

CATALYTIC DECHLORINATION OF PCDD/Fs UNDER MILD CONDITIONS

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Introduction

The emission of polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) at municipal and hazardous waste incinerators is strictly regulated to reduce pollution. Although the firing systems have been designed and operated to minimize the formation of PCDD/Fs, the integration of disposal procedures such as adsorption and dust collection is indispensable at present facilities in order to achieve the stringent limiting value for PCDD/F emissions.

In recent years, destruction methods of PCDD/Fs have been widely studied. Catalytic oxidation with V₂O₅-TiO₂ catalysts has been adopted in some facilities to decompose PCDD/Fs from exhaust gases in the temperature region of ca. 200°C¹. On the laboratory scale, supercritical water systems are known to be capable of oxidizing PCDD/Fs contained in solid wastes², but high temperature and high pressure (>374.1°C, >22.12MPa) are required to generate the supercritical conditions. It is possible to decompose PCDD/Fs under ambient conditions using direct light irradiation³ or photocatalyst⁴, although the photodegradation rate is not very high. We report here a new method for catalytic dechlorination of PCDD/Fs; the dechlorination reaction proceeds in the presence of noble metal catalysts even at room temperature to give a very high conversion and an excellent yield of chlorine-free products.

Methods and Materials

The dechlorination reaction of PCDD/Fs was carried out in a solution of NaOH in 2-propanol (6 ml) in the presence of carbon-supported noble metal catalysts (3-10 mg) at temperatures between 23°C and 55°C. The reaction mixture, in a test tube under an atmosphere of N₂ or air, was stirred vigorously; temperature was controlled by immersion in a water bath. The initial concentration of PCDD/Fs was around 140-290µg/ml; a large excess of NaOH (2000µg/ml) was present. Analysis of the concentrations of substrates and products was carried out using GC-MS (GC: HP6890, MS: HP5973) equipped with a column of HP-5MS (30 m x 0.25 mm, 0.25µm film-thickness).

Substrates, 2,7-dichlorodibenzo-*p*-dioxin (2,7-DCDD), 1,2,6,7-tetrachlorodibenzo-*p*-dioxin (1,2,6,7-TCDD), and 2,8-dichlorodibenzofuran (2,8-DCDF) were obtained from AccuStandard Inc. Rh-Pt/C (Rh: 3wt %, Pt: 1wt%) catalyst was prepared by a method described in a previous paper⁵; Pd/C (Pd: 5wt%) was obtained from N. E. Chemcat Co. Ltd. These catalysts were selected due to very high activities for dechlorination of organic chlorides such as chlorobenzenes and PCBs⁵⁻⁸. Prior to use, Rh-Pt/C and Pd/C were heated under a flow of N₂ and H₂, respectively, at 200°C for 30 min.

Results and Discussion

The time profile for dechlorination of 2,8-DCDF with Pd/C at 30°C is shown in Fig. 1. The concentration of 2,8-DCDF in the solution decreased sharply, and the concentration of chlorine-free product, dibenzofuran (DF), increased gradually to attain the ultimate yield (> 90%). During the reaction, mono-chlorodibenzofuran (MCDF) increased in concentration to a maximum value then decreased until it disappeared, indicating that dechlorination of 2,8-DCDF proceeds stepwise.

Table 1 summarizes the experimental results of dechlorination of 2,7-DCDD and 1,2,6,7-TCDD at 23°C or 35°C for 3 h. The amount of catalyst was 10 mg, which is larger than that in Fig.1. After the reaction was completed, the catalyst and the liquid phase were separated by centrifuge, and then the substrates and products adsorbed on the catalyst were extracted with toluene, because the amount of dibenzo-*p*-dioxin (DD) adsorbed on the catalyst was too large to be negligible. The conversion and yield were evaluated from the sum of the amounts present in the liquid phase and adsorbed on the catalyst. Even at 23°C, very high conversion of 2,7-DCDD (99.9%) was obtained using Pd/C under both aerobic and anaerobic conditions (Runs 1 and 2). The tolerance to air has already been observed in the dechlorination reaction of chlorotoluenes⁸. When Rh-Pt/C was used as the catalyst, a higher temperature was required to complete dechlorination of 2,7-DCDD, and a small amount of partially dechlorinated PCDD (denoted as light-CDD), with a chlorine number less than that of the substrate, was detected (Runs 3 and 4). The yield of DD from 2,7-DCDD was over 70% in all cases. Dechlorination of 1,2,6,7-TCDD was also completed using Pd/C or Rh-Pt/C at temperatures below 35°C; high yields of DD were obtained with negligible amounts of light-CDD (Runs 5 and 6).

Table 1. Dechlorination of polychlorinated dibenzo-*p*-dioxin^a

Run	PCDD	Catalyst	Temp. (°C)	Gas phase	Initial conc. (µg/ml)	Conv. ^b (%)	Yield (%) ^b	
							light-CDD ^c	DD
1	2,7-DCDD	Pd/C	23	N ₂	215	99.9	0.02	80.1
2	2,7-DCDD	Pd/C	23	Air	236	99.9	0.02	74.5
3	2,7-DCDD	Rh-Pt/C	23	N ₂	213	97.6	7.6	70.0
4	2,7-DCDD	Rh-Pt/C	35	N ₂	209	99.8	0.1	69.6
5	1,2,6,7-TCDD	Pd/C	23	N ₂	167	99.9	< 0.01	74.1
6	1,2,6,7-TCDD	Rh-Pt/C	35	N ₂	139	99.8	0.06	59.9

^a Reaction conditions: 2-propanol (6.0ml); NaOH (2000µg/ml); catalyst (10 mg); reaction time (3 h)

^b Estimated from the sum of the amounts in the liquid phase and adsorbed on the catalyst

^c Partially dechlorinated PCDD

We studied previously the reaction mechanism of catalytic dechlorination of chlorobenzenes in the same system. From the experiments using D-labeled 2-propanol, it was proved that the reaction includes hydrogen transfer from 2-propanol to the aromatic chlorides⁶. We believe that the dechlorination reaction of PCDD/Fs proceeds in the same manner. The postulated reaction scheme of MCDD, as an example, is as follows.

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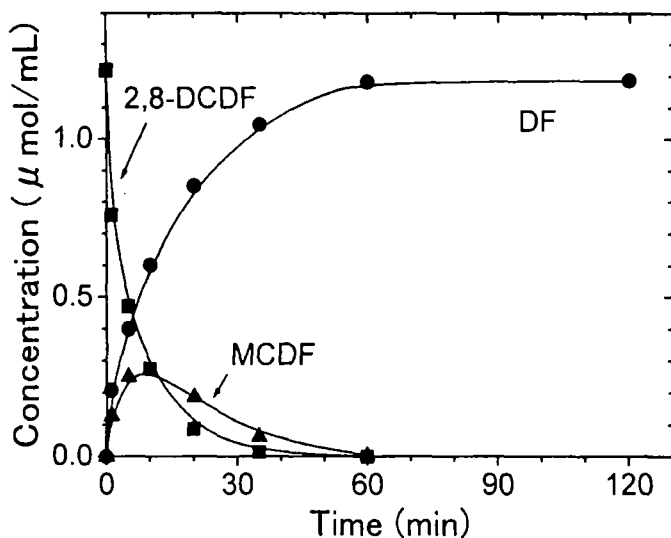


Figure 1. Catalytic dechlorination of 2,8-DCDF at 30°C.
Reaction conditions; 2-propanol (6 ml), 2,8-DCDF (288μg/ml),
Pd/C (3 mg), NaOH (2000μg/ml), in Air

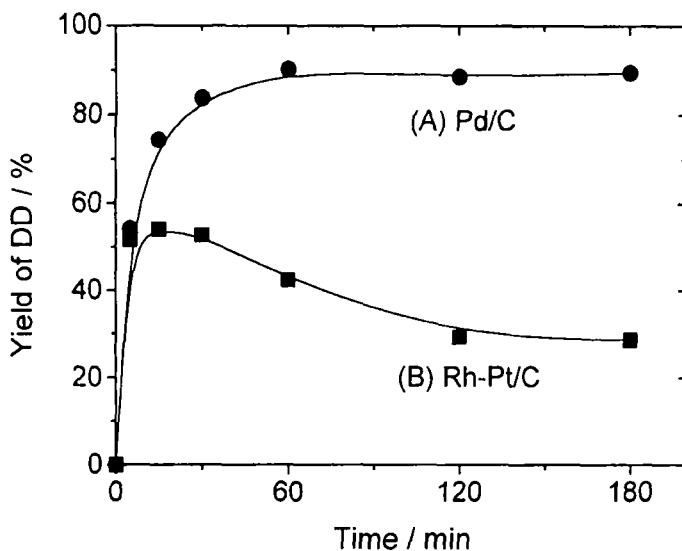
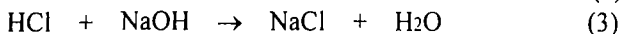
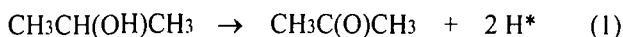


Figure 2. Catalytic dechlorination of 2,7-DCDD at 55°C.
Reaction conditions; 2-propanol (6 ml), NaOH (2000μg/ml), in N₂,
(A) Pd/C (3 mg), 2,7-DCDD (286μg/ml),
(B) Rh-Pt/C (10 mg), 2,7-DCDD (187μg/ml)

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First, catalytic dehydrogenation of 2-propanol proceeds on the noble metal catalyst⁹. The active hydrogen species (H^*) transfer to MCDD on the catalyst; as a result, hydrodechlorination of MCDD occurs to give DD. The chlorine released in the form of HCl is neutralized by NaOH dissolved in the solution, resulting in the formation of NaCl and H_2O . In the case of polychlorinated species, this dechlorination cycle is repeated until DD is formed.

Figure 2 shows the time profile of DD yield in the solution during catalytic dechlorination of 2,7-DCDD with Pd/C and Rh-Pt/C at higher temperature (55°C). In the presence of Pd/C, DD yield attained 90% within 1 h. On the other hand, the reaction with Rh-Pt/C exhibited a different time profile; DD increased to a maximum value (54%) and then gradually decreased, indicating that DD might change to a different species at higher temperature. In the same conditions, DF was rather stable; a decrease in concentration was hardly observed (not shown in figure).

In conclusion, catalytic dechlorination of PCDD/Fs such as 2,7-DCDD, 2,8-DCDF and 1,2,6,7-TCDD proceeds efficiently in a solution of NaOH in 2-propanol by using noble metal catalysts under mild conditions, including hydrogen-transfer hydrodechlorination. Further investigation with respect to higher chlorinated PCDD/Fs is in progress in our laboratory.

References

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