



Synergy of iron and copper oxides in the catalytic formation of PCDD/Fs from 2-monochlorophenol

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HIGHLIGHTS

- Iron and copper often cohabit on particulate matter in combustion systems.
- Under pyrolysis, synergy of CuO and Fe₂O₃ produced almost 5-fold yields of PCDD/F compared to single CuO or Fe₂O₃.
- CuO influences the PCDD/F congener profile while Fe₂O₃ affects the PCDD/F yields.

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ABSTRACT

Transition metal oxides present in waste incineration systems have the ability to catalyze the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) through surface reactions involving organic dioxin precursors. However, studies have concentrated on the catalytic effects of individual transition metal oxides, while the complex elemental composition of fly ash introduces the possibility of synergistic or inhibiting effects between multiple, catalytically active components. In this study, we have tested fly ash surrogates containing different ratios (by weight) of iron (III) oxide and copper (II) oxide. Such Fe₂O₃/CuO mixed-oxide surrogates (in the Fe:Cu ratio of 3.5, 0.9 and 0.2) were used to study the cooperative effects between two transition metals that are present in high concentrations in most combustion systems and are known to individually catalyze the formation of PCDD/Fs. The presence of both iron and copper oxides increased the oxidative power of the fly ash surrogates in oxygen rich conditions and led to extremely high PCDD/F yields under pyrolytic conditions (up to >5% yield) from 2-monochlorophenol precursor. PCDD/F congener profiles from the mixed oxide samples are similar to results obtained from only CuO, however the total PCDD/F yield increases with increasing Fe₂O₃ content. Careful analysis of the reaction products and changes to the oxidation states of active metals indicate the CuO surface sites are centers for reaction while the Fe₂O₃ is affecting the bonds in CuO and increasing the ability of copper centers to form surface-bound radicals that are precursors to PCDD/Fs.

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1. Introduction

The vast majority of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) in the environment originate from anthropogenic sources (Aries et al., 2006; Pitea et al., 2008; Addink and Altwicker, 2004; Gullett et al., 2000). The primary origin of PCDD/Fs can be traced to the condensation of halogenated aromatics over catalytic surfaces, particularly metal-rich fly ash, in the cool zone of

incineration systems.

PCDD/Fs can be formed by way of three primary pathways: de novo formation from carbonaceous deposits assisted by metal chlorides, gas-phase formation involving organic precursors, and surface-mediated reactions between gas-phase organic precursors and metal oxides. The latter process occurs in the cool zone of an incinerator, where the temperature falls between 200 and 600 °C (Hatanaka et al., 2002; Hell et al., 2001; Milligan and Altwicker, 1995; Ryu et al., 2005). These surface-mediated reactions are responsible for up to 70% of all combustion-generated PCDD/Fs (Altwicker, 1991; Lomnicki and Dellinger, 2003).

A mechanism was proposed and validated, in which transition metal oxides present on the effluent particulates from high temperature zones form and stabilize surface-bound organic radicals

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(Dellinger et al., 2007; Lomnicki et al., 2008; Khachatryan et al., 2011). This mechanism yields pollutant-particle systems that have been termed environmentally persistent free radicals (EPFRs). EPFRs are very stable and have lifetimes of hours or days under ambient conditions. EPFRs associated with a metal oxide substrate are precursors to PCDD/Fs as they react to form dioxins by following two alternative mechanisms: (1) the Langmuir-Hinshelwood mechanism, in which two adjacent surface-bound EPFRs undergo surface condensation or (2) the Eley-Rideal mechanism in which a surface-bound EPFR reacts with a gas-phase precursor molecule (Lomnicki and Dellinger, 2002, 2003; Addink and Olie, 1995; Lippert et al., 1991).

To fully understand the mechanism and yields of PCDD/Fs on the surface of fly ashes, model fly ash surrogates have been investigated. Surrogates containing either iron or copper oxide impregnated onto a silica matrix have been studied extensively and these transition metal oxides were found to contribute to PCDD/F formation (Lomnicki and Dellinger, 2003; Nganai et al., 2008, 2010; Gullett et al., 1990; Olie et al., 1998; Ryan and Altwicker, 2004). The initial focus on iron and copper oxide was due to their relatively high concentrations in fly ashes and their known redox properties (Ryan and Altwicker, 2004; Cains et al., 1997; Seames, 2003; Takasuga et al., 2000). It was found that while copper tends to be more catalytically active than iron, iron is typically present in fly ash in much higher concentrations than copper. Both Fe_2O_3 and CuO have been shown to form phenoxyl-type EPFRs as intermediates in the formation of PCDD/Fs (Alderman et al., 2005; Kiruri et al., 2014). These fly ash surrogates were appropriate tools to formulate a reaction mechanism as they are uniform in their composition and their chemical makeup is easily reproducible, as opposed to fly ash, whose metal content varies significantly depending on its source. Mixed oxide catalysis between iron and copper has displayed synergistic effects in a variety of applications (Siriwardane et al., 2013; Zhu et al., 2010; Deng et al., 2004; He et al., 2013; Schuchardt et al., 1995), however, it has never been tested in the surface-mediated precursor pathway of PCDD/F formation. Recent study by Liao et al. found no synergy of copper chloride and iron oxide in de novo PCDD/F formation (Liao et al., 2016). The use of primarily single-oxide surrogates in PCDD/F formation studies discounts the presence of synergistic effects between various components in real world fly ash. To study the cooperative effects of mixed oxide catalysts on PCDD/F formation could lead to our better understanding of the roles that various metals play for the formation of PCDD/F in real fly ash.

This work focused on Fe_2O_3 and CuO co-impregnated onto silica powder to simulate the structure of combustion-generated fly ash and analyze the potential synergy between two metals in PCDD/F formation. Previous research involved single oxide fly ash surrogates containing 5% (w/w) of either Fe_2O_3 or CuO (Lomnicki and Dellinger, 2002; Nganai et al., 2008). For the sake of comparison, three mixed oxide surrogates were made with a total metal oxide content of 5% (w/w) and varying ratios of co-impregnated Fe_2O_3 and CuO . The three mixed oxide surrogates contained Fe_2O_3 : CuO ratios (by weight) of 4, 1, and 0.25, which corresponds to Fe:Cu ratios (by weight) of 3.5, 0.9, and 0.2, respectively. The molar ratios of Fe:Cu are 4, 1 and 0.25 respectively.

2. Experimental

2.1. Fly ash surrogate synthesis

Incipient wetness method was used to prepare the mixed oxide fly ash surrogates. An aqueous solution of copper (II) nitrate and iron (III) nitrate was introduced into silica gel powder (Aldrich, grade 923, 100–200 mesh size) in the appropriate amount for

incipient wetness to occur. Various ratios of $\text{Fe}^{3+}/\text{Cu}^{2+}$ were used to produce 1% $\text{Fe}_2\text{O}_3/4\%$ CuO , 2.5% $\text{Fe}_2\text{O}_3/2.5\%$ CuO and 4% $\text{Fe}_2\text{O}_3/1\%$ CuO on silica (by weight). The samples were rotated on Rotavap for 24 h at room temperature, dried 12 h at 120 °C, and calcined in air for 7 h at 450 °C.

2.2. PCDD/F formation reaction

The System for Thermal Diagnostic Studies (STDS) was used to investigate the surface-mediated reactions of 2-monochlorophenol (2-MCP), which is a known PCDD/F precursor (Milligan and Altwicker, 1995), over a $\text{Fe}_2\text{O}_3/\text{CuO}/\text{Silica}$ surface. Detailed description of the system can be found in ref (Rubey and Grant, 1988). Briefly, a thermal reactor (4.0 mm i.d. fused silica reactor) is set in a high-temperature furnace housed within an isothermal oven that facilitates precise temperature control over all transfer lines to and from the reactor (180 °C). A GC-MS system is interfaced in-line with the thermal reactor for analysis of combustion products.

A small amount of mixed oxide catalyst (40 mg) was placed between quartz wool plugs in the thermal reactor. To avoid condensation of the reaction products, all transfer lines were maintained at a constant temperature of 180 °C. Prior to each experiment, the mixed oxide catalyst was oxidized in situ at 450 °C for 1 h under an air flow of 5 cc/min to oxidize the surface of the fly ash surrogate. 2-MCP (Aldrich, $\geq 99\%$) was introduced into the flow stream by a digital syringe pump (KD Scientific, model-100) through a GC injection port maintained at 185 °C. Two carrier gases were used: air ($\sim 21\%$ O_2) for oxidation experiments and pure nitrogen for pyrolytic experiments. The rate of injection was set to maintain a constant gas phase concentration of 50 ppm of 2-MCP with a residence time of 0.2 s. Reaction temperatures range from 200 to 550 °C. In between runs the transfer lines were baked out at 210 °C in air flow and blank run was performed to check for trace residue of products. The reaction time at each temperature is 75 min and at the same time products were collected. For the studies at each temperature, a fresh batch of fly ash was used.

The products from the reaction were analyzed using an in-line Varian CP-3800 GC system. A 30 m, 0.25 mm i.d., 0.25 μm film thickness column was used (HP-5MS) for product separation. The temperature was held at -60 °C for the reaction period followed by a ramp from -60 to 300 at a rate of 10 °C min^{-1} . Detection and quantification of the products were obtained on a Varian Saturn 2000 mass spectrometer, which was operated in full-scan mode from 15 to 450 amu for the duration of the GC run. Identification of the eluting compounds was done based on the mass spectrum of the eluent and the retention time comparison to a standard. The amount of the formed products was calculated based on the calibration curves using respective standard solutions. The following standards were used for the calibration of PCDD/F products based on the peak area in the chromatogram: dibenzofuran (DF), 1-chlorodibenzo-*p*-dioxin (MCDD), 4-chlorodibenzofuran (MCDF), 2,7-/2,8-dichlorodibenzo-*p*-dioxin (DCDD). For the selected PCDD/F compounds, calibration was based on the MS response to the similar compounds: The calibration curve for DCDD was used to calculate DCDF, trichlorodibenzo-*p*-dioxin (TriCDD) and tetrachlorodibenzo-*p*-dioxin (TetraCDD). The yields of the products were calculated by use of the expression:

$$Y = \frac{[\text{PROD}] \times A}{[2 - \text{MCP}]_0} \times 100\% \quad (1)$$

where [PROD] is the concentration of specific product formed (in moles), $[2 - \text{MCP}]_0$ is the initial concentration of 2-MCP (in moles), and A is the molar stoichiometric factor. Quantitative standards

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