1.5 °C/min, and finally increased to 270 °C at 2.5 °C/min. An electron ionization system was used with an ionization energy of 70 eV. The qualitative determination of the produced PCNs was based on m/z , the retention time of $^{13}\text{C}_{10}$ -labeled PCNs, and the relative retention time intervals between adjacent compounds. The quantitative determination of unreacted CN-75 and produced PCNs was performed in selected ion monitoring mode using the two abundant ions in the molecular ion clusters and those of the corresponding or adjacent $^{13}\text{C}_{10}$ -labeled CN-75 standards. The selected mass-to-charge ratios of PCN analysis are given in Table S1 of the Supporting Information (SI).

For analysis of the hydroxyl species of PCNs by HPLC/Q-ToF-MS/MS, the samples were extracted with HPLC grade methanol, filtered through a 0.45- μm mesh membrane, and concentrated to approximately 100 μL . Analysis of the hydroxyl-PCNs in the samples was performed with a HPLC/Q-ToF-MS/MS apparatus (Micromass Q-ToF micro, Waters, USA), equipped with a SUPELCO SILLC-18 C_{18} column (Sigma; 4.6 $\times$ 250 mm; particle size 5 μm). Elution was performed at a flow rate of 0.5 mL/min with a 0.1% acetic acid in water–acetonitrile gradient (acetonitrile concentrations of 0% (isocratic, 5 min), 70% (isocratic, 5 min), 70–90% (linear, 5 min), 90–100% (linear, 5 min), 100% (isocratic, 5 min), 0% (isocratic, 4 min)). The mass analyzer was operated in negative ionization (EI^-) mode and the optimized parameters were as

follows: source temperature, 120 °C; desolvation temperature, 200 °C; capillary voltage, 2.50 kV; desolvation gas flow, 600 L/h; cone gas flow, 50 L/h.

Samples for analysis of organic acids by IC were extracted with deionized water, then filtered through a 0.45- μ m mesh membrane for IC measurements. The analysis was conducted on a DIONEX AS 5000 equipped with an AS-AP automated sampler. A Dionex AS11-HC guard column (50 $\times$ 4 mm i.d.) and a Dionex AS11-HC analytical column (250 $\times$ 4 mm i.d.) were used. The analysis was performed at 30 °C, using potassium hydroxide eluent that was generated from a Dionex EG online and run with a linear gradient at a flow rate of 1.0 mL min⁻¹.

Density Functional Theory Calculations. Theoretical calculations were carried out using the Gaussian 03 program. The charge of the natural bond orbitals in CN-75, the molecular electrostatic potential of CN-75, and the energy of the two HpCN radicals were calculated by the DFT method at the B3LYP/6-311++ g(d,p) theory level.

RESULTS AND DISCUSSION

Kinetic Study. The time-dependent degradation behavior of CN-75 (990.1 nmol) over as-prepared micro/nano Fe₃O₄ was investigated at 300 °C (The optimization of degradation conditions was examined, which can be seen from Figure S1 and its explanation in the SI.). The black squares in Figure 1

Figure 1. Residual CN-75 content as a function of heating time. Inset shows the pseudo-first-order kinetic plot of the reaction.

represent the changes in the residual CN-75 amount dependent on the heating time at 300 °C via a quasi-exponential-type decay. CN-75 rapidly decomposed from 990.1 to 92.1 nmol in 5 min, and further decreased to 0.8 nmol in 60 min. This result suggests that micro/nano Fe₃O₄ is an effective catalyst for the degradation of CN-75, similar for that of decachlorobiphenyl (CB-209) and hexachlorobenzene.^{18,19} A linear $\ln([R_{CN-75}]/[I_{CN-75}])$ vs time plot was obtained that corresponds to pseudo-first-order reaction kinetics (inset in Figure 1). The initial rate of decomposition of CN-75 can be described by the pseudo-first-order kinetic law with respect to CN-75 concentration, as shown in eq 1:

$$\ln([R_{CN-75}]/[I_{CN-75}]) = -k_{obs}t \quad (1)$$

where k_{obs} is the pseudo-first-order initial rate constant (min⁻¹) as calculated from the experimental data, I_{CN-75} is the initial number of moles of CN-75, and R_{CN-75} is the number of moles of the remained CN-75 following heating for a given time period, t (min).

The pseudo-first-order rate constant for the degradation of CN-75 over the synthesized Fe₃O₄ is 0.10 min⁻¹ ($R^2 = 0.89$). For comparison, the degradation behavior of CB-209 over the synthesized Fe₃O₄ was also assessed, as shown in SI Figure S2. The decomposition profile of CB-209 also conforms to pseudo-first-order kinetics, with a calculated rate constant of 0.14 min⁻¹ ($R^2 = 0.97$). As observed, the rate constant of CN-75 degradation is comparable with that of CB-209 degradation over the prepared Fe₃O₄. However, these two values are lower than the pseudo-first-order rate constant of HCB degradation over the synthesized Fe₃O₄, i.e., 0.96 min⁻¹ ($R^2 = 0.94$), as reported by Jia et al.¹⁹ Thus, the degradation behaviors of different chlorinated aromatic hydrocarbons are highly dependent on their molecular sizes and chemical properties such as π -conjugated effects exerted by the chlorinated aromatic hydrocarbons. The stronger π -conjugated effects in CN-75 and CB-209 relative to that in HCB might impede on the activity of the catalyst to decompose CB-209 and CN-75. However, as-prepared Fe₃O₄ micro/nano material is efficient not only for the degradation of CN-75, but also for that of CB-209 and hexachlorobenzene confirmed in the previous studies,^{18,19} suggesting the feasibility for the synergetic disposal of their homologues by lower-temperature catalytic degradation.

In addition, the photolysis of CN-75 in hexane, with a different sensitizer or quencher, similarly exhibited pseudo-first-order kinetics.¹² The photolysis rate constant varied over the range 0.053–1.1 h⁻¹ (0.00088–0.018 min⁻¹), which is smaller by factors of 6–114 than that for CN-75 degradation over synthesized Fe₃O₄. From the data presented by this literature,¹² it can be estimated that the photodegradation efficiency of CN-75 only reached to around 70% in aerated hexane for a reaction time of 3 h, while the degradation efficiency of CN-75 over the synthesized Fe₃O₄ reached to 95.6% for a short reaction time of 10 min (Figure S1 in the SI). On the other hand, the high-temperature incineration is the most widely used method for the disposal of POPs up to now. To our best knowledge, there have not yet been reports on the technical specification for centralized incineration disposal engineering on PCN waste. In view of similar chemical structure between PCNs and PCBs, the high-temperature incineration techniques of PCB wastes could be taken as a reference. The incineration system can achieve an above 99% removal efficiency for PCB wastes. However, the incineration temperature is required to be maintained at 1200 °C (± 100 °C) for 2-s dwell times or 1600 °C (± 100 °C) for 1.5-s dwell times,²⁰ resulting in significantly high disposal costs. These comparison results indicated that the catalytic degradation technique might be very promising for the disposal of PCNs as an alternative.

Product Analysis. As observed in Figure 2, a series of hydrodechlorinated products was identified that included (a) heptachloronaphthalenes (HpCNs), (b) hexachloronaphthalenes (HxCNs), (c) pentachloronaphthalenes (PeCNs), (d) tetrachloronaphthalenes (TeCNs), (e) trichloronaphthalenes (TrCNs), and (f) dichloronaphthalenes (DiCNs). With increasing reaction time, the amount of all newly formed lower chlorinated naphthalenes increased at the early stages of the reaction before a decrease was noted. The detection of newly formed lower chlorinated naphthalene homologues and

Figure 2. Distribution of the hydrodechlorination products (a) HpCNs, (b) HxCNs, (c) PeCNs, (d) TeCNs, (e) TrCNs, and (f) DiCNs following degradation of CN-75 over as-prepared Fe_3O_4 at 300 °C as a function of heating time.

their time-dependent distribution pattern indicated the occurrence of successive reductive hydrodechlorination reactions during the degradation of CN-75 on the prepared Fe_3O_4 . A similar reaction pathway has also been observed during the degradation of CB-209 and HCB over as-prepared Fe_3O_4 .^{18,19}

Figure 2 also showed that the lower chlorinated homologues displayed nonuniform distribution profiles of the PCN isomers. In regard to the two isomers of HpCNs, as show in Figure 2a, the content of CN-73 was markedly higher than that of CN-74. The content of CN-73 corresponded to ~97.3% of the total amount of the two HpCN isomers at a reaction time of 5 min. Higher contents of CN-73 are also released during thermal industrial processes in the coking industry,⁹ secondary nonferrous metallurgical facilities,¹⁰ and municipal solid waste combustion.²¹ Jalil et al.²² reported that the hydrodechlorination pathway involves the transfer of electrons from the catalyst to the parent chlorinated compound. Following dissociation of the chloride anion, the neutral radical that forms can undergo further reduction to form an aryl anion, which is then protonated to produce lower chlorinated aromatics. On the

basis of this proposed mechanism, the formation process of the two HpCN isomers, from CN-75, is described in Scheme 1a. The transformation of Fe_3O_4 into $\alpha\text{-Fe}_2\text{O}_3$ during the thermal reaction, which has been confirmed in previous studies,¹⁹ can provide free electrons, leading to the formation and adsorption of the leaving chloride ion on the Lewis acid sites and subsequent association with iron ions (see Figure S3 and its explanation in the SI). It is well-known that the surface of metal oxides is covered with adsorbed water. Thus, the water adsorbed onto the iron oxide surface can act as hydrogen donor groups, enabling hydrodechlorination to occur. Further details about the adsorbed water phenomenon can be obtained from Figure S4 and its explanation in the SI Section.

From Scheme 1a, it can be judged that the leaving of chlorine group from CN-75 and the formation of HpCN radicals played important roles for producing CN-74 and CN-73. The concept of natural orbitals was first introduced by Per-Olov Löwdin²³ in 1955 to describe the unique set of orthonormal one-electron functions that are intrinsic to the N-electron wave function. The natural bond orbitals are one of a sequence of natural

Scheme 1. (a) Proposed Formation Steps of the Two HpCN Isomers; (b) Proposed Hydrodechlorination Pathways Toward the Degradation of CN-75 over As-Prepared Fe₃O₄; (c) Oxidative Attack Mechanism for CN-75 Degradation over Fe₃O₄

localized orbital sets that include atomic, hybrid, and (semi-) localized molecular orbitals, intermediate between basis atomic orbitals and molecular orbitals. The natural bond orbital analysis can give a representation of the charge distribution that may be used to analyze chemical effects and rationalize

chemical reactivity.²⁴ To investigate the difference observed in the experimental yields of the two HpCN isomers, the charge of the natural bond orbitals in CN-75 and the energy of the two HpCN radicals were calculated by the DFT method, as shown in Table 1. The larger charge difference between the C atoms

Table 1. Charge of Natural Bond Orbitals in CN-75 and Energy of the Two HpCN Radicals

Chemical	Atom	Charge (a.u.)	Atom	Charge (a.u.)	Charge difference (a.u.) at α - and β -positions	Energy (kcal mol ⁻¹)
1C (α)	-0.14936	11Cl (α)	0.770250	0.919610 (α)	
	2C (β)	-0.10594	12Cl (β)	0.644639	0.750579 (β)	
	3C (β)	-0.09218	13Cl (β)	0.644588	0.736760 (β)	
	4C (α)	-0.08866	14Cl (α)	0.770322	0.858992 (α)	
	5C (α)	-0.07372	15Cl (α)	0.770323	0.844043 (α)	
	6C (β)	-0.09957	16Cl (β)	0.644577	0.744147 (β)	
	7C (β)	-0.10666	17Cl (β)	0.644646	0.751306 (β)	
	8C (α)	-0.15086	18Cl (α)	0.770260	0.921120 (α)	
	9C	-0.46590				
	10C	-0.67837				-2260665.3
α -radical						-2260653.1
β -radical

Figure 3. (a) HPLC chromatogram of chemical species following degradation of CN-75 over as-prepared Fe₃O₄ at 300 °C. (b) Distribution profile of organic acids formed following degradation of CN-75 over as-prepared Fe₃O₄ at 300 °C.

and Cl atoms at the α -position when compared with that at β -position favored the abstraction of chlorine at the α -position. On the basis of the stability viewpoint, CN-73 radical is

preferentially formed and more stable than CN-74 radical because the energy of CN-73 radical is lower than that of CN-74 radical (by 12.2 kcal mol⁻¹). Zhai et al. previously reported

the total energy (TE), the standard heat energy of formation (ΔH_f^0), and the standard free energy of formation (ΔG_f^0) of 75 polychlorinated naphthalenes using DFT that were heavily dependent on the number and position of the chlorine atoms.²⁵ In this study, the calculated TE, ΔH_f^0 , and ΔG_f^0 of CN-73 are lower than those of CN-74. The isomers that featured chlorine atoms at either set of positions i.e., 1 and 8, or 4 and 5 were determined as nonstable. Thus, it can be concluded that the formation of abundant CN-73 was thermodynamically favorable and promoted by steric effects. Contrarily, regarding technical PCN-mixtures of the Halowax series, the content of CN-73 is lower than that of CN-74, with ratios of 0.2–0.4. The difference might be due to the different formation pathways. PCN mixtures in the Halowax series are produced by chlorination of molten naphthalene with chlorine gas in the presence of FeCl_3 and/or SbCl_5 as catalysts,²⁶ based on electrophilic substitution mechanism.²⁷

The TE, ΔH_f^0 , and ΔG_f^0 of CN-66/67 and CN-52/60 were the lowest among those obtained for the HxCNs and PeCNs isomers.²⁵ On the basis of the steric effect viewpoint, the isomers with fewer chlorine atoms substituted at the ortho-positions were more stable. As observed in Figure 2b and c, the content of the thermodynamically stabilized CN-66/67 amounted to ~91.5% of the total content of the HxCN isomers and CN-52/60 amounted to ~81.1% of the total content of PeCN isomers at a reaction time of 5 min. It is also reported that CN66/67 and CN-52/60 are relatively abundant isomers for thermal industrial processes²¹ compared with their far lower contents in Halowax mixtures.²⁶

As shown in Figure 2d, the corresponding contents of the detected TeCN isomers, relative to the total TeCN isomers content, varied between 5.8% and 23.2%. On the other hand, the corresponding amounts of the detected TrCN isomers, relative to the total TrCN isomers content, varied between 4.0% and 21.8% (Figure 2e). The observed difference in contents among the detected TeCN isomers and TrCN isomers is small when compared with those of the detected HpCN isomers, HxCN isomers, and PeCN isomers, respectively, with significantly higher amounts of CN-73, CN-66/67, and CN-52/60. On the basis of the thermodynamic data reported by Zhai et al.,²⁵ the TE, ΔH_f^0 , and ΔG_f^0 values among the two respectively detected TeCN and TrCN isomer groups was rather approximate and contrary to those among the detected HpCN isomers, HxCN isomers, and PeCN isomers. Moreover, all the detected TeCN and TrCN isomers feature fewer chlorine atoms that were substituted at either positions 1 and 8 or 4 and 5, with similar steric effect. These might be the reason why the small content difference was observed within the two TeCN and TrCN isomer groups.

Among the detected DiCN isomers, as shown in Figure 2f, CN-11/8 isomers contributed to ~58.5% of the total detected DiCN isomers. CN-11 isomer has chlorine atoms substituted at C atoms in positions 2 and 6, and CN-8 isomer has chlorine atoms substituted at C atoms in positions 1 and 7. Consequently, the repulsive effect exerted by chlorine atoms substituted at either positions 1 and 8, or 4 and 5 decreased significantly. On the other hand, both CN-11 and CN-8 isomers featured lower TE, ΔH_f^0 , and ΔG_f^0 values when compared with those of other detected DiCN isomers. Taken together, these two aspects above might result in the higher contents observed for the CN-11 and CN-8 isomers relative to those of the other detected DiCN isomers. Higher contents of

CN-11/8 isomer are also reported during waste combustion experiments using a laboratory-scale fluidized-bed reactor.²¹

Lichtenberger et al.²⁸ reported the formation of chlorophenol via nucleophilic attack of O^{2-} on dichlorobenzene adsorbed onto $\text{V}_2\text{O}_5/\text{TiO}_2$ at 200–400 °C. Zhang et al.²⁹ confirmed the presence of pentachlorophenol during the degradation of hexachlorobenzene over ultrafine $\gamma\text{-Al}_2\text{O}_3$ at 300 °C. However, there have been few studies reporting the existence of hydroxyl species during the degradation of PCNs over metal oxides. In this study, HPLC/Q-ToF-MS/MS was used to determine the presence of hydroxyl species during the degradation of CN-75 over the as-prepared Fe_3O_4 . However, hydroxyl species were not detected under the same CN-75 reaction dosage as that used for the detection of the newly formed PCN products.

Thus, to further evaluate the existence of hydroxyl species during the reaction, the dosage of CN-75 was increased from 990.1 to 4950.5 nmol. Figure 3a shows the HPLC chromatogram of the chemical species following reaction between 4950.5 nmol CN-75 and 50 mg of Fe_3O_4 at 300 °C for 10 min. Hydroxyl species were identified based on comparison with the mass spectra and retention times of the external standards. As listed in SI Table S2, hydroxyl -TrCN, -TeCN, -PeCN, and -HxCN were detected as degradation products. However, all the different hydroxyl species could not be identified because of limitations associated with the external standards. The existence of a series of naphthol species substituted with different chlorine atoms confirmed that partial oxidation of CN-75 and newly produced PCNs over the as-prepared Fe_3O_4 could occur. It is noted that the hydroxyl-HpCN species could not be detected during the degradation of 4950.5 nmol of CN-75 over 50 mg of as-prepared Fe_3O_4 catalyst following 10 min of degradation. This is most likely because the conversion reactions involving the formed hydroxyl-HpCN species occurred too quickly or at a level below the detection limit of the analytical equipment.

Literature reports have indicated that chlorinated aromatic compounds containing hydroxyl groups can be easily ring-cracked into smaller organic molecules such as formate and acetate.²⁸ In the current study, such ring-cracked products in the reaction between 990.1 nmol CN-75 and 50 mg of Fe_3O_4 at 300 °C were detected by IC. Formic and acetic acids were determined as the main ring-cracked degradation products, as shown in Figure 3b. The amount of acetic acid rapidly increased to a maximum of 116.4 nmol at about 10 min of heating time, followed by a decrease with the heating time. In contrast, the content of formic acid increased steadily as a function of heating time; the maximum content of formic acid was 59.3 nmol at 60 min of heating time. These additional oxidation products indicated that Fe_3O_4 facilitated the ring-cracking oxidation pathway of chlorinated aromatics.

Proposed Degradation Mechanism. Competition between hydrodechlorination and oxidative reactions has often been reported for the degradation of chlorinated benzenes over metal oxides.^{18,30,31} Lin et al.³⁰ reported the concurrent formation of lower chlorinated (dichlorobenzenes and monochlorobenzene) and oxidation (chlorinated phenols) products upon degradation of 1,2,4-trichlorobenzene over Co_3O_4 . Similar reaction routes have been reported for the formation of lower polychlorinated biphenyls and hydroxy compounds during the degradation of CB-209 over Fe_3O_4 .¹⁸

On the basis of intermediate products identification, it is possible to establish the hydrodechlorination pathways of CN-75.^{32,33} In the present degradation reaction system, CN-75

produced a range of hydrodechlorination products from HpCNs to DiCNs via successive elimination of chlorine atoms. As shown in Scheme 1b, the hydrodechlorination pathways varied widely. The major hydrodechlorination pathways were determined by identifying the major intermediates at each stage of the process.³⁴ Thus, based on the amounts obtained for the detected PCN isomers, the predominant hydrodechlorination pathway of CN-75 on the prepared micro/nano Fe₃O₄ likely involved CN-75 → CN-73 → CN-66/67 → CN-52/60 → CN-8/11, as highlighted in Scheme 1b. The degradation of CN-75 to CN-73 proceeded via elimination of a chlorine atom at one of the α-positions in CN-75. A similar dechlorination reaction was also detected toward the formation of CN-66/67, whereby a chlorine atom at one of the α-positions of the two rings in CN-73 is removed. In contrast, CN-52/60 formed upon removal of a chlorine atom at one of the β-positions of the two rings in CN-66/67. However, there is no predominant isomer distinguished among the detected TeCN and TrCN isomers. Thus, it is rather difficult to determine the main hydrodechlorination pathway at these two stages. At the onward step, the hydrodechlorination to CN-11/8 featuring two chlorine atoms locating at two different benzene rings is the predominant pathway. The lower energy principle and steric effect account for the predominant formation of CN73, CN-66/67, CN-52/60, and CN-8/11 relative to that of their corresponding isomers and the small difference in the contents observed among the two classes of detected TeCN and TrCN isomers.

The onset of oxidation reaction is believed to be dependent on the existence of reactive oxygen species.³⁵ Therefore, the availability of oxygen species on micro/nano Fe₃O₄ that may be involved in CN-75 oxidation was investigated by O₂-TPD, as shown in Figure 4a. Generally, the desorption order of oxygen species is as follows: O₂ (adsorbed) — O₂[−] (adsorbed) — O[−] (adsorbed) — O^{2−} (lattice).³⁶ The prepared Fe₃O₄ features four desorption peaks at 130, 390, 490, and 690 °C, respectively. The peak at 130 °C corresponds to physically adsorbed oxygen O₂. The peaks obtained at the higher temperatures, 390 and 490 °C, can be attributed to O₂[−] (adsorbed) and O[−] (adsorbed). The peak at 690 °C (i.e., > 600 °C) can be attributed to O^{2−} (lattice). O^{2−} is often reported to be nucleophilic while O₂[−] and O[−] are determined to be electrophilic.³⁷ The existence of these active oxygen species on Fe₃O₄ catalysts was hypothesized to contribute to the occurrence of oxidation reactions during the degradation of CN-75.³⁵ The contribution of surface active oxygen species to the oxidation reaction has also been reported during the catalytic degradation of 1,2-dichlorobenzene over Ca-doped FeO_x hollow microspheres.³⁸

The molecular electrostatic potential (MESP) of CN-75, as shown in Figure 4b, was calculated by DFT at the B3LYP, 6-311++G (d,p) theory level and used to characterize the chemical reactivity. The red area corresponds to a “negative MESP”, whereby the energy level of the outer electron is higher and the nucleus is weakly attracted to the outer electron. As a result, Cl atoms located in the “negative MESP” region tend to donate electrons. Conversely, the blue area corresponds to a “positive MESP”, whereby the energy level of the outer electron is lower and the nucleus is strongly attracted to the outer electron. Consequently, C atoms located in the “positive MESP” region can accept electrons from other chemical species. In addition to providing a distribution of the energy level of the outer electron, MESP is an indicator of the

Figure 4. (a) O₂-TPD profile of micro/nano Fe₃O₄. (b) Molecular electrostatic potential of CN-75.

electronic density of a molecule. The “negative MESP” region, as indicated in red, corresponds to a low-electron density region, whereas the “positive MESP” area, marked as blue, represents a high-electron density area.

On the basis of the MESP of CN-75 and the oxygen species present on micro/nano Fe₃O₄ in combination with the detected oxidation products, the oxidation-based degradation pathway is proposed, as shown in Scheme 1c. The reaction pathway, involving the formation of naphthol species, is similar to the Mars–van Krevelen mechanism.^{30,39} Similar oxidative degradation routes have been reported for the detection of phenolate compounds during the degradation of HCB over Al₂O₃²⁹ and the degradation of chlorobenzene over iron and titanium oxide catalysts.⁴⁰ First, dissociative adsorption of CN-75 on the central iron cations occurs, followed by the attack of carbon atom potential to accepting the electrons by reactive nucleophilic oxygen O^{2−} species. This results in C–Cl bond cleavage and subsequent Fe–Cl bond formation, and the generation of naphthol species as partial oxidation products.^{28,41} Following consumption of the nearby lattice oxygen O^{2−}, further species can be regenerated from stepwise electron gain by the adsorbed oxygen O₂ on the surface of Fe₃O₄, as follows:³⁶

As observed in Figure 4b, the naphthalene ring is represented by the dark blue area that is indicative of a denser-electron distribution region when compared with other areas of CN-75.

The electrophilic O_2^- and O^- species with strong reactivity can attack the π electron cloud of naphthalene ring with highly dense electron population.³⁶ This will lead to cracking of the naphthalene ring into low-molecular-weight products such as formic and acetic acids.

As described above, in the progress of CN-75 degradation over as-prepared Fe_3O_4 , the hydrodechlorination and oxygen-attacking pathways occurred competitively. This phenomenon may be explained by the presence of different types of active centers on catalysts. However, it is noted that the two competitive reaction pathways, hydrodechlorination and oxidative degradation, are not independent of each other, and newly formed PCN via hydrodechlorination can be also attacked by the reactive oxygen species to form the corresponding chlorinated phenols and small molecules such as formic and acetic acids.

■ ASSOCIATED CONTENT

■ Supporting Information

Figures and tables addressing (1) selected mass-to-charge ratios (m/z) of PCN analysis, (2) hydroxyl-PCN degradation products, (3) change of the degradation efficiency of CN-75 dependent on the reaction temperature and catalyst dosage, (4) residual CB-209 content as a function of heating time, (5) Cl 2p XPS spectra of Fe_3O_4 samples after 10 min of heating time, and (6) FTIR spectra of H_2O adsorption on Fe_3O_4 . This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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