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PCDD/F Adsorption and Destruction in the Flue Gas Streams of MWI and MSP via Cu and Fe Catalysts Supported on Carbon

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Received January 24, 2008. Revised manuscript received April 3, 2008. Accepted May 9, 2008.

Catalytic destruction has been applied to control polychlorinated dibenzo-*p*-dioxin and dibenzofuran (PCDD/Fs) emissions from different facilities. The cost of carbon-based catalysts is considerably lower than that of the metal oxide or zeolite-based catalysts used in the selective catalytic reduction (SCR) system. In this study, destruction and adsorption efficiencies of PCDD/Fs achieved with Cu/C and Fe/C catalysts from flue gas streams of a metal smelting plant (MSP) and a large-scale municipal waste incinerator (MWI), respectively, are evaluated via the pilot-scale catalytic reactor system (PCRS). The results indicate that Cu and Fe catalysts supported on carbon surface are capable of decomposing and adsorbing PCDD/Fs from gas streams. In the testing sources of MSP and MWI, the PCDD/F removal efficiencies achieved with Cu/C catalyst at 250 °C reach 96%, however, the destruction efficiencies are negative (−1,390% and −112%, respectively) due to significant PCDD/F formation on catalyst promoted by copper. In addition, Fe/C catalyst is of higher removal and destruction efficiencies compared with Cu/C catalyst in both testing sources. The removal efficiencies of PCDD/Fs achieved with Fe/C catalyst are 97 and 94% for MSP and MWI, respectively, whereas the destruction efficiencies are both higher than 70%. Decrease of PCDD/F destruction efficiency and increase of adsorption efficiency with increasing chlorination of dioxin congeners is also observed in the test via three-layer Fe/C catalyst. Furthermore, the mass of 2,3,7,8-PCDD/Fs retained on catalyst decreases on the order of first to third layer of catalyst. Each gram Fe/C catalyst in first layer adsorbs 10.9, 6.91, and 3.04 ng 2,3,7,8-PCDD/Fs in 100 min testing duration as the operating temperature is controlled at 150, 200, and 250 °C, respectively.

1. Introduction

The catalysts commonly used in the selective catalytic reduction (SCR) process are made of metal oxides or zeolites,

with the optimal operating temperature ranging from 200 to 430 °C. Recently, the SCR catalyst which operates at a lower temperature (180–190 °C) is also available (1). Operating at this temperature would avoid extensive heating of the gas streams. In comparison with the SCR catalysts, various types of carbons exhibit high catalytic activity in NO_x reduction at relatively low temperatures (2–4). The cost of carbon material is considerably lower than that of SCR. These advantages over the metal oxide or zeolite-based catalysts make carbon an excellent alternative for NO_x removal by SCR. In addition, relevant study (5) demonstrates that the NO conversion efficiency exceeding 90% can be achieved with carbon-based catalysts (Cu/C and Fe/C) with the operating temperature lower than 200 °C, hence the carbon-based catalysts can potentially serve as effective catalysts for NO_x removal. Previous studies indicate that SCR catalysts (TiO₂-based V₂O₅–WO₃) applied to reduce NO_x emission are also effective in the decomposition of PCDD/Fs (6, 7).

During the past decade, commercial SCR catalysts have been developed for the combined dioxin/NO_x removal by increasing the oxidation potential of the catalysts with a higher vanadium content (7, 8). Another study (9) also indicates that catalytic decomposition and removal efficiencies of semivolatile compounds (such as PCDD/Fs and PCBs) strongly depend on volatility and oxidative behavior of the compounds. Both properties are closely related to the chlorination level of the compound. The volatility of PCDD/Fs decreases with increasing chlorination level as can be derived from the vapor pressure of the PCDD/F. Highly chlorinated PCDD/Fs are retained on the catalyst surface longer, therefore, increasing the chance of oxidation. Up to now, a variety of catalysts have been developed for PCDD/F removal. Among the noble metals, Pt, Pd, and Rh are commonly used. Those catalysts can achieve as high as 90% removal efficiency at 300 °C; however, relatively high cost has limited its application (10–12). For the effective destruction of PCDD/Fs, the temperature lower than 210 °C might be sufficient in pilot plants, however, temperature of 240–260 °C is typically needed in the field tests (13). At 200 °C, metal oxides (Cu and Fe) supported on carbon show higher SCR activity for NO_x removal than the oxides supported on other materials such as TiO₂-based V₂O₅–WO₃ (14). Since the cost of Cu or Fe catalyst supported on carbon is considerably lower than that of commercial SCR catalysts, the possibility of Cu and Fe catalysts supported on carbon in reducing PCDD/F emission is anticipated.

For end-of-pipe treatment, activated carbon injection (ACI) is predominantly used for reducing PCDD/F emissions from MWIs. In contrast to SCR system, the ACI process has some disadvantages. Activated carbon adsorbs PCDD/Fs but does not destroy them and this physical process merely transfers vapor-phase PCDD/Fs to solid-phase PCDD/Fs (15). Although the catalysts composed of noble metals (such as vanadium and titanium) are effective in decomposing PCDD/Fs from flue gas streams, the cost of those catalysts is relatively high. Hence, developing dedioxin catalysts with low cost is essential in reducing PCDD/F emissions from different facilities. The aim of this study is to investigate the removal and destruction efficiencies of PCDD/Fs achieved with two nonnoble metal catalysts (Cu/C and Fe/C) from the flue gas streams of a metal smelting plant (MSP) and municipal wastes incinerator (MWI), respectively.

2. Experimental Section

2.1. Preparation of Cu/Fe Catalysts Supported on Carbon.

In this study, porous carbon prepared by Hureha Ltd. Co.

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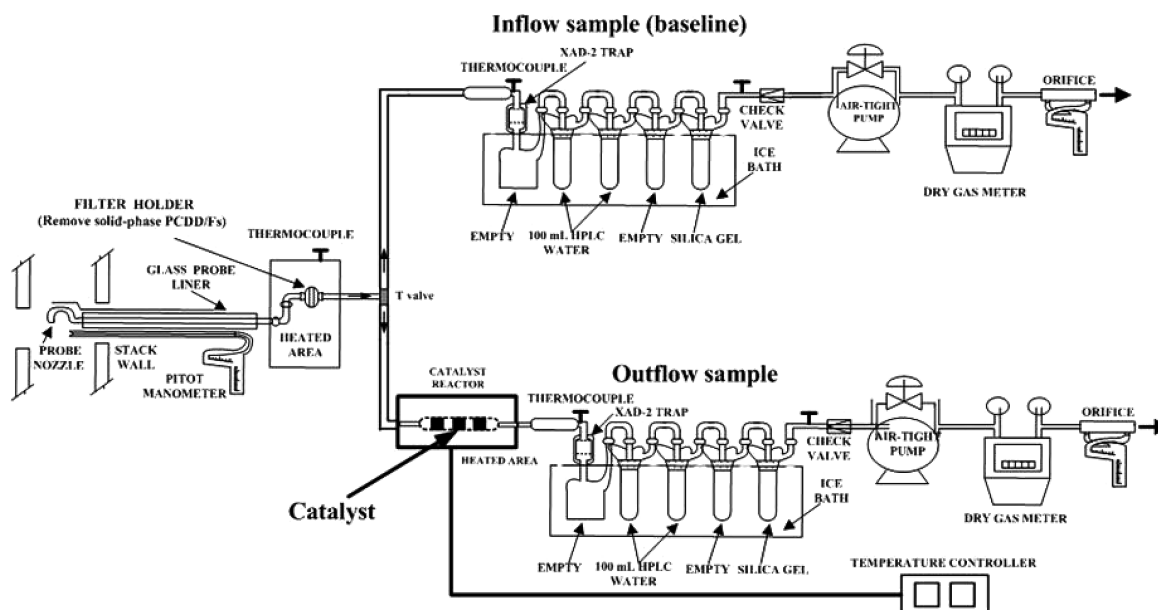


FIGURE 1. Schematics of the pilot-scale catalytic reactor system (PCRS).

(Japan) is used as the support for two nonnoble metal catalysts. The average diameter of porous carbon particles (G-BAC) was 6 mm. In metal impregnation, $\text{Cu}(\text{NO}_3)_2$ and $\text{Fe}(\text{NO}_3)_3$ were mixed with porous carbon, respectively, and the resulting products are designated as Cu/C and Fe/C catalysts. The process was initiated by stirring the porous carbon and nitrate mixtures at 90 °C for two hours under N_2 environment. The resulted slurry was dried at 110 °C for 12 h after stirring, followed by heat treatment in N_2 at 350 °C for two hours to give metal-impregnated catalysts. The pore structures of the catalysts were characterized by N_2 adsorption at -196 °C with an automated adsorption apparatus (Micromeritics, ASAP 2010). A JEOL JEM-1200-EX-TEM tunneling electron microscope was used to study the morphology of catalyst surface. The BET surface areas of Cu/C and Fe/C catalyst are around 600 m^2/g , and the pore volumes of those catalysts are around 0.294 cm^3/g . The analysis also indicates that these catalysts are mainly microporous (<20 Å). Although two different metals including Fe and Cu were used in impregnation, the physical characteristics of the impregnated samples were similar. Owing to the similarity in pore structures, the influence of physical characteristics on the catalytic activity was considered to be minor in the following discussion.

2.2. Pilot-Scale Catalytic Reactor System (PCRS). A pilot-scale catalytic reactor system (PCRS) was constructed for the evaluation of PCDD/F removal and destruction efficiencies with temperature variation. The PCRS consists of two Graseby Anderson stack sampling systems (MST 2010) as shown in Figure 1. One stack sampler located upstream of the catalytic reactor is used to collect vapor-phase PCDD/Fs with XAD-2 as inlet concentration (baseline sample), whereas the other stack sampler is located downstream of the catalytic reactor to collect PCDD/Fs as outlet concentration. A 0.5 g amount of Cu/C or Fe/C catalyst is filled in the reactor for examining the effectiveness of the catalyst in removing PCDD/F from the flue gases of the MSP and MWI investigated, respectively. The space velocity of the catalytic reactor system was controlled at 18 000 h^{-1} . In this study, the solid-phase PCDD/Fs and particulate matter had been removed by fiber glass filter installed prior to PCRS and only vapor-phase PCDD/Fs passing through the catalytic reactor are concerned.

2.3. Sampling Locations. The MSP investigated is equipped with electrostatic precipitator (EP) and selective catalytic reduction (SCR) as major APCDs for controlling

particulate and gaseous emissions. The MWI investigated is equipped with cyclone (CY), dry sorbent injection (DSI), and bag filter (BF) as major APCDs for controlling acid gas and particulate emissions. The capacity of the MSP and MWI investigated are 250 and 450 tons/day/unit, respectively. Table 1 indicates the experimental parameter of the PCRS applied in the MSP and MWI, respectively. The PCDD/F-containing gas stream (vapor-phase PCDD/Fs) were sampled from the flue gases of MSP (downstream of EP) and MWI (downstream of CY), respectively. To determine the PCDD/F removal and destruction efficiencies achieved with Cu/C and Fe/C catalysts, the PCDD/F concentrations of the gas streams prior to the reactor (inlet), downstream of the reactor (outlet) and on the catalyst are measured simultaneously.

2.4. Sample Collection and Analysis. The flue gas sampling was conducted with the Graseby Anderson stack sampling system complying with the U.S. Environmental Protection Agency (USEPA) Method 23. The vapor-phase sample was collected by XAD-2 resin. To avoid the error and bias caused by sampling PCDD/Fs bound to the particulate matter, isokinetic sampling had to be conducted to collect representative samples. Before sampling, the XAD-2 was also spiked with known amounts of USEPA Method 23 surrogate standard solution to confirm that no PCDD/Fs would penetrate through the sampling system. Once the sampling was completed, the samples were brought back to the laboratory under refrigeration. They were then spiked with known amounts of USEPA Method 23 internal standard solution. Thereafter, the XAD-2 and filter samples were Soxhlet extracted with toluene for 24 hours. The toluene extract was then concentrated to about 1 mL by rotary evaporation and was replaced by 5 mL hexane for pretreatment process. Having been treated with concentrated sulfuric acid, the sample was then subjected to a series of cleanup columns including sulfuric acid silica gel column, acidic aluminum oxide column and celite/carbon column. Finally, the cleaned up solution was spiked with known amounts of Method 23 recovery standard solution, and then analyzed for 17 2,3,7,8-substituted PCDD/F congeners with high resolution gas chromatography (HRGC) (Hewlett-Packard 6890 plus)/high resolution mass spectrometer (HRMS) (JEOL JMS-700) equipped with a fused silica capillary column DB-5 MS (60 m \times 0.25 mm \times 0.25 μm , J&W). The mass spectrometer was operated with a resolution greater than 10 000 under positive EI conditions, and data were obtained in the selected ion monitoring (SIM) mode.

TABLE 1. Operating Conditions of PCRS in the MSP and MWI, Respectively (SV^a: 18 000 h⁻¹^a, testing duration = 100 min)

facility	catalyst	temperature (°C)	O ₂ (%)	H ₂ O _(g) (%)	HCl (ppm)	sampling flow rate (lpm)
MSP	Cu/C catalyst	150	15.8	8.9	150	3.8
		200	15.6	6.9		
		250	15.9	9.2		
	Fe/C catalyst	150	15.8	8.9		
		200	15.6	6.9		
		250	15.9	9.2		
MWI	Cu/C catalyst	150	10.3	19.4	1500 to 2000	3.8
		200	10.6	20.4		
		250	10.4	20.9		
	Fe/C catalyst	150	10.3	19.4		
		200	10.6	20.4		
		250	10.4	20.9		

^a Space velocity (h⁻¹) = gas flow rate passing through the catalyst bed (m³/hr)/volume of the catalyst bed (m³).

TABLE 2. PCDD/F Removal and Destruction Efficiencies Achieved with Cu/C and Fe/C Catalyst in the MSP and MWI, Respectively (SV^a: 18 000 h⁻¹, Testing Duration = 100 min)

facility	catalyst	temperature (°C)	PCDD/F _{inflow} (ng-PCDD/Fs)	PCDD/F _{outflow} (ng-PCDD/Fs)	PCDD/F _{on catalyst} (ng-PCDD/Fs)	removal efficiency (%)	destruction efficiency (%)
MSP	Cu/C	150	2.43	0.108	1.65	95.6	27.6
		200	2.87	0.215	2.65	90.9	-19.6
		250	3.78	0.158	56.1	95.8	-1,390
	Fe/C	150	2.43	0.071	1.95	97.1	17.0
		200	2.87	0.145	1.24	94.9	51.6
		250	3.78	0.106	0.702	97.2	78.6
MWI	Cu/C	150	7.38	0.330	4.54	95.5	33.9
		200	9.23	1.16	2.24	87.5	63.2
		250	8.31	0.340	17.3	95.9	-112
	Fe/C	150	7.38	1.68	2.06	93.2	49.2
		200	9.23	1.29	1.81	90.0	66.4
		250	8.31	1.50	1.05	93.9	69.2

^a Space velocity (h⁻¹) = gas flow rate passing through the catalyst bed (m³/hr)/volume of the catalyst bed (m³).

3. Results and Discussion

3.1. PCDD/F Removal and Destruction Efficiency Achieved with Cu/C and Fe/C Catalysts. PCDD/F removal and destruction efficiencies describing the ability of the catalyst applied to remove and destroy PCDD/Fs, respectively, are defined as follows:

$$\text{removal efficiency (\%)} = \left[\frac{\text{mass of PCDD/F}_{\text{inflow}} - \text{mass of PCDD/F}_{\text{outflow}}}{\text{mass of PCDD/F}_{\text{inflow}}} \right] \times 100 \quad (1)$$

$$\text{destruction efficiency (\%)} = \left[\frac{\text{mass of PCDD/F}_{\text{inflow}} - (\text{mass of PCDD/F}_{\text{outflow}} + \text{mass of PCDD/F}_{\text{on catalyst}})}{\text{mass of PCDD/F}_{\text{inflow}}} \right] \times 100 \quad (2)$$

Table 2 lists the results of PCDD/F-containing gas streams being treated with Cu/C and Fe/C catalysts in the MSP and MWI investigated, respectively. The results indicate that the PCDD/F removal efficiencies achieved with Cu/C and Fe/C catalysts are not significantly affected by operating temperature. Our results indicate that lower PCDD/F removal efficiencies achieved with Cu/C and Fe/C catalysts are observed at 200 °C. Additionally, PCDD/F removal efficiencies do not increase with increasing operating temperature. That is attributed to the fact that removal efficiency achieved with carbon-based catalysts is influenced by the PCDD/F destruction and adsorption at different operating temperatures.

In the case of Fe/C catalyst testing, higher PCDD/F destruction efficiency was observed at 250 °C, however, higher PCDD/F adsorption efficiency was observed at 150 °C. Hence, the PCDD/F removal efficiencies achieved with a carbon-based catalyst observed at 150 and 250 °C are always comparable.

Since Cu and Fe catalysts are supported on carbon which functions as effective adsorbent, the removal efficiencies of PCDD/Fs achieved with Fe/C and Cu/C catalysts are greater than 90% for both facilities tested. For the case of MSP, the results indicate that the destruction efficiency of PCDD/Fs over Fe/C catalyst increases from 17.0 to 78.6% as the temperature is increased from 150 to 250 °C. On the other hand, destruction efficiencies of PCDD/Fs achieved with Cu/C catalyst at 150 °C is 27.6%. As temperature is increased to 250 °C, destruction efficiency of PCDD/Fs with Cu/C catalyst decreases dramatically to -1390%. That is attributed to the fact that significant amounts of PCDD/Fs were generated on Cu/C catalyst, causing the destruction efficiency to decrease to a negative value. Previous study (16) recognized copper as an effective catalyst in PCDD/F formation in some circumstances. Relevant study (17) also indicates that as the operating temperature of SCR is >250 °C, PCDD/Fs are probably formed via de novo synthesis within SCR. As for the case of MWI, the results indicate that the decomposition of PCDD/Fs over Fe/C catalyst increased with increasing temperature. At 250 °C, Fe/C catalyst reached the highest PCDD/F destruction efficiency (69.2%). However, Cu/C catalyst had a negative destruction efficiency of PCDD/Fs

TABLE 3. Comparison of PCDD/F Destruction and Removal Efficiencies Achieved with Commercial V₂O₅/TiO₂ Catalyst and Fe/C Catalyst Applied

catalyst type	operating temperature (°C)	space velocity (h ⁻¹)	destruction efficiency (%)	removal efficiency (%)
V ₂ O ₅ /TiO ₂ catalyst (8)	100	40 000	No destruction	82.1
	150		92.5	98.6
	230		98.7	98.8
Fe/C catalyst (this study)	150	18 000 ^a	49.2	97.1
	200		66.4	94.9
	250		78.6	97.2

^a Space velocity (h⁻¹) = the flow passed through the catalyst bed (m³/hr)/ volume of the catalyst bed (m³).

(-112%) at 250 °C. The reason for those phenomena became obvious as the PCDD/Fs remained on Cu/C and Fe/C catalysts were further analyzed. At 150 °C, 80.0 and 28.0% of PCDD/Fs are adsorbed on Fe/C catalyst tested in the MSP and MWI, respectively. Only 43.3 and 19.6% of PCDD/Fs were recovered at 200 and at 250 °C, and only 18.6 and 12.7% of total PCDD/Fs remained on Fe/C catalyst for the MSP and MWI, respectively (Table 2). A previous study (8) conducted with Ti/V catalyst indicated that PCDD/Fs were effectively removed via adsorption at low temperature (100 °C), whereas PCDD/F concentrations were reduced mainly by destruction at temperature above 150 °C. This results in high destruction efficiency of PCDD/Fs over Fe/C catalyst at 250 °C. Interestingly, Cu/C catalysts that were originally designed to decompose PCDD/Fs, become the activator of PCDD/F formation at 250 °C. At 250 °C, negative PCDD/F destruction efficiencies over Cu/C catalyst were observed for both MSP and MWI. This is due to significant formation of PCDD/Fs on Cu/C catalyst. Factors affecting PCDD/F formation are summarized as follows: (1) gas composition: O₂ is essential for de novo synthesis, the presence of HCl, SO₂, CO, and H₂ has little influence and H₂O_(g) may affect the homologue profile. (2) solid-phase material: Carbon of degenerated graphitic structure, chlorine and metallic catalyst (Cu²⁺ is a strong catalyst) are essential for de novo synthesis. (3) temperature: Remarkable PCDD/Fs formation occurs at 250~300 °C insignificant PCDD/F formation is observed below 200 °C or above 400 °C (18). Carbon material is used as support of Cu catalyst in this study and causes significant PCDD/F formation at 250 °C. Hence, destruction efficiency of PCDD/Fs achieved with Cu/C catalyst become negative with significant PCDD/F formation at 250 °C. Actually, adsorption and destruction of PCDD/Fs with a carbon-based catalyst is complicated and depends on a number of parameters. In general, the HCl concentration in the flue gas would affect PCDD/F formation. However, the flue gas sampling results indicate that the PCDD/F concentrations on TEQ basis measured in MSP range from 2.40 to 3.56 ng-TEQ/Nm³ which is considerable higher than that measured in MWI (1.07 to 1.67 ng-TEQ/Nm³). In general, higher PCDD/F inlet concentrations result in lower PCDD/F destruction efficiency achieved with a catalyst. That may be the reason why the PCDD/F adsorption and destruction efficiencies achieved with a carbon-based catalyst are not comparable with the HCl concentration measured in the flue gases in two facilities.

In general, the PCDD/F destruction efficiency achieved with a catalyst is significant at a high operating temperature (250 °C). As the operating temperature was set at 150 °C, PCDD/F destruction efficiencies achieved with Fe/C catalyst at two facilities are not significant (<50%). At 200 °C, PCDD/F destruction efficiencies achieved with Fe/C catalyst increase to 51.6 and 66.4% in MSP and MWI, respectively. A previous study (4) indicated that the metal oxides (Cu and Fe) supported on carbon show a higher activity for NO_x removal

than the oxides supported on other materials such as TiO₂-based V₂O₅-WO₃. That is attributed to the fact that the pollutants were effectively removed with a carbon-based catalyst via adsorption and destruction at low temperature. The adsorption capacity of the carbon-based catalyst applied in this study is significantly enhanced with the treatment of sulfuric acid, which would introduce acidic functional groups on the carbon surface. This results in higher destruction efficiency of PCDD/Fs over Fe/C catalyst at operating temperatures higher than 200 °C. Compared with V₂O₅/TiO₂ catalysts that are widely used for PCDD/F decomposition in industrial processes, Fe/C catalyst has lower catalytic activity for PCDD/F decomposition at 250 °C. PCDD/F destruction efficiencies achieved with Fe/C catalyst at 250 °C tested in the MSP and MWI investigated reach 78.6 and 69.2%, respectively. Performance of Fe/C catalyst for PCDD/F destruction at the MSP and MWI tested are slightly lower than that of the commercial V₂O₅/TiO₂ catalyst in the laboratory (Table 3). In addition, the destruction efficiencies of PCDD/Fs achieved with catalysts are mainly affected by two other factors in addition to the catalyst activity, i.e., operating temperature and space velocity.

3.2. Comparison of Adsorption Efficiency of Pcds/Fs over Fe/C Catalyst with Temperature Variation. Two mechanisms including adsorption and decomposition have to be considered regarding PCDD/F removal achieved with carbon support catalysts. Those phenomena were both affected by the variation of operating temperature and characteristics of catalysts. Table 2 indicates that the PCDD/F destruction efficiency varies significantly with the different metals supported on carbon. Due to significant PCDD/F formation on Cu/C catalyst, Fe/C catalyst is selected to evaluate the PCDD/F adsorption efficiency with temperature variation. PCDD/F adsorption efficiencies is calculated as follows:

$$\text{adsorption efficiency (\%)} = \frac{\text{mass of PCDD/F}_{\text{on catalyst}}}{\text{mass of PCDD/F}_{\text{inflow}}} \times 100(3)$$

Figure 2 shows the PCDD/F adsorption efficiency over Fe/C catalyst with temperature variation in the MSP and MWI investigated. Fe/C catalysts adsorb 37.1 to 83.8% PCDDs and 12.9 to 79.6% PCDFs for the flue gases of MSP at temperature range of 250–150 °C. In the case of MWI, around 16.6–56.9% PCDDs and 11.7–19.5% PCDFs in the flue gas are adsorbed by Fe/C catalyst at temperature of 250–150 °C. The PCDD/F adsorption efficiencies over Fe/C catalyst decreased with increasing temperature. That is attributed to the fact that the PCDD/Fs tend to distribute in vapor phase as temperature is increased. In addition, the adsorption efficiencies of PCDDs over Fe/C catalyst are higher than that of PCDFs observed in two sources due to the lower vapor pressure of PCDD congeners (1.51–24.7 Pa at 150 °C) compared with PCDF congeners (1.79–29.1 Pa at 150 °C)

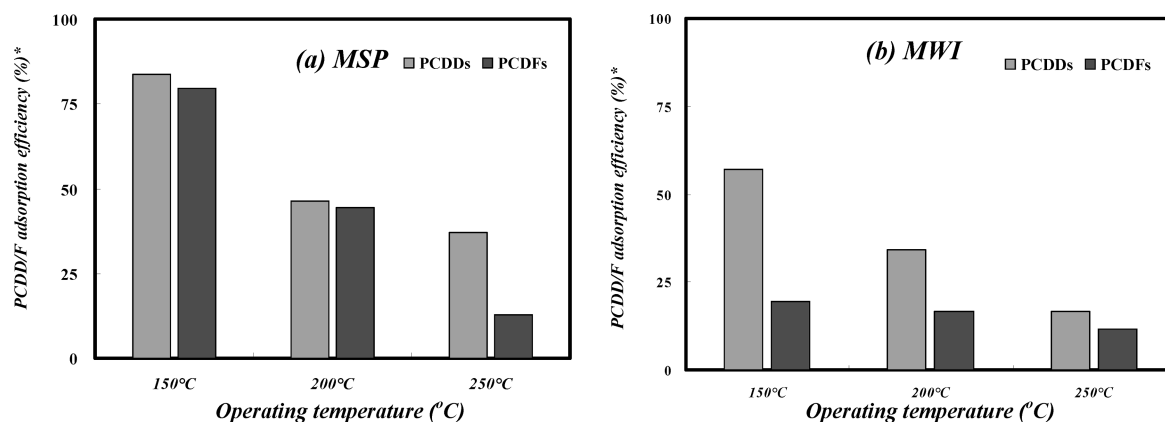


FIGURE 2. PCDD/F adsorption efficiency achieved with Fe/C catalyst at different operating temperatures in (a) MSP, and (b) MWI (SV=18 000 h⁻¹, testing duration = 100 min).

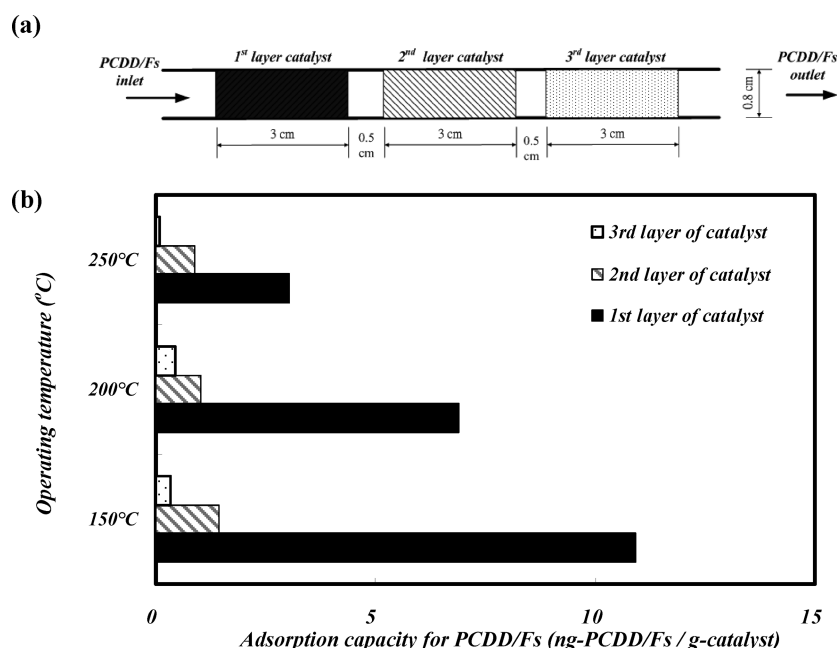


FIGURE 3. (a) Schematics of the Fe/C catalyst bed for the test of PCDD/F adsorption capacity, (b) Variation of PCDD/Fs adsorbed on three-layer Fe/C catalyst at different operating temperatures in the MSP investigated ($n = 6$) (SV=18 000 h⁻¹, testing duration = 100 min).

(19). Interestingly, PCDD/F adsorption efficiency also varies with different location (layer) of the catalyst bed. As indicated in Figure 3(a), the catalyst bed is composed of three-layer Fe/C catalyst. Figure 3(b) also compares the mass of PCDD/F adsorbed on three-layer Fe/C catalyst with different operating temperatures in the MSP investigated. Each gram of Fe/C catalyst in first layer adsorbs 10.9, 6.91, and 3.04 ng-PCDD/Fs in 100 min testing duration as the operating temperatures are controlled at 150, 200, and 250 °C, respectively. Based on total PCDD/F mass adsorbed on the catalyst bed, the percentage of PCDD/Fs retained on the first layer of catalyst decreases from 86 to 76% as the temperature is increased from 150 to 250 °C. Additionally, the mass of 2,3,7,8-PCDD/Fs retained on the catalyst decreases on the order of first to third layer of catalyst. That may be caused by the variation of PCDD/F mass transfer rates on different layers of the catalysts.

3.3. Comparison of Adsorption and Destruction Efficiency of PCDD/F Congener over Fe/C Catalyst with Temperature Variation. Figure 4 shows the interesting trend of the PCDD/F destruction and adsorption efficiencies with temperature variation in two facilities. The PCDD/F destruction efficiency achieved with Fe/C catalyst increases with increasing operating temperature. On the other hand, the

PCDD/F adsorption efficiency decreases with increasing temperature. The adsorption and destruction efficiencies of each congener over the catalyst vary significantly due to different characteristics of each PCDD/F congener. Figure 5 shows the adsorption and destruction efficiencies, respectively, of PCDD/F congeners over Fe/C catalyst at 150 and 250 °C. As the MWI flue gas passed through the catalyst bed, Fe/C catalyst adsorbed 10.4~73.8 and 5.84~27.2% PCDD/Fs at 150 and 250 °C, respectively. The adsorption efficiency of PCDD/F congener increases with increasing chlorination level of PCDD/F congeners and decreases with increasing operating temperature. Generally, highly chlorinated PCDD/Fs in flue gases are more easily adhered to the particles due to lower vapor pressures (20). Prior to the PCRS, the particulate matter had been effectively removed by the glass fiber filter. Therefore, the results obtained in PCRS experimentation excluding the interference of particulate matter indicate that highly chlorinated PCDD/F congeners are more effectively adsorbed by a carbon-based catalyst bed. Interestingly, adsorption efficiencies of PCDD congeners over Fe/C catalyst are higher than that of PCDF congeners due to the difference of vapor pressures between PCDD and PCDF congeners.

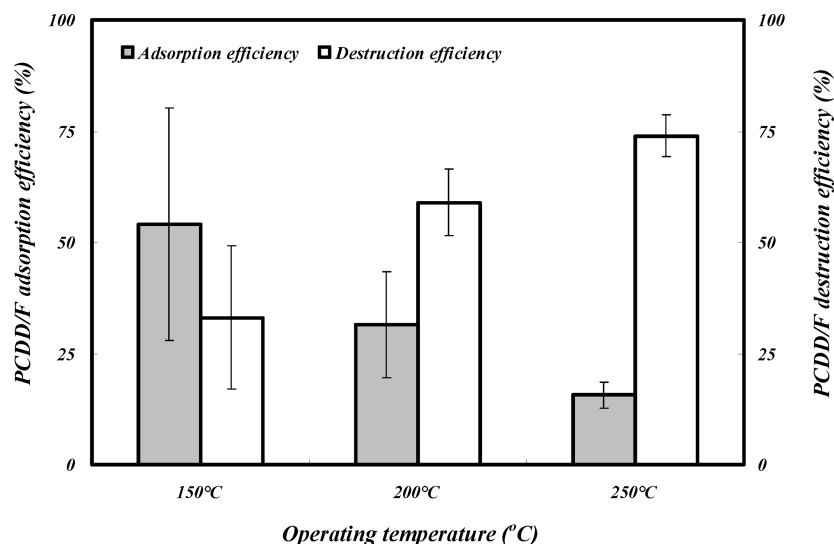


FIGURE 4. PCDD/F adsorption and destruction efficiencies achieved with Fe/C catalyst at different operating temperatures in the MSP and MWI investigated ($n = 6$) (SV = 18 000 h⁻¹, testing duration = 100 min).

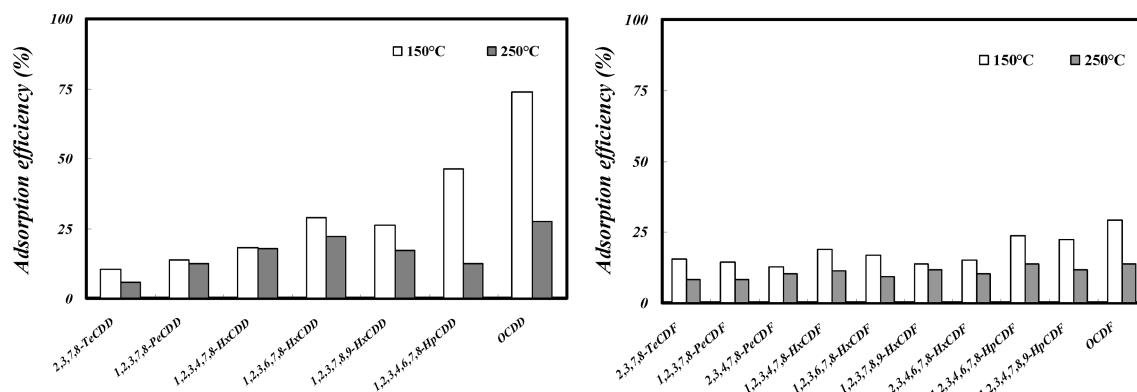


FIGURE 5. Adsorption efficiency of PCDD/F congeners achieved with Fe/C catalyst at 150 and 250 °C in the MWI investigated (SV = 18 000 h⁻¹, testing duration = 100 min).

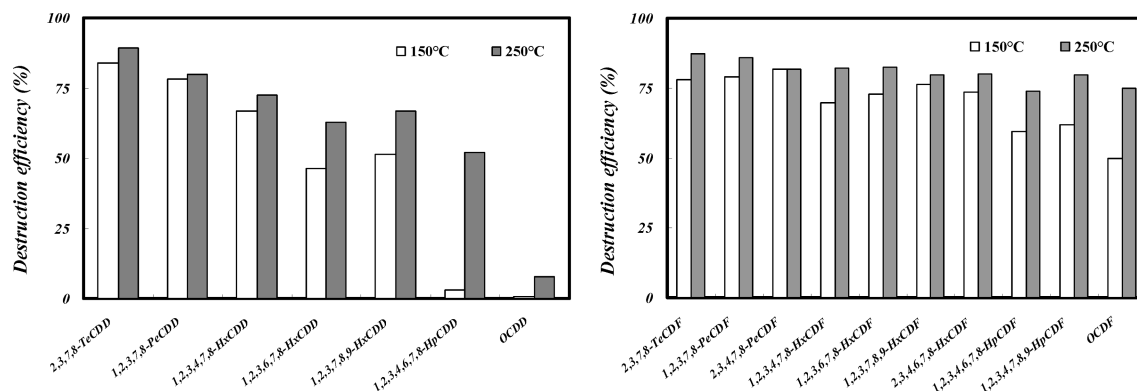


FIGURE 6. Destruction efficiency of PCDD/F congeners achieved with Fe/C catalyst at 150 and 250 °C in the MWI investigated (SV = 18 000 h⁻¹, testing duration = 100 min).

Figure 6 indicates that around 0.56~83.9% and 7.72~89.3% PCDD/F congeners were decomposed by Fe/C catalyst at 150 and 250 °C, respectively. Low activity in the decomposition of highly chlorinated PCDD/F over Fe/C catalyst is observed. Especially, Fe/C catalyst has the lowest activity in the decomposition of OCDD (0.56%) and 1,2,3,4,6,7,8-H7CDD (3.11%) at 150 °C in the MWI investigated. 2,3,7,8-T4CDD (89.3%) and 2,3,7,8-P4CDF (87.2%) are two congeners of the highest destruction efficiency of all 17 2,3,7,8-substituted PCDD/F congeners over Fe/C catalyst at 250 °C. Overall speaking, the destruction efficiencies of PCDFs

are higher than that of PCDDs, and the destruction efficiency of PCDD/F congeners decreases with increasing chlorination. Additionally, our results indicate that the PCDD/F congeners achieved with a catalyst were converted to the chlorinated products such as trichloro-, dichloro-, and monochlorodibenzo-*p*-dioxin/furans via the dechlorination mechanism. Therefore, the dechlorination proceeds stepwise to give the chlorine-free product or biphenyl. Previous study (21) also indicated that the PCDD/F congeners achieved with a catalyst possibly react to form trace amounts of CO₂, H₂O(g), and HCl.

Dependences of destruction and adsorption efficiencies of the PCDD/F congeners on operating temperature are totally different. Previous study (22) indicates that highly chlorinated PCDD/F congeners have more stable chemical structures and smaller reaction rate constants (h^{-1}) compared with lowly chlorinated congeners. For example, the reaction rate constants of OCDD and OCDF photodegraded by UV range from 0.0080 to 0.0087 h^{-1} , whereas that of TCDD/F vary from 0.0104 to 0.0202 h^{-1} . Hence, highly chlorinated PCDD/F congeners are more difficult to decompose by catalyst, and even poison the catalysts due to their lower vapor pressure and high adsorption efficiency on the catalyst. The decrease of PCDD/F destruction efficiency and increase of adsorption efficiency with increasing chlorination is attributed to the physical characteristics of PCDD/F congeners and the removal mechanism of Fe/C catalyst. In conclusion, Fe/C catalyst is of higher destruction efficiencies compared with Cu/C catalyst in two testing sources and of lower capital cost compared with the commercial SCR catalysts. The destruction efficiencies of PCDD congeners are relatively lower than that of PCDFs, and the destruction efficiencies of lowly chlorinated congeners are higher than that of highly chlorinated congeners over Fe/C catalyst.

Acknowledgments

We gratefully acknowledge the financial support provided by NSC (NSC94-EPA-Z-008-002) and NCU-ITRI (04-03-02). Assistance provided by Prof. W. H. Ding of Department of Chemistry, National Central University in analyzing the samples is also acknowledged.

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