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Contribution of Aluminas and Aluminosilicates to the Formation of PCDD/Fs on Fly Ashes

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Abstract

Chlorinated aromatics undergo surface-mediated reactions with metal oxides to form Environmentally Persistent Free Radicals (EPFRs) which can further react to produce polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs). Previous work using laboratory-made fly ash surrogates composed of transition metal oxides deposited on silica powder has confirmed their ability to mimic fly ash in the production of PCDD/Fs. However, little is known about the propensity of aluminas and aluminosilicates, other components of fly ash, to form PCDD/Fs. A fly ash sample containing both alumina and mullite, an aluminosilicate, was tested for PCDD/F formation ability and compared to PCDD/F yields from the thermal degradation of 2-monochlorophenol (2-MCP) precursor over γ -alumina, α -alumina, and mullite. A packed-bed flow reactor was used to investigate the thermal degradation of 2-MCP over the various catalysts at 200–600 °C. Fly ash gave similar PCDD/F yields to surrogates made with similar transition metal content. γ -alumina, which is thermodynamically unfavorable, was very catalytically active and gave low PCDD/F yields despite a high destruction of 2-MCP. Mullite and α -alumina, the thermodynamically favorable form of alumina, yielded higher concentrations of dioxins and products with a higher degree of chlorine substitution than γ -alumina. The data suggest that certain aluminas and aluminosilicates, commonly found in fly ash, are active catalytic surfaces in the formation of PCDD/Fs in the post-flame cool zones of combustion systems and should be considered as additional catalytic surfaces active in the process.

1. Introduction

Polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs) are a particularly toxic class of compounds that originate from a variety of anthropogenic sources^{1–6}. Over 70% of all PCDD/Fs are formed through surface-mediated reactions over catalytic surfaces in the post-flame, cool zone of combustion systems at temperatures between 200–600°C^{7–9}. Reactions following the ‘precursor’ pathway involve a chlorinated aromatic molecule acting as a precursor to dioxin formation^{10–17}. Previous research on the mechanism for the surface-

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mediated formation of PCDD/Fs has confirmed the involvement of surface radicals bound to metal centers on the fly ash surface^{8, 9, 18, 19}. Though the original mechanistic studies were performed over copper oxide clusters on silica, the mechanism applies to any surface center that can form surface radicals. Formation of such radicals has been shown to occur on many metals at low post-combustion temperatures^{20–22}.

To fully understand the mechanism and yields of PCDD/Fs on the surface of fly ashes, fly ash surrogates have been investigated. Using a bottom up approach, systems containing either iron or copper oxides on a silica matrix were studied extensively and these metals were found to contribute to PCDD/F formation^{8, 18, 19, 23–25}. The initial focus on iron and copper oxide was due to their relative high concentrations in fly ashes and their known redox properties^{25–28}. Silica powder is used as a matrix substrate in the fly ash surrogates as it is a major constituent of fly ashes and at the same time is inert in PCDD/F formation. However, the composition of fly ashes is much more complex and no data is available whether other components contribute to the catalytic formation of PCDD/Fs.

Aluminas and aluminosilicates are major components of fly ashes where the aluminum concentration can reach 13–16% by mass²⁹. While there has been some research involving the *de novo* pathway for PCDD/F formation on alumina, surprisingly little research has been performed involving the surface-mediated precursor pathway on alumina, though it is known to be catalytically active^{30–32}. In here, we are presenting pioneering studies on the contribution of aluminas and aluminosilicates to PCDD/F emissions. We have chosen to study PCDD/F formation from 2-monochlorophenol (2-MCP) precursor over the following systems: γ -alumina, α -alumina, mullite, and a fly ash sample. 2-MCP was selected due to its extensive use in PCDD/F research leading to well characterized product profiles that high yields. Mullite is an aluminosilicate that is commonly found in fly ash and can reach concentrations of up to 20% by mass³³. α -alumina is the most thermodynamically stable form of alumina and, unlike γ -alumina, can be found in fly ashes. Although γ -alumina does not occur in fly ash, it is known for possessing strong catalytic activity and investigating its influence on PCDD/F formation could lead to a new method for prevention or destruction of dioxins.

2. Materials and Methods

2.1. PCDD/F Formation Experiments

All fly ash and surrogate samples were used as received without chemical treatment. Fly ash was obtained from the EPA Test Burn Installation at the Research Triangle Park and used as is. Both α - and γ -alumina (Sigma-Aldrich, #342718 #267740) along with mullite (Alfa Aesar, #22881) were used after sieving to ensure a particle mesh size between 100–120 corresponding to the fly ash surrogate particle size of 125–150 μm . 2-MCP was obtained from Sigma Aldrich (99+%, #185779) and used without further purification.

Surface-mediated reactions of 2-MCP over various catalytic metal oxide surfaces were studied using the System for Thermal Diagnostic Studies (STDS)³⁴. The STDS consists of a quartz reactor placed in a high-temperature furnace enclosed within the oven of a gas chromatograph maintained at 180 °C. The GC oven (Varian 3800) allows uniform

temperatures of the silica lined transfer lines (1 mm ID) and prevents condensation of reaction products. Products are transferred directly to the second gas chromatograph-mass spectrometer (Varian Saturn 2000) where they are cryogenically trapped at -60°C liquid nitrogen temperature in the head of a capillary column (30 m, 0.250 mm i.d., 0.25 μm film thickness HP5-MS GC column (Agilent)). After finishing each reaction (75 min), the column is heated at $15^{\circ}\text{C}/\text{min}$ up to 300°C . Products were identified using the NIST Mass spectra library and the eluted amounts were calculated based on calibration curves using corresponding standards.

For the PCDD/F formation studies, a quartz reactor was loaded with solid catalyst between quartz wool plugs and the catalytic bed length was kept at a constant 3.5 mm in all trials. 2-MCP was injected into the gas stream using a digital syringe pump (New Era Pump Systems Inc.) at a rate to maintain the gas phase concentration of 50 ppm.

Prior to each experiment, all catalytic material was oxidized in situ in 5 mL/min air flow at 450°C for 1 hr to ensure the surface was clean of adsorbed water and residual organic material. In the case of the fly ash, thermal desorption experiments performed under air flow at temperatures of 250 – 550°C had shown that the activation conditions were sufficient to clean the fly ash surface of organic species and did not lead to any additional formation of PCDD/Fs.

PCDD/F formation experiments were performed at temperatures ranging from 200 – 600°C . Product yields were calculated using the following equation:

$$\text{product yields} = (x[\text{product}]/[2\text{-MCP}]_0) \times 100,$$

where, [product] is the number of moles of product formed, $[2\text{-MCP}]_0$ is the number of moles of precursor fed to the reactor, and x is a stoichiometric factor representing number of precursor molecules required to form one product molecule. This factor is equal to 1 for single-ring aromatic products and 2 for dioxin-like compounds consisting of two rings. Each data point represents an average of 3–5 experimental runs.

2.2. Acid Digestion and ICP-OES Analysis

Microwave-assisted acid digestion was used to dissolve the fly ash for ICP-OES analysis. A 1:1:3:5 mixture of HF, HCl, HNO_3 , and H_2O was used to digest the fly ash for 60 minutes at 200°C . After digestion, samples were diluted with ultrapure water and the aqueous samples were analyzed by a Spectra Ciros CCD ICP-OES (Spectro Analytical Instruments) using the Smart Analyzer Vision program. The instrument was calibrated using single element analytical standards purchased from PlasmaCAL (SCP Science). All spectral lines obtained from digested fly ash were compared to those obtained from analytical standards for identification and quantification.

2.3. BET Analysis

A Quantachrome Autosorb-1 was used to analyze the surface properties of the catalytic material under nitrogen as the sorbent gas on a dried powder sample. Surface area, average

pore size, and total pore volume were calculated by the Autosorb software. More information on the analysis of surface morphology can be found in the Supporting Information.

2.4. XPS Analysis

Elemental composition of the fly ash surface was determined using a Kratos Axis-165 XPS using a monochromatic Al-K α radiation source.

2.5. XRD Analysis

The fly ash was analyzed with a Bruker-Siemens D5000 XRD using Cu-K α radiation and a solid state detector while operating in θ -2 θ mode with a diffraction angle range of 10–45°. Diffrac AT software was used to qualitatively analyze the crystalline components within the fly ash.

3. Results

3.1. Fly Ash Characterization

The elemental composition of the studied fly ash in this work is presented in Table 1. The composition is quite typical compared to other fly ashes presented in literature^{35–39} with iron being the most abundant transition metal component at ~4.5% by mass. The concentration of other transition metals falls within bounds typically found in fly ashes. From the perspective of PCDD/F formation, the concentration of copper in fly ashes is of importance, as copper is considered one of the most potent PCDD/F formation catalysts and has been studied extensively in the past^{9, 19, 20, 40, 41}. The fly ash studied in here contains only 0.02 % Cu, which is within the range observed in fly ashes from waste incineration processes^{35–39}. Copper concentration can be as high as ~4.5%, especially in e-waste reclamation systems⁴². Since iron content is so dominant in the fly ash, it is anticipated to be a driving force in PCDD/F formation from precursors. Our previous experiments have been performed using a Fe₂O₃/silica system containing 5% iron oxide that translates to ~3.5% Fe in the synthetic fly ash (Table 1), and showed a high yield of PCDD/Fs from such systems^{8, 18}.

The two other major components of fly ash as listed in Table 1 are Al and Si. Though the concentrations of those elements are high, little is known on their propensity to catalyze the formation of PCDD/F from precursors. These two elements form the inorganic matrix of the fly ashes and are usually in the form of oxides. SiO₂ is believed to be inert in the PCDD/F formation; however, other forms of the oxide can exist. X-Ray Diffraction analysis of the fly ash confirmed the majority of Si is present in the form of quartz (SiO₂). The presence of aluminosilicates has also been detected in the form of mullite (Al₆Si₂O₁₃). Silica and mullite are commonly found in fly ashes in considerable quantities as they are formed during the particle inception process during cooling in the post-flame zone from vaporized Si and Al from fuel³⁹. Though no crystalline forms of aluminum oxides were detected (except aluminosilicates), it does not exclude small crystallite or amorphous phases of other aluminum oxides to be present. In particular, one would anticipate α -alumina to be present, as this is the most thermodynamically stable form of aluminum oxides.

Surface area of the fly ash has been found to be relatively small at 13.65m²/g (Table 2) when compared to the different types of aluminas. Similarly, the mullite sample has a very small surface area of <2m²/g. Compared to α - and γ -alumina, both the fly ash and mullite can be considered systems without significant pore structure. Thus, surface activity in these two catalysts is most likely related to the external surface of the particles. The average pore diameter of α -alumina is ~2 Å and though the pore system is very well developed, it is essentially not accessible for aromatic molecules. Aromatic rings have a width of >2.5 Å. It is difficult to consider the overall surface area of α -alumina as a contributing factor, as most of the surface is unavailable. Therefore, α -alumina has available surface area similar to that of fly ash and mullite.

3.2. PCDD/F Formation

Decomposition profiles of 2-MCP over studied surfaces varied significantly (cf. Figure 1). The highest 2-MCP destruction yield was observed for γ -alumina (>99.9% destruction over studied temperature range) and the fly ash surrogate 5% Fe₂O₃/Silica (>90% destruction). It is evident, that these two catalysts are very active and activate 2-MCP on their surfaces at temperatures below 250 °C. The high catalytic activity of γ -alumina is related to its crystal structure. Along with surface hydroxyl groups, γ -alumina has unique Al³⁺ Lewis acid sites that aid in adsorption of substituted organic species^{43, 44}. The activation of the catalyst under air flow at 450 °C prior to the experiment removes hydroxyl coverage from Al³⁺ sites and makes them available for adsorption of the precursor. The significantly higher surface area of γ -alumina is also a contributing factor to high degradation of 2-MCP.

For the other three samples, a gradual increase of 2-MCP degradation with increasing reaction temperature was observed, however, temperatures above 400 °C are required to achieve ~95% degradation. Though the degradation at 250 °C was much lower for the fly ash, stronger temperature dependence resulted in higher conversions at temperatures above 450 °C. The 2-MCP decomposition over fly ash differed from that of the Fe₂O₃/silica surrogate despite having a similar concentration of iron. Because iron is known to be particularly active in this temperature region, it seems likely that not all the iron in the fly ash may be available as active surface sites or it is present in a different coordination environment. This correlates with XPS results that show a weak iron signal under high-resolution scan. The majority of the iron in the fly ash may be within the particles and not available for precursor adsorption.

Destruction of 2-MCP resulted in formation of PCDD/Fs for all studied systems. Briefly, the surface-mediated mechanism for PCDD/F formation consists of the chemisorption of a precursor molecule to the catalytic surface to form an environmentally persistent free radical (EPFR). The EPFRs are then able to react with each other to form PCDFs or upon further transformation react with gas-phase precursor molecules to form PCDDs⁹. According to this mechanism, only simple PCDDs and PCDFs such as dibenzo-p-dioxin (DD), 1-Monochlorodibenzo-p-dioxin (1-MCDD), dibenzofuran (DF) and 4,6-dichlorodibenzofuran (4,6-DCDF) are anticipated to be formed from 2-MCP as a result of the direct condensation reactions. Indeed, such species were the dominant PCDD/F observed products, while small yields of higher chlorinated (di-, tri-, and tetrachlorodibenzo-p-dioxins) were also detected.

No other higher chlorinated species (penta-, hexa-, hepta-, or octa-) were detected. Individual isomers of dioxin congeners, such as 4,6-dichlorodibenzofuran and 2,4-dichlorodibenzofuran, were not differentiated. These indicate a limited chlorination process of PCDD/Fs. It is unlikely that the higher chlorinated species (more than dichloro) were formed by direct condensation of the precursors, as the amounts of higher chlorinated phenols and benzenes in the reaction were insignificant compared to the observed PCDD/F yields. Only dichlorophenol and trichlorobenzene are formed in high enough yields to produce secondary condensation products – dichlorodibenzo-p-dioxins and tri and tetrachlorodibenzofurans. However the lack of higher chlorinated furans indicates that is not the case. The presence of only higher chlorinated dibenzo-p-dioxins as a reaction product indicates surface chlorination of adsorbed PCDD⁹. The PCDD/F product yields and 2-MCP decomposition curves are presented in Figures 1–4 as a function of temperature under oxidative conditions.

4. Discussion

A stark contrast in the yields of PCDD/Fs was observed for different aluminas. The analysis of the reaction products for γ -alumina has indicated very low yields of PCDD/Fs in the studied temperature region with a maximum at ~ 450 °C (0.01% yield of dibenzo-*p*-dioxin). The high activity of γ -alumina towards decomposition of 2-MCP in the studied temperature region results in an unfavorable condition for surface condensation processes. It is likely that PCDD/F products are formed in the highly developed pore system – this is supported by observation of EPFR formation over γ -alumina⁴⁵. With an average pore diameter of ~ 20 Å, precursor molecules are able to enter but PCDD/F products would be trapped (“ship-in-a-bottle” effect) and prone to secondary decomposition processes.

2-MCP oxidation over α -alumina produced PCDD/Fs with yields up to $\sim 0.3\%$ (cf. Figure 2). The maximum formation was observed at 500 °C, a temperature higher than the maximum yield temperatures for copper oxide and iron oxide surrogates (350 °C and 450 °C, respectively)^{18, 19}. Smaller yields and shift of the maximum formation towards higher temperature indicates α -alumina is less active in the formation of PCDD/Fs compared to the transition metal ions such as copper and iron. However, in spite of its lower activity, aluminum-containing compounds are found in fly ash in concentrations many times higher than transition metals, therefore their contributions cannot be discounted. This is also true for mullite, which exhibited similar yield of PCDD/Fs to α -alumina ($\sim 0.3\%$ at 550 °C). The higher temperature of maximum yield compared to α -alumina indicates that mullite active sites have higher activation energy, likely due to the differences in the coordination environment of active sites. One can assume a similar mechanism of PCDD/F formation is taking place on both α -alumina and mullite surface as on transition metal oxides. Although future work using model fly ashes containing alumina and aluminosilicates could better quantify the contributions from these compounds, they could be the primary contributors to PCDD/F formation under certain incinerator conditions.

The EPA Test Burn Installation fly ash was used to compare the formation of PCDD/F with surrogate samples (cf. Figure 3). Observed maximum PCDD/F yield of $\sim 1.0\%$ at 450 °C is significantly higher than both mullite and α -alumina and even slightly higher than the

Fe₂O₃/silica surrogate (a maximum yield of ~0.6%). This is surprising as iron oxide is known to strongly contribute to PCDD/F formation in the post-combustion cool zone⁸. The studied fly ash contains iron, mullite, and amorphous alumina. However, PCDD/F yields over fly ash are almost 80% higher compared to iron oxide surrogate and show a different formation temperature profile (cf. Figure 4). A further discourse between the activity of iron oxide and studied fly ash is more evident when comparing the congener pattern formed from 2-MCP reaction. Fly ashes produced mainly 1-MCDD, while iron oxide formed mixture of 4,6-DCDF, DF, DD and 1-MCDD. Some formation of secondary chlorination products were detected for fly ash (DCDD).

This observation is significant from the perspective of potential predictive models of PCDD/F formation based on fly ash composition as well as understanding the factors governing their yields. The presence of high concentration of metal (iron in this case) does not necessary translate to similar catalytic activity observed on pure metal oxide compositions. One of the potential explanations is surface availability of such metal oxides. Lab-made surrogates have their entire transition metal content available for adsorption. In real fly ash, a portion of the metal oxides is contained within the particle, covered by other components, and is not available for precursor adsorption. At the same time, we have shown both alumina and aluminosilicates to affect the formation of PCDD/Fs. Recent studies of the adsorption of phenol on γ -alumina at 230 °C have indicated the formation of surface phenoxyl radicals, similar to those formed on transition metal oxide fly ash surrogates that further react to form PCDD/Fs⁴⁵.

Predicting PCDD/Fs in Fly Ash

The sum of PCDD/F yields from the Fe₂O₃/silica surrogate, α -alumina, and mullite is shown in Figure 5 alongside the total PCDD/F yield from fly ash. Currently referred to as the 'predicted yield,' this sum represents the three primary PCDD/F contributors found in this particular fly ash. The fly ash and the predicted yield share a similar maximum yield and temperature formation profile. The slight shift in the maximum is attributed to the higher temperatures required by aluminas and aluminosilicates to form PCDD/Fs. The high baseline at low temperatures seen in the predicted yield is due to higher concentrations of PCDFs resulting from Fe₂O₃ activity.

These results indicate that combustion-generated particulate matter can be viewed as a sum of its parts with regard to PCDD/F formation. The additive and possibly cooperative effects from the complex mixture of transition metals, alumina, and aluminosilicates leads to a significantly higher PCDD/F yield than any one component. Once such effects are well understood, a mathematical equation can be designed (the development of the model is currently in progress) that accurately identifies the expected PCDD/F surface concentrations and other quantifiable data like PCDD/PCDF ratios through input of the concentrations of various fly ash components. In a simple form, the equation will be a sum of yields from various components weighted based on each components concentration in the combustion system. Factors such as differing product profiles, surface availability, and catalytic synergy between components would allow the equation to grow to a more complex state.

5. Conclusions

Non-transition metals have been largely discounted in the past as nonparticipants in the formation of PCDD/Fs. While this may be true for some non-transition metals that are prevalent in fly ash, as in the case of SiO₂, other common components, such as aluminas and aluminosilicates, do play roles in PCDD/F formation. Particularly under oxidative conditions and at the higher temperatures of the cool zone range, aluminas and aluminosilicates can make significant contributions to PCDD/F formation. Specifically, α -alumina and mullite, both found in real world fly ash, exhibited maximum PCDD/F yields of 0.4% from the catalytic oxidation of 2-MCP. A real world fly ash sample containing both alumina and mullite reached a maximum of 1.0% PCDD/F yield. The mechanism for PCDD/F formation on aluminum-containing compounds has not been completely investigated. Similar to transition metal oxides, the initial step involving a surface-bound radical does take place on aluminas and therefore it can be inferred that condensation of surface-bound radicals is still the primary pathway for PCDD/F formation on these components.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Highlights

- Aluminosilicates are catalytically active in the formation PCDD/Fs
- Aluminosilicates are particularly active in oxygen rich conditions of the combustors exhaust
- Prediction of PCDD/F in combustion sources can be based on the additive catalytic activity of fly-ash components

Figure 1. 2-MCP oxidative decomposition over the Fe₂O₃/silica surrogate, fly ash, α -alumina, mullite, and γ -alumina. Lines represent trends.

Figure 2. PCDD/F yields from the oxidation of 2-MCP over α -alumina and mullite. Lines represent formation trends.

Figure 3. PCDD/F yields from the oxidation of 2-MCP over the Fe₂O₃/silica surrogate, fly ash, α -alumina, mullite, and γ -alumina. Lines represent formation trends.

Figure 4.
PCDD/F yields from the oxidation of 2-MCP over the Fe₂O₃/silica surrogate and fly ash.
Lines represent formation trends.

Figure 5. Comparison of PCDD/F yields from fly ash and predicted yields from a sum of studied fly ash components.

Table 1

Elemental composition of fly ash from the EPA test Burn Installation

	Fly Ash Surrogates	Fly Ash
Si	44.41	46.49
Al	-	10.43
Fe	3.50	4.46
Ti	-	1.01
Ca	-	0.28
Mg	-	0.16
Mn	-	0.034
Cu	3.99	0.020
Zn	-	0.016

Table 2

Surface morphology parameters of materials used in the experiments

Sample	Surface Area (m ² /g)	Total Micropore Volume (cm ³ /g)	Average Pore Diameter (Å)
Fly Ash	13.65	6.49×10^{-3}	19.03
α -Alumina	175.70	9.49×10^{-3}	2.16
γ -Alumina	267.50	1.29×10^{-1}	19.37
Mullite	1.57	7.44×10^{-4}	21.28