

# Field investigation and laboratory development of VO<sub>x</sub>/TiO<sub>2</sub> catalyst at low temperature: decomposition and kinetics analysis of PCDD/Fs and 1,2-DCBz

Ma YF, Li XD, Lin XQ, Yan JH

State Key laboratory of Clean Energy Utilization of Zhejiang University, Hangzhou, China, 310027,  
[happyjoe@zju.edu.cn](mailto:happyjoe@zju.edu.cn)

## 1. Introduction

Polychlorinated-*p*-dibenzodioxins and dibenzofurans (PCDD/Fs), discharged from municipal solid waste incineration (MSWI) have received the global attention because of their extreme toxicity and high risk to human health<sup>1-3</sup>. Catalytic technology can decrease the emission amount of PCDD/F by catalytic decomposition, other than transformation without amount reduction.

Some previous studies reported the positive catalytic effect of deNO<sub>x</sub> catalysts on PCDD/F removal<sup>4-5</sup>. And the catalysts of TiO<sub>2</sub>-based transition metal oxide are considered as the ideal option due to the low price and strong resistance to chlorine poisoning of transition metal oxide<sup>6-7</sup>. V<sub>2</sub>O<sub>5</sub>, the active component, shows the advantages of high activity, high selectivity and strong resistance to sulfur compared to other transition metal oxides, such as CrO<sub>x</sub>, MnO<sub>x</sub>, FeO<sub>x</sub>, CoO<sub>x</sub>, CuO<sub>x</sub> and MoO<sub>x</sub><sup>8-9</sup>. Yu et al. had reported the PCDD/F removal efficiency (RE) increased from 94.3% to 96.7% as increasing the reaction temperature of VO<sub>x</sub>/TiO<sub>2</sub> from 160°C to 200°C, and the maximum RE was reached at 300°C<sup>10</sup>. Previous studies have shown that adding a second catalytic component to the Vanadia catalyst can effectively improve the catalytic activity<sup>11-12</sup>, and V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> has been globally used. Boos et al. reported V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> honeycomb catalyst removed 96% PCDD/F from the flue gas under 280 °C<sup>13</sup>. Goemans et al. reported the V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>/TiO<sub>2</sub> catalyst simultaneously reduced the PCDD/Fs and NO<sub>x</sub> with RE of 99% and 90%, respectively, at 230 °C<sup>14</sup>. Yu et al. added the second metal catalytic components of WO<sub>x</sub>, MoO<sub>x</sub>, MnO<sub>x</sub> and CeO<sub>x</sub> into the VO<sub>x</sub>/TiO<sub>2</sub> catalyst, and the PCDD/F degradation efficiency of increase rate order from high to low order is CeO<sub>x</sub>, MnO<sub>x</sub>, WO<sub>x</sub>, MoO<sub>x</sub>. The VO<sub>x</sub>-CeO<sub>x</sub>/TiO<sub>2</sub> has a PCDD/F degradation efficiency of 92.5% at 200°C. The previous studies were mainly carried out in laboratory experiments based on powder catalysts. However, the powder catalysts have no macroscopic geometric structure and mechanical strength, which is not convenient for field application. The mainstream monolithic catalysts are currently honeycomb catalysts and the granular catalyst, especially in the de-NO<sub>x</sub> field by SCR technology.

However, less studies had reported the current statuses of PCDD/F removal by commercial selective catalytic reduction (SCR) designed for deNO<sub>x</sub>, especially at the low operating temperature (160-200°C). In addition, the laboratory experiments were mainly carried out under clean condition and based on powder catalysts, which would show big difference with field condition. This study not only investigated the RE of PCDD/Fs by commercial SCR but also tested their conversion efficiency (CE) of 1,2-DCBz. In addition, a series of new VO<sub>x</sub>/TiO<sub>2</sub> catalysts were developed and their CE of 1,2-DCBz were also tested.

## 2. Materials and methods

### 2.1 Field investigation of SCR

Total 5 SCR of different domestic MSWI system were investigated in this study. Two sampling positions of flue gas were set for each SCR (inlet and outlet, respectively) to observe the influence of SCR on PCDD/F emissions. Sampling PCDD/Fs in the flue gas of MSWI was conducted under stable operation and lasts for 4 h (2 h for each one Sample), thus two parallel samples at each sampling position were obtained. And the influence of operation temperature were also studied.

### 2.2 Laboratory development of new catalyst

To better investigate the catalytic efficiency of some commercial catalysts mentioned above, the 1,2-dichlorobenzene (1,2-DCBz) catalytic experiments were carried out by the instrument shown in Figure 1. The catalyst was loaded in a vertical quartz tube reactor (18 mm i.d., 28 cm length). The reactor was then installed in an electric furnace and the temperature was controlled by a regulator. The reaction temperature was measured by a K-type thermocouple closed to the catalyst bed. The flow rate was controlled at 100 mL/min by the mass flowmeter, and a 1.2 mL granular catalyst was carried out for tests with the purpose of gas hourly space velocity (GHSV) maintaining at 3,000 h<sup>-1</sup>.

In this study, we also developed some new honeycomb catalysts in laboratory. Their conversion efficiencies (CE) of 1,2-DCBz were also tested as the operating temperature increases from 150 to 200 °C.

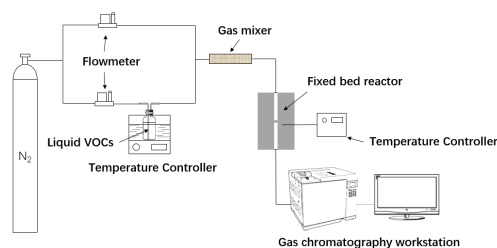


Figure 1. System diagram of the catalytic instrument of 1,2-DCBz.

### 2.3 Sampling and analysis

PCDD/Fs in flue gases were collected by an isokinetic sampler (Model KNJ23, KNJ, Korea) followed the US EPA method 23a. The pretreatment procedures of PCDD/F samples follow the US EPA method 1613. The purified samples are analyzed through a high-resolution gas chromatography/high-resolution mass spectrometry (HRGC/HRMS) (JMS-800D, JEOL, Japan). The toxic equivalents (TEQ) are calculated using NATO/CCMS factors<sup>15</sup>. The concentration of PCDD/Fs in gaseous samples is normalized to dry air of 11% O<sub>2</sub> at 101.3 kPa and 0 °C.

To better evaluate the activity of the catalyst and the influence of applied period, Brunner–Emmet–Teller (BET) measurements (TRISTAR 3020, Micromeritics Instrument Corporation, USA) was used to analyze the physical characteristics of these catalysts.

## 3. Results and discussion

### 3.1 Field investigation of SCR

#### 3.1.1 The RE of PCDD/Fs

In this study, we investigated five commercial SCR and carried out the RE test of PCDD/Fs, and the detail information was summarized in Table 1. As mentioned above, all five SCR was applied monolithic catalysts in type of honeycomb or granular, which are the mainstream due to their stronger mechanical strength, smaller bed pressure drops and more convenience of unloading and cleaning. In addition, the operation temperatures of these SCR were distributed at high temperature (408.6~427.7°C), middle temperature (220.7~224.3°C) and low temperature (~180°C). That is, their installing positions were distributed at post-combustion area, the front of fabric filter and the back of fabric filter. The different installing positions also means different concentrations of PCDD/Fs and other pollutants, such as dust, NO<sub>x</sub>, SO<sub>2</sub>, HCl, etc., which would also influence the catalytic efficiency of PCDD/Fs.

The SCR-1 were operated at high temperature (408.6~427.7°C) with an inlet concentration of PCDD/Fs (8.33 ng I-TEQ/Nm<sup>3</sup>). It was applied for few months before our tests, however, the RE of PCDD/Fs was low as 6.05%. The SCR-2 were operated at middle temperature (220.7~224.3°C) with an even higher inlet concentration of PCDD/Fs (18.15 ng I-TEQ/Nm<sup>3</sup>) than SCR-1. And the RE of PCDD/Fs was negative (-221.30 ng I-TEQ/Nm<sup>3</sup>) and released much PCDD/Fs into flue gas. Both of SCR-1 and SCR-2 showed bad and even terrible RE of PCDD/Fs, which could be attributed to the following reasons: (1) operating temperature, the operating temperature ranged at the regeneration temperature of PCDD/F (200-500°C), which could release PCDD/Fs in the reduction process of PCDD/Fs; (2) fly ash, both SCR-1 and SCR-2 were installed at the front of fabric filter, and high concentration of fly ash prepared good regeneration surface and catalytic metals and benefit the PCDD/F regeneration and release; (3) high inlet concentration of PCDD/Fs, the high concentration of PCDD/Fs would cause big challenge for these SCR units due to their original designed objections of NO<sub>x</sub> other than PCDD/Fs; (4) bad operation of incinerator system, the operating temperature of SCR-1 was distributed at a wide range, which could not benefit the application of SCR.

**Table 1.** The RE of PCDD/Fs by different SCR.

SCR	SCR-1	SCR-2	SCR-3	SCR-4	SCR-5		
<b>Catalyst type</b>	Honeycomb	Honeycomb	Honeycomb	Honeycomb	Granular		
<b>Catalyst code</b>	/	/	Cata-1 (V <sub>2</sub> O <sub>5</sub> -MoO <sub>3</sub> /TiO <sub>2</sub> )		Cata-2 (V <sub>2</sub> O <sub>5</sub> /TiO <sub>2</sub> )		
<b>Operating temperature (°C)</b>	408.6~427.7	220.7~224.3	~180	~180	~200	~180 ~160	
<b>PCDD/Fs</b> (ng I-TEQ/Nm <sup>3</sup> ; %)	<b>Inlet</b>	8.33	18.15	0.1412	0.0284	0.057	0.091 0.15
	<b>Outlet</b>	6.16	58.3	0.0257	0.0236	0.0086	0.0075 0.0069
	<b>RE</b>	6.05	-221.30	81.80	16.90	95.43	91.74 84.98

The initial air pollution control devices (APCDs) contained the semi-dry spray neutralizer and active carbon injection coupled with fabric filter. The above results also suggest that the SCR should be installed after the fabric filter, which can better protect the SCR. However, it brings a new challenge of the RE of PCDD/Fs by SCR.

at low temperature (<200°C). In addition, the lower the operating temperature will save more energy and bring higher economy benefit due to the temperature of flue gas at the outlet of fabric filter was lower as 150°C. Thus, we also investigated the SCR-3, SCR-4 and SCR-5, which were operated stably at low temperature (~180°C). The SCR-3 and SCR-4 were the same catalyst in honeycomb type, while the SCR-5 was designed as granular type. As for SCR-3, the inlet concentration of PCDD/Fs was 0.1412 ng I-TEQ/Nm<sup>3</sup>, which was reduced to 0.0257 ng I-TEQ/Nm<sup>3</sup> with a good RE of 81.80%. As for SCR-4, the inlet concentration of PCDD/Fs was 0.0284 ng I-TEQ/Nm<sup>3</sup>, which was reduced to 0.0236 ng I-TEQ/Nm<sup>3</sup> with the RE of 16.90%. The different RE of SCR-3 and SCR-4 could be attributed to the different incineration system and different inlet concentration of PCDD/Fs. As for SCR-5, the inlet concentration of PCDD/Fs was 0.091 ng I-TEQ/Nm<sup>3</sup>, which was reduced to 0.0075 ng I-TEQ/Nm<sup>3</sup> with a high RE of 91.74%. At the same temperature (~180°C), the SCR-5 showed better RE on PCDD/Fs than SCR-3 and SCR-4, which could be attributed to the different incineration system and different major catalytic components shown in Table 1.

To better investigate the influence of operating temperature, the SCR-5 was selected to test the RE of PCDD/Fs by decreasing the operating temperature (200°C, 180°C and 160°C), and the results were shown in Table 1. The inlet concentration of PCDD/Fs ranged from 0.057 to 0.15 ng I-TEQ/Nm<sup>3</sup>. The RE of PCDD/Fs distributed as 95.43%, 91.74% and 84.98%, respectively, with the decreasing operating temperature. This study tried to explain these phenomena by the catalytic reaction rate (*k*) and apparent activation energy (*E<sub>a</sub>*) of PCDD/Fs according to the Arrhenius equation<sup>16-17</sup>, which can provide a reference for future or other relevant studies (Table 2). As shown in Table 2, the *k* of PCDD/Fs was decreased as the decreasing operating temperature. Based on the *k* and operating temperature, the *E<sub>a</sub>* of PCDD/Fs was calculated as 14.40 kJ/mol, which was far lower than the activation energy of PCDD/F by thermal decomposition (approximately 250 kJ/mol on average)<sup>18</sup> due to the catalytic reaction. In addition, the *E<sub>a</sub>* of PCDFs (17.11 kJ/mol) was higher than the PCDDs (11.26 kJ/mol). The coefficient relationships (*R*<sup>2</sup>) were as high as 0.90~1.00, which showed the accurate values of the calculated *E<sub>a</sub>*.

**Table 2.** The *k* (s<sup>-1</sup>) and *E<sub>a</sub>* (kJ/mol) of PCDD/Fs at different temperatures.

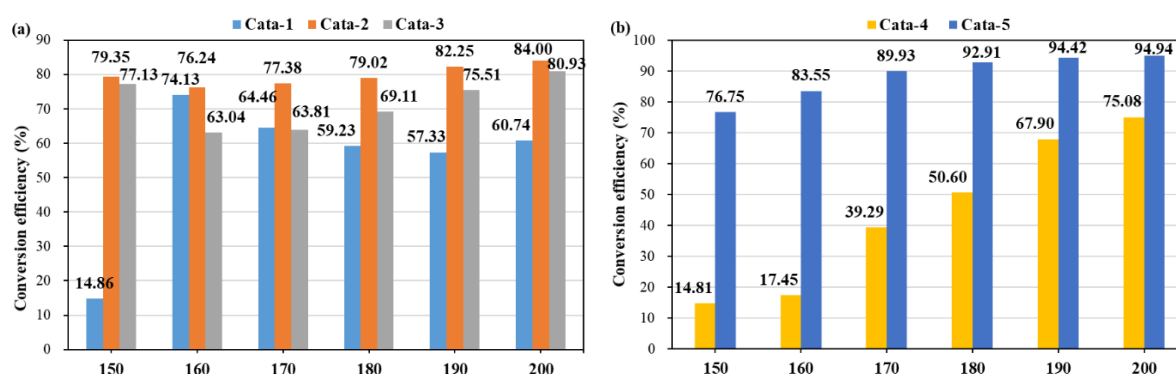
PCDD/Fs	<i>k</i>			<i>E<sub>a</sub></i>	<i>R</i> <sup>2</sup>
	200°C	180°C	160°C		
PCDD	4.96	4.05	3.80	11.26	0.90
PCDF	5.47	4.46	3.66	17.11	1.00
PCDD/F	5.25	4.25	3.74	14.40	0.97

### 3.1.2 Decomposition of 1,2-DCBz by commercial catalysts

Table 2 summarized the detailed information of three commercial catalysts (Cata-1, Cata-2 and Cata-3) and two new catalysts developed in laboratory (Cata-4 and Cata-5). And the conversion efficiency (CE) of 1,2-DCBz by these catalysts were shown in Figure 2. The gas hourly space velocity (GHSV) was about 3000 h<sup>-1</sup>.

**Table 2.** The collected commercial catalysts and new catalysts developed in laboratory.

	Catalyst code	Major component	Catalyst type	Meso-pore area of BET (m <sup>2</sup> /g)
Commercial catalysts	Cata-1	V <sub>2</sub> O <sub>5</sub> (3.63%), MoO <sub>3</sub> (6.76%)	Honeycomb	55.36
	Cata-2	V <sub>2</sub> O <sub>5</sub> (6.58%)	Granular	89.52
	Cata-3	V <sub>2</sub> O <sub>5</sub> (2.99%), WO <sub>3</sub> (2.62%)	Honeycomb	74.53
New catalysts	Cata-4	V <sub>2</sub> O <sub>5</sub> (3.58%), CeO <sub>2</sub> (3.28%)	Honeycomb	77.56
	Cata-5	V <sub>2</sub> O <sub>5</sub> (3.63%), CeO <sub>2</sub> (3.35%), WO <sub>3</sub> (3.07%)	Honeycomb	/



**Figure 2.** RE of 1,2-DCBz by (a) commercial catalysts and (b) new catalysts developed in laboratory.

As shown in Figure 2(a), the CE of 1,2-DCBz by Cata-1 ranged from 14.86% to 74.13% at the reaction temperature range of 150-200°C. The CE sharply increased from 14.86% (150°C) to 79.35% (160°C), then it decreased slowly to 60.74% (200°C). While the Cata-2 initially showed a high CE of 1,2-DCBz (79.35%) at 150°C, and it firstly decreased to 76.24% (160°C) then increased to 84.00% (200°C). That is, the CE of 1,2-DCBz ranged from 76.24% to 84.00% at the temperature range of 150-200°C. Similarly, the Cata-3 also showed same changing trend of CE, the Cata-2 initially performed a high CE of 1,2-DCBz (77.13%) at 150°C, and it firstly decreased to 63.04% (160°C) then increased to 80.93% (200°C). The CE of 1,2-DCBz ranged from 63.04% to 80.93% at the temperature range of 150-200°C. The results showed significant difference on the CE of 1,2-DCBz at 150°C, which could be influenced by the different catalytic components of Cata-1, Cata-2 and Cata-3. However, it was also hard to confirm whether it caused by some error during the experiment process of Cata-1. The Cata-2 and Cata-3 showed good CE of 1,2-DCBz, but both were firstly decreased then increased as the increasing reaction temperature. Generally, Cata-1 performed the lowest CE of 1,2-DCBz, which might be also influenced by the lower meso-pore area of BET (55.36 m<sup>2</sup>/g), while the meso-pore area of BET were higher as 89.52 m<sup>2</sup>/g and 74.53 m<sup>2</sup>/g, respectively for Cata-2 and Cata-3. The reason could be attribute to the good volatility of 1,2-DCBz, and adsorption of 1,2-DCBz at the surface the catalyst was weakened as the temperature increased. Thus, the adsorbed 1,2-DCBz at the surface the catalyst was released and decreased the CE, and this phenomenon was weakened by the increasing temperature.

### 3.2 Catalyst development

Based on the previous studies of our group, some new catalysts were developed in laboratory, and the detailed information was summarized in Table 2. The conversion efficiency (CE) of 1,2-DCBz by these catalysts were shown in Figure 2(b).

The CE of 1,2-DCBz by Cata-4 was low and similar with Cata-1 at 150°C, and the CE increased from 14.81% to 75.08% as the reaction temperature increased from 150°C to 200°C. The Cata-5 generally showed much higher RE of 1,2-DCBz under each reaction temperature. The RE of 1,2-DCBz at 150°C was 76.75%, and it increased to 94.94% as the increasing temperature. In addition, the RE of 1,2-DCBz had been higher than 92% at 180°C, and the increasing value of RE had also decreased with each 10°C of increasing step.

At lower temperature range (150-180°C), Cata-4 showed the lowest CE of 1,2-DCBz, while Cata-1 showed the lowest CE of 1,2-DCBz at higher temperature range (190-200°C). At similar proportions of catalytic components, the group of V<sub>2</sub>O<sub>5</sub> and WO<sub>3</sub> still showed better CE of 1,2-DCBz than the group of V<sub>2</sub>O<sub>5</sub> and MoO<sub>3</sub> or the group of V<sub>2</sub>O<sub>5</sub> and CeO<sub>2</sub>. The high proportion of V<sub>2</sub>O<sub>5</sub> could also achieve good CE of 1,2-DCBz. The group of V<sub>2</sub>O<sub>5</sub>, CeO<sub>2</sub> and WO<sub>3</sub>, showed the best CE of 1,2-DCBz due to one more second catalytic component compared with other catalysts.

### Acknowledgements:

This study was supported by the National Key Research and Development Program of China (2020YFC1910100).

### References:

1. Gao H, Ni, Y, Zhang, H et al. (2009) *Chemosphere*. 77(5): 634-639.
2. Gullett B K, Bruce, K R, Beach, L O (1990) *Waste Management & Research*. 8(3): 203-214.
3. Ni Y, Zhang, H, Fan, S et al. (2009) *Chemosphere*. 75(9): 1153-1158.
4. M.B. Chang, K.H. Chi, and G.P. Chang-Chien (2004) *Chemosphere*. 55:1457-1467.
5. X. Liu, J. Wang, X. Wang, and T. Zhu (2015) *Chemosphere*. 133: 90-96.
6. D.P. Debecker, R. Delaigle, P.C. Hung, et al. (2011) *Chemosphere*. 82: 1337-1342.
7. S. Ji, X. Li, Y. Ren, et al. (2013) *Chemosphere*. 92: 265-272.
8. C.H. Cho, and S.K. Ihm (2002) *Environmental ence & Technology*. 36: 1600.
9. R. Weber, T. Sakurai, and H. Hagenmaier (1999) *Applied Catalysis B: Environmental*. 20: 249-256.
10. M.F. Yu, X.Q. Lin, X.D. Li, et al. (2016) *Environmental Science & Pollution Research International*. 23: 16249-16258.
11. M. Yu, W. Li, X. Li, et al. (2016) *Chemosphere*. 156: 383-391.
12. F. Bertinchamps, C. Grégoire, and E.M. Gaigneaux (2006) *Applied Catalysis B: Environmental*. 66: 1-9.
13. R. Boos, R. Budin, H. Hartl, et al. (1992) *Chemosphere*. 25: 375-382.
14. M. Goemans, P. Clarysse, J. Joannès, P., et al. (2003) *Chemosphere*. 50: 489-497.
15. Bhavsar S P, Reiner, E J, Hayton, A et al. (2008) *Environment International*. 34(7): 915-921.
16. Q. Wang, P.C. Hung, S. Lu, et al. (2016) *Chemosphere*. 159: 132-137.
17. S. Lu, Q. Wang, W.R. Stevens, et al. (2014) *Applied Catalysis B: Environmental*. 147: 322-329.
18. K. Tagashira, I. Torii, K. Myouyou, K., et al. (1999) *Chemical Engineering Science*. 54: 5599-5607.