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Chlorinated Aromatic Hydrocarbons in Heterogeneous Combustion Reactions of C_2 Aliphatics.

Part II. Ethylene and Ethane

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Introduction

The relevance in combustion processes of fast, heterogeneous reactions of short-chain aliphatic compounds in the formation of chlorinated aromatic compounds has been postulated in previous investigations(1-4) and in Part I of this series. We have chosen C_2 aliphatics as model compounds to study the formation of simple chlorinated aromatics such as chlorinated benzene and chlorinated phenols. Gas-phase and heterogeneous combustion and pyrolysis reactions of ethylene have been reported(5-8), showing production of aromatic compounds. We believe that investigations of heterogeneous reactions with ethylene and ethane, together with information learned in reactions with acetylene (Part I), will provide invaluable information regarding fundamental aromatic compound formation in combustion systems.

Experimental

Ethylene and ethane were reacted with HCl in synthetic air under heterogeneous combustion conditions at temperatures from 300-600°C and gas-phase residence times of < 2 s. Model catalyst mixtures of SiO_2, SiO_2/Al_20_3 and SiO_2/CuO were compared with extracted and annealed municipal waste incinerator (MWI) flyash. Approximately 30-40 mg C_2H_4 or C_2H_6 were reacted in 30 min experiments. Reaction products were eluted from the catalytic material in the reaction tube and from the Carbotrap adsorbent tube. The sample extracts were concentrated, the phenolic compounds derivatised using acetic anhydride, and the final sample extracts were analysed quantitatively by GC-MSD for chlorinated benzenes and phenols and qualitatively for additional volatile and semi-volatile products.

Results

Chlorinated benzenes (Cl_xBz) and chlorinated phenols (Cl_xPh) were detected in both gas-phase products as well as catalyst-adsorbed products. In C_2H_4 reactions over flyash, the

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rate of Cl_xBz production increased exponentially to 600°C (Figure 1) (Cl_5Bz: $1.6x10^4$ ng/g C_2H_4 HCB: $6x10^3$ng/g C_2H_4), while Cl_xPh (PCP) production remained constant from 400-600°C ($1.5x10^3$ng/g C_2H_4). For C_2H_6 reactions at 600°C, Cl_xBz production was very similar to the C_2H_4 reaction (Cl_5Bz: $1.6x10^4$ ng/g C_2H_6 HCB: $5x10^3$ng/g C_2H_6), whereas total Cl_xPh (PCP) production was an order of magnitude greater ($1.2x10^4$ng/g C_2H_6). The CuO catalysed gas-phase Cl_xBz patterns most closely matched those produced in the reactions with MWI flyash (Figures 2 and 3). The Al_2O_3 catalysed reactions distinguished themselves from the others in unique Cl_xBz and Cl_xPh congener patterns that were dominated by the dichloro-homologue group (Figures 2 and 3), and in the observation of non-chorinated aromatic reaction products, in contrast to a predominance of chlorinated aliphatic compounds in the CuO and flyash catalysed reactions. These results suggest that Cu is a critical catalytic component of the flyash. They also point to a very different but intriguing aromatic formation mechanism catalysed by Al_2O_3.

References

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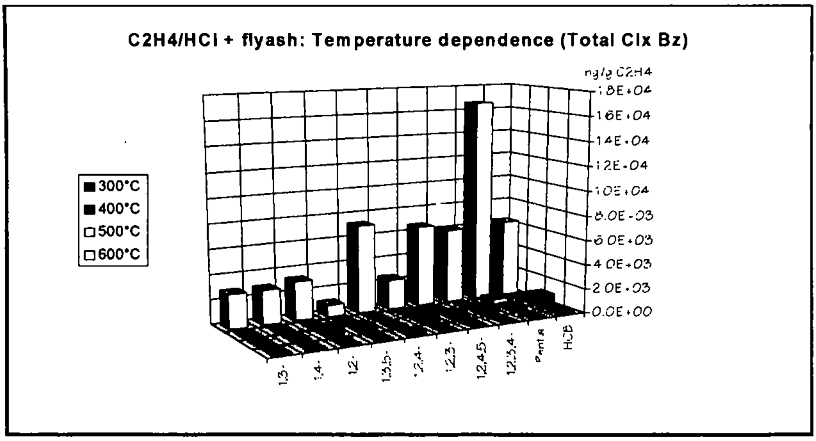

Figure 1. Temperature dependence of total Cl_xBz production in the flyash catalysed reaction of ethylene/HCl.

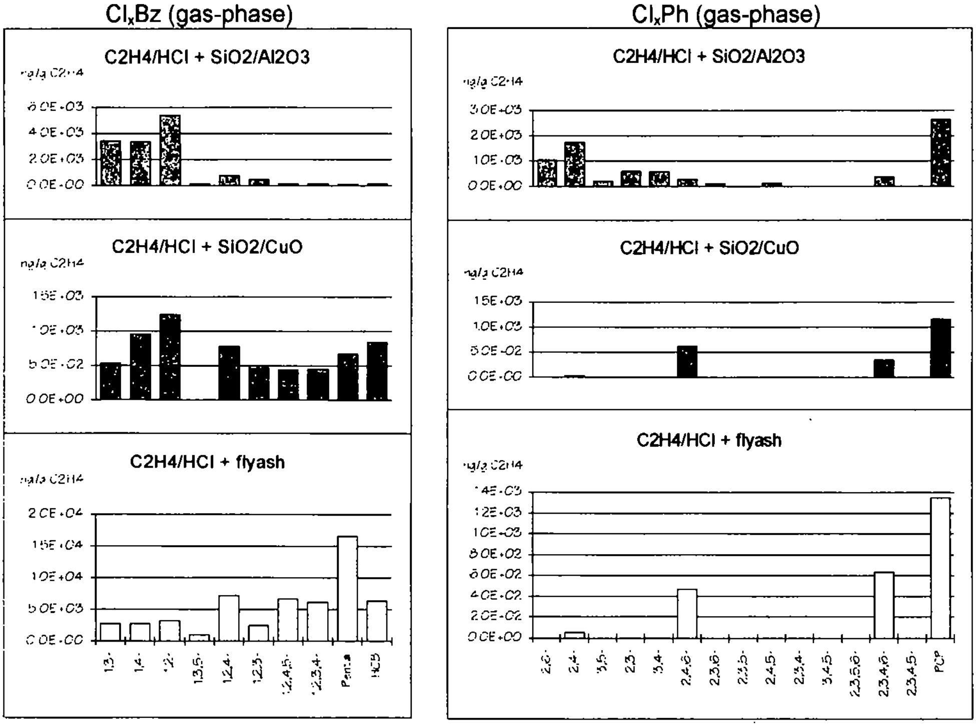

Figure 2. Congener patterns of gas-phase Cl_xBz and Cl_xPh production in the 600°C reactions of ethylene/HCl with various catalysts.

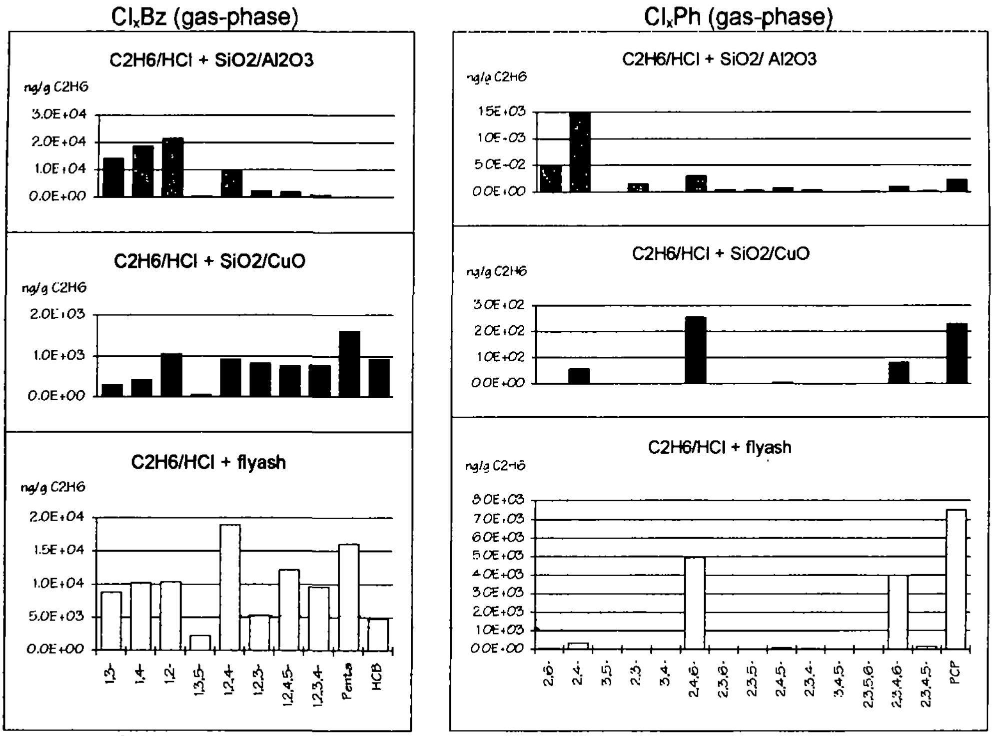

Figure 3. Congener patterns of gas-phase Cl$_x$Bz and Cl$_x$Ph production in the 600°C reactions of ethane/HCl with various catalysts.