

Thermal degradation of octachloronaphthalene over as-prepared Fe₃O₄ micro/nano
material and its hypothesized mechanism

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Table S1 The selected mass-to-charge ratios (m/z) of PCN analysis.

PCN Congeners	m/z	Type of m/z
DiCN	196	M
	198	M+2
TrCN	230	M
	232	M+2
TeCN	266	M+2
	268	M+4
PeCN	300	M+2
	302	M+4
HxCN	334	M+2
	336	M+4
HpCN	368	M+2
	370	M+4
OCN	402	M+2
	404	M+4

Table S2 Hydroxyl-PCN degradation products.

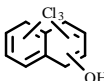
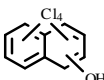
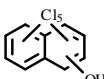
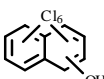
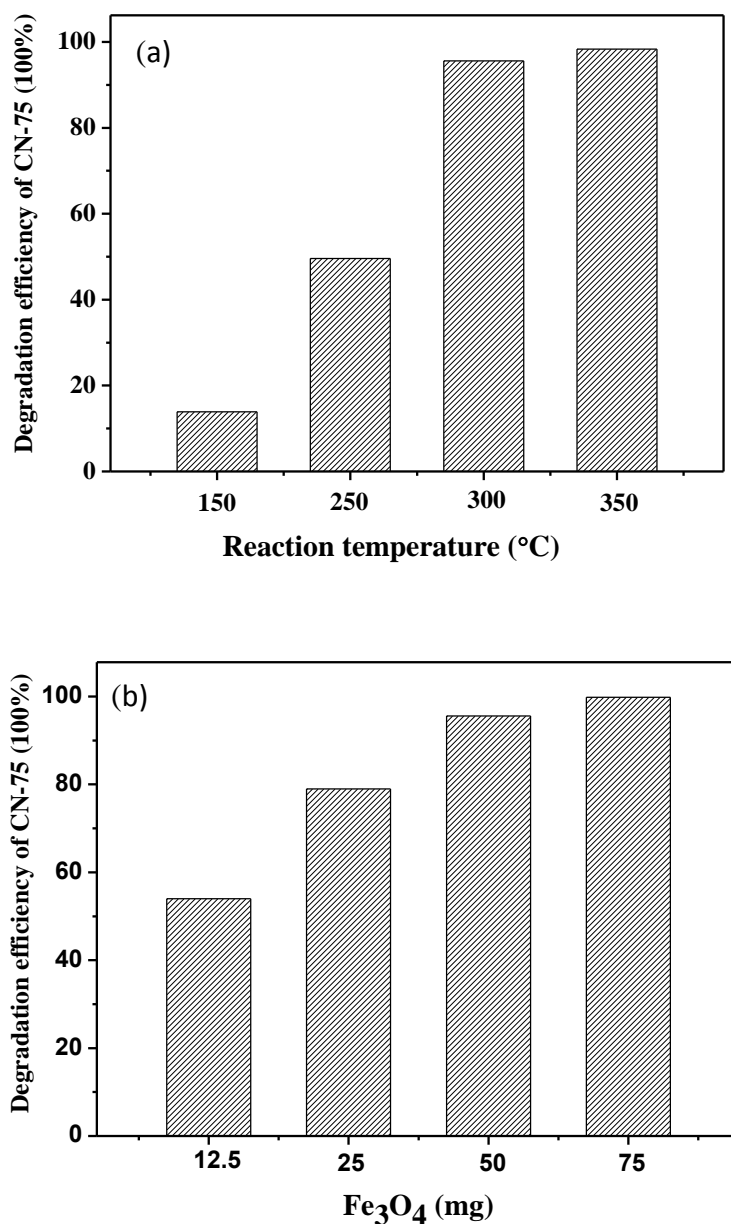
Peak number	Retention time (min)	Compound name	Chemical structure
P1, P2	15.51, 16.08	OH-TrCN	
P3, P4, P5, P7	16.63, 17.06, 17.41, 17.99	OH-TeCN	
P6, P8, P10	17.53, 18.47, 19.86	OH-PeCN	
P9, P11	19.52, 20.29, 20.79	OH-HxCN	

Figure S1 The change of the degradation efficiency of CN-75 dependent on (a) the reaction temperature with the fixed 50 mg of as-prepared Fe_3O_4 and (b) the catalyst dosage with the fixed reaction temperature at 300 °C.



Supplementary explanation for **Figure S1**.

The determination of the optimized degradation conditions has been examined by varying the reaction temperature and catalyst dosage under fixed amount of CN-75 (990.1 nmol) in a short reaction time of 10 min, as shown in Figure S1. The

degradation efficiency of CN-75 on as-prepared Fe₃O₄ was calculated by:

$$\text{Degradation efficiency (\%)} = (1 - R_{\text{CN-75}} / I_{\text{CN-75}}) \times 100$$

where $I_{\text{CN-75}}$ is the initial number of moles of CN-75, and $R_{\text{CN-75}}$ is the remaining number of moles of CN-75 after the reaction. Figure S1 (a) showed the change of the degradation efficiency of CN-75 dependent on the reaction temperature with the fixed 50 mg of as-prepared Fe₃O₄. The degradation efficiency of CN-75 was less than 50% at lower than 250 °C, but suddenly reached up to 95.6% at 300 °C. Afterwards, when the reaction temperature was further raised to 350 °C, the degradation efficiency of CN-75 reached 98.8% just with a small increase step of 3.2%. Figure S4 (b) represented the variation of the degradation efficiency of CN-75 as a function of the catalyst dosage with the reaction temperature fixed at 300 °C. The degradation efficiencies of CN-75 increased from 53.7% to 95.6% when the dosages of as-prepared Fe₃O₄ increased from 12.5 to 50 mg, respectively. However, when the dosages of as-prepared Fe₃O₄ was further raised to be 75 mg, the degradation efficiency of CN-75 reached 99.3% just with a small increase step of 3.7%. Therefore, based on the energy efficiency and reagent consumption, the optimal conditions for the degradation of 990.1 nmol CN-75 is set for the reaction temperature of 300 °C and 50 mg of as-prepared Fe₃O₄.

Figure S2 Residual CB-209 content as a function of heating time. Inset shows the pseudo-first-order kinetic plot of the reaction.

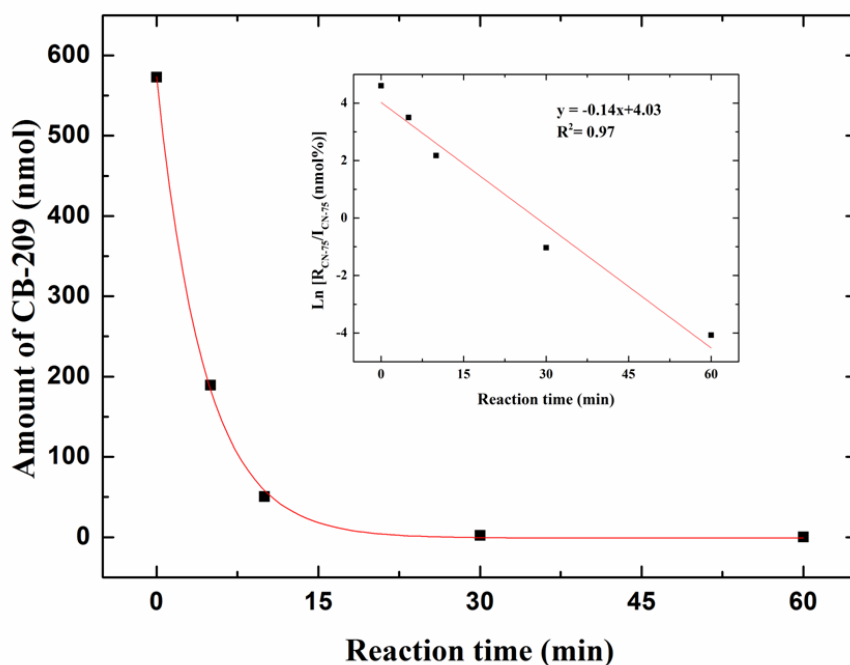
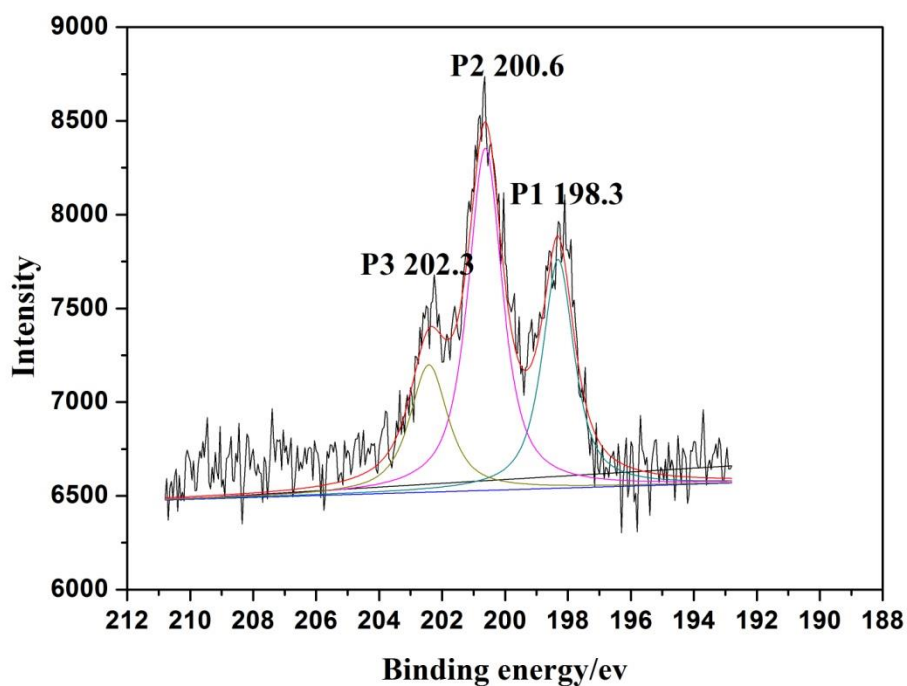


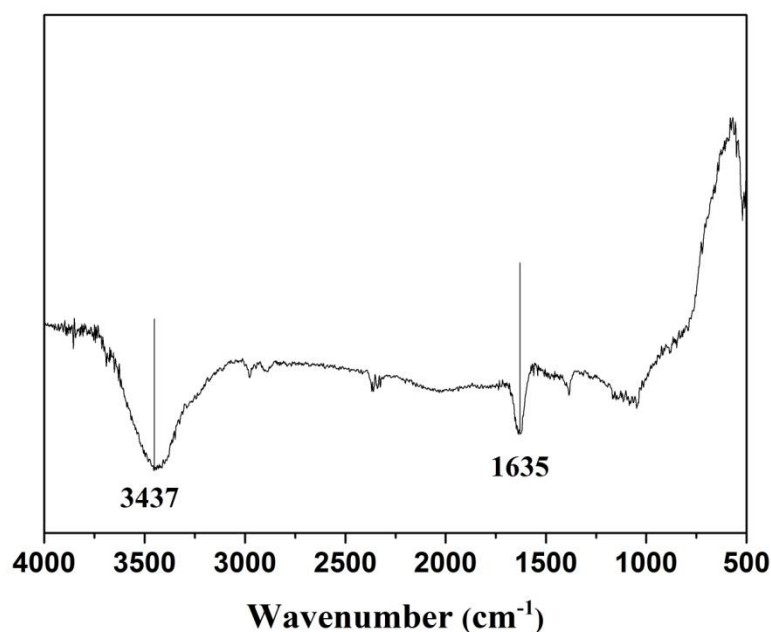
Figure S3 Cl2p XPS spectra of Fe_3O_4 samples after 10 min of heating time.



Supplementary explanation for **Figure S3**.

The association of the free chloride ion with Lewis acid iron ions took place during the degradation of CN-75 over as-prepared micro/nano Fe_3O_4 . The $\text{Cl}2p$ core-level XPS spectra of the catalytic samples after 10 min of heating time are shown in Figure S3. Three peaks (denoted as P1, P2, and P3) were observed. The peak at 198.3 eV corresponds to Cl bonding to Fe^{3+} , with a net charge of -1 , indicating possible formation of FeCl_3 in the degradation of CN-75. This finding is in agreement with the binding energy data for Cl species in FeCl_3 samples¹.

Figure S4 FTIR spectra of H_2O adsorption on Fe_3O_4 .



Supplementary explanation for **Figure S4**.

As can be seen in Figure S4, fourier transform infrared spectrometry (FTIR) absorption measurements were performed to study the water adsorption on the surface of Fe_3O_4 . It is reported that when water from the vapor phase condenses onto a surface of oxide particles phase, the H_2O bending mode at 1595 cm^{-1} of water vapor forms a relatively sharp, well-defined band centered near 1645 cm^{-1} for the vibration

caused by bending mode is less affected²⁻⁴. And in the case of Fe₃O₄, H₂O bending adsorption bands centered at 1635 cm⁻¹. In contrast, the shape of the surface O-H stretching band depends to a much greater extent on the detailed nature of the chemical and physical surface properties⁵. In this study, the coverage of adsorbed water on oxide particles Fe₃O₄, the broad O-H stretching absorption band for Fe₃O₄ is centered at 3437 cm⁻¹.

References:

- (1) Fleutot, S.; Dupin, J. C.; Renaudin, G.; Martinez, H. Intercalation and grafting of benzene derivatives into zinc-aluminum and copper-chromium layered double hydroxide hosts: an XPS monitoring study. *Phys. Chem. Chem. Phys.* **2011**, *13* (39), 17564-17578.
- (2) Luck, W. A. P. Infrared fundamental region. *Struct. Water. Aq. Solut.* **1974**, 221-245.
- (3) Eisenberg, D.; Kauzmann, W. *The Structure and Properties of Water*; Oxford University Press: New York, 1969.
- (4) Pimental, G. C.; McClellan, A. L. *The Hydrogen Bond*; Freeman: San Francisco, CA, 1960.
- (5) Goodman, A. L.; Bernard, E. T.; Grassian, V. H. Spectroscopic Study of Nitric Acid and Water Adsorption on Oxide Particles: Enhanced Nitric Acid Uptake Kinetics in the Presence of Adsorbed Water. *J. Phys. Chem. A.* **2001**, *105*, 6443-6457.