Homologue Profiles of PCDD/Fs from Graphite

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Introduction

The importance of carbon in the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/Fs) are generally acknowledged[1)-5)]. However, there is no or less information on the carbon surfaces. The characterization of the carbon surfaces used in the experiments are necessary to elucidate the mechanism of PCDD/Fs formation from unburned carbon from municipal waste incinerators. On the other hand, it is known that the surface oxygen complexes formed on the soot during the soot oxidation process with copper chloride[6)].

In this study PCDD/Fs formation from graphite and copper chloride was mainly examined. Since graphite has the basic structure of carbon, the results could be easily compared with the case of other smaller polycyclic compounds which were thought to be possible precursors of PCDD/Fs.

Material and Methods

Graphite particles were sieved to a particle size < 125μm and mechanically mixed with copper compounds (CuCl or CuO). The mixture was placed in a quartz tube reactor heated at 400℃ for 2 hours. The products desorbing from graphite surface were collected in an ice-cooled water trap and a florisil trap.

The products in the traps were extracted with ethyl acetate. The graphite particles after the reaction were soxhlet-extracted with toluene over 12 hours. The extracted samples were respectively concentrated with a rotary evaporator to a few ml and were cleaned up with chromatographic columns filled with acidified, alkaline and neutral silicagel. After the sample volumes being finally reduced to 200-300μl, the samples were injected into GC-MS Hitachi M-80B with a DB-5 column (30m, 0.25mm i.d.) for PCDD/Fs analysis. GC-MS Varian Saturn3 with a TC-1701 column was used for identification and semi-quantitative analysis of by-products.

The formation of PCDD/Fs from the following combinations of starting materials was examined.

1. Graphite/CuCl
2. Graphite/CuO/HCl
3. Graphite/CuCl/Dibenzo-*p*-Dioxin

The inlet oxygen into the reactor was controlled at 10% by N_2 and air with the desired concentration of HCl. The total mass flow rate was 200ml/min.

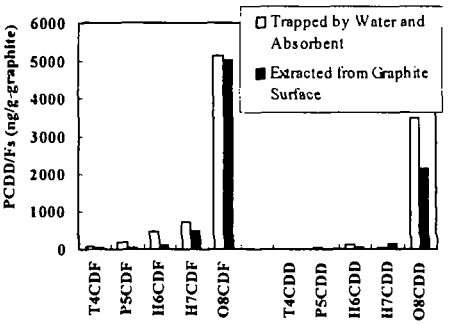

Fig.1 PCDD/Fs Formation from Graphite and 5% CuCl

N_2:100ml/min, Air 100ml/min, Temperature:400℃, Reaction Time:2 hours

Results and Discussion

The major products which could be confirmed from graphite and 5%CuCl were tri- to hexa- chlorobenzenes and hexachlorobenzofuran. Some of the minor products were nona- and deca-chlorobiphenyls. The homologue profile of PCDD/Fs is shown in Fig.1. O8CDD/F were the dominant homologues. The yields of hepta- to tetra- chloro-dibenzofurans decreased as the degree of chlorination lowered. The lower chlorinated dibenzo-*p*-dioxins were negligibly small. It is considered that necessity of chlorine termination of the aromatic rings could lead to this homologue profile.

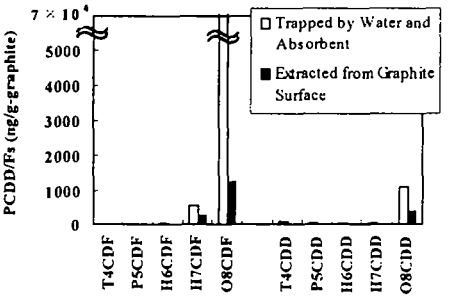

Fig.2 PCDD/Fs Formation from Graphite/CuO and HCl(500ppm)

1000ppmHCl(N_2 Balance):100ml/min, Air 100ml/min, Temperature:400℃, Reaction Time:2 hours

In the case that the same amounts of copper and chlorine as 5%CuCl were introduced as CuO and HCl, the formation of O8CDF desorbing from graphite surface to the gas phase was drastically promoted as shown in the Fig.2. One of the reasons for this drastic change is probably that the chlorine onto the graphite surface was gradually supplied and as a result the chlorination efficiency on the graphite surface increased.

The isomer patterns of Graphite/5%CuCl and Graphite/CuO/500ppmHCl were compared with that of electric precipitator flyash. The flyash was collected from a continuous fluidized bed incinerator for municipal waste. The isomer patterns of hexa- and hepta-chlorodibenzofuran is shown in Fig.3. It is very interesting that the isomer patterns of H6CDF and H7CDF from chlorination of graphite are almost the same as those from the municipal waste incinerator, although there could be other formation mechanisms of PCDFs on the flyash. This similar patterns are seen on the other PCDFs.

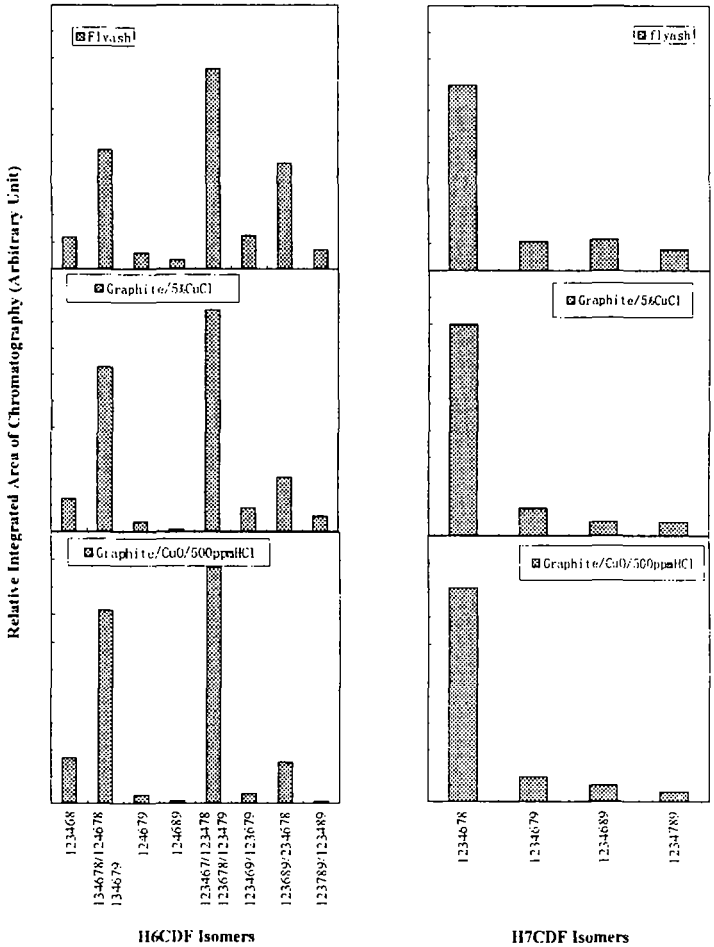

Fig.3 Comparison of H6CDF and H7CDF Isomer Patterns from Electric Precipitator Flyash of A Continuous Fluidized Bed Incinerator, Graphite/5%CuCl and Graphite/CuO/500ppmHCl

The homologue profile (Fig.4) of PCDD/Fs from graphite and 0.5%CuCl also showed that O8CDF was dominant and the yields of the hexa- to tetra-chlorodibenzofurans decreased as the degree of chlorination lowered. These results that most products were highly chlorinated compounds suggests that chlorination is one of the most important processes for their production from the graphite which has the rigid polycyclic surface.

The effect of the smaller polycyclic compounds on the homologue profile of PCDD/Fs was examined with Dibenzo-p-dioxin. The resultant profile is described in Fig.5. The yield of the lower chlorinated dibenzo-p-dioxins slightly increased in comparison with the profile of 5%CuCl (Fig.1). It is also clear that the formation of O8CDF was interfered.

Further works with other compounds composed of several aromatic rings need to be done in order to make it clear to what extent these smaller polycyclic precursors contribute to the PCDD/Fs formation.

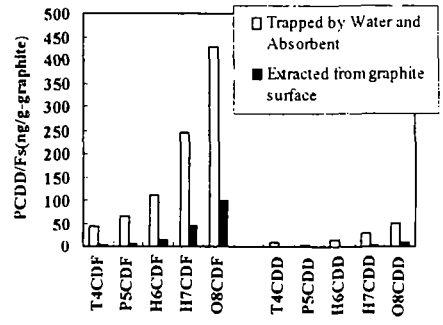

Fig.4 PCDD/Fs Formation from Graphite and 0.5% CuCl

N_2:100ml/min, Air 100ml/min, Temperature:400℃, Reaction Time:2 hours

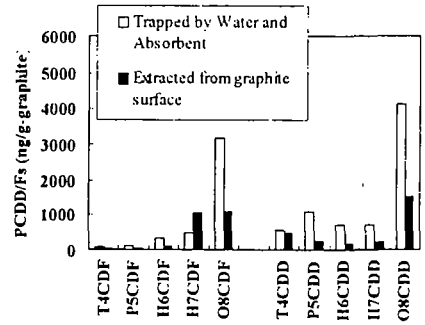

Fig.5 PCDD/Fs Formation from Graphite and 5% CuCl with Dibenzo-p-Dioxin

N_2: 100ml/min, Air:100ml/min, Temperature: 400℃
Reaction Time: 2 hours, Dibenzo-p-Diozin: 0.09wt%

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