CATALYTIC DECHLORINATION OF PCDDS, PCDFS AND CO-PCBS WITH SUPPORTED PALLADIUM CATALYSTS

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Introduction

The emission of PCDDs, PCDFs and co-PCBs at municipal and hazardous waste incinerators is strictly regulated. For newly constructed municipal solid waste incinerators, the regulatory limit in Japan is 0.1 ng-TEQ/m^3 on a scale of > 4 tons/h. To achieve the strict limiting value, it is necessary to integrate disposal procedures such as adsorption and dust collection. However, disposal of the absorbent and dust, which contain PCDD/Fs and co-PCBs in high concentration, is a problem to be solved. Also, soil pollution by PCDD/Fs and co-PCBs is reported, so that the remediation procedure is expected to be developed. Recently, a process with volatilization and decomposition has been suggested, in which PCDD/Fs and co-PCBs in fly ash were volatilized to gas phase by heating in gas flow at 400ºC and decomposed by catalyst[1]. Remediation of soil contaminated by PCDD/Fs has been investigated, which includes ethanol washing[2] and irradiation of UV light[3]. A chemical reagent (KPEG) produced by mixing solid potassium hydroxide with a polyethylene glycol formulation is capable of dechlorinating PCDD/Fs at temperatures between 70ºC and 150ºC and has been used to treat activated carbon and soils contaminated with PCDD/Fs[4,5].

We previously reported that catalytic dechlorination of 2,7-D_2CDD and 1,2,6,7-T_4CDD occurs efficiently in a solution of NaOH in 2-propanol in the presence of supported noble metal catalysts such as Pd/C and Rh-Pt/C under mild conditions (< 35ºC)[6]. In this study, we examined the reaction conditions to complete dechlorination of 2,7-D_2CDD, 2,8-D_2CDF and 1,2,3,4-T_4CDD with Pd/C and Pd/Al_2O_3. Furthermore, we made an experiment on dechlorination of PCDD/Fs and co-PCBs, which were extracted from fly ash by using 2-propanol as a solvent.

Methods and Materials

The catalysts used in this study were two supported palladium catalysts (Pd/C and Pd/Al_2O_3), which contain 5 wt% of Pd. The specific surface area and dispersion were as follows: Pd/C (1088 m^2/g, 27 %), Pd/Al_2O_3 (205 m^2/g, 15 %). The substrares, 2,7-D_2CDD, 2,8-D_2CDF and 1,2,3,4-T_4CDD were purchased from AccuStandard Inc. Fly ash containing PCDD/Fs and co-PCBs was obtained from a waste incinerator. The TEQ value of fly ash was 32 ng-TEQ/g.

The dechlorination reaction of 2,7-D_2CDD, 2,8-D_2CDF and 1,2,3,4-T_4CDD was carried out in a solution of NaOH in 2-propanol in the presence of Pd/C or Pd/Al_2O_3 at 30-45ºC. The molar amount of NaOH was much larger than that of chlorine contained in the substrate. The reaction mixture was vigorously stirred in a test tube. The concentrations of substrates and products were determined with a GC–MS instrument (GC: HP6890; MS: HP5973).

In order to perform dechlorination of actual dioxins, PCDD/Fs and co-PCBs in fly ash was extracted by 2-propanol with a solvent extractor (DIONEX, ASE-200). To the 2-propanol solution containing the extracts, NaOH was dissolved and Pd/C was added. Then, the mixture was vigorously stirred and heated at 82ºC (reflux condition) in a flat bottom flask with a condenser. The analysis of

PCDD/Fs and co-PCBs was done by using a high-resolution GC-MS (GC:HP-6890; MS: Micromass AutoSpec Ultima). The TEQ value was calculated based on WHO-TEF (1998).

Results and Discussion

Dechlorination of a mixture of 2,7-D_2CDD and 2,8-D_2CDF

Dechlorination of a mixture of 2,7-D_2CDD (102 µg/ml) and 2,8-D_2CDF (115 µg/ml) was carried out in a solution of NaOH (2000 mg/ml) in 2-propanol (5 ml) in the presence of Pd/Al_2O_3 (8 mg) at 30ºC. Figure 1 shows the time profile of the dechlorination reaction. The concentrations of 2,7-D_2CDD and 2,8-D_2CDF decreased sharply at almost the same rate, and the substrates disappeared within 60 min. Small amounts of monochlorinated species (M_1CDD and M_1CDF) were detected during the reaction. The concentrations of these monochlorinated species increased to a maximum value and then gradually decreased to zero, implying that dechlorination proceeds stepwise. The concentrations of chlorine-free products, dibenzo-p-dioxin (DD) and dibenzofuran (DF), increased gradually, and the yields were estimated to be 90% and 98%, respectively, after 150 min of reaction. The dechlorination of D_2CDD and D_2CDF proceeded efficiently independent of the parent molecular structure bonding to chlorine, although the rate of formation of DF was slightly higher than that of DD. The molar amount of Pd exposed on the catalyst was estimated to be 0.58 µmol, which is less than the total molar amount of substrates, 4.4 µmol, indicating that the dechlorination reaction proceeds catalytically.

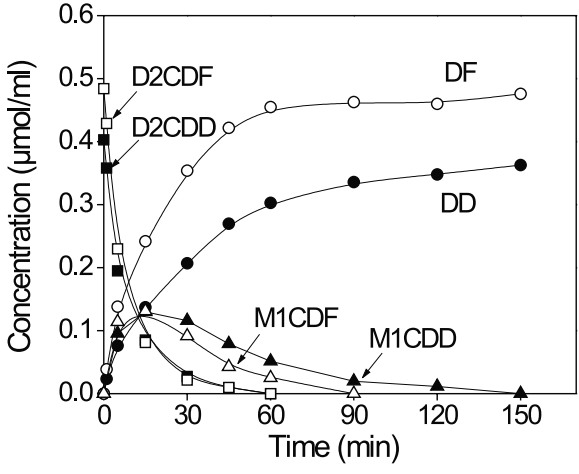

Figure 1. Dechlorination of a mixture of 2,7-D_2CDD and 2,8-D_2CDF with Pd/Al_2O_3 at 30ºC

Dechlorination of 1,2,3,4-T_4CDD

The catalytic system was applied for dechlorination of a higher chlorinated substrate, 1,2,3,4-T_4CDD, in which chlorines are very crowded. Figure 2 shows the time profile of DD, when dechlorination of 1,2,3,4-T_4CDD (260 µg/ml) was performed in a solution of NaOH (2000 µg/ml) in 2-propanol (6 ml) with Pd/C (10 mg) at 45 ºC. Catalytic dechlorination of 1,2,3,4-T_4CDD proceeded successfully, although a higher temperature and a larger amount of catalyst than those for dechlorination of 2,7-D_2CDD (30 ºC, 3 mg) was necessary (see a solid line for 1,2,3,4-T_4CDD and a dotted line for 2,7-D_2CDD). This indicates that higher chlorinated dioxins are likely to need severe

conditions to complete dechlorination. The yields of DD were leveled off (less than 80 %), because the catalyst support (active carbon) is capable of adsorbing a large amount of DD [6].

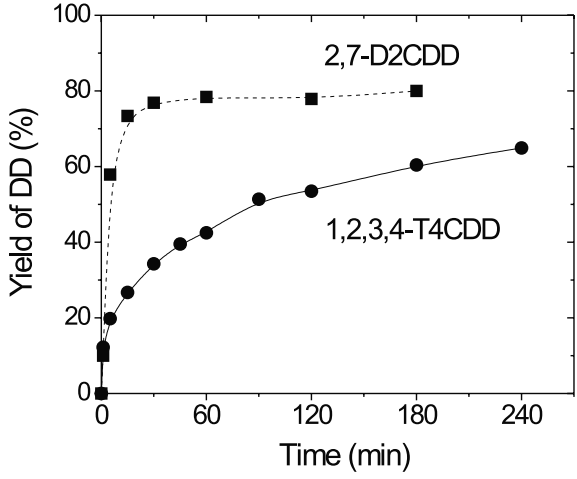

Figure 2. Dechlorination of 1,2,3,4-T_4CDD and 2,7-D_2CDD with Pd/C

Dechlorination of PCDDs, PCDFs and co-PCBs extracted from fly ash

Fly ash contaminated by PCDD/Fs and co-PCBs was extracted by 2-propanol with a solvent extractor under 1500 psi at 150 ºC for 15 min. To the 2-propanol solution (25 ml) containing the extracts, NaOH (58 mg) and Pd/C (50 mg) were added. Then, dechlorination reaction was carried out at 82 ºC for 2 h. After the reaction, the catalyst was recovered and the species adsorbed on the catalyst were extracted by toluene two times with the solvent extractor (1500 psi, 150ºC, 15 min) to minimize the loss of material balance. The extracts were mixed with the liquid phase, followed by GC-MS analysis. Figure 3 shows the profiles of PCDD/F homologues and co-PCB isomers before and after the reaction. The total TEQ value before the reaction was 16 pg-TEQ/ml. After the reaction, the concentrations of higher chlorinated PCDDs decreased and that of T_4CDDs slightly increases, indicating higher chlorinated species shift to lower chlorinated ones because of dechlorination. A similar shift was observed for PCDFs, although the concentrations of homologues entirely decreased. As for co-PCBs, higher chlorinated isomers almost disappeared and the concentration of a specific lower chlorinated isomer increased. The conversions of total PCDDs (T_4CDDs-O_8CDD), total PCDFs (T_4CDFs-O_8CDF) and total co-PCBs were estimated to be 60 %, 79 % and 78 %, respectively. The total TEQ value after the 2 h-reaction was 6.1 pg-TEQ/ml, which is 62 % down compared to the value before the reaction. Thus, it was found that dechlorination of PCDD/Fs and co-PCBs proceeds in the catalytic system. However, the efficiency was not so high, because the catalyst amount and the reaction time was not enough to complete dechlorination. The optimization of reaction conditions is in progress in our laboratory.

References

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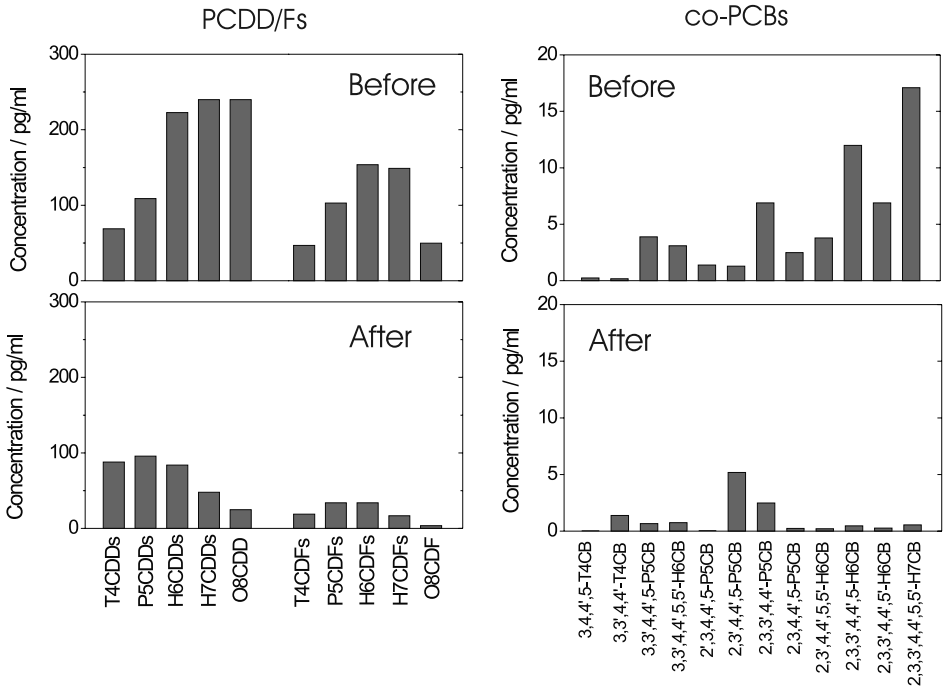

Figure 3. Dechlorination of PCDDs, PCDFs and co-PCBs extracted from fly ash

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