PERGAMON

Chemosphere 45 (2001) 129–136

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

PCDD/DF formations by the heterogeneous thermal reactions of phenols and their TiO_2 photocatalytic degradation by batch-recycle system

Hajime Muto [a,*], Koki Saitoh [b], Hitoshi Funayama [c]

[a] *Environmental Research Center, Akita University, 1-1-1 Hondo, Akita 010-8543, Japan*
[b] *Tohkem Products Co., 3-1-6 Barajima, Akita 010-0065, Japan*
[c] *Akita National College of Technology, 1-1 Iijima Bunkyoh-chou, Akita 011-8511, Japan*

Received 6 September 2000; accepted 18 October 2000

Abstract

Polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDD/DFs) formation by the thermal reactions of phenols with $CuCl_2$ under oxygen flux were carried out in relation to their formation mechanisms. To evaluate the effect of photocatalytic degradation of titanium dioxide (TiO_2) thin film prepared by the sol–gel method, the photocatalysis of PCDD/DFs in acetonitrile/water solution by batch-recycle system was conducted. For the thermal reaction system of powder mixtures of 2,4,5-trichlorophenol (2,4,5-TCP) and $CuCl_2$, the formation rates were 8.1 μg/g-2,4,5-TCP/min for total PCDD/DFs and 6.9 μg/g-2,4,5-TCP/min for PCDDs, and total PCDD/DF rate was higher by approximately 40 fold compared to phenol vapor/oxygen/$CuCl_2$ powder system. For the system of 2,4,5-TCP, PCDDs were mainly formed via *ortho*-phenoxyphenols (POP) intermediate by the condensation of 2,4,5-trichlorophenate. For PCDD/DF photocatalytic degradations, most PCDD congeners photodecomposed rapidly and the rates presented more than 70% (as dechlorination rates of 76% for PCDDs) at 24 h after irradiation, using PCDD/DFs formed with 2,4,5-TCP. The rate constants were in the order of $4.8–6.1 \times 10^{-3}$ min^{-1} , assuming the pseudo-first-order reactions for their low levels.

Keywords: PCDD/DFs; Thermal formation; Photodecomposition; Phenol; 2,4,5-TCP; Sol–gel method; Batch-recycle reactor; TiO_2 thin film

---

1. Introduction

PCDD/DFs occur in the incineration of municipal solid wastes and industrial and infectious wastes, the combustion of building materials and wood, and from industrial production proccess (Hiraoka and Okajima, 1994). Environmental pollution happens by the disposal and usage of chemical hazardous wastes and agricultural chemicals containing PCDD/DFs as contaminants. In combustion sources the PCDD/DF reduction has been conducted by the optimum operation and control of incinerators and the treatment equipments for flue gas, according to the guideline of regulations for PCDD/DFs. Advanced oxidation and biological processes have also been investigated to reduce PCDD/DFs in source and environment (Foester and Hites, 1992; Adriaens et al., 1995). In the liquid-phase photolysis the reductive dechlorination and hydroxidation of PCDDs in solvents was reported (Buser, 1976), and PCDD/DF degradation rates in the photolysis on solid surface were generally small compared to the liquid-phase photolysis (Nestrick

---

[*] Corresponding author. Tel.: +81-18-884-6192; fax: +81-18-884-6453.

E-mail address: hmuto@med.akita-u.ac.jp (H. Muto).

0045-6535/01/$ - see front matter

PII: S0045-6535(00)00552-X

and Lamparski, 1980; Choudry and Webster, 1987; Buser, 1988). Atkinson (1991) presented that simulated rate constants of PCDD/DF congeners (k_{OH}) with OH radical in the troposphere were in the order of 0.4–37 $cm^3/mol/s$ (their half-lives: 0.4–39 days). On the other hand, the studies on the heterogeneous photocatalytic degradation of organic compounds in liquid and gas phases with TiO_2 powder or its thin film have been advanced (Mathews, 1986; Rosenberg et al., 1992; Pichat et al., 1996), because of the stronger reduction/oxidation forces of electron and hole occurred by the irradiation of more than the bandgap energy of TiO_2 (Linsebigler et al., 1995).

We report here PCDD/DF formation by heterogeneous thermal reactions of phenols with $CuCl_2$ under the oxygen flux, in relation to their formation mechanisms, and the photocatalytic degradation of PCDD/DFs in acetonitrile/water solution using TiO_2 thin film prepared by the sol–gel method.

2. Materials and methods

2.1. Reagents

Phenol, 2,4,5-TCP, $CuCl_2$, titanium tetraisopropoxide, isopropanol, hydrogen peroxide, hydrochloric and sulfuric acids, dichloromethane, methanol, *n*-hexane, toluene, *n*-nonane, acetone, diethylene glycol, multilayer-silica gels, and alumina were reagent grade quality and obtained from Wako Pure Chemical Industries (Osaka, Japan), and XAD-II resin (Amberlite) and glass fiber filters (Advantec) were from Organo (Tokyo, Japan) and Tokyo Roshi Kaisha (Tokyo, Japan), respectively. Native and $^{13}C_{12}$-internal standard mixtures of PCDD/DF isomers of tetra- through octa-CDD/DF were purchased from Cambridge Isotope Laboratories (Woburn, MA).

2.2. Experimental

2.2.1. Thermal formation of PCDD/DFs

Fig. 1 shows an experimental apparatus for PCDD/DF formations by heterogeneous thermal reactions of phenols with $CuCl_2$ under the oxygen flux, and materials and conditions for their formations are shown in Table 1. 2,4,5-TCP powder weighing 23.5 g were mixed with 148 g of $CuCl_2$ powder and the mixture was put and divided into a few parts with quartz wools in a reaction fused silica tube (46 mm-i.d. × 500 mm-length), and the tube was equipped with a electric furnace being kept at 400°C set temperature. Continuously, oxygen gas was supplied at 10 ml/min of flow rate into the tube (85 ml/min as total flux with nitrogen gas) and PCDD/DFs formed were trapped with a PCDD/DF collector (Asada et al., 1987). The thermal reactions of 2,4,5-TCP with $CuCl_2$ for PCDD/DF formations were continued for 13 h. Phenol was prepared as 10% distilled water solution in a buffer flask and phenol vapor formed from the flask heated (60°C) was supplied to the tube put with 264 g of $CuCl_2$ powder at 30 ml/min of oxygen flux (250 ml/min as total gas flux). The vapors generated were 200 g for

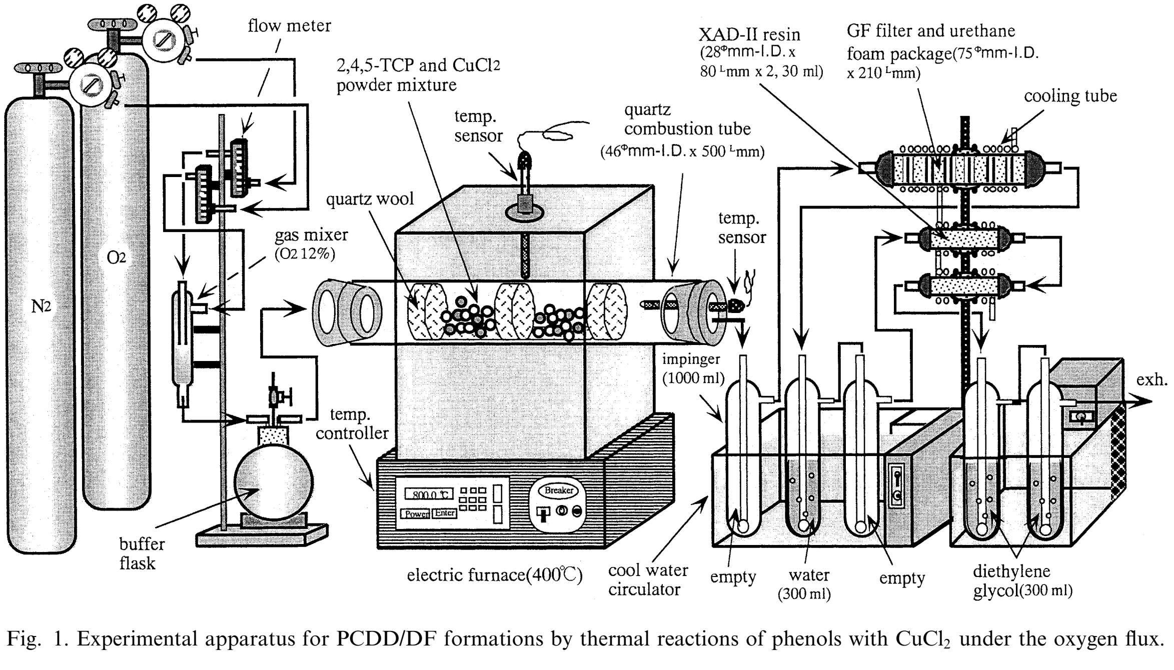

Fig. 1. Experimental apparatus for PCDD/DF formations by thermal reactions of phenols with $CuCl_2$ under the oxygen flux.

Table 1
Materials and conditions for PCDD/DF formations[a]

Terms/phenols	2,4,5-TCP	Phenol
Materials		
Organics (g)	23.5	200 as vapor (10% phenol solution; solution temperature 60°C)
$CuCl_2$(g)	148	264
Absorbents		
XAD-II; amberlite (g)	25	75
Urethan foam and GF filter (g)	3.2	7.2
Quartz wool (g)	3.5	9.6
Distilled water (ml)	300	300
Diethylene glycol (ml)	300	300
Gas flux		
N_2 gas rate (ml/min)	75	220
O_2 gas rate (ml/min)	10	30
Furnace temperature (°C)	400	400
Test time (h)	13	18

[a] Phenol was prepared in a buffer flask and its vapor was supplied to reaction tube with $CuCl_2$ powder divided to a few parts with quartz wool (see Fig. 1).

18 h of test time. For two reaction systems the reaction gas temperatures in the tube were 240 ± 5.2°C at 400°C set temperature.

2.2.2. Preparation of TiO_2 thin film

Procedure to prepare TiO_2 thin film on Pyrex glass plate by sol–gel method is shown in Fig. 2. By the hydrolysis reactions of titan isopropoxide (8.22 ml as titan alcoxide) with isopropanol (1.78 ml), amorphous monomers of titania oxides were formed and after standing for 1 h, continuously filtrated and monomer residues were dried at 60°C for more than 8 h. With 300 ml of 20 wt%-H_2O_2, 1 g of the residue was mixed at 60°C for 5 h and colloidal oligomer (titania sol) was formed by the condensation reactions of these monomers. To get Pyrex glass plate coated with TiO_2 thin film by gel formation reations, an aliquot of the sol solution diluted five times was dipped onto the plate and then dried at 45°C, and further calcinated at 500°C for 1 h. The sequential procedure of dipping, drying, and calcination was repeated two times.

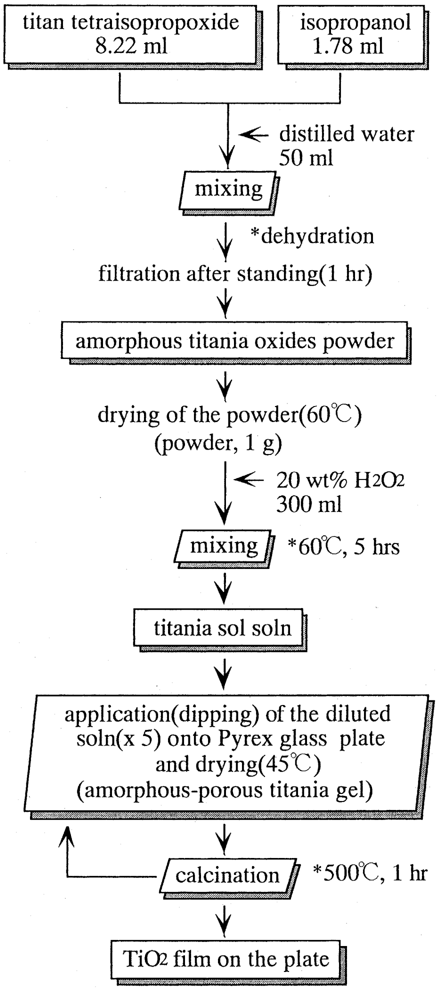

Fig. 2. Procedure to prepare TiO_2 film by sol–gel method.

2.2.3. Photocatalytic degradation of PCDD/DFs

Fig. 3 shows a schematic diagram of apparatus of PCDD/DF photocatalysis using TiO_2 batch-recycle system. PCDD/DFs formed by the thermal reactions of 2,4,5-TCP with $CuCl_2$ was dissolved into acetonitrile/distilled water (3:2) solution in reservior (500 ml, <0°C) being cooled by methanol chiller. Then, the solutions was mixed with a magnetic stirrer, acompanied with the supply of oxygen gas (100 ml/min), and cycled with a liquid pump (200 ml/min) to the reservior via an acrylic batch-recycle photoreactor where a Pyrex plate coated with TiO_2 thin film (70 mm × 120 mm, 2 mm thickness) and a quartz plate as irradiation window (100 mm × 150 mm, 2 mm thickness) were set. After cycling for 30 min, the solution (0°C) in the reactor was irradiated with a high pressure mercury lamp (Toshiba-H400PL, 400 W), and PCDD/DF photocatalysis test was started. Initial concentrations were 2.1 ppm for PCDDs and 0.25 for PCDFs. The lamp was cooled by air cooler and the distance of between the center of lamp and irradiation window was kept at 75 mm. Time-dependent sampling was carried out and sample volume and number were 1 ml and two samples by each time stage, respectively. Then, total reaction volume was 500 ml and the space velocity in the reactor was 105 ml/min.

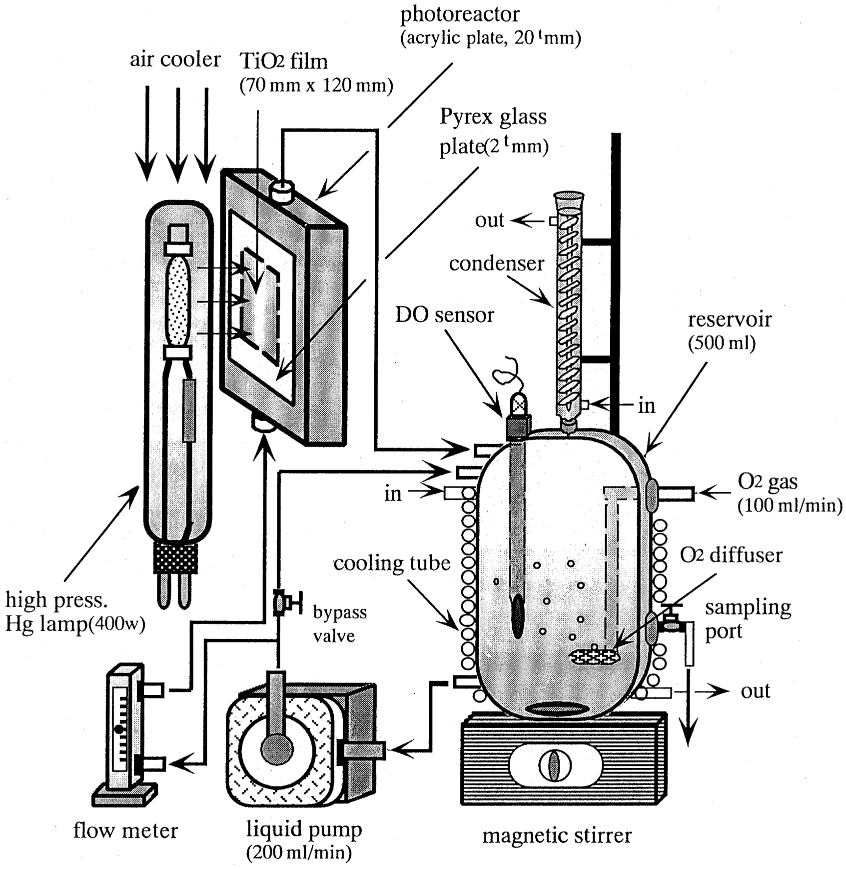

Fig. 3. Schematic diagram of apparatus for PCDD/DF photocatalytic degradation using TiO_2 batch-recycle system.

2.3. Analytical

The analytical procedures for PCDD/DFs in samples formed from phenols were same manners to those for flue gas from municipal solid waste incinerators (Asada et al., 1987). Urethane foam were treated with 200 ml of 2 mol/l-HCl solution and filtrated. PCDD/DFs in filtrate were extracted two times with 100 ml of dichloromethane. Those in residue and XAD-II resin were Soxhlet-extracted with 200 ml of toluene for 24 h. Washings, drains, and diethylene glycol solution were mixed and PCDD/DFs in the solution were extracted two times with 100 ml of dichloromethane. The dichloromethane and toluene extracts were mixed and concentrated. After the addition of internal standard of $^{13}C_{12}$-2,3,7,8-PCDD/DF isomer mixtures to the extract, the procedures of multilayer-silica gel and alumina column chromatographies for PCDD/DFs were continuously carried out. PCDD/DF eluents were concentrated up to 100 μl with nonane solution and the qualitative and quantitative analyses were proceeded by high-resolution gas chromatography/low-resolution mass spectrometry/single ion monitoring (HRGC/LRMS/SIM). For the procedures of photocatalized samples, to 1 ml of sample solution of acetonitrile/distilled water (3:2), 2 ml of *n*-hexane were added and shaked, and PCDD/DFs in the sample were transfered to *n*-hexane layer by the partition repeated three times, and followed to the multi-layer-silica gel chromatography and then GC/MS analysis. Conditions for HRGC/LRMS/SIM used to determine PCDD/DFs are described in details elsewhere (Muto et al., 1991).

3. Results and discussion

3.1. PCDD/DF formation by the thermal reaction of phenols with $CuCl_2$

Formation rates of PCDD/DF congeners by the thermal reactions of phenols with $CuCl_2$ under the oxygen flux are shown in Fig. 4. In heterogeneous thermal reaction system of powder mixtures of 2,4,5-TCP and $CuCl_2$ under the oxygen flux, the formation rates were 8.1 μg/g-2,4,5-TCP/min for total PCDD/DFs, 6.9 μg/g-2,4,5-TCP/min for PCDDs, and 1.2 μg/g-2,4,5-TCP/min

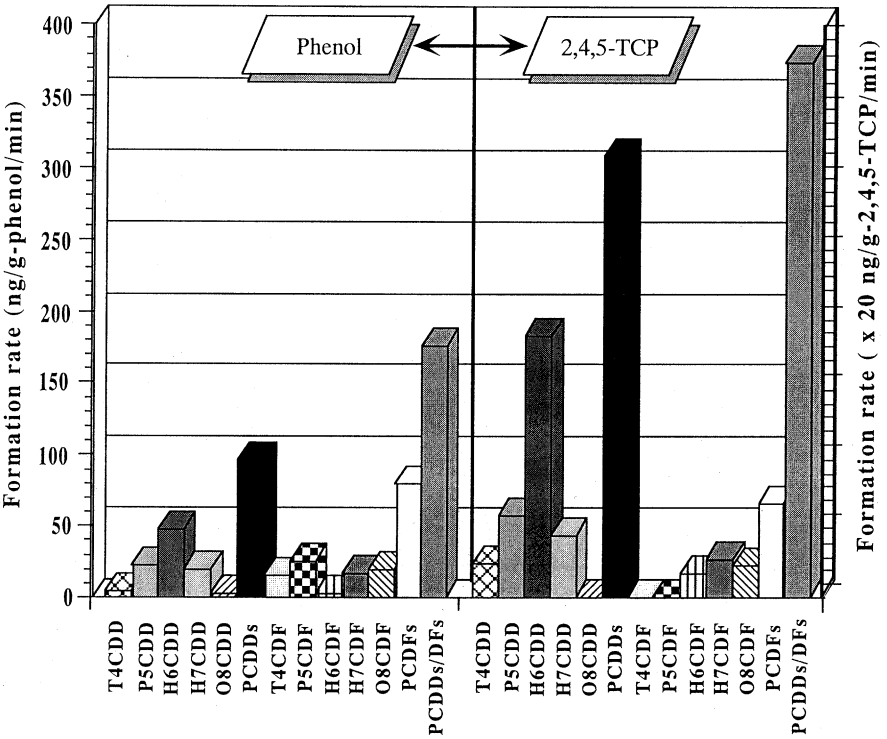

Fig. 4. Formation rates of PCDD/DF congeners by thermal reactions of phenols with $CuCl_2$ under the oxygen flux.

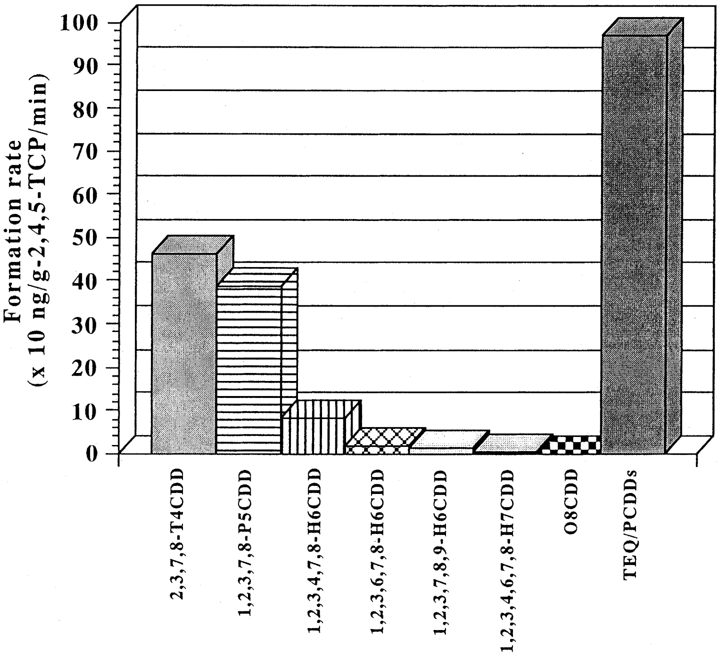

Fig. 5. Formation rates of 2,3,7,8-chlorine substituted PCDDs by thermal reactions of 2,4,5-TCP with $CuCl_2$ under the oxygen flux.

Table 2
Quantitative results of specific isomer analysis of PCDD/DF congeners, formed by the thermal reactions of 2,4,5-TCP with $CuCl_2$ under the oxygen flux, and their 2,3,7,8-TCDD toxic equivalents (TEQs) in hexane stock solution[a]

	measured (μg/ml)	1-TEF	TEQ (μg-TEQ/ml)
2,3,7,8-Tetra-CDD	85	×1	85
1,2,3,7,8-Penta-CDD	140	×0.5	71
1,2,3,4,7,8-Hexa-CDD	150	×0.1	15
1,2,3,6,7,8-Hexa-CDD	31	×0.1	3.1
1,2,3,7,8,9-Hexa-CDD	28	×0.1	2.8
1,2,3,4,6,7,8-Hepta-CDD	87	×0.01	0.87
Octa-CDD	1.7	×0.001	0.002
2,3,7,8-Tetra-CDF	0.04	×0.1	0.004
1,2,3,7,8-Penta-CDF	0.08	×0.05	0.004
2,3,4,7,8-Penta-CDF	0.08	×0.5	0.04
1,2,3,4,7,8-Hexa-CDF	2.8	×0.1	0.28
1,2,3,6,7,8-Hexa-CDF	0.10	×0.1	0.010
1,2,3,7,8,9-Hexa-CDF	0.11	×0.1	0.011
2,3,4,6,7,8-Hexa-CDF	0.18	×0.1	0.018
1,2,3,4,6,7,8-Hepta-CDF	8.3	×0.01	0.083
1,2,3,4,7,8,9-Hepta-CDF	2.7	×0.01	0.027
Octa-CDF	82	×0.001	0.082
Tetra-CDDs	86	–	–
Penta-CDDs	210	–	–
Hexa-CDDs	670	–	–
Hepta-CDDs	160	–	–
Octa-CDD	1.7	–	–
Total PCDDs	1100	–	180
Tetra-CDFs	0.14	–	–
Penta-CDFs	1.6	–	–
Hexa-CDFs	60	–	–
Hepta-CDFs	99	–	–
Octa-CDF	82	–	–
Total PCDFs	240	–	0.56
Total PCDDS and PCDFs	1400	–	180

[a] Limits of detection: tetra- and penta-CDD/DFs, 0.01 μg/ml; hexa- and hepta-CDD/DFs, 0.01 μg/ml; octa-CDD/DFs, 0.05 μg/ml.

for PCDFs, and PCDD/DF total rate was higher by approximately 40 folds than that by the reaction system of phenol vapor/oxygen with $CuCl_2$ powder. PCDFs rate in the phenol formation system was 80 ng/g-phenol/min and low by about one-fifteenths compared to the 2,4,5-TCP system, but total rate of lowly chlorinated DFs of tetra- and penta-CDF congeners was 40 ng/g-phenol/min and more higher than the 2,4,5-TCP system being their negligible rates. Fig. 5 shows the formation rates of 2,3,7,8-chlorine substituted PCDDs by the thermal reactions of 2,4,5-TCP with $CuCl_2$ under the oxygen flux. The formation rates of 2,3,7,8-tetra-CDD and 1,2,3,7,8-penta-CDD were 464 and 387 ng/g-2,4,5-TCP/min (982 ng/g-2,4,5-TCP/min for all 2,3,7,8-chlorine substituted PCDDs). The quantitative results of specific isomer analysis of PCDD/DF congeners and their toxic equivalents (TEQs) in hexane solution, formed by the 2,4,5-TCP system, are shown in Table 2.

For the mechanisms of PCDD/DF formation from chlorophenols in gas-phase reactions, it was reported that the pyrolysis of chlorinated phenates at a temperature of about 280°C results in the formation of definite PCDD congeners (Higginbotham et al., 1968; Weber and Hagenmaier, 1999) suggested that after the formation of phenoxy radicals, PCDD/DFs are formed via intermediates of POPs by the condensation of phenates and dihydroxybiphenyls (DOHBs) formed by the dimerization of two phenoxy radicals, and the formation of the DOHBs and their condensation to PCDFs show a strong dependency on the reaction temperature, the substitution pattern of the chlorophenols and the oxygen concentration. In our PCDD/DF formation system with phenol vapor and $CuCl_2$ powder, it was considered that PCDD/DFs were formed via intermediates of the POPs and DOHBs, since the formation rates of PCDDs were nearly equal to those of PCDFs. However, for the system with 2,4,5-TCP, it was suggested that PCDDs were mainly formed via the POP intermediates by the condensation of 2,4,5-trichlorophenate, because that the formations of PCDF congeners were a little. Particularly large quantities of 2,3,7,8-tetra-, 1,2,3,7,8-penta- and 2,3,7,8-chlorine substituted hexa-CDDs, which are the highest thermodynamic stability for each group of PCDD homologues (Wehrmeier et al., 1998), were formed by the sequential-thermal reactions with $CuCl_2$, but highly chlorination reactions such as 1,2,3,4,6,7,8-hepta- and octa-CDDs formations were not appeared. These PCDD/DF formation might be by the heterogeneous pyrolysis of phenates of phenol and 2,4,5-TCP with $CuCl_2$ at gas temperature of about 240°C under the oxygen flux, though it was reported that in gas-phase reactions chlorophenols react in the presence of oxygen above 250°C to PCDDs and above 340°C not only to PCDDs but also to PCDFs (Weber and Hagenmaier, 1999).

3.2. Batch-recycle photocatalytic degradation of PCDD/DFs using TiO_2 thin film

From the X-ray diffraction analysis, amorphous TiO_2 powder obtained by the hydrolysis reactions of titan isopropoxide of titan alcoxides was an anatase-type TiO_2, and its peak intensities and patterns appeared that both crystallization and particle size of the TiO_2 may be small. Nishide and Mizukami (1992) carried out the sol formation reactions of titania oxides monomers with water/70%-nitric acid and coated the sol on soda glass and silicon wafer as 0.1 μm of thin layer. In our sol formations, however, it was found that H_2O_2 solution is a more favorite reagent.

Fig. 6 shows the changes in concentrations of PCDD congeners (a) and dechlorination rates calculated as total PCDDs (b) in PCDD/DF photocatalysis by a plate type batch-recycle photoreactor with a TiO_2 thin film plate, using PCDD/DFs formed with 2,4,5-TCP. Each PCDD congener photodecomposed rapidly and at 24 h after irradiation the disappearance rates of most congeners presented more than 70%. The photocatalytic degradations of the lowly chlorinated DD congeners of tetra- and penta-CDDs were slower, and this may be by the sequential photodechlorinations of highly chlorinated DDs of hexa- through octa-CDD. Then, if the disappearances of PCDD/DFs are by their dechlorinations, an equation of the dechlorination rates (Z_D) is the following: $Z_D = \Sigma(C_j, \theta \times W_j)/\Sigma(C_j, 0 \times W_j)$ $(j = 4, \ldots, 8)$, where $C_j, 0$ is the initial concentration of a PCDD/DF congener, C_j, θ the concentration of a PCDD/DF congener at a time θ, and W_j is chlorine content of a PCDD/DF congener. According to the equation, the dechlorination rates were calculated as 76% for PCDDs (see Fig. 6(b)), 100% for PCDFs and 79% for PCDD/DFs at 24 h after irradiation from the disappearance rates of PCDD/DF congeners.

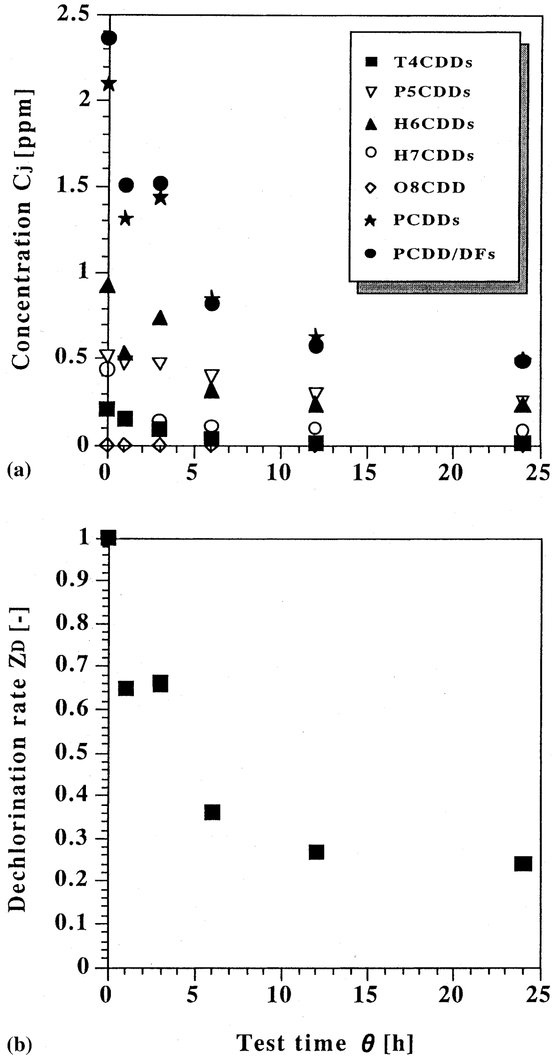

Fig. 6. Changes in concentrations of PCDD congeners (a) and dechlorination rates calculated as total PCDDs (b) in TiO_2 thin film photocatalytic degradation, using PCDD/DFs formed by thermal reaction of 2,4,5-TCP with $CuCl_2$.

For the photodegradations of PCDD/DFs in aqueous solution and in organic solvents, Kim and O'Keefe (2000) suggested that photolytic half-lives of di-, tetra- and octa-CDDs at the 300 nm were in the order of 4.3–680 min in 60% acetonitrile/water solution and di- and tetra-CDDs had higher first-order photodegradation rate constants of 1.6×10^{-1} and 3.2×10^{-2} min^{-1}, respectively, and also, it was reported that the half-lives of tetra- and octa-CDDs and their CDFs at 254 nm were in the range of 2.3–88 min in *n*-hexane solution, showing the higher rate constant of 2,3,7,8-TCDF (2.7×10^{-2} min^{-1}; Muto and Takizawa, 1991). Dulln et al. (1986) photolized 2,3,7,8-TCDD in water/acetonitrile (9:1) solution, and reported that its conversion rates were 62% at 313 nm for 24 h and 49% at sunlight for 26.3 h. On the other hand, Muto et al. (1991) presented that for the heterogeneous photolysis of PCDDs in suspension solution of fly ash with water and/or water/acetonitrile (2:3) at 254 nm, the pseudo-first order rate constants of all PCDD congeners were in the order of $0.75–1.7 \times 10^{-3}$ min^{-1}.

For the TiO_2 thin film photocataysis of PCDD/DFs formed with 2,4,5-TCP by the batch-recycle system, the photodegradation rate constants of total PCDDs, and PCDFs and PCDD/DFs and their half-lives were in the order of $4.8–6.1 \times 10^{-3}$ min^{-1} and of 1.9–2.4 h, assuming the pseudo first-order reactions for low levels of PCDD/DFs. Compared to the liquid-phase photolyses of PCDD/DF isomers mentioned above, these rate constants were about one order of magnitude small, but the same order as those in the heterogeneous photolysis of PCDDs (Muto et al., 1991), in spite of UV irradiation of more than 300 nm. It was found that the milder photocatalytic degradation system using TiO_2 catalyst was useful for the PCDD/DF reduction.

References

Adriaens, P., Fu, Q., Grbic-Galic, D., 1995. Bioavailibility and transformation of highly chlorinated dibenzo-*p*-dioxins and dibenzofurans in anaerobic soils and sediments. Environ. Sci. Technol. 29, 2252–2260.

Asada, S., Matsushita, H., Morita, M., Hamada, Y., 1987. Determination of chlorodibenzo-*p*-dioxins and chlorobenzofurans discharged from several municipal incinerators in Japan. Chemosphere 16, 1907.

Atkinson, R., 1991. Atmospheric lifetimes of dibenzo-*p*-dioxins and dibenzofurans. Sci. Total Environ. 104, 17–33.

Buser, H.R., 1976. Preparation of qualitative standard mixtures of polychlorinated dibenzo-*p*-dioxins and dibenzofurans by ultraviolet irradiation of the octachloro compounds. J. Chromatogr. 129, 303–307.

Buser, H.R., 1988. Rapid photolytic decomposition of brominated and brominated/chlorinated dibenzodioxins and dibenzofurans. Chemosphere 17, 889–903.

Choudry, G.G., Webster, G.R.B., 1987. Environmental photochemistry of polycholorinated dibenzofurans (PCDFs) and dibenzo-*p*-dioxins (PCDDs): a review. Toxicol. Environ. Chem. 14, 43–61.

Dulln, D., Drossman, H., Mill, T., 1986. Products and quantum yields for photolysis of chloroaromatics in water. Environ. Sci. Technol. 20, 72–77.

Foester, C.J.B.D., Hites, R.A., 1992. Photodegradation of polychlorinated dioxins and dibenzofurans adsorbed to fly ash. Environ. Sci. Technol. 26, 502–507.

Higginbotham, G.R., Huang, A., Firestone, D., Verret, J., Ress, J., Campell, A.D., 1968. Chemical and toxicological evaluations of isolated and synthetic chloro derivatives of dibenzo-*p*-dioxin. Nature 220, 702–703.

Hiraoka, M., Okajima, S., 1994. Source control technologies in MSW incineration plants. Organohalogen Compd. 19, 275.

Kim, M.-K., O'Keefe, P.W., 2000. Hotodegradation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans in aqueous solutions and in organic solvents. Chemosphere 41, 793–800.

Linsebigler, A.L., Lu, G., Yates Jr, J.T., 1995. Photocatalysis on TiO_2 surface: principles, mechanisms, and selected results. Chem. Rev. 95, 735–758.

Mathews, R.W., 1986. Photo-oxidation of organic material in aqueous suspensions of titanium dioxide. Water Res. 20, 569.

Muto, H., Takizawa, Y., 1991. The liquid-phase photolyses of tetra- and octa-CDDs and their CDFs in hexane solution. Chem. Lett., 273–276.

Muto, H., Shinada, M., Takizawa, Y., 1991. Heterogeneous photolysis of polychlorinated dibenzo-*p*-dioxins on fly ash in water-acetonitrile solution in relation to the reaction with ozone. Environ. Sci. Technol. 25, 316–322.

Nestrick, T.J., Lamparski, L.L., 1980. Identification of tetrachlorodibenzo-*p*-dioxin isomers at the 1-ng level by photolytic degradation and pattern recognition techniques. Anal. Chem. 52, 1865–1874.

Nishide, T., Mizukami, F., 1992. Preparation and properties of TiO_2 films by complexing agent-assited sol–gel method. J. Ceram. Soc. Jpn. 100, 1122–1126.

Pichat, P., Mas, D., Guillard, C., Luck, F., 1996. TiO_2 photocatalytic degradation of mono-chloroaceic acid and 2,4-dichlorophenoxyacetic acid (2,4-D) in liquid water effect of ozonized air. In: Second International Conference on TiO_2 Photocatalytic Purification and Treatment of Water and Air, Cincinnati, OH, USA, p. 39.

Rosenberg, I., Brock, J.R., Heller, A., 1992. Collection optics of TiO_2 photocatalyst on hollow glass microbeads floating on oil slicks. J. Phys. Chem. 96, 3423.

Weber, R., Hagenmaier, H., 1999. Mechanism of the formation of polychlorinated dibenzo-*p*-dioxins and dibenzofurans from chlorophenols in gas phase reactions. Chemosphere 38, 529–549.

Wehrmeier, A., Lenoir, D., Schramm, K.-W., Zimmermann, R., Hahn, K., Henkelmann, B., Kettrup, A., 1998. Patterns of isomers of chlorinated dibenzo-*p*-dioxins as tool for elucidation of thermal formation mechanisms. Chemosphere 36, 2775.