Surface Catalyzed Chlorobenzene Transformation Reactions in Post-Combustion Zone

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Introduction

It has been shown that condensation of chlorophenols is a major pathway for the formation of polychlorinated dibenzodioxins and furans (PCDD/F)[1,2] but the role of other compounds like chlorobenzenes is not clear. It has been shown that chlorobenzenes have lower PCDD/F formation rates than phenols. Born et al.[2] showed that when a mixture of chlorobenzene and chlorophenol was passed over fly ash bed, chlorophenol was completely converted but chlorobenzene was unaffected. This shows that chlorobenzenes are inert with respect to oxidation and oxychlorination. However, it should be noted that experiments of Born et al.[2] were focused on fate of chlorophenol and only in the first experiment they passed a mixture of chlorophenol and chlorobenzene and found chlorobenzene to be inactive. They[2] did not use HCl in the experiments in which chlorobenzene was used as reactant over fly ash. Altwicker et al.[3] investigating the role of chlorobenzenes in de novo PCDD/F formation reactions observed that presence of chlorobenzenes leads to decline in PCCD/F yields over fly ash. Results of Altwicker et al.[3] indicate that chlorobenzenes are not precursors of PCDD/Fs. However, chlrobenzenes are regularly used as indicators for continous indirect monitoring of PCDD/F emissions. Blumenstock et al.[4] observed that lower chlorinated benzenes show a high correlation with the international toxicity equivalent (I-TEQ) value of PCDD/F, which implies that chlorobenzene and PCDD/F formation are connected in some way. Chlorobenzenes may not have a major role in the formation of PCDD/F, however, it can form phenol/chlorophenols in presences of a chlorine source. Procaccini et al.[5] showed conversion of benzene to chlorobenzene and chlorophenol by reaction with chlorine radicals in the cool zone of a plug-flow combustor.

It is evident from above discussion that relationship between chlorobenzenes and PCDD/Fs is not completely understood. Also, the above mentioned studies lack information about the role of chlorobenzene with respect to presence and changes in catalyst surface or the chlorine source. Hence the current study was designed to investigate how these variables impact the fate of chlorobenzenes in the post-combustion (cool) zone of a combustor.

Materials and Methods

In this study, the catalyst was prepared by impregnating florosil (85% SiO_2, MgO) with a solution of $CuNO_3$. The catalyst was then dried and calcined at 600 °C for 24 hrs. The final concentration of Cu in the catalyst was 2 wt%. The catalyst was placed as a packed bed between

two quartz wool plugs inside the reactor. This reactor system has been described in detail elsewhere[6]. A schematic of the reactor system used in the present study is shown in Figure 1.

The experiments were conducted at temperatures of 300, 400, 500 and 600ºC in a mixture of air and Helium (10% oxygen). For each experiment the fixed bed was made of 0.1 g of catalyst. The total reaction time was 60 minutes. After each experiment catalyst was desorbed for 15minutes in Helium. Desorption is done to desorb all the PAHs that are adsorbed in the bed and on the surface. The monochlorobenzene reactor inlet concentration was 25 mg/m^3 and 201 mg/m^3 for low and high concentration cases respectively. The concentration of HCl was 3000 mg/m^3 for both reactant concentrations. The reactor effluent was collected in a XAD trap which was maintained at the room temperature. The reaction products were extracted from XAD trap using dichloromethane and then concentrated. The products were then analyzed using mass spectroscopy. To quantify the products D8- anthracene was used as an internal standard. The internal standard was added in an auxiliary flow (20ml/min) at the start of the reaction, this flows through the auxiliary column bypasses the reactor and joins at the junction flow where it mixes with the reaction products.
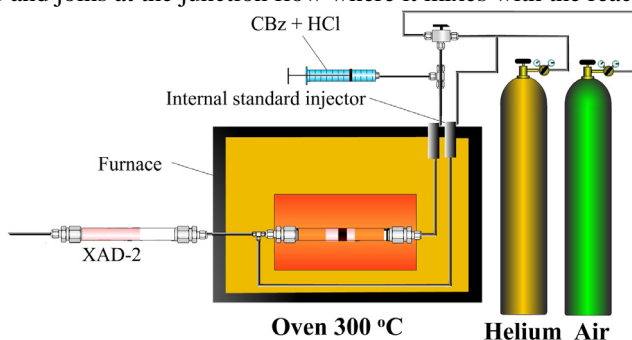

Figure 1. Schematic of catalytic reactor system.

Results and Discussion

To investigate the impact of surface and chlorine source on monochlorobenzene conversion reactions, three sets of experiments were conducted; a) without catalyst or chlorine source, b) without catalyst but with chlorine source and c) with both catalyst and chlorine source. The results of all three sets of experiments at 300ºC are shown in figure 2. Examination of figure 2 shows that conversion of monochlorobenzene is enhanced by the addition of both chlorine source and catalyst. Increase in monochlorobenzene conversion with addition of HCl can not be explained by gas-kinetics only plausible explanation is that perhaps addition of HCl activates the surface of quartz reactor which leads to increase in monochlorobenzene conversion. It should be noted that there was no chance of quartz reactor being contaminated by previous experiments as new quartz tube was used for each experiment. Figure 3 compares the results of this study using CuO (+HCl) as catalyst with those obtained in our previous gas-phase study[1] and with results of Born et al.[2]. This comparison shows that presence of HCl and CuO lower the initial temperature of monochlorobenzene conversion from 700ºC for gas-phase study[1] to 500 ºC. Born et al.[2] didn't observe conversion of chlorobenzene till 600 ºC over fly ash. However HCl was not present in their system.
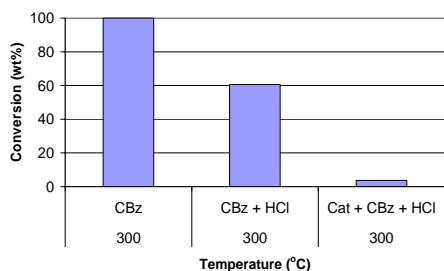
Figure 2. Conversion of monochlorobenzene at 300ºC in three different reaction environments.
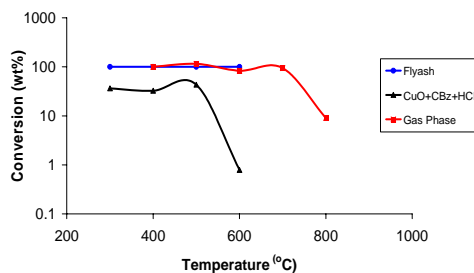

Figure 3. Comparison of monochlorobenzene oxidation profiles.

Tetrachloroethylene was one of the major products observed in this study. Figure 4 shows tetrachloroethylene at 300°C for three sets of experiments. Presences of both HCl and CuO enhanced formation of tetrachloroethylene. Figure 5 shows that tetrachloroethylene yield decreases with increase in temperature. This probably is due to the fact that at higher temperature reaction channels leading to other products are becoming more accessible thus decreasing formation of tetrachloroethylene. Other major products observed in the study were chlorobenzenes. Chlorobenzenes ranging from di- to hexa- were observed in this study. Figure 6 shows the isomer distribution of chlorobenzene at various temperatures obtained by passing monochlorobenzene over CuO in presences of HCl. Dichlorobenzene was the dominant chlorobenzene at all temperatures. The chlorobenzene isomer distribution observed from chlorination of monochlorobenzene is different than the chlorobenzene isomer distribution that is observed in MWI flue gas or from de novo experiments.
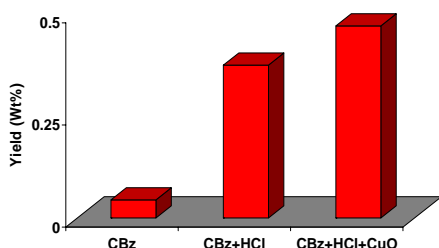

Figure 4. Yield of tetrachloroethylene at 300ºC from oxidation of monochlorobenzene in three different reaction environments.
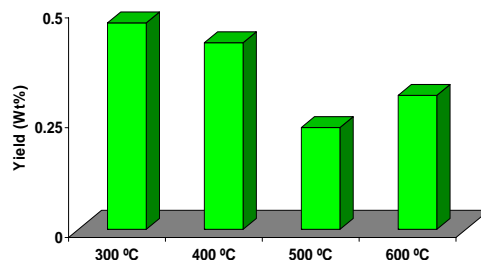

Figure 5. Yield of tetrachloroethylene from oxidation of monochlorobenzene over CuO catalyst in the presence of HCl.

Phenols, PCDD/F and chlorinated-PAHs were not observed in this study. These results are different than the results of our previous gas-phase monochlorobenzene oxidation study[1] where phenol, chlorophenols, dibenzodioxin, dibenzofurans, 4-chlorodibenzofuran, 4,6-

dichlorodibenzofuran and naphthalene were observed as products over a temperature range of 550-750°C. It was expected that presences of copper catalyst and HCl will enhance the conversion of monochlorobenzene to chlorinated phenols and PCDD/Fs. However it appears that under the conditions of this study presence of copper and HCl enhanced complete oxidation of monochlorobenzene. Also in this study catalyst surface did not show any signs of sooting. This means that monochlorobenzene was not involved in molecular growth reactions that lead to soot formation. The results of this study indicate that in presences of CuO and HCl monochlorobenzene preferentially oxidizes to CO and CO_2 since tetrachloroethylene and higher chlorobenzenes are the only products observed.
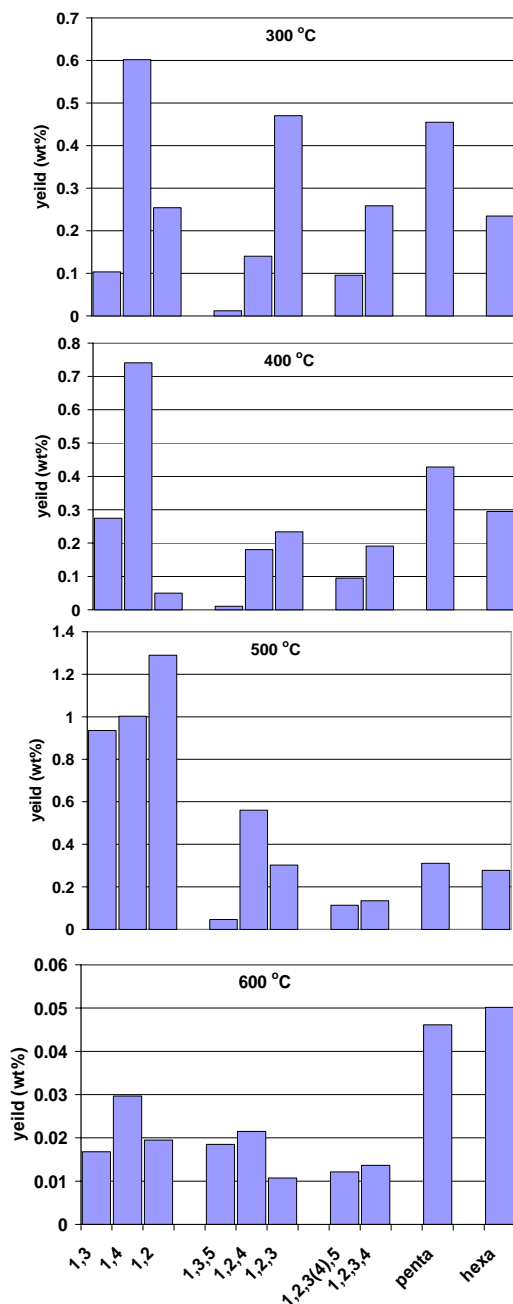
The results of this study combined with results of Born et al.[2] and Altwicker et al.[3] show that chlorobenzenes are not significant precursors of PCDD/Fs. The reason why chlorobenzenes correlate well with total PCDD/F yields is most likely due to the fact that chlorobenzenes and PCDD/Fs are formed from same reactant source, like PAHs or soluble organic fraction of soot, but by parallel pathways that are related to each other.

Figure 6. Isomer distribution of chlorobenzenes from oxidation of monochlorobenzene over CuO catalyst in the presence of HCl.

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