

PCDD/F FORMATION MECHANISM: EFFECT OF SURFACE COMPOSITION ON CHLORINATION AND CONDENSATION REACTIONS

Sukh Sidhu and Pulak Nath

Environmental Science and Engineering, University of Dayton, 300 College Park, Dayton, OH 45469

Introduction

The post-combustion zone immediately following the incineration (flame) zone is a potential pollutant formation zone as it contains excess O₂ (3-9 %), sufficient residence time (from sub seconds to minutes) and catalytically active fly ash particles. This is an ideal reaction environment for the C₁ and C₂ compounds exiting the flame zone to undergo condensation and chlorination reactions. Heterogeneous reactions of short-chain aliphatic and chlorinated aliphatic combustion products in both high-temperature and low-temperature post-combustion zones can be important in the formation of larger organic pollutants (e.g. polychlorinated biphenyls, polychlorinated dibenzo-p-dioxins/dibenzofurans, chlorophenols, chlorobenzenes, etc). Fly ash formed in the combustion process provides the active surface for chlorination/condensation reactions in the post-combustion zone. The presence of several metals in fly ashes gives rise to the question whether there is one specific metal or a complex of metals that is responsible for the chlorination. Although fly ash contains many metallic species, most researchers investigating the PCDD/F formation mechanism have used copper as the catalytic surface in their pollutant formation studies because copper is a known commercial oxychlorination catalyst. The specific catalytic effects of various copper compounds in the formation of PCDD/F from aliphatic and aromatic compounds have been examined by us and a number of other investigators^{1,2}. In limited studies, iron compounds have also been used as PCDD/F formation catalysts, although these iron studies have produced contradictory results^{3,4}. Review of commercially important polymerization reactions shows that at varying temperatures and pressures, C₂ and C₄ olefinic polymerization reactions may be catalyzed by HCl-activated Al₂O₃, SiO₂ (aromatization also observed), aluminosilicates (1 % Al₂O₃ in SiO₂), and Fe oxides on aluminosilicates⁵. Isomerisation reactions such as cis-trans isomerisation, olefin-bond shifts and carbon-skeleton isomerisation can also occur over metal oxides like SiO₂/Al₂O₃, SiO₂/MgO₂, etc.⁵ These commercial catalytic processes indicate that non-copper metals can contribute to the surface catalyzed reactions in the post-combustion zone. However, little attention has been given to the catalytic activities of non-copper metals present in the fly ash. For this paper, we investigated the impact of other fly ash metal surfaces (Fe, K, Al, Si) on pollutant formation and compared their catalytic activity with that of actual oxidized fly ash and a CuCl₂ catalyst.

Methods and Materials

In this study, chlorination and condensation reactions of aliphatic (ethylene and propylene) and aromatic (benzene) precursors were investigated on three different catalytic surfaces. The composition of all three catalytic surfaces is shown in Table 1. Chlorides for model fly ashes were purchased from Aldrich and used as received. The OX-fly ash was obtained from U.S. EPA National Risk Management

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Research Laboratory. Silicon (iv) Oxide (99.995 %) was obtained from Alfa Aesar and was treated in two steps to remove organic contaminants. The two steps involved heating the silicon oxide at 700 °C in air for 3-5 days and then heating at 800-900 °C in flowing helium for 5 hours. An aqueous solution of CuCl_2 (2 %) and metal chlorides (0.85 % FeCl_3 , 0.85 %

Table 1. Fly Ash Composition

Fly ash	Surface Composition
Model fly ash #1	CuCl_2 (0.6-0.7 %) on Silicon(iv) Oxide Support
Model fly ash #2	Mixed metal Chlorides (FeCl_3 - 0.26 %; AlCl_3 - 0.27 % KCl - 0.17 %) on Silicon(iv) Oxide Support
OX-fly ash ⁶	Cu (0.17 %); Fe (1.11%); Mg (0.85 %); Ca (4.22 %); Ni (0.01 %); Si (8.86 %); P (0.6 %); Pb (1.43%); Al (2.41%); Zn (4.46%)

AlCl_3 and 0.55 % KCl) was used to impregnate the cleaned silica support. Following incipient wetness, the catalysts were dried overnight at 80 °C and then in a vacuum dryer at 40 °C for 1 hour. All experiments were conducted using a fixed bed flow reactor system described in detail elsewhere⁷. For all experiments, a constant inlet flow rate of carbon (~85 ng/min) in 4 % O_2 was maintained. For OX-fly ash experiments, HCl gas (5-7 ppm) was introduced in the inlet flow as a source of chlorine. The experiments were conducted at 300 °C, 400°C and 500 °C. The amount of catalysts was kept constant (.23 gm) in the fixed bed reactor and the total reaction time was 60 minutes. Residence times varied from 75 to 120 milliseconds. The products were trapped in a DB-5 capillary column (30 m; ID 0.25 mm film thickness 0.25mm) at -60 °C. Then gas chromatographic separation was carried out using a linear temperature program -60 °C//10 °C/min.//280 °C//1min. Products were analyzed by means of a mass selective detector (HP5970B MSD). Quantification for reaction products was accomplished using standard calibration curves.

Results and Discussion

The total ion chromatogram showed that tetrachloroethylene was the major product for all of the experiments. Tetrachloroethylene yields and yields of other chlorinated aliphatics were not quantified, as the focus of this study was to investigate formation of chlorinated aromatic products. In this paper, we will only present and discuss chlorobenzene yields as the chlorobenzenes are a known indicator of formation of higher chlorinated pollutants like PCDD/Fs, PCBs and PCNs. The selected ion method (SIM) was used to monitor major ions from chlorobenzenes. The monitoring showed that major aromatic products were chlorobenzenes. Chromatograms showed chlorobenzenes from mono to hexa chloro benzenes. The mole% yields of all of the experiments are presented in figures 1 and 2.

A comparison of results for the same precursor over different surfaces (fly ash #1, fly ash #2 and OX-fly ash) shows how the difference in surface composition affects the chlorination and condensation process. Fly ash #1 produced very small amounts of benzenes with ethylene and propylene precursors at any temperature. At the same time, chlorobenzenes were produced at all temperatures with significant yields of chlorobenzenes at 500 °C. Over a temperature range of 300 °C to 400 °C, fly ash #1 gave minimal chlorobenzene yields. This leads to the conclusion that fly ash #1 surface, i.e. CuCl_2 surface, chlorinates the aliphatic precursors first and then these chlorinated aliphatics condense to form chlorinated aromatics. In benzene experiments over fly ash #1, a significant amount of monochlorobenzene was observed at 400 °C and 500 °C. Higher chlorinated benzene yields were not

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significant in these benzene experiments. This means that the fly ash #1 surface cannot chlorinate aromatic rings very effectively. Fly ash #2, on the other hand, produced more benzene from aliphatic precursors at 300 °C and 400 °C and the amount decreased at 500 °C. At the same time, the amount of chlorobenzenes produced in these experiments increased gradually with temperature. This is a clear indication that over fly ash #2, the aliphatic precursors first undergo condensation and then they are chlorinated to different chlorobenzenes. Experiments with benzene showed that between 300 °C and 400 °C, very low yields of chlorobenzenes were produced, but at 500 °C the chlorobenzene amounts increased significantly. This means that fly ash #2 is more active at 500 °C and can effectively chlorinate aromatic rings. Therefore, fly ash #2 surface, i.e. $\text{AlCl}_3 + \text{FeCl}_3 + \text{KCl}$ surface, induces condensation first and then chlorination occurs (over the temperature range of investigation). Fly ash #3, which is the oxidized fly ash surface, produced benzenes as well as chlorobenzenes at all temperatures and the amount of products increased with temperature. The increase in benzene production suggests that there is condensation taking place at all temperatures and that the tendency increases with temperature. On the other hand, increase in the formation of chlorobenzenes suggests that the aliphatic precursors are also chlorinated and then condensing to form chlorobenzenes. Since benzene and chlorobenzenes were formed simultaneously, it can be concluded that both chlorination and condensation occurs simultaneously in these experiments. When aliphatic precursor experiments were repeated with benzene, it was seen that the chlorobenzene amount produced was small compared to aliphatic experiments. So, even though with fly ash #3 chlorination and condensation appears to occur simultaneously, it can be concluded that most chlorobenzene products are the result first of chlorination of aliphatic chains and then condensation.

From these results, it is clear that metal ions (Cu, Fe or Al) do not behave in the same manner when it comes to chlorination and condensation. Cu (fly ash #1) has the tendency to chlorinate the aliphatic precursors first and then go on to ring formation. In contrast, the mixed metal ions (Fe and Al) had the tendency to condense aliphatic precursors before chlorination. The oxidized fly ash, on the other hand, showed both chlorination and condensation tendencies but overall behaved more like CuCl_2 surfaces. Froese and Hutzinger⁸ also found that CuCl_2 behaves more like actual fly ashes than AlCl_3 or FeCl_3 surfaces.

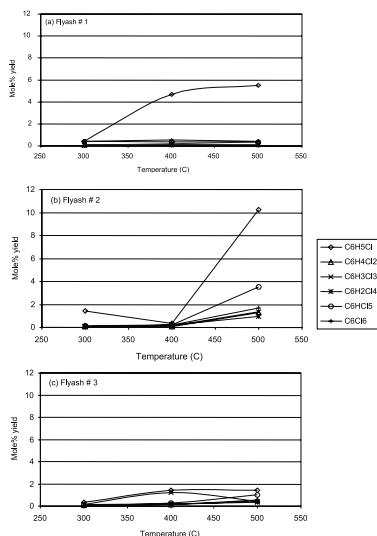


Figure 1. Chlorobenzene yields obtained when benzene (85 ng/min carbon) was passed over (a) flyash #1; (b) flyash #2; (c) flyash #3 and HCl (1700ppm).

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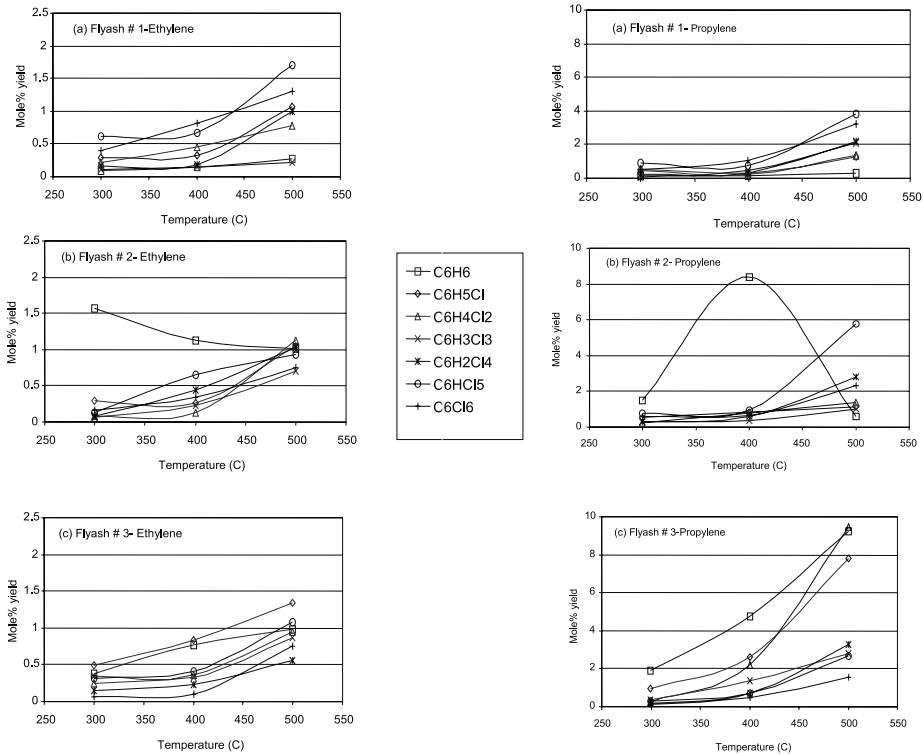


Figure 2. Benzene and chlorobenzene yields obtained when ethylene (85 ng/min carbon) and propylene (85 ng/min carbon) were individually passed over (a) flyash #1; (b) flyash #2; (c) flyash #3 and HCl (1700 ppm).

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