EFFECT OF OXYGEN ON BEHAVIOR OF PCDD/Fs FORMED DURING HEAT TREATMENT OF PVC AND COPPER OXIDE MIXTURE

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Introduction

A new regulation on the emissions of PCDD/Fs has been enforced and, in such background, a number of new technologies to reduce PCDD/Fs emissions have been developed. This leads to significant decreases in the emissions of PCDD/Fs and relating compounds. Most of these technologies are based on stable and high temperature combustion, and rapid cooling and succeeding filtrating/scrubbing of the waste gas. Although there are many reports on the control/suppression of formation rate and/or the promotion of decomposition of PCDD/Fs, the detailed mechanisms have not been clarified yet.

The present paper reports a fundamental study on the formation/decomposition of PCDD/Fs using a sealed quartz ampoule as a reactor. Powder mixture of PVC (Poly-Vinyl-Chloride) and CuO as oxygen source and catalyst was used as a sample. Especially, the effect of oxygen on the formation of PCDD/Fs was investigated in this study because the oxygen promotes the formation of chlorine gas by the deacon reaction, and then the complete combustion by the further supplying of oxygen is effective on the promotion of the decomposition of PCDD/Fs in the combustion process. In this study, the effect of oxygen was experimentally investigated by changing the molar ratio of CuO/PVC as a sample. Moreover, the acceptability of the thermodynamic consideration on the formation and decomposition of PCDD/Fs has been investigated by comparing the thermodynamic calculation with the experimental results. The thermodynamic equilibrium calculation has been carried out using the thermodynamic functions of PCDD/Fs obtained by the molecular orbital method with density functional theory.

Materials and Methods

Powder mixture of PVC and CuO vacuum-sealed in the quartz cell was kept in the furnace at the fixed temperature. A detail of experimental procedure has been presented in the previous paper[1]. Mass of PVC, reaction temperature and retention time were fixed to 40mg, 300 °C and

48h, respectively. Molar ratios of CuO/PVC have been varied from 1 to 5 in order to investigate the effect of oxygen on the formation of PCDD/Fs. 5 of the molar ratio corresponds to the stoichiometric one that the oxygen in CuO completely reacts with carbon and hydrogen in PVC. After the heat treatment, the quartz amples were immediately cooled down in the air on the outside of furnace.

Results and Discussions

Experimental consideration

Figure 1 shows the change in the formation amount of PCDD/Fs with the molar ratios of CuO/PVC. The values of formation amount of PCDD/Fs converted to those corresponding to 1 g of PVC were shown in the logarithmic scale. It is obvious that the total amount of PCDD/Fs formed deceases drastically with the increase in the molar ratio of CuO/PVC. Though the oxygen is necessary for the formation of chlorine gas chlorinating the organic compounds, it has been reported that oxygen also promotes the decomposition of PCDD/Fs by the dechlorinated reaction.[2] The formation

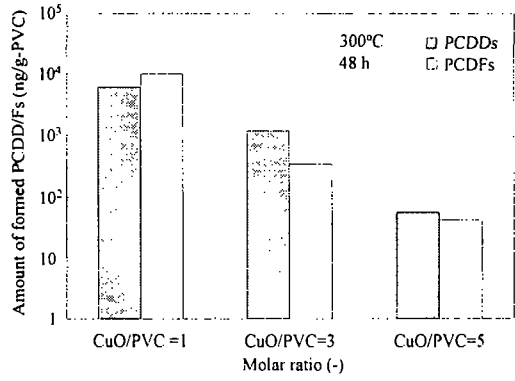

Fig.1 Change in the amount of PCDD/Fs with molar ratio of CuO/PVC at 300 °C.

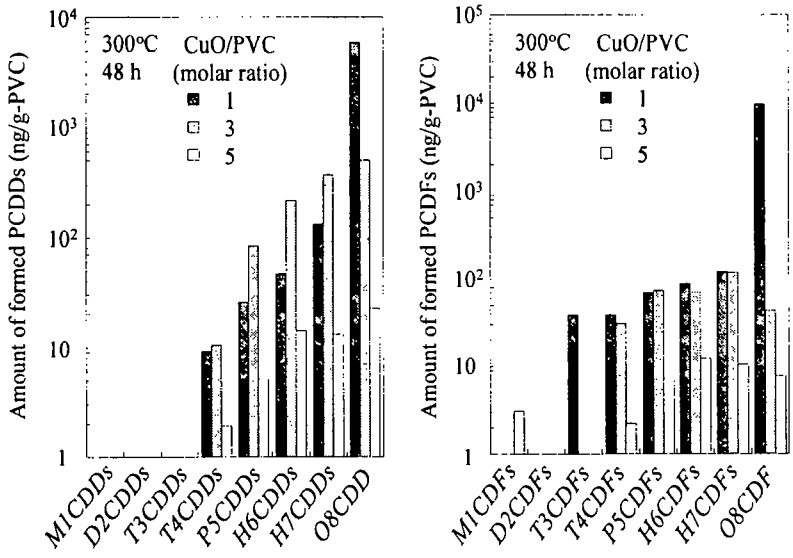

Fig.2 Effect of molar ratio of CuO/PVC on the homologue profiles obtained at 300 °C.

of PCDD/Fs is supposed to be restrained when the atmosphere of reaction field become oxygen-rich excessively. The most effectible oxygen content for the formation of PCDD/Fs in the present experimental condition cannot be specified from the results shown in Fig.1. It has been also reported that the amount of PCDD/Fs formed decreases with decreasing in the content of oxygen from 10% to 1% in the nitrogen atmosphere on the heat treatment experiment using the mixture samples of carbon and fly ash,[3] so it can be suggested that some content of oxygen is necessary for the formation of PCDD/Fs.

Figure 2 shows the comparison of homologue profiles of PCDD/Fs on the varying of the molar ratio of CuO/PVC. There was found a tendency that the formation amounts of homologues increased in order of degree of chlorination. When the molar ratio of CuO/PVC is 1, the fraction of O8CDD has become remarkably larger than the other results of higher molar ratio of CuO/PVC.

Thermodynamic consideration

Thermodynamic equilibrium calculation has been carried out using the software of F*A*C*T. Thermodynamic functions of PCDD/Fs employed in the present equilibrium calculation have been already obtained by the molecular orbital method with density functional theory, which is considered as one of the most accurate method at present.[4] The initial conditions of the equilibrium calculations are adjusted to the experimental ones. Gas and solid phases are considered as the equilibrium phases, and the formation of solid carbon is ignored in the present calculations. Figure 3 shows the relationship of the calculated amount of formed PCDD/Fs and the molar ratios of CuO/PVC at 300 °C. The amounts of PCDDs and PCDFs are shown in this figure, respectively. It is obvious that the formed PCDD/Fs drastically decrease with the increase in the molar ratio of CuO/PVC. This calculated tendency of the effect of oxygen on the formation of PCDD/Fs agrees well with the experimental results shown in Fig.1, although the absolute values of formation amount of PCDD/Fs are much different between the experimental and calculated ones, especially on the higher molar ratio of CuO/PVC.

Figure 4 shows the experimental results of the change in the formation amount of PCDD/Fs with retention time obtained at 300 °C. In this experiment, the molar ratios of CuO/PVC are fixed to 5. As mentioned in detail in the previous paper[1], it is shown in Fig.4 that the PCDD/Fs are formed at once in the range of shorter retention time and afterwards the decomposition proceeds by the further keeping at 300 °C. On the other hands,

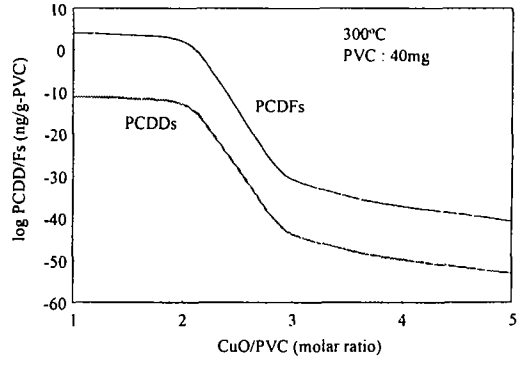

Fig.3 Results of thermodynamic calculation with the varying of molar ratio of CuO/PVC.

the formation amount of PCDD/Fs by the thermodynamic calculation at the molar ratio of 5 shown in Fig.3 are extremely smaller than that of experimental results shown in Fig.4. It is considered that the much longer retention time is necessary for the complete achievement of the equilibration at such low temperature as 300 °C. From these results shown in Fig.3 and 4, it can be suggested that the formation of PCDD/Fs may occur locally before the achievement of equilibration on the reaction system of CuO and PVC, so it can be dangerous to depend only on the thermodynamic consideration for the formation and decomposition of PCDD/Fs in the combustion process.

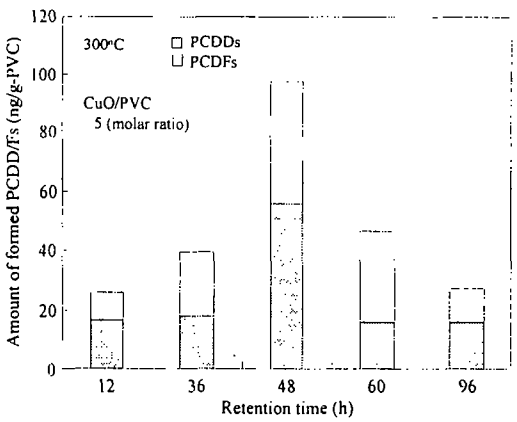

Fig.4 Relation between the amount of PCDD/Fs formation and retention time at 300 °C.

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