Catalytic Decomposition of PCDD/Fs over Nano-TiO₂ Based V₂O₅/CeO₂ Catalyst at Low Temperature

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ABSTRACT

Catalytic decomposition of PCDD/Fs (Polychlorinated dibenzo-p-dioxins and furans) over nano-TiO₂ based V₂O₅/CeO₂ catalyst is investigated at 180°C based on a stable PCDD/Fs generating system. Step impregnation method is used to prepare the powder catalyst, and catalyst characterization is conducted by XRD and TPR. Effects of oxygen, water vapour and sulphur dioxide on PCDD/Fs destruction are studied in terms of destruction efficiency. Oxygen plays a positive role on PCDD/Fs destruction by accelerating the conversion of V⁴⁺Oₓ and V⁵⁺Oₓ, Ce³⁺Oₓ and Ce⁴⁺Oₓ. The destruction efficiencies of PCDD/Fs increase from 67.6% to 77.8% with oxygen contents increasing from 11 vol.% to 21 vol.% In the absence of oxygen, PCDD/Fs can still be destroyed with destruction efficiency of 33.7% due to the lattice oxygen atoms stored by V₂O₅ and CeO₂. Water vapour negatively affects the destruction of PCDD/Fs by competitive adsorption. On the other hand, negative destruction efficiencies of TCDD and TCDF are observed in the presence of water, and the values become lower with water vapour contents increasing. This result demonstrates water vapour facilitates the removal of Cl⁻ present on the catalyst surface. SO₂ inhibits the activity of catalyst by poisoning active sites of catalyst. With SO₂ concentration increasing from 0 to 100 ppm, destruction efficiencies of PCDD/Fs significantly decrease from 67.6% to 51.9%. Finally, catalyst regeneration is also investigated at 180°C in the presence of oxygen. Most of PCDD/Fs residues in the catalyst will be destroyed, and catalyst is regenerated without PCDD/Fs contaminated.

Keywords: PCDD/Fs; V₂O₅-CeO₂/TiO₂ catalyst; Oxygen; Water vapour; SO₂.

INTRODUCTION

Incineration, rapidly reducing waste volume and also recovering heat, has become the preferred technology for municipal solid waste disposal. However, dioxins and other aromatic compounds emission from incinerators are proved to be harmful for human health, and thus the extensive development of incinerators is rejected by society (Gao et al., 2009; Yan et al., 2011; Cheruiyot et al., 2015; Li et al., 2015; Tiwari et al., 2015). Dioxins, including polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), have been incorporated into the Annex C compounds of the Stockholm Convention (Stockholm Convention, 2006) due to their chemical properties of stability, lipophilicity and persistence. Therefore, various feasible and effective technologies for the control of dioxins emission are eagerly developing to prevent harmful influence on the environmental and human health (Wielgosiński, 2010; Wang et al., 2009; Chen et al., 2015). Previous studies indicate activated carbon injection technology has an excellent performance on the removal of gaseous PCDD/Fs, and thus has become a widely applied technology in the waste incinerators (Hajizadeh et al., 2011; Kawashima et al., 2011). However, the total PCDD/Fs concentration, including both vapour phase and particulate phase PCDD/Fs, emission from solid waste incinerators increases due to the increase of carbon source and metal catalysts (i.e., CuCl₂, FeCl₂, etc. in commercial activated carbon) in fabric filter (Chang and Lin, 2001). Thus, catalytic destruction of PCDD/Fs, completely destroying aromatic compounds without creating secondary pollutants, has become a focused and developable method for dioxins control.

V₂O₅-WO₃/TiO₂ catalyst is originally designed for the removal of NOₓ by selective catalytic reduction (SCR), and also found to be useful for the decomposition of PCDD/Fs (Liljelind et al., 2001; Finocchio et al., 2006). Actually, TiO₂ has been used and studied as a photocatalyst in a photocatalytic air cleaner to decompose dioxins in the air (Daikoku et al., 2015). Vanadium oxide is identified as the active sites and presents a best oxidative activity compared to other metal oxides, for instance, CrO₃, MnO₃, and FeO₃.
etc. (Liu et al., 2001; Yim et al., 2002; Lou et al., 2009).
Catalytic destruction of vapour phase PCDD/Fs over vanadium oxide based catalysts achieves the best activity with the operating temperature controlled at above 200°C (Weber et al., 1999; Debecker et al., 2011). Nevertheless, in order to avoid the catalyst poisoning and enhance the operation life of catalyst, the catalytic part is usually placed behind the baghouse filter where the temperature of flue gas falls below 180°C. Therefore, the development and application of new transition metal oxide catalysts for the destruction of PCDD/Fs at below 180°C have become an urgent and significant research area.

Cerium oxide (CeO$_2$) has high oxygen storage capacity and facile redox properties, and thus attracts plenty of attention on pollution control (Chen et al., 2010; Yu et al., 2011). It is reported that CeO$_2$ catalyst presents a higher activity compared to other reported catalysts on the destruction of chlorinated volatile organic compounds (Guillemot et al., 2007; de Rivas et al., 2009, 2012). Catalytic destruction of trichloroethylene at low temperature over CeO$_2$ catalyst was investigated, and trichloroethylene was completely destroyed at 205°C (Dai et al., 2007).

Usually, the complex flue gas composition of MSW incinerators, such as H$_2$O and SO$_2$, plays various roles on the activity of catalysts. Previous study indicates catalytic activity of CeO$_2$ catalyst is inhibited in the presence of excess water with a content of 3 vol.% in the feed steam (Dai et al., 2007). In addition, a significant promotional effect on the activity of catalyst, proportional to water amount in the feed, was observed at temperatures below 290°C, whereas water vapour had a strong deactivating effect at temperatures above 290°C (Hetrick et al., 2011). SO$_2$, reacting with active sites of the catalysts, had the inhibiting effects on catalytic degradation of polycyclic aromatic hydrocarbons (PAHs) over vanadium based catalyst, and even the acceleration effect on the formation of PAHs were observed (Chang et al., 2009).

In the present work, V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst is developed to destroy PCDD/Fs at low temperature (180°C) based on a lab-scale dioxins generating system. This system can produce a stable and continuous flow of vapour phase PCDD/Fs flow. The influences of oxygen, water vapour and SO$_2$ on the activity of V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst are investigated at 180°C. Finally, catalyst regeneration in the presence of oxygen at 180°C is also discussed.

MATERIALS AND METHODS

Catalyst Preparation

Step impregnation method was used to prepare V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst. Nano-TiO$_2$, purchased from Xuanchengjingrui New Material Co. Ltd, was served as the catalyst support. Firstly, cerium nitrate dissolved in the appropriate amount of deionized water, and then nano-TiO$_2$ support was impregnated with the cerium nitrate solution along with sufficient stirring. The wet catalyst sample was aged in the atmosphere for 24 h and dried at 105°C for 4 h. Then, the catalyst sample was ground to powder by a planetary ball mill. The powder was calcined at 450°C for 2 h in atmosphere to obtain CeO$_2$/TiO$_2$ catalyst. Secondly, the CeO$_2$/TiO$_2$ catalyst was sufficiently impregnated by the hot water solution with ammonium meta-vanadate and oxalic acid dissolved. Start the preparation procedure, which is same with preparation of CeO$_2$/TiO$_2$ catalyst, to obtain V$_2$O$_5$-CeO$_2$/TiO$_2$ catalysts. The V$_2$O$_5$ and CeO$_2$ loading are both controlled at 5 wt.% through adjusting the amount of precursors including cerium nitrate and ammonium meta-vanadate.

Catalyst Characterization

The main physical properties of catalysts, including specific surface area, pore volume and average pore diameter, were detected with an automated Brunauer-Emmet-Teller (BET) and pore analyser (Quanta Chrome, USA) using a N$_2$-physisorption. X-ray diffraction (XRD) patterns were determined in the range 10–80° at a rate of 0.02° min$^{-1}$ by a X-ray diffractometer (PANalytical-X'Pert PRO, Holland) with CuKα radiation (λ = 0.154 nm). H$_2$-temperature programmed reduction (H$_2$-TPR) profiles were recorded on a Micromeritics Autochem II 2920 equipped with a thermal conductivity detector (TCD). The temperature increased from 50°C to 1000°C with a heating rate of 10°C min$^{-1}$. 5 vol.% of hydrogen in argon was introduced as a reducing gas with a flow rate of 30 mL min$^{-1}$.

Experimental System

Catalytic destruction tests are developed on a lab-scale dioxins generating system which can continuously supply a stable vapour phase PCDD/Fs steam, as shown in Fig. 1. This system mainly consists of a mass flowmeter, a temperature controller, a quartz tube with preheater and an injector/nebulizer of PCDD/Fs solution. PCDD/Fs stock solution is prepared from fly ash of a medical waste incinerator by Soxhlet extraction. PCDD/Fs concentration, required in this study, is determined by adjusting the amount of solvent (nonane). After injection, the solution is atomized through the nebulizer. Most of nonane is removed at preheating area to eliminate the influence of solvent on PCDD/Fs destruction. A gas mixture of N$_2$ and O$_2$ is used as the carrier gas, and the flow rate is controlled at 1 L min$^{-1}$ by a mass flow controller.

Catalytic destruction of PCDD/Fs over V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst is investigated on a lab-scale reaction system. The mixture of the prepared catalyst (2 g) and quartz sand places in a vertical quartz tube. Gas hourly space velocity (GHSV) is controlled at 11000 h$^{-1}$ through adjusting the amount of quartz sand, and the operating temperature is controlled at 180°C by a temperature controller. Adjust oxygen content in carrier gas to investigate the effects of oxygen on PCDD/Fs destruction. In order to investigate the effects of SO$_2$ and H$_2$O, an extra gas stream (60 mL min$^{-1}$) is introduced into the reactor from a bypass. Deionized water is continuously and stably injected into the bypass, heated by a heater band and then vaporized at 180°C, through an injection pump (Pump 11, Harvard, China) to produce water vapour. Reaction time of each run is 1 h. In order to eliminate cross contamination, the quartz reactor is cleaned by toluene after each run. Exhaust is collected by XAD-2 polymeric resin and toluene. Finally, the clean fluid, exhaust and catalyst are collected and analysed for PCDD/Fs. Although catalytic
regeneration tests are developed one time in this study, all catalytic activity tests on the effects of oxygen, water vapour and SO₂ are conducted two times to ensure the accuracy of data, and average value of two sets of experiments is established as the destruction efficiency.

**Analysis**

PCDD/Fs samples were firstly Soxhlet extracted with toluene for twenty four hours with 13C-labelled internal standards spiked, and then purified according to US EPA method 1613. The clean-up procedure involved a multi-silicagel column and a basic-alumina column. Analysis was conducted by a high-resolution gas chromatograph (HRGC, 6890N, Agilent, USA) coupled to a high-resolution mass spectrometer (HRMS, JMS800D, JEOL). The detection limits of HRGC/HRMS are defined as 0.1 pg for TCDD/F and PeCDD/F, 0.2 pg for HxCDD/F and HpCDD/F, 0.5 pg for OCDD/F. A DB-5 chromatographic column (60 m × 0.25 mm inside diameter, 0.25 µm film thickness) was used. The temperature program was as developed as described by Chen et al. (2008). The mass spectrometer was operated at a resolution of 10000 under positive electron ionization conditions (38 eV electron energy). An auto-sampler in the splitless mode was used to inject the sample of 1 µL. The PCDD/Fs were quantified using a molecular base ion (M), and an M²⁺ ion or an M⁴⁺ ion (Chen et al., 2008).

The recovery rate (R) of each internal standard is obtained in order to guarantee the reliability of the data, and calculated as follows according to EPA method 1613:

\[
R = \frac{A_{rs}}{A_{es}} \times \frac{Q_{rs}}{Q_{es}} \times 100% \times \frac{1}{RRF_{rs}}
\]  

where, \( A_{es} \) and \( A_{rs} \) are the area of the extract and injection internal standard; \( Q_{es} \) and \( Q_{rs} \) represent the amount of the extract and injection internal standard; \( RRF_{rs} \) implies the response factor for injection to extract internal standard.

In this study, recovery rate for each congener is established between 48.2%–108.9%, which conforms to the recovery rate standard of 40%–130%. I-TEQ is calculated using the international toxic equivalence factor (I-TEF).

Only seventeen toxic 2, 3, 7, 8-substituted PCDD/F congeners are discussed based on I-TEQ concentration. Two parameters, removal efficiency and destruction efficiency (referred to as “RE”, “DE” for short), are calculated as follows:

\[
RE = \frac{(PCDD/F_{inlet} - PCDD/F_{exhaust})}{PCDD/F_{inlet}} \times \frac{100%}{RRF_{rs}}
\]

\[
DE = \frac{(PCDD/F_{inlet} - PCDD/F_{catalyst+tube+exhaust})}{PCDD/F_{inlet}} \times \frac{100%}{RRF_{rs}}
\]

where, \( PCDD/F_{inlet} \) implies the initial PCDD/Fs concentration; \( PCDD/F_{exhaust} \) represents the PCDD/Fs concentration in the exhaust collected by XAD-2 polymeric resin and toluene; \( PCDD/F_{catalyst+tube+exhaust} \) is the summation of PCDD/Fs concentration in the exhaust, catalyst and cleaning fluid.
RESULTS AND DISCUSSION

Characteristics of Catalysts

The main physical properties of the prepared catalysts, including nano-TiO2 support, CeO2/TiO2 and V2O5-CeO2/TiO2 catalysts, are present in Table 1. The BET specific surface area and pore volume of nano-TiO2 are 125.3 m² g⁻¹ and 0.26 cm³ g⁻¹, respectively, which indicates nano-TiO2 is an excellent catalyst support. After the first impregnation with cerium nitrate and then calcination, the surface area and pore volume decrease. It’s mainly contributed to the fact that pore space was blocked by metal oxide and nano-TiO2 was agglomerated under high temperature calcination. Unexpectedly, pore diameter increases to 85.5 Å for CeO2/TiO2 catalyst. The surface area and pore volume are further diminishing with the further impregnation of vanadium, while pore diameter also decreases rather than increase.

The XRD peaks at 25.3°, 38°, 47.7°, and 54.8° appear in the XRD patterns of CeO2/TiO2 and V2O5-CeO2/TiO2 catalysts, as shown in Fig. 2(a). This result indicates that nano-TiO2 support belongs to anatase TiO2, and the conversion from anatase to rutile phase of TiO2 isn’t observed during the catalysts preparation. The peaks, contributed by microcrystalline CeO2 and V2O5, aren’t observed from XRD patterns, which is associated with high dispersion and amorphous state of CeO2 and V2O5 on the support.

The reducibility of the CeO2/TiO2 and V2O5-CeO2/TiO2 catalysts is present in Fig. 2(b). A weak peak at 618°C, Table 1. Physical property of the prepared catalysts.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore volume (cm³ g⁻¹)</th>
<th>Average pore diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>125.3</td>
<td>0.26</td>
<td>82.6</td>
</tr>
<tr>
<td>CeO2/TiO2</td>
<td>87.3</td>
<td>0.19</td>
<td>85.5</td>
</tr>
<tr>
<td>V2O5-CeO2/TiO2</td>
<td>69.6</td>
<td>0.14</td>
<td>80.9</td>
</tr>
</tbody>
</table>

Fig. 2. (a) X-ray diffraction patterns and (b) temperature-programmed reduction profiles of the prepared catalysts.
produced by the reduction of Ce, is observed in the profile of CeO$_2$/TiO$_2$ catalyst. Relevant study also indicates a quite smaller band of H$_2$ consumption at T > 773 K, with a maximum at approximately 1000 K, is typical of the reduction of subsurface Ce$^{4+}$ ions (Arena et al., 2007). However, in the TPR profile of V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst, the large intensity and the shift of reduction peak to a lower temperature of 520°C indicate that the oxidation ability and oxygen storage capacity of V$_2$O$_5$ are stronger than those of CeO$_2$.

**Catalytic Activity Evaluation**

**Initial Concentration of PCDD/Fs**

In order to generate a stable PCDD/Fs flow, PCDD/Fs generating system needs to reasonably run for a period of time before catalytic destruction tests conducting. At the outlet of generating system, three PCDD/Fs samples are repeatedly collected with XAD-2 polymeric resin and toluene. The average concentration of the three samples is intended to be initial concentration of the input to catalytic destruction system. The initial concentrations of PCDD/Fs, PCDDs, PCDFs and 17 toxic congeners are summarized in Table 2. Initial concentration of PCDD/Fs is 4.84 ng I-TEQ Nm$^{-3}$, PCDFs, with the concentration of 3.69 ng I-TEQ Nm$^{-3}$, is the main contributor of I-TEQ. The I-TEQ concentration of 2, 3, 4, 7, 8-PeCDF contributes 29.1% of initial concentration.

**Effects of Oxygen on PCDD/Fs Destruction**

In order to investigate effects of oxygen on PCDD/Fs destruction over V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst at 180°C, three different oxygen contents (0%, 11% and 21% by volume) are investigated. The average DE values increase from 67.6% to 77.8% with oxygen content increasing from 11 vol.% to 21 vol.% Therefore, oxygen plays a great promoting role on PCDD/Fs destruction. Significantly, the decomposition of PCDD/Fs still happens even in the absence of oxygen with a DE value of 33.0%. Usually, V$_2$O$_5$ is considered as active sites and presents the strongest destruction ability for organic pollutants compared to other transition metal oxides including CrO$_3$, CuO$_2$, MnO$_2$, etc. (Cho and Ihm, 2002). High valent V$^{5+}$O$_x$ species on the catalyst surface are regarded as active sites to oxidize organic pollutants, and then reduced to V$^{4+}$O$_x$ species; afterwards, V$^{4+}$O$_x$ species are re-oxidized by O$_2$, provided by the carrier gas, and recovered to V$^{5+}$O$_x$ (Xu et al., 2012; Ji et al., 2013). In addition, CeO$_2$ is also frequently studied in the environmental catalysis as its high oxygen-storage capacity and facile redox cycle of Ce$^{3+}$/Ce$^{4+}$ (Skårmann et al., 2002; Zimmer et al., 2002; Dai et al., 2007). The addition of CeO$_2$ is believed to improve the catalyst oxygen storage capacity and facilitate the oxygen mobility over catalyst (Wu et al., 2008). Therefore, high oxygen content accelerates the conversion rate from V$^{5+}$O$_x$ to V$^{4+}$O$_x$ and Ce$^{3+}$O$_x$ to Ce$^{4+}$O$_x$, and then results in higher DE values. Once oxygen is absent in the reaction system, lattice oxygen atoms, stored by V$_2$O$_5$ and CeO$_2$, can still complete the circulation between high valent metal and low valent metal until they are depleted.

Fig. 3(a) presents the DE values of PCDDs and PCDFs over V$_2$O$_5$-CeO$_2$/TiO$_2$ catalyst achieved with different oxygen contents. DE values of PCDDs are apparently higher compared to PCDFs. The gaps of DE values between PCDDs and PCDFs vary from 5.0% to 12.1% with the variation of oxygen content. When oxygen content is 11 vol.% the DE value of PCDDs reaches 76.8% while that of PCDFs is 64.7%, and the gaps reach maximum of 12.1%. Usually, highly chlorinated organic compounds can convert into lowly chlorinated compounds through dechlorination mechanism in catalytic decomposition of chlorinated organic pollutants (Choi et al., 2004; Yang et al., 2008). After dechlorination, the formation of lowly chlorinated PCDD/F congeners with high TEF results in the increase of TEQ concentration.

### Table 2: Initial I-TEQ concentration of 17 toxic PCDD/F congeners (pg I-TEQ Nm$^{-3}$).

<table>
<thead>
<tr>
<th>Congener</th>
<th>Data 1</th>
<th>Data 2</th>
<th>Data 3</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>2378-TCDD</td>
<td>252.7</td>
<td>281.6</td>
<td>273.6</td>
<td>269.3</td>
</tr>
<tr>
<td>12378-PeCDD</td>
<td>361.2</td>
<td>322.3</td>
<td>352.4</td>
<td>345.3</td>
</tr>
<tr>
<td>123478-HxCDD</td>
<td>57.6</td>
<td>47.6</td>
<td>46.5</td>
<td>50.6</td>
</tr>
<tr>
<td>1235678-HxCDD</td>
<td>223.9</td>
<td>220.7</td>
<td>216.6</td>
<td>220.4</td>
</tr>
<tr>
<td>123789-HxCDD</td>
<td>146.5</td>
<td>157.0</td>
<td>146.3</td>
<td>149.9</td>
</tr>
<tr>
<td>1234678-HpCDD</td>
<td>103.1</td>
<td>106.8</td>
<td>95.6</td>
<td>101.8</td>
</tr>
<tr>
<td>OCDD</td>
<td>11.4</td>
<td>12.5</td>
<td>10.9</td>
<td>11.6</td>
</tr>
<tr>
<td>2378-TCDF</td>
<td>158.2</td>
<td>230.7</td>
<td>190.6</td>
<td>193.2</td>
</tr>
<tr>
<td>12378-PeCDF</td>
<td>118.5</td>
<td>107.4</td>
<td>116.0</td>
<td>114.0</td>
</tr>
<tr>
<td>123478-PeCDF</td>
<td>1551.3</td>
<td>1323.3</td>
<td>1341.7</td>
<td>1405.4</td>
</tr>
<tr>
<td>123478-HxCDF</td>
<td>588.1</td>
<td>496.1</td>
<td>560.7</td>
<td>548.3</td>
</tr>
<tr>
<td>1235678-HxCDF</td>
<td>490.0</td>
<td>474.6</td>
<td>474.9</td>
<td>479.8</td>
</tr>
<tr>
<td>234678-HxCDF</td>
<td>248.1</td>
<td>234.0</td>
<td>286.0</td>
<td>256.0</td>
</tr>
<tr>
<td>123789-HxCDF</td>
<td>544.4</td>
<td>490.7</td>
<td>518.6</td>
<td>517.9</td>
</tr>
<tr>
<td>1234678-HpCDF</td>
<td>144.4</td>
<td>151.8</td>
<td>147.2</td>
<td>147.8</td>
</tr>
<tr>
<td>1234789-HpCDF</td>
<td>17.3</td>
<td>20.5</td>
<td>22.6</td>
<td>20.1</td>
</tr>
<tr>
<td>OCDF</td>
<td>5.9</td>
<td>4.7</td>
<td>5.5</td>
<td>5.4</td>
</tr>
<tr>
<td>PCDDs</td>
<td>1156.4</td>
<td>1148.4</td>
<td>1141.8</td>
<td>1148.9</td>
</tr>
<tr>
<td>PCDFs</td>
<td>3866.3</td>
<td>3533.8</td>
<td>3663.7</td>
<td>3688.0</td>
</tr>
<tr>
<td>PCDD/Fs</td>
<td>5022.8</td>
<td>4682.2</td>
<td>4805.6</td>
<td>4836.9</td>
</tr>
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</table>
PCDFs possess more highly chlorinated congeners than PCDDs. Therefore, DE values of PCDDs are always higher compared to those of PCDFs over V_2O_5-CeO_2/TiO_2 catalyst. However, the increase rate of destruction efficiency for PCDFs is obviously higher compared to PCDDs with oxygen content increasing to 21 vol.%.

Fig. 3(b) indicates DE values of seventeen PCDD/F congeners over V_2O_5-CeO_2/TiO_2 catalyst achieved with different oxygen contents. DE values of seventeen PCDD/F congeners keep rising with the increase of chlorination level as a whole. At low temperature, highly chlorinated congeners are of lower vapour pressures, which induces higher deposition rate on the surface of catalyst, and thus they are more easily contact and further react with active sites compared to lowly chlorinated congeners. What’s more, dechlorination will generate more lowly chlorinated congeners, and further decrease the DE value of lowly chlorinated congeners. TCDD and TCDF are extraordinarily noticeable with negative DE values in the absence of oxygen. It indicates that dechlorination always happens whether in the presence or absence of oxygen. Therefore, oxygen presents a greater influence on the oxidation of PCDD/Fs instead of dechlorination. Usually, it can be proposed that the destruction of aromatic compounds may occur by three different reaction pathway (Xu et al., 2012): firstly, aromatic rings are oxidized or opened, and then resulting in the formation of non-aromatic acyclic intermediates by oxidation; secondly, low chlorinated aromatic is formed due to hydrodechlorination; finally, chlorine atoms are replaced by surface oxygen species, providing by active sites of catalyst. Therefore, oxygen present can accelerate the first and last step, and thus oxidize PCDD/Fs. However, oxygen has little influence on the hydrodechlorination.

Effects of Water Vapour on PCDD/Fs Destruction
Catalytic destruction of PCDD/Fs over V_2O_5-CeO_2/TiO_2 catalyst with different oxygen contents at 180°C.
catalyst is conducted to investigate the effects of water vapour (0 vol.%, 3 vol.%, 9 vol.% and 15 vol.%) on the activity of catalyst. Generally, water vapour plays two important roles on the destruction of organic chlorinated pollutants by catalysis (Krishnamoorthy et al., 2000; Poplawski et al., 2000; Lomnicki et al., 2003). Firstly, competitive adsorption between water vapour and organic pollutants on catalyst surface, and also a diffusion block due to the cluster-forming ability of water molecules inhibit the catalytic activity. On the other hand, water vapour facilitates the removal of Cl⁻ present on the catalyst surface via the following reaction (Yang et al., 2008):

\[
\text{Cl}^- + \text{H}_2\text{O}(g) \rightarrow \text{HCl} + \text{OH}^- \quad (3)
\]

In the present work, the inhibiting effect on PCDD/Fs destruction is observed in the presence of water due to the competition adsorption between PCDD/F molecules and water vapour on the catalyst. The average DE values are 63.9%, 54.6% and 46.6% when water vapour content are controlled at 3 vol.%, 9 vol.% and 15 vol.%, respectively. However, the DE value reaches 67.6% in the absence of water. Fig. 4(a) shows the DE values of PCDDs and PCDFs, respectively, achieved with various water vapour contents. The DE values of both PCDDs and PCDFs decrease with water vapour contents increasing. Compared to PCDFs, PCDDs are always easier to be destroyed. However, with water vapour contents increasing, the gaps between the DE values of PCDDs and PCDFs decrease. This result demonstrates the inhibition effect of water vapour on PCDDs destruction is greater than PCDFs destruction.

Fig. 4(b) shows the DE values of 17 toxic PCDD/F congeners over V₂O₅-CeO₂/TiO₂ catalyst achieved with different water vapour contents. DE values of PCDD/F
congeners basically increase with chlorination level increasing due to vapour pressure and dechlorination mechanism. For the destruction efficiencies of TCDD and TCDF, negative values are obtained in the presence of water, and these values become lower with water vapour contents increasing. Namely, more TCDD and TCDF are generated with more water vapour introduced. This result confirms the acceleration effect of water vapour on the removal of Cl⁻.

Effects of Sulphur Dioxide on PCDD/Fs Destruction

Effects of sulphur dioxide on PCDD/Fs destruction over V₂O₅-CeO₂/TiO₂ catalyst are studied at 180°C. In the absence of SO₂, the average destruction efficiency is 67.6%, and then decreases to 62.4% with 50 ppm SO₂ introduced. With SO₂ concentration further increasing to 100 ppm, the destruction efficiency only reaches 51.9%. Obviously, SO₂ plays a negative role on PCDD/Fs destruction. Previous study indicates V₂O₅ is an effective catalyst for SO₂ oxidation in the presence of O₂, and the adsorbed SO₂ on catalyst surface can be oxidized to S⁶⁺ (Zhu et al., 2001). If surface sulphate species are linked to the vanadium sites, it is possible that the vanadium species are converted into new chemical forms such as VOSO₄ which can deposit on the surface of catalyst (Krishnamoorthy et al., 2000; Wang and Li, 2010). Therefore, SO₂ can irreversibly deactivate the active sites of catalyst, such as vanadium sites. Although Ce doping can effectively enhance SO₂ resistance of catalyst since it can inhibit the formation of sulphate on catalyst surface (Wu et al., 2009), the inhibiting effect of SO₂ still plays a main role on the activity of V₂O₅-CeO₂/TiO₂ catalyst. Therefore, the flue gas desulfurization devices shall be placed in front of the catalytic part once V₂O₅-CeO₂/TiO₂ catalyst is applied in solid waste incinerators.

Fig. 5(a) shows the DE values of PCDDs and PCDFs,  

![Fig. 5. Destruction efficiencies of (a) PCDDs and PCDFs and (b) 17 toxic congeners over V₂O₅-CeO₂/TiO₂ catalyst with different sulphur dioxide concentration at 180°C.](image-url)
respectively, at 180°C achieved with different SO₂ concentration. The DE values of both PCDDs and PCDFs decrease with the increase of SO₂ concentration. Similarly, PCDDs are always easier to be destroyed compared to PCDFs. With SO₂ concentration increasing, the gaps between the DE values of PCDDs and PCDFs increase instead of decreasing as with the effects of water vapour. This result demonstrates SO₂ plays a greater inhibition role on PCDFs destruction compared with PCDDs.

Fig. 5(b) shows the DE values of 17 toxic PCDD/F congeners over V₂O₅-CeO₂/TiO₂ catalyst achieved with different SO₂ concentration. With chlorination level increasing, DE values of 17 PCDD/F congeners basically increase due to vapour pressure and dechlorination mechanism in the absence and presence of SO₂. The DE values of each PCDD/F congener decrease with the increase of SO₂ concentration. Thus, SO₂ mainly inhibits the oxidation of PCDD/Fs by deactivation instead of dechlorination.

Catalyst Regeneration

In fact, PCDD/Fs residues in the used V₂O₅-CeO₂/TiO₂ catalyst still need to be removed in order to regenerate catalyst. Thermal treatment regeneration has been investigated as one of the cheapest and most versatile methods in the presence of oxygen (Sabio et al., 2004). Therefore, it is proposed that PCDD/Fs residues will continuously desorb and react with active sites at 180°C in the presence of oxygen. Finally, the used catalyst will be regenerated without PCDD/Fs contamination.

V₂O₅-CeO₂/TiO₂ catalyst with weight of 3 g was initially placed in the reaction system with PCDD/Fs flow introduced. The operating temperature was set as 180°C. Carrier gas consisted of 11 vol.% oxygen and 89 vol.% nitrogen. Sample at the outlet of reaction system per 2 h, and the total reaction time was 10 h. Afterwards, the catalyst sample was divided into two equal parts: one was used to analyse the quantity of PCDD/Fs residues in the catalyst; another one was selected to conduct regenerating experiment. Thus, half of catalyst sample was arranged in the reaction system without PCDD/Fs flow introduced at 180°C to develop catalyst regenerating tests. The sampling time of each run was 2 h. The atmosphere also contained 11 vol.% oxygen and 89 vol.% nitrogen. After 10 h desorption, the catalyst sample was collected and analysed for PCDD/Fs.

Fig. 6 shows the RE values of PCDD/Fs during different reaction time with PCDD/Fs flow introduced. As time goes on, PCDD/Fs concentration emission from the catalytic reaction system increases due to the decrease of catalytic activity. DE value of PCDD/Fs for 10 h reaches 62.6% over V₂O₅-CeO₂/TiO₂ catalyst, which is smaller than that of PCDD/Fs for 1 h with the DE value of 67.6%. Finally, the concentrations of residual PCDD/Fs, PCDDs and PCDFs in the catalyst are 0.18, 0.02 and 0.16 ng I-TEQ g⁻¹, respectively. PCDFs, dominating the I-TEQ of PCDD/Fs, account for 88.9%.

After developing catalyst regeneration tests, PCDD/Fs residues in the catalyst, decrease to 2.8%, as shown in Fig. 7. Gaseous PCDD/Fs, desorbed from the catalyst, only account for 13.8%. Most of PCDD/Fs are destroyed over V₂O₅-CeO₂/TiO₂ catalyst. Among the PCDD/Fs desorbed from the catalyst, desorption quantity of PCDD/Fs is obviously larger than that of PCDFs, as Fig. 8 shown. It is mainly contributed to the fact that highly chlorinated PCDD/F congeners are of lower volatility compared to lowly chlorinated congeners, and PCDFs possess more highly chlorinated congeners than PCDDs. At the first 2 h, the desorption quantity of gaseous PCDD/Fs reaches a maximum of 5.0%. As time goes on, there is barely gaseous PCDD/Fs emission from the catalyst. What’s more, it can be deduced from the linear curve fitting that zero PCDD/Fs emission from the used V₂O₅-CeO₂/TiO₂ catalyst will be achieved after 13 h.

Fig. 6. Removal efficiencies of PCDD/Fs during different reaction time.
CONCLUSIONS

Catalytic destruction of PCDD/Fs over V_2O_5-CeO_2/TiO_2 catalyst is investigated at 180°C based on a stable PCDD/Fs generating system. Effects of oxygen, water vapour and sulphur dioxide on the catalytic activity are studied. Oxygen plays a positive role on PCDD/Fs destruction by accelerating the conversion from V^{4+} to V^{5+}, and from Ce^{3+} to Ce^{4+}. DE value of PCDD/Fs reaches a maximum value of 77.8% with oxygen content controlled 21 vol.%. In the absence of oxygen, 33.7% of PCDD/Fs can still be destroyed due to lattice oxygen atoms stored by V_2O_5 and CeO_2. Water vapour is considered to suppress the destruction of PCDD/Fs by competitive adsorption. However, negative DE values of TCDD and TCDF are observed in the presence of water, and more TCDD and TCDF are generated with more water vapour introduced. Therefore, water vapour can also facilitate the removal of Cl^- present on the catalyst surface. SO_2 can poison the active sites of catalyst, and then inhibits the DE value of PCDD/Fs. With SO_2 concentration increasing from 0 to 100 ppm, DE values of PCDD/Fs significantly decrease from 67.6% to 51.9%. Catalyst regeneration is also investigated at 180°C in the presence of oxygen. Zero dioxins emission from the used catalyst can be observed after 13 h of desorption and destruction.

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