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Ferric Oxide Mediated Formation of PCDD/Fs from 2-Monochlorophenol

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Abstract

The copper oxide, surface-mediated formation of polychlorinated dibenzop-dioxins and dibenzofurans (PCDD/F) from precursors such as chlorinated phenols is considered to be a major source of PCDD/F emissions from combustion sources. In spite of being present at 2–50x higher concentrations than copper oxide, virtually no studies of the iron oxide-mediated formation of PCDD/F have been reported in the literature. We have performed packed bed, flow reactor studies of the reaction of 50 ppm gas phase 2-monochlorophenol (2-MCP) over a surface of 5% iron oxide on silica over a temperature range of 200–500 °C. Dibenzo-p-dioxin (DD), 1-monochlorodibenzo-p-dioxin (1-MCDD), 4,6-dichlorodibenzofuran (4,6-DCDF), and dibenzofuran (DF) were formed in maximum yields of 0.1, 0.2, 0.3, and 0.4 %, respectively. The yield of PCDD/F over iron oxide peaked at temperatures 50–100 °C higher in temperature than over copper oxide. The maximum yields of DD, 1-MCDD and 4,6-DCDF were 2x and 5x higher over iron oxide, respectively, than over copper oxide, while DF was not observed at all for copper oxide. The resulting PCDD/PCDF ratio was 0.39 versus 1.2 observed for iron oxide and copper oxide, respectively, which is in agreement with PCDD to PCDF ratios in full-scale combustors that are typically <<1. The combination of 2–50x higher concentrations of iron oxide than copper oxide in most full-scale combustors and 2.5x higher yields of PCDD/F observed in the laboratory, suggest that iron oxide may contribute as much as 5–125x more than copper oxide to the emissions of PCDD/F from full-scale combustors.

INTRODUCTION

Combustion is the dominant source of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) in the environment (1–5). It is believed that ~70 % of PCDD/F emissions are due to transition metal-mediated, surface reactions in the post-flame, cool zone at temperatures between 300 and 500 °C (6–8).

Previous research has focused on copper oxide mediated formation from elemental carbon (“*de novo*” pathway) (9–11) and chlorinated phenols (“precursor” pathway) (12–14). The focus on copper oxide is likely the result of its significant concentration in municipal waste incinerators where PCDD/F were first discovered in combustion systems and the well-known redox activity of copper oxides (15–17). However, iron oxide, which is also redox active, is almost always the highest concentration transition metal in combustion systems (18–20) and one might expect iron to mediate or catalyze the formation of PCDD/Fs. Probably because iron is a very effective oxidizing agent, research on the role of iron has focused on destruction rather than formation of PCDD/F (21–25).

Our recent work on the mechanism of chemisorption of phenols and other substituted aromatic species on transition metal surfaces suggests that reactions involving iron oxide

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have the potential to be a significant source of PCDD/F emissions(26). Specifically, substituted aromatic species chemisorb to metal oxide or hydroxide surface sites to form a phenoxy-type, persistent free radical (PFR) (27,28). These surface-associated phenoxy radicals may then react with each other to form PCDD/F and other products (29,30).

Consequently, we have performed a study of the formation of PCDD/F and other reaction products from a 2-monochlorophenol (2-MCP) precursor over a surface of iron oxide supported on a silica substrate. This study was performed using a temperature-controlled, packed bed, flow-reactor interfaced to an in-line GC-MS for product analysis using conditions identical to those used in our previously reported studies of PCDD/F formation from 2-MCP over a copper oxide/silica surface (31). Although a much wider range of reaction environments and compositions of fly-ash exist in full-scale combustors, the conditions in this study are comparable to those used in the published literature and allow direct comparison of the role of iron oxide to copper oxide on the formation of PCDD/F under specific, well-defined combustion conditions.

EXPERIMENTAL

Surface-mediated reactions of 2-chlorophenol over $\text{Fe}_2\text{O}_3/\text{SiO}_2$ were studied using the System of Thermal Diagnostic Studies (STDS) which is described in detail elsewhere (32). Briefly, the system is composed of a thermal reactor located in a high-temperature furnace housed within a GC oven that facilitates precise temperature control as well as reproducible sample introduction. A computer-interfaced control module is used to set and monitor all experimental parameters. A GC-MS system is interfaced in-line with the thermal reactor for chemical analysis of the reactor effluent.

We and others have reported multiple studies of the gas-phase reactions of 2-MCP and other chlorinated phenols. These studies clearly demonstrate that 2-MCP does not decompose in the gas-phase until above 500 °C and gas-phase reactions are unimportant over the 200–500 °C range of this study (33).

Catalyst Preparation

The iron oxide catalyst was prepared to allow direct comparison with results for copper oxide previously published in the literature (31,34–36). Accordingly, it was prepared using the same method, materials, and metal oxide concentration. Model fly-ashes were used for several reasons.

It is very difficult to discern the effect of a specific metal within the complex mixture contained in a typical fly-ash generated in a combustion system, and it is impossible to compare the results of those to a pure iron or copper oxide. In addition, the combustion-generated fly-ashes typically used in these studies are collected at the end of the combustion system after they have been exposed to multiple organics, and their activities might be altered compared to that of fresh, in-situ generated fly-ashes. Finally, these fly-ashes are only representative of the specific system being studied under the operating conditions at the time of collection. Thus to compare their relative reactivities, we chose to use model systems of pure iron oxide/silica and copper oxide/silica.

Although sub-oxides of some metals have been reported, the principal oxide of copper or iron in a combustor is expected to be the highest oxidation state. This is due to the high-temperature and oxygen rich environment in the flame in which the metals are vaporized or entrained. Consequently, our samples of $\text{Fe}_2(\text{III})\text{O}_3$ and $\text{Cu}(\text{II})\text{O}$ represent the majority of both metals in most combustion systems (37).

The method of incipient wetness was used to prepare the catalytic material that serves as a surrogate for combustion-generated, iron-rich fly-ash. A water solution of iron (III) nitrate (Aldrich) was used to prepare a catalyst of 5% iron (III) oxide on silica. Silica gel powder (Aldrich, grade 923 100–200 mesh) was introduced into the solution of iron (III) nitrate in the amount for incipient wetness to occur. The sample was allowed to age for 24 hr at room temperature and dried at 120 °C for 12 hr before calcination in air for 5 hrs at 450 °C. The sample was then ground and sieved to a mesh size of 100–120 which corresponds to a particle size of 125–150 microns.

Reaction Conditions

50 mg of the resulting 5% iron(III) oxide/silica catalyst was placed between quartz wool plugs in a 0.3 cm i.d. fused silica reactor in the STDS. To avoid condensation of the reaction products, all transfer lines were maintained at a constant temperature of 180 °C. Prior to each experiment, the catalytic material was oxidized *in situ* at 450 °C for 1 hr at an air flow-rate of 5 cc/min to activate the surface. The reactant, 2-monochlorophenol (2-MCP) (Aldrich) was introduced into the flow stream using a digital syringe pump (KD Scientific, Model-100) through a vaporizer maintained at 180 °C. Nitrogen was used as a carrier gas, and the rate of injection was selected to maintain a constant concentration of 50 ppm of 2-MCP for temperatures ranging from 200 to 550 °C. The overall flow rate of the reaction gas stream was maintained at 5 cc/min. All data are for a precursor reaction time or 1 hr over the catalytic bed with concomitant collection of the products on the head of capillary column.

The precursor concentration is higher than usually observed in stack measurements at full-scale facilities (38). However, due to low reaction yields, it is generally accepted by the scientific community for the laboratory studies of PCDD/F formation (39–41). In fact, the use of the STDS in our studies allows us to lower the precursor concentration to below that typically reported in the literature.

Product Analysis

The products of reaction were analyzed using an in-line Agilent 6890 GCMSD system. For product separation, a 30 m, 0.25 mm i.d., 0.25 micron film thickness column was used (Restek RTS 5MX) with a temperature hold at –60 °C for the reaction period followed by a temperature programmed ramp from –60 to 300 at 10 °C/min. Detection and quantification of the products were obtained on an Agilent 5973 mass spectrometer, which was operated in the full-scan mode from 15–350 amu for the duration of the GC run.

The yields of the products were calculated using the expression: $\text{Yield} = ([\text{product}] \cdot A / [2\text{-MCP}]_0) \times 100$, where; $[\text{product}]$ is the concentration of specific product formed (in moles) and $[2\text{-MCP}]_0$ is the initial concentration of 2-MCP (in moles) injected into the reactor and A is the molar stoichiometric factor (two in this case, since one PCDD/F molecule is formed from two 2-MCP molecules). Each data point reflects an average result of 3 experimental runs. All data were plotted using the Igor Pro 6.0 (Wave Metrics Inc.) software. The yield curves presented in the graphs are the result of mathematical fits generated by Igor. Quantitative standards were used to calibrate the MS response for all products.

RESULTS AND DISCUSSION

The temperature dependence of the surface-mediated pyrolysis of 2-MCP over $\text{Fe}_2\text{O}_3/\text{SiO}_2$, and the yield of major organic products are presented in Figures 1–3 (and Table 1 in Supporting Materials). At the lowest temperature studied (200 °C), 90% of the 2-MCP undergoes surface mediated decomposition (cf. Figure 1). Above 350 °C the reaction rapidly accelerates resulting in almost complete degradation of 2-MCP by 500 °C.

Apart from the lower molecular weight products, not analyzed quantitatively in this study (CO, CO₂, C₂ and C₃ organics), the main products were chlorophenols and chlorobenzenes. The yields of chlorophenols were in general higher than that of chlorobenzenes and included: 2,3- and 2,6- dichlorophenol (2,3-DCP + 2,6-DCP) – 0.4% maximum yield at 350 °C; 2,3,6 and 2,4,6-trichlorophenol (2,3,6-DCP + 2,4,6-DCP) – 7.0 % maximum yield at 250 °C; and phenol – 1.3% maximum yield at 350 °C (cf. Figure 1).

Among chlorobenzene products, the yields of hexachlorobenzene (HCBz) – 0.9% maximum yield at 500°C; and tetrachlorobenzenes (1,2,3,4 TeCBz + 1,2,3,5 TeCBz) – 1.4% maximum yield at 500 °C were the highest (cf. Figure 2). Other chlorobenzenes detected were: monochlorobenzene (MCBz) – < 0.1 % yield at 250 °C; 1,2,4 and 1,2,3 trichlorobenzene (1,2,4-TriCBz + 1,2,3-TriCBz) – 0.3% maximum yield at 450 °C; and pentachlorobenzene (PCBz) – < 0.1% yield at 350 °C. Benzene (Bz) was formed with a constant yield of ~0.1% from 300–550 °C (cf. Figure 2).

Each of these products were formed as low as 250 °C, while 1,2-DCBz and Bz were detected even at 200 °C. However, 1,2-DCBz was present in the 2-MCP reagent as a minor contaminant (0.3% by mole), and its concentration declined with increasing temperature. Thus, its presence at this temperature should be considered to be un-destructed reactant. This is not the case for benzene, whose measured concentration increased by two orders of magnitude with increasing temperature, indicating formation of benzene as a reaction product (cf. Figure 2).

At 200–250 °C, significant yields PCDD/F were observed, comparable with the yields of chlorinated benzenes (cf. Figure 3). Dibenzo-*p*-dioxin (DD), 1-monochlorodibenzo-*p*-dioxin (1-MCDD), 4,6-dichlorodibenzofuran (4,6-DCDF), and dibenzofuran (DF) were all detected as the products of 2-MCP pyrolysis over Fe₂O₃/Silica surface. The maximum yields of 4,6-DCDF and 1-MCDD were 0.3 %, and 0.1 % at 250 °C and 350 °C, respectively, while DD and DF exhibited maximum yields of 0.2 and 0.4% at 400 °C and 450 °C, respectively. Chloronaphthalene, naphthalene and biphenyl were also detected in trace quantities, their yields increasing with increasing temperature to a maximum at 450–500 °C (cf. Table 1).

Adsorption, Chlorination and Destructive Desorption on Fe₂O₃/Silica

In our previously reported studies, we have demonstrated using FTIR spectroscopy that chlorinated phenols chemisorb to the surface of copper oxide by initial hydrogen-bonding of the copper oxide terminal hydroxide groups and the phenol hydroxide substituents (28). Subsequent elimination of water and HCl above 150 °C leads to the formation of a chemisorbed phenoxide. (cf. Scheme 1). Hydroxyl groups are present on almost every terminal plane of metal oxides as a completion of unsatisfied charges and valences of metal ions at terminal positions (26,31,42). Iron oxide is no different than other metal oxides, and its interaction with gas-phase 2-MCP is expected to be similar to that of copper oxide.

Based on previous experimental results, two pathways of chemisorption have been identified for chlorophenols: i) elimination of H₂O (upper path in scheme 1) and ii) elimination of both H₂O and HCl (lower path in Scheme 1) (43).

We have previously demonstrated using electron paramagnetic resonance spectroscopy (EPR) (43) and X-ray Absorption Near Edge Spectroscopy (XANES) (42) that in the case of CuO, the resulting chemisorbed species, **I** and **IV**, are subject to electron transfer between the adsorbed molecule and metal center (Cu⁺² for CuO) resulting in the formation of persistent free radicals, species **II**, **III** and **V** that are associated with the concomitantly formed reduced metal centers (Cu⁺¹ for CuO) (43,44). We have recently performed EPR

analyses of samples of Fe₂O₃/silica dosed with 2-MCP and confirmed behavior similar to that on CuO with the formation of persistent free radicals as low as 150 °C.

The chemisorbed chlorophenoxy species are strongly bound to the surface and can undergo multiple chlorination reactions. This is reflected in the formation of polychlorinated phenols and polychlorinated benzenes (cf. Figs. 1 & 2) as was also observed for the CuO/silica system that we have previously studied (31). The mechanism of the chlorination reaction of adsorbed species has never been experimentally demonstrated. We and others have suggested that the most likely mechanism is the formation of surface hypochlorite species that are very potent chlorinating agents (26,31,42).

Significant quantities of dechlorination products, benzene and phenol, were also formed. Their formation is probably related to the stronger oxidative properties of Fe₂O₃/silica versus CuO/silica.

In fact, at 200 °C, 40% more 2-MCP reacted over Fe₂O₃/silica (90% at 200 °C) than over CuO (50% at 200 °C), though the rapid destruction of 2-MCP was not initiated until 350 °C (cf. Fig. 1). These observations suggest strong adsorption and retention of the adsorbed 2-MCP on the surface of Fe₂O₃/silica.

Gas-phase chlorinated phenols are formed via the scission of a weak or partial metal-oxygen bond of intermediate **II** in Scheme 1 to form a free chlorophenoxy radical that is converted to a chlorinated phenol by scavenging a hydrogen atom. The formation of gas-phase chlorinated benzenes can result from scission of the carbon-oxygen bond to form a free chlorophenyl radical that scavenges a hydrogen to form chlorobenzenes. The scission of the seemingly stronger carbon-oxygen bond seems improbable; nevertheless, it has been experimentally observed for phenols (45). However, the higher yields of chlorinated phenols indicates that scission of the weaker, partial metal-oxygen bond is preferred over the scission of the carbon-oxygen bond needed to form chlorinated benzenes.

Formation of un-chlorinated phenol or benzene from 2-MCP requires removal of a chlorine substituent. Such a reaction occurs when adsorption proceeds through the lower path of Scheme 1. The scission of one carbon-oxygen bond and one metal-oxygen bond in intermediate **V** followed by scavenging of hydrogen atoms forms phenol. The scission of two carbon-oxygen bonds of **V** followed by scavenging of two hydrogen atoms results in the formation of benzene. The higher yield of phenol again suggests that the cleavage of the partial, weaker metal-oxygen bond is preferred. Surface-associated or gas-phase by-products of the decomposition of 2-MCP, such as carbonyls and olefins, provide the source of hydrogen atoms for scavenging.

Surface-Mediated PCDD/F Formation

The formation of DD, 2-MCDD and 4,6-DCDF from 2-chlorophenoxy radical is likely via mechanisms previously described by us for the reaction of 2-MCP over a CuO/silica surface (31). However, the formation of DF and higher yields of 4,6-DCDF imply an additional mechanism of formation of PCDFs over Fe₂O₃/silica surfaces.

The bi-dentate intermediate **V** depicted in Scheme 1 can form a surface-associated phenoxy radical, **VI**, via back-electron transfer as depicted in the initial step in Scheme 3 which then converts to the keto-mesomer, **VII**. Two of the surface-associated keto-mesomers then react to form DF (Scheme 2, species VIII–XII) via a mechanism similar to that previously proposed for formation of 4,6-DCDF from chlorophenoxy radical (34–36).

This back-electron transfer occurs at 400 – 450 °C as evidenced by the maximum in both the phenol and DF formation curves. In contrast, 4,6-DCDF exhibits a maximum yield at 300 °C and is formed directly from the initially formed chlorophenoxy radical which is formed at lower temperatures.

Copper- vs Iron-Mediated Formation of PCDD/F

The majority of laboratory studies of the surface-mediated formation of PCDD/F have focused on copper and copper oxide (9–11,46–47). Our current results indicate that iron is also a mediator of formation of PCDD/F. Figure 4 presents the comparison of the PCDD/F product yields over copper oxide and iron oxide surfaces under otherwise identical conditions.

Based on comparison of our data with data generated under comparable conditions for CuO, the maximum yield of total PCDD/Fs is 2.5x greater over iron oxide than copper oxide. Over iron oxide, PCDFs were the dominant products with 4,6-DCDF (formed from 2-chlorophenoxy radical) dominating at temperatures < 350 °C and DF (formed from phenoxy radical) dominating above 350 °C. In contrast, for copper oxide, PCDD and PCDF product yields were comparable. DF was not observed for copper oxide at all, and the only PCDD/F products of 2-chlorophenoxy reactions detected were DD, 1-MCDD, and 4,6-DCDF.

These data indicate that the differences in PCDD/F formation over copper and iron oxides surfaces result from different chemisorption mechanisms. For copper oxide, the chemisorption at the hydroxyl constituent via upper pathway in Scheme 1 to form 2-chlorophenoxy radical is dominant. In the case of iron oxide, two chemisorption reactions are evident: 1) the upper pathway in Scheme 1 where 2-chlorophenoxy radical is formed, and 2) the lower pathway in Scheme 1 where the bi-dentate species is formed. The 2-chlorophenoxy radical proceeds to form 4,6-DCDF while the bidentate species reacts further at temperatures >350 °C to produce phenoxy radical that forms DF.

Implications for Full-Scale Emissions

Iron and copper oxide surfaces can both mediate the formation of PCDD/F in the post-combustion, cool-zones of combustion systems under pyrolytic conditions. Of course, most combustion systems have regions of pyrolysis and oxidation, various pollutants may participate in competitive co-adsorption, and fly-ash that is more complex than the simple iron oxide/silica and copper oxide/silica substrates we used in these studies, all of which can lead to varied results.

However, for the simplified, comparable conditions presented in this paper, the data suggests that iron may potentially play a more important role than copper. The concentration of iron in fly-ash and other types of combustion-generated particulate matter is 2–50x higher than copper (cf. Table 2 in Supporting Materials). Because the total PCDD/F yield is also 2.5x higher for iron oxide than copper oxide, a simple calculation indicates that iron may result in 5–125x more PCDD/F than copper. It should be pointed out, that many other factors can affect the reactivity of copper or iron in the combustion systems, however since both of them are subject to those limitations, the overall yield factors between the copper and iron should still be valid.

Furthermore, as presented in this study, iron oxide promotes PCDF formation over PCDD formation as well as partial dechlorination that has not been observed for copper oxide. The PCDD to PCDF ratios in our lab studies are 0.38 for iron oxide and 1.2 for copper oxide. The iron oxide PCDD to PCDF ratio is in far better agreement with typical field

measurements in which the PCDD to PCDF ratio is $\ll 1(6,48)$ (cf. Table 3 in Supporting Materials)

The bi-dentate chemisorption of chlorophenols on iron oxide promotes loss of an additional chlorine in the pathway of PCDF formation. This is also in agreement with typical full-scale results in which the homologue class distribution of PCDFs are typically shifted to one less chlorine than the homologue class distribution for PCDDs (13,49) (cf. Table 3 in Supporting Materials).

It is possible that the role of iron on PCDD/F formation has been overlooked because iron is highly oxidative above 500 °C resulting in destruction rather than formation of PCDD/F and other chlorinated hydrocarbons. Laboratory experiments over the temperature range typically used for studies of copper may have missed the PCDD/F formation window for iron.

The observation of formation of PCDD/F over iron oxide surfaces suggests that additional studies of the impact of iron in combustion-generated particulate matter should be conducted. These include laboratory studies under oxidative conditions, addition of relatively high-concentration species such as water, SO_x and NO_x that can also adsorb on surfaces, use of more complex fly-ash samples, and field studies. Development of new reaction kinetic models of formation of PCDD/F over iron would be particularly useful as the current models significantly overpredict PCDD concentrations but under predict PCDF concentrations in full-scale combustion systems based solely on copper-mediated reactions of chlorophenols (50).

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Credit

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Figure 1.
Yields of phenols from the pyrolysis of 2-MCP over an $\text{Fe}_2\text{O}_3/\text{silica}$ surface.

Figure 2.
Yields of chlorobenzenes from the pyrolysis of 2-MCP over an $\text{Fe}_2\text{O}_3/\text{silica}$ surface.

Figure 3.
PCDD/F yields from the pyrolysis of 2-MCP over an $\text{Fe}_2\text{O}_3/\text{silica}$ surface.

Figure 4. Comparison of PCDD/Fs yields from the pyrolysis of 2-MCP over Fe₂O₃/silica (—) and CuO/silica (.....) surfaces

Scheme 1.

Scheme 2.