

COUPLING EFFECT OF IRON AND COPPER COMPOUNDS ON THE FORMATION OF UP-POPS DURING IRON ORE SINTERING

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Introduction

Unintentionally produced-persistent organic pollutants (UP-POPs), such as chlorobenzenes (CBzs), polychlorinated biphenyls (PCBs), and polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs), have been found to be concentrated in fly ash during various anthropogenic thermal processes, such as municipal solid waste incineration, iron ore sintering, metallurgical smelting and chlorinated chemicals production. The formation of these POPs is extremely undesirable because of their hypertoxicity and threat to human health and the environment. Metal catalysts are one of the most important factors in the formation of POPs. Vogg and Stieglitz found that the formation of POPs was promoted by fly ash due to the presence of transition metal compounds, and extensive studies have been carried out to investigate the effects of metal catalysts (such as Fe, Mg, Mn, Ni, Cu, Cr, Co and Ti) on the formation of POPs¹. Copper compounds are the most active catalysts for the formation of chlorinated aromatics by promoting the oxidation and chlorination of carbon². Sun et al. reported that the catalytic activity on *de novo* formation was $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \gg \text{Cu}_2\text{O} > \text{Cu} > \text{CuSO}_4 > \text{CuO}$ for CBzs and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O} \gg \text{Cu}_2\text{O} > \text{CuO} > \text{Cu} > \text{CuSO}_4$ for PCBs³. Although copper compounds have proven to be important catalysts for forming chlorinated aromatics, the effect of iron should not be neglected due to its much greater amounts than copper in fly ash. Based on the above analysis, both iron and copper oxides were tested as catalysts for the formation of POPs. However, the synergetic effect of iron and copper compounds on the formation of POPs has rarely been studied. In this study, the influence of Cu and Fe oxides and of their potential synergetic effects on formation of POPs in iron ore sintering was examined. CBzs, PCBs, and PCDD/Fs were selected as target compounds, since they were the most abundant and representative compounds formed by *de novo* synthesis. This work aimed to (i) compare the catalytic activity of CuO, Fe₂O₃ and CuFe₂O₄, (ii) reveal the synergetic effect of Cu and Fe oxides, and (iii) investigate the effect of trace metal oxides (PbO and MnO) on the formation of CBzs, PCBs and PCDD/Fs during iron ore sintering.

Materials and methods

The SFA was prepared based on the actual composition of fly ash in iron ore sintering. Experiments were conducted to study three main areas of interest:

- (1) The synergistic effect of CuO and Fe₂O₃ (11 wt. % in total) on the formation of CBzs, PCBs and PCDD/Fs was investigated by adjusting the Cu/Fe molar ratio to 0:11 (SFAFe), 1:10 (SFA1:10), 4:7 (SFA4:7), 10:1 (SFA10:1) and 11:0 (SFACu).
- (2) Effect of different metal oxide species (CuO, Fe₂O₃ and CuFe₂O₄, 11 wt. % in total) on the formation of CBzs and PCBs was studied.
- (3) Effect of trace metals was investigated by adding 0.5 wt.% of PbO or MnO to the SFA.

The experimental system and procedure has been described previously³. The SFA (5.0 g for each test) was placed in a ceramic cup and heated at 350 °C in a horizontal tubular furnace. Simulated air (100 mL/min, 21% O₂ and 79% N₂) was selected as the carrier gas. The SFA was heated in the furnace for 30 min, and then the carrier gas was held for another 30 min to guarantee all of the products were absorbed. The condensable products were absorbed by ~200 mL of toluene cooled in an ice trap, and the solid matrix was also retained for the POPs analysis.

Each sample was spiked with ¹³C-labeled internal standard. The residue remaining in the fly ash was Soxhlet extracted using ~200 mL of toluene for 20-24 h. Both the adsorption and extraction liquids were pre-treated with a series of condensation and purification methods. The samples were concentrated to a volume of about 2-3 mL, and the concentrated liquids were then purified with a series purification column containing an acid silica gel column, a multi-layer silica gel column and an AC column. The purified liquid was further condensed to 50 µL for analysis.

CBzs and PCBs in the samples were analyzed by the isotope dilution method using a high-resolution gas chromatograph/low-resolution mass spectrometer (HRGC/LRMS) (GCMS-QP2010 Plus, Shimadzu Co., Ltd., Japan). The detailed analytical method can be found in US Environmental Protection Agency (USEPA) Method 8280B. For the PCDD/F analysis, the samples were spiked with ¹³C-labeled injection internal standard (EPA-1613IS). PCDD/Fs were analysed by a high-resolution gas chromatograph/high-resolution mass spectrometer (HRGC/HRMS; Thermo Fisher Scientific, USA) equipped with a DB-5MS fused silica column. The instrumental analytical method was in accordance with US EPA Method 1613A.

The element compositions on the surface of the SFA at room temperature (RT) and 350 °C were recorded using an in situ X-ray photoelectron spectrometer (XPS) (ESCALAB 250Xi; Thermo Fisher Scientific) under a vacuum of 7.1×10^{-5} Pa. The survey scan was performed at a voltage of 15 kV and a current of 10.8 mA. Al K α ($h\nu = 1,486.6$ eV) was selected as the radiation source. The C1s (284.6 eV) and Si2p (103.4 eV) photoelectron peaks were used for charge calibration.

Results and discussion:

1. In situ analysis of the synergistic effect of Fe₂O₃-CuO on the formation of CBzs, PCBs and PCDD/Fs

The effect of Cu/Fe ratio on CBz, PCB and PCDD/F production is presented in **Figure 1**. The production of POPs showed little increase with the presence of only Fe₂O₃ compared with the blank test, indicating that Fe₂O₃ exhibited no strong catalytic effect on the formation of these substances. When the ratio of Fe₂O₃ : CuO increased from 0:11 (Fe₂O₃ only) to 1:10 and then to 4:7 in the SFA, the formation of CBzs, PCBs and PCDD/Fs increased significantly. When the Cu/Fe ratio reached 10:1, the production of POPs exhibited dramatic growth and attained a maximum of 8.0×10^4 ng/g-fly ash for CBzs, 168 ng/g-fly ash for PCBs and 25 ng/g-fly ash for PCDFs. However, a further increase in the Cu/Fe ratio to 11:0 led to a dramatic decrease in these yields to 3.2×10^3 , 47 and 11 ng/g-fly ash, respectively. With a constant metal concentration of 11.0 wt.%, the formation of chlorinated aromatics was mainly catalyzed by CuO in the SFA. However, the substitution of CuO with a small quantity of Fe₂O₃ promoted the catalytic activity of CuO and, subsequently, POPs formation.

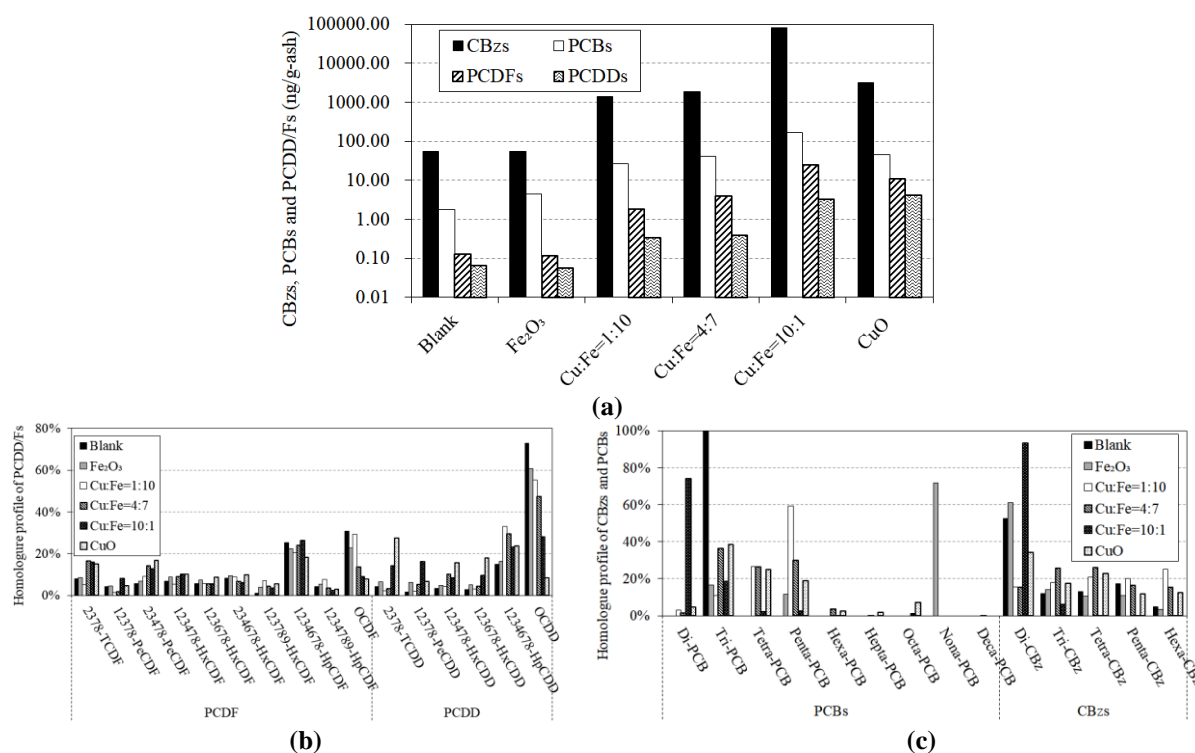


Figure 1. Effect of Cu/Fe ratio on the (a) amount and (b, c) homologue profiles of CBzs, PCBs, PCDD/Fs.

An in situ XPS analysis of SFA with different Cu/Fe ratios (SFAFe, SFA1:10, SFA4:7, SFA10:1 and SFACu) at RT and 350 °C was carried out to demonstrate the synergetic mechanism of CuO and Fe₂O₃. The target elements were O, C, Cl, Cu and Fe, which are the major elements related to the formation of CBzs, PCBs and PCDD/Fs. The spectral deconvolution of Cu2p, Fe2p, Cl2p, O1s and C1s are shown in **Figure 2**.

As shown in **Figure 2(a)**, only SFA1:10, SFA10:1 and SFACu exhibited obvious features in the Cu2p region. For all SFA the Cu2p spectra showed one dominant peak at ~ 933.3 eV, along with the shake-up satellite peaks at 938-946 eV. The presence of satellite peaks and their binding energy indicated the existence of Cu²⁺ on the SFA surface. The Cu2p_{3/2} spectra can be deconvoluted into two peaks for SFA10:1 and SFACu at both temperatures, confirming the coexistence of Cu²⁺ at 934.6 eV and also Cu⁺ or Cu⁰ at 933.4 eV in the fly ash. It is difficult to distinguish between Cu⁺ and Cu⁰ peaks, since the Cu2p core-level binding energies (B.E.) of these two species are very close. Moreover, the XPS spectra of the SFA10:1 at 350 °C also showed an additional minor peak of Cu-Cl at 932.8 eV, indicating the generation of CuCl during the thermal treatment of SFA. By contrast, only the Cu²⁺ peak was observed for SFA1:10. Therefore, the results indicate that the formation of CBzs, PCBs and PCDD/Fs is positively correlated to the Cu-Cl and Cu⁺/Cu⁰ ratio. This can be explained by the fact that (1) more Cu²⁺ was reduced by heating the SFA and, simultaneously, the formation of Cl₂ with a higher chlorination

capability was promoted via the Deacon reaction. Therefore, the oxidation and chlorination of carbon was enhanced, leading to increased formation of CBzs, PCBs and PCDD/Fs; and (2) CuCl, Cu₂O and metallic Cu exhibit higher activity than CuO for CBz, PCB and PCDD/F formation. The Fe2p spectra of SFAFe, SFA1:10 and SFA10:1 are presented in **Figure 2(b)**. Three peaks were resolved at B.E. of ~712.4 eV, ~710.9 eV and ~709.8 eV, respectively corresponding to Fe₂O₃, Fe₃O₄ and FeO, through the deconvolution of Fe2p_{3/2} peaks for SFAFe and SFA1:10. Accordingly, the Fe2p_{1/2} peaks were also deconvoluted into three peaks at ~726.6 eV, 724.6 eV and ~723.1 eV. In addition, the presence of satellite peaks confirmed the presence of Fe³⁺. Therefore, the superior oxidation performance of the CuO/Fe₂O₃ system with a ratio of 10:1 can be attributable to (1) the higher reduced level of Fe species and enhanced carbon oxidation and chlorination; and (2) the strong interaction between Cu and Fe⁴. The Cl2p spectra (**Figure 2c**) were deconvoluted into two peaks, corresponding to Cl bonding with C (Cl-C) at 199.8-200.4 eV and ionic Cl⁻ at 198.2-198.8 eV. **Figure 2(d)** shows that the O1s spectra can be resolved as two peaks, which are assigned to lattice oxygen (O_{lat}) at 529.2-531.6 eV and oxygen-containing adsorbates (O_{ads}) at ~532 eV. The ratio of O_{ads} has proved to be the dominant active oxygen species for the oxidation reactions⁵, which was considered to be crucial for the formation of CBzs, PCBs and PCDD/Fs. Deconvolution of the C1s spectra was also performed, as shown in **Figure 2(e)**, since carbon is also an essential element for POPs formation. Five peaks were resolved, which were assigned as C-C groups at ~284.5 eV, C-H groups at ~285.5 eV, C-Cl groups at ~288.5 eV, C=O groups at ~293.0 eV, and O-C=O groups at ~295.5 eV. In addition, SFA10:1 and SFACu exhibited much higher ratios of C=O, O-C=O and C-Cl compared with the SFA1:10 and SFAFe, demonstrating higher levels of carbon oxidation and chlorination.

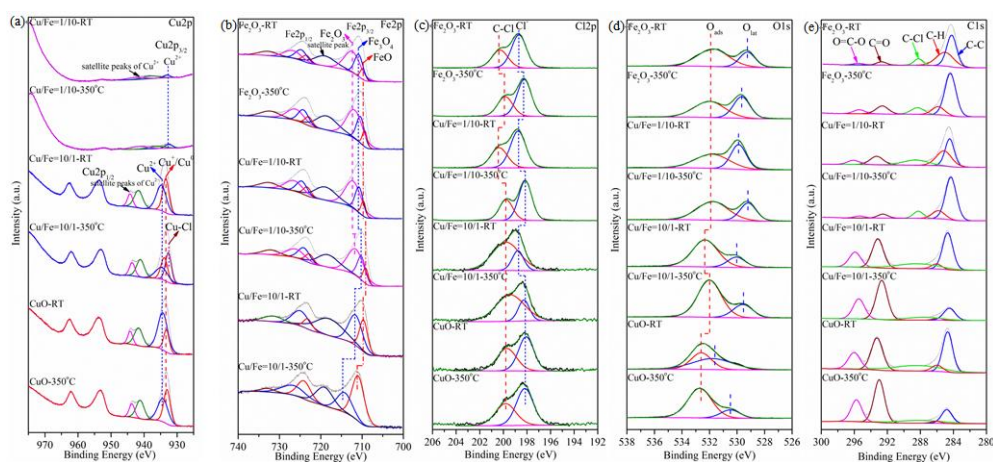


Figure 2. In situ XPS spectra of (a) Cu2p, (b) Fe2p, (c) Cl2p, (d) O1s and (e) C1s for SFA at room temperature and 350 °C.

2. Effect of copper and iron species on the formation of CBzs and PCBs

Various species of metal oxides show different effects on the formation of chlorinated aromatics. The production of CBzs and PCBs during the annealing of SFA with different kinds of Cu and Fe oxides (together, 11 wt. %) is shown in **Figure 3**. CBzs and PCBs showed yields of 56 and 1.8 ng/g-fly ash in the blank test, respectively. The addition of Fe₂O₃ had no obvious influence: 54 ng/g-fly ash for CBzs and 4.5 ng/g-fly ash for PCBs. However, the yield of CBzs and PCBs increased sharply to 3,200 and 47 ng/g-fly ash by adding only CuO to the SFA, about 57- and 26-fold increases compared to the blank test.

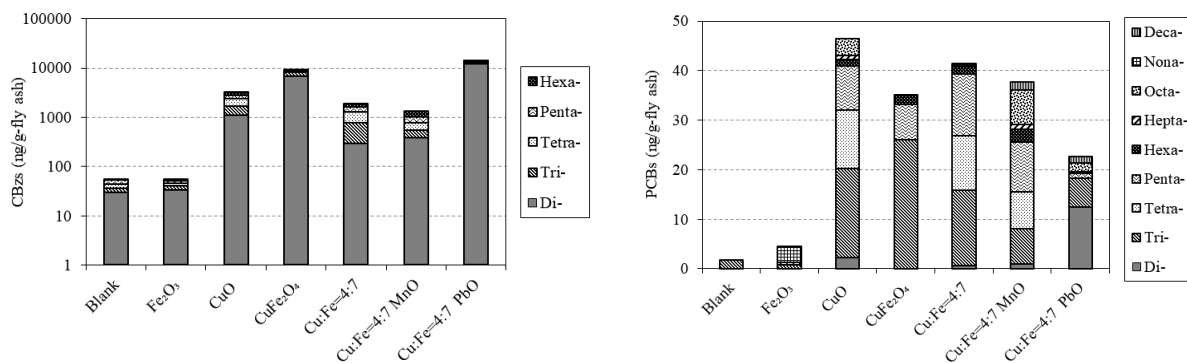


Figure 3. Effect of metal species on the formation of CBzs and PCBs.

3. Effect of other trace metal oxides on the formation of CBzs and PCBs

There are a range of metal elements in trace amounts in fly ash, such as Al, Mg, Pb, Cr, Cu, Mn, that might also influence the formation of chlorinated aromatics during iron ore sintering. In this study, 0.5 wt.% of PbO and MnO was added to the SFA to investigate the effect of trace metals on the formation of CBzs and PCBs (Figure 3). The production of both CBzs and PCBs decreased slightly from 1.9×10^3 ng/g-fly ash to 1.4×10^3 ng/g-fly ash for CBzs, and from 41 ng/g-fly ash to 38 ng/g-fly ash for PCBs after adding MnO to the SFA. However, the yield of CBzs increased sharply to 13,000 ng/g-fly ash, while the generated amount of PCBs showed a decrease to 23 ng/g-fly ash with PbO addition. Fujimori et al. prepared SFA with KCl, AC, PbO and SiO₂, and found that PbO had a suppressing effect on the formation of chlorinated aromatics, since PbO inhibits the oxidation of the carbon matrix and blocks the formation of CBzs⁶. However, the formation of CBzs was obviously promoted in our investigation. PbO might have a synergetic effect with CuO and/or Fe₂O₃ thereby promoting the formation of chlorinated aromatics.

4. Mechanism analysis of CBz, PCB and PCDD/F formation

The chlorinated aromatics formed in the SFA at 350 °C were mainly generated by *de novo* synthesis from carbon in the presence of chlorides and metal catalysts⁷. The formation mechanism of CBzs, PCBs and PCDD/Fs was deduced based on the *in situ* XPS analysis of the SFA and product analysis during thermal treatment of SFA10:1 (Figure 4). CuO and Fe₂O₃ were the dominant catalysts for CBz, PCB and PCDD/F formation in SFA. On one hand, they react with Cl⁻ to form CuCl₂ and FeCl₃, which provides further potential catalysts for *de novo* synthesis, since they serve as both catalysts and chlorine sources. The Deacon reaction was promoted in the presence of CuCl₂ and FeCl₃, and consequently more Cl₂ was produced for the chlorination of the native carbon in the SFA⁸. On the other hand, CuO and Fe₂O₃ could be reduced to Cu/Cu₂O and FeO/Fe₃O₄ in the presence of native carbon in SFA. Therefore, the oxidation and chlorination of native carbon was promoted. Native carbon in the SFA could be chlorinated and oxidized to form short-chain chlorinated hydrocarbons, such as CH₂Cl₂ and CHCl₃, in the presence of Cu/Fe catalysts and a chlorine source. With increasing carbon chain length, chlorinated aromatic CBzs and PCBs were formed. Finally, PCDDs and PCDFs were synthesized by hydroxyl (OH) attack on CBzs and PCBs, followed by HCl elimination.

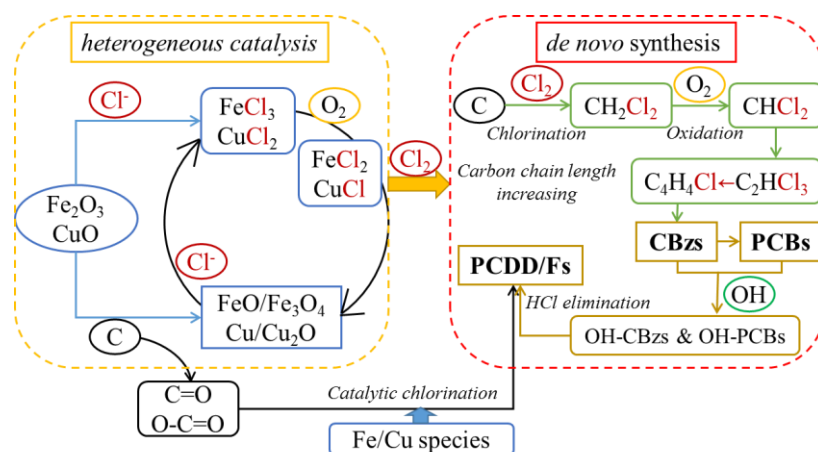


Figure 4. Formation mechanism of CBzs, PCBs and PCDD/Fs.

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