CATALYTIC DESTRUCTION OF CHLOROBENZENE AND MODEL DIOXIN COMPOUNDS WITH IRON OXIDE IN A SMALL SIZE INCINERATOR

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Key Words: Catalyst, chlorinated compounds, combustion, dioxin, furan

ABSTRACT

The current study was intended to investigate the catalytic destruction of iron oxide in chlorobenzene and model dioxin compounds combustion. First, chlorobenzene was used to correlate dioxin formation with chloro content of chlorobenzene. Further, the regenerated ferric oxide catalyst was used at different combustion temperatures to evaluate its impact on dioxin formation. Finally, a referenced dioxin material was used to examine the capability of ferric oxide catalytic oxidation. The results indicate that PCDD/F concentrations are linearly dependent on chloro content in the feed stream. PCDD/F concentrations are significantly affected by gas temperature in the presence of ferric iron catalyst. Furthermore, the PCDD/F concentrations were significantly reduced, or from 0.78 ng-TEQ/Nm$^3$ (580 °C) to less than 0.1 ng-TEQ/Nm$^3$ at temperature greater than 750 °C at the catalyst loading 100 g/hr. The destruction efficiency of the model dioxin compound is greater than 95% (in terms of TEQ) at catalyst of 300 g/hr. Among the various dioxin congeners, the destruction of the most toxic congener 2,3,7,8-TeCDD is the most effective.

INTRODUCTION

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are the most concerned air toxics generated from combustion practices. Many studies have been performed concerning dioxin emission control from municipal solid waste incinerators (MSWI), and to a lesser extent, on industrial waste combustion [1]. In Japan, the total dioxin emission was estimated to be 3000 g-TEQ/year, of which one third was released from the industrial waste incinerators [2]. In Taiwan, in addition to 19 regional municipal waste incinerators, there are over 4000 small size incinerators used for combusting a variety of industrial wastes [3]. These small size incinerators with numerous types including different furnaces were widespread everywhere in the island. It is therefore complicated and difficult to develop an effective means to control dioxin generation.

Two major mechanisms have been proposed for dioxin generation: precursor formation from existing smaller chlorinated molecules and de novo synthesis [4]. Both mechanisms occur simultaneously and/or independently [5]. The alternatives used in combustion facilities to control PCDD/Fs to compile with regulations can be categorized into three approaches: waste management; in-line inhibition; and end of process treatment [6,7]. The widely employed technologies for end of pipe treatment are activated carbon adsorption and catalytic destruction [8]. With these technologies, it is highly possible to meet the stringent emission standards, say below 0.1 ng-TEQ/Nm$^3$ in flue gas [7]. Almost all MSWIs in Taiwan use activated carbon adsorption process to ensure satisfactory dioxin removal before flue gas is emitted into ambient environment. However, activated carbon may react with chlorine atom or molecules to form species that can react to form PCDD/Fs [9]. Additionally, the disposal of spent activated carbon contaminated with dioxin becomes problematic as it creates another hazardous wastes to treat [8].

Catalytic materials were initially developed on industrial gas cleaning systems to destroy waste pollutants such as hydrocarbons, aromatics, halogenated derivatives, and NOx [10]. For example, some organic compounds, such as methane, toluene and styrene have been catalytically oxidized to carbon dioxide and water by noble metals (e.g., Pt and Pd), and MnO/Fe$_2$O$_3$ catalysts [11-13]. Recent efforts in developing catalysts have been focused on the PCDD/F removal. As a result, there are several metal
oxides such as PdO, CuO, V$_2$O$_5$, MoO$_3$, TiO$_2$, and Fe$_2$O$_3$ that have been demonstrated for their capability in suppressing dioxin formation [14]. For example, the removal efficiencies of PCDD/Fs up to > 99% could be achieved with the TiO$_2$/V$_2$O$_5$ -based catalyst [10, 15].

Imai et al. [16-19] have successfully applied hematite (α-Fe$_2$O$_3$) to catalyze oxidation of CO to near 100% destruction, and reduction of dioxin more than 80% in different small MSWIs. Recently, Weber et al. [14] used fly ash-containing Fe$_2$O$_3$ to reduce concentration of 1,2,3,4,6,7,8,9-octachlorodibenzo-p-dioxin in an industrial waste incinerator. Therefore, adding metal oxides catalyst either in the mixture with waste or in the gas stream to reduce dioxin formation and emission has become a promising means for small size incinerators [20].

Dioxin formation as function of CO, temperature and chloro content are well known factors in MSWI [21]. However, that is little research as their effects under catalytic conditions. Consequently, in the previous study [22], iron oxide, regenerated from the ferrite sludge, was used for successful CO destruction and dioxin suppression in a pilot-scale incinerator. For the present study, the catalytic destruction of iron oxide for chlorobenzene and model dioxin compounds was furthermore discussed. First, chlorobenzene was used to correlate dioxin formation with chloro content of chlorobenzene. Further, the ferric oxide catalyst was used at different combustion temperatures to evaluate its impact on dioxin formation. Finally, a referenced dioxin material was used to examine the capability of ferric oxide catalytic oxidation. It is the intention of this work to develop an environmentally acceptable and cost-effective technology to reduce the risk of dioxin emission from small size incinerators.

**MATERIALS AND METHODS**

**Catalyst**

The catalyst (iron oxide) used in this study was regenerated by raw ferric iron sludge (M$_x$Fe$_{3-x}$O$_3$), which was obtained from a nearby pilot wastewater treatment plant. After separation from wastewater by a magnetic process, the ferric iron sludge was heat-treated, ground and milled to fine particles. The metallic allotrope pattern of the particle was 90% α-Fe$_2$O$_3$ (by X-Ray Powder Diffraclat Meter). Laser Diameter Analyzer shows its mean diameter is about 1.5 μm (uniformity dispersion between 0.12 and 0.18μm), and the BET specific surface area of 5.6 m$^2$/g by Micrometrics. The preparation, regeneration and characterization of the regenerated ferric iron oxide were described in details elsewhere [22].

**Combustion Operation**

Experiments

The schematic diagram of the pilot incinerator

A. chlorobenzene or model dioxin sample feed; B. iron oxide addition. X. solid sampling point; C. dioxin sampling point.

1. first combustion chamber; 2. second combustion chamber; 3. catalytic reactor; 4. ferric iron sludge; 5. dryer/furnace; 6. miller; 7. cooling tower; 8. heat exchanger; 9. bag filter; 10. wet scrubber; 11. re heater (demister); 12. chimney.

Fig. 1. Schematic diagram of the incinerator system.

and the associated air pollution control devices are shown in Fig. 1. The incineration system has two combustion chambers with the upper temperatures controlling at 550 °C and 850 °C in Chamber 1 ($V = 1.4$ m$^3$) and 2 ($V = 1.4$ m$^3$), respectively. Chlorobenzene or reference dioxin compound, which was well mixed in heptane solvent, was delivered into Chamber 1 at a fixed rate of 20 L/hr. Two separate blowers were operated to provide the adequate oxygen to each chamber. The volume of combustion air in Chamber 1 and Chamber 2 are 12.2 and 0.4 Nm$^3$/min, respectively. The average flue gas rate is about 12.7 Nm$^3$/min to maintain the pressure of chambers under a slight suction condition (negative pressure). The iron oxide reaction chamber is located immediately after Chamber 2. The iron oxide was applied at a preset rate of either 100 or 300 g/hr by pulsejet into the catalytic reactor ($V = 0.68$ m$^3$). This injection involves no extra air into the reaction chamber. Based on the temperature (close to 850 °C), gas residence time of about 0.8 second (@ CO$_2$) and turbulence condition (Reynolds number about 10$^4$), it is expected that conditions are favorable for the catalytic reactions, and there was no solid material present in the catalytic reactor. As in the case of real incinerator systems, the processes shown in Fig. 1 also include a flue gas cooling system, filter, wet scrubber and a second heating device.
The combustion experiments consist of two parts. The first experiment, chlorobenzene was used to examine the effects of chloro concentration in chloro-
benzene on dioxin formation, because chlorobenzene decomposition is of interest as the past studies have indicated that it has high potential to contributing to dioxin formation [23,24]. The chlorobenzene was preset at five different concentrations (1-8% by weight of heptane, w/w; or 0.31-2.5% chloro/chlorobenzene). Thereafter, in the case of chloro concentration that yielded a relative highest PCDD/F concentration, addition of 100 g/hr of ferric oxide was applied to test the effectiveness of catalytic reaction on suppressing dioxin formation at various reaction temperatures.

In the second part of experiments, model PCDD/Fs were used to observe the oxidative capability of ferric iron oxide in terms of the destruction efficiency (DE) and removal efficiency (RE). The certified referenced [25] dioxin compound (Merck, Taiwan) and their concentrations are presented in Table 1.

The DE and RE were calculated by the respective equation shown below [26]:

\[ RE = \left( \frac{(PCDD/F)_{in}}{PCDD/F}_{out} - (PCDD/F)_{catalyst} - (PCDD/F)_{in} \right) \times 100\% \]

\[ DE = \left( \frac{(PCDD/F)_{in} - (PCDD/F)_{catalyst}}{(PCDD/F)_{in}} - (PCDD/F)_{catalyst} \right) \times 100\% \]

where subscripts “in”, “out” and “catalyst” refer to the dioxin mass in sampling points A, C and X (Fig. 1), respectively. Again, the inlet dioxin concentrations are shown in Table 1.

The difference between RE and DE is whether PCDD/Fs resident on the catalyst or not. In other words, RE is the overall efficiency, including that of catalytic destruction and adsorption on catalyst, if any. The DE includes the term of dioxin adsorbed onto catalyst.

### Results and Discussion

#### Effect of Chloro Concentration on PCDD/Fs

Figure 2 shows the combustion of chlorobenzene with five different chloro concentrations (0.31-2.5%) on PCDD/F formation without applying iron oxide. In these experimental runs, temperatures in Chamber 1 and 2 were controlled at 450 °C and 780 °C, respectively. Because there was no solid material present in the combustion chambers, the interference induced from dust particle adsorption of dioxin in the flue gas

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**Analysis**

Stack flue gas samples (sampling point C in Fig. 1) were used for analyses of PCDD/F concentrations, according to the US EPA modified method 23 [22].

The solid samples (sampling point X in Fig. 1) were air dried and crushed to less than 200 meshes. For analysis, a 10-gram sample was extracted with toluene at 150 °C and 13790 kPa using a Dionex ASE 200 accelerated solvent extraction system, with three extracting cycles per sample. After extraction, the crude extracts were transferred to hexane and treated with concentrated H2SO4. Purification was accomplished by an automated cleanup system based on the use of multi-layer silica, basic alumina column and AX-21 carbon adsorbents. Purified extracts were analyzed in a high-resolution gas chromatograph, equipped with a DB-5MS fused silica capillary column (J&W Scientific, CA, USA) with splitless injection, coupled with a high-resolution mass spectrometer was used for the quantification of PCDD/Fs. The methods and procedures of analyzing PCDD/Fs follow US EPA modified method 1613 [27]. Lab blank and lab matrix spike were also taken, and the value of blank is 0.004 ng-TEQ.

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**Fig. 2. Effect of chloro concentration on PCDD/F formation at T_{Chamber 1} = 450 °C, and T_{Chamber 2} = 780 °C.**

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**PCDD/F versus Cl concentration**

\[ (PCDD/F)_{Cl} = 0.261 (Cl) + 0.052 \]

\[ R^2 = 0.895 \]

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**Lab blank and lab matrix spike were also taken, and the value of blank is 0.004 ng-TEQ.**
stream was excluded. Nonetheless, the PCDD/F concentrations ranging from 0.16 to 0.72 ng-TEQ/Nm³ are clearly dependent on chloro content with the following correlation:

\[
(\text{PCDD/Fs})_{\text{3}} = 0.261(\text{Cl}) + 0.052
\]

Table 2. PCDD/F concentrations in the flue gas and the total TEQ of five different chloro contents of chlorobenzene.

<table>
<thead>
<tr>
<th>Dioxin congener</th>
<th>0.31%</th>
<th>0.77%</th>
<th>1.25%</th>
<th>1.75%</th>
<th>2.5%</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCDDs (ng/Nm³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,7,8-TeCDD</td>
<td>0.01</td>
<td>0.01</td>
<td>0.02</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDD</td>
<td>0.03</td>
<td>0.04</td>
<td>0.05</td>
<td>0.11</td>
<td>0.13</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDD</td>
<td>0.01</td>
<td>0.04</td>
<td>0.07</td>
<td>0.11</td>
<td>0.11</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDD</td>
<td>0.03</td>
<td>0.04</td>
<td>0.16</td>
<td>0.17</td>
<td>0.22</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDD</td>
<td>0.03</td>
<td>0.05</td>
<td>0.16</td>
<td>0.17</td>
<td>0.31</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDD</td>
<td>0.03</td>
<td>0.27</td>
<td>0.07</td>
<td>1.27</td>
<td>1.65</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8,9-OCDD</td>
<td>0.30</td>
<td>0.38</td>
<td>0.52</td>
<td>1.01</td>
<td>2.34</td>
</tr>
<tr>
<td>PCDFs (ng/Nm³)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3,7,8-TeCDF</td>
<td>0.65</td>
<td>0.18</td>
<td>0.07</td>
<td>0.25</td>
<td>0.96</td>
</tr>
<tr>
<td>1,2,3,7,8-PeCDF</td>
<td>0.10</td>
<td>0.02</td>
<td>0.01</td>
<td>0.25</td>
<td>0.16</td>
</tr>
<tr>
<td>2,3,4,7,8-PeCDF</td>
<td>0.12</td>
<td>0.09</td>
<td>0.23</td>
<td>0.32</td>
<td>0.31</td>
</tr>
<tr>
<td>1,2,3,4,7,8-HxCDF</td>
<td>0.26</td>
<td>0.16</td>
<td>0.31</td>
<td>0.36</td>
<td>0.86</td>
</tr>
<tr>
<td>1,2,3,6,7,8-HxCDF</td>
<td>0.09</td>
<td>0.08</td>
<td>0.28</td>
<td>0.39</td>
<td>0.36</td>
</tr>
<tr>
<td>1,2,3,7,8,9-HxCDF</td>
<td>0.01</td>
<td>0.01</td>
<td>0.44</td>
<td>0.62</td>
<td>0.53</td>
</tr>
<tr>
<td>2,3,4,6,7,8-HxCDF</td>
<td>0.08</td>
<td>0.12</td>
<td>0.02</td>
<td>0.28</td>
<td>0.71</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8-HpCDF</td>
<td>0.10</td>
<td>0.26</td>
<td>1.05</td>
<td>1.46</td>
<td>1.84</td>
</tr>
<tr>
<td>1,2,3,4,7,8,9-HpCDF</td>
<td>0.03</td>
<td>0.08</td>
<td>0.23</td>
<td>0.41</td>
<td>0.47</td>
</tr>
<tr>
<td>1,2,3,4,6,7,8,9-OCDF</td>
<td>0.40</td>
<td>0.18</td>
<td>0.43</td>
<td>2.05</td>
<td>2.89</td>
</tr>
<tr>
<td>Total PCDD/Fs (ng-TEQ /Nm³)</td>
<td>0.21</td>
<td>0.15</td>
<td>0.32</td>
<td>0.56</td>
<td>0.72</td>
</tr>
</tbody>
</table>

where the unit of chloro is percent (%) by weight in chlorobenzene. This observation is expected, since there have been numerous reports indicating a significant correlation between chloro content and dioxin formation [1, 28-29].

The ratio of $\Sigma$PCDF/ $\Sigma$PCDD ranged from 1.4 to 4.2, indicating that the PCDFs are predominant in all samples analyzed (Table 2), as was also reported by Stanmore [4]. Further, 2,3,4,7,8-PeCDF with its International Toxicity Equivalence Factor (I-TEF) = 0.5 is the congener most contributing to the overall TEQ as also mentioned by others [30]. Table 2 data also indicate that among PCDDs/PCDFs, the more-chlorinated congeners, the higher the concentration, e.g., OCDD and OCDF are highest among PCDDs and PCDFs, respectively.

**Effect of Gas Temperature on PCDD/F Formation**

As indicated above, PCDD/F concentrations depend on chloro content of the feeding material. To test the capability of iron oxide catalyst on reducing PCDD/F formation potential, a relative highest 2.5% Cl concentration was used at five different temperatures while 100 g/hr of iron oxide was injecting into the reactor chamber. The five temperatures for Chamber 1 and 2 were 150, 450 °C; 250, 550 °C; 350, 650 °C; 450, 750 °C; and 550, 850 °C, respectively. Temperatures in catalytic reactor were very close to Chamber 2. Figure 3 presents the results of toxicity equivalent PCDD/F concentrations versus gas temperature in the catalytic reaction chamber. The emitted PCDD/F versus Gas Temperature

Fig. 3. Effect of catalytic reaction chamber temperature on PCDD/F formation in the presence of catalyst (100 g/hr) for chloro content 2.5%. The five temperatures for Chambers 1 and 2 were 150, 450 °C; 250, 550 °C; 350, 650 °C; 450, 750 °C; and 550, 850 °C, respectively.

PCDD/F concentrations ranged from 0.03 to 0.78 ng-TEQ/Nm³, depending on gas temperature.

For temperatures between 450 and 550 °C, the
The effect of catalytic oxidation of iron oxide is not noticeable (Fig. 3). This could be due to an incomplete combustion of chlorobenzene resulting in PCDD/F formation. For temperatures between 650 and 850 °C, this is a significant reduction of PCDD/Fs by comparing to the results shown in Figure 2 (0.72 ng-TEQ/Nm³ for 2.5% chloro content). Particularly, the dioxin TEQ values were below the emission standard of PCDD/Fs (0.1 ng-TEQ/Nm³) at temperature greater than 750 °C.

Based on literature results, PCDD/Fs should be rapidly destroyed in a well-mixed gas phase at temperatures above 700 °C [31]. However, Sidhu et al. [32] reported that PCDD concentrations were virtually unchanged between 700 and 800 °C. In fact, these dioxin-like compounds are consistently found in the flue gases of a real incinerator at temperature up to 800 °C [21]. The reason could be attributed to the continuous presence of precursor species at elevated temperatures [33]. Nonetheless, it is suggested that, in the presence of iron oxides, the process temperature can be operated Chamber 2 at around 850 °C (550 °C @ Chamber 1) to ensure a low emission of dioxin compounds.

### The DE and RE of PCDD/Fs

For the referenced dioxin experiments, the dioxin material was well mixed in the heptane solvent and subsequently combusted at 550 °C @ Chamber 1 and 850 °C @ Chamber 2. The iron oxide used in two separate tests was 100 and 300 g/hr. The amount of PCDD/F adsorbed on iron oxide was also measured for each experiment. An insignificant fraction of PCDD/Fs (about 5 ng total, or 0.1% of input) was detected on the iron oxide catalyst collected in the bag filter (Table 3). Hence, the values of DE were close to RE, indicating that the mechanism of destroying PCDD/F would be catalytic oxidation but not adsorption. Figure 4 shows DE and RE of PCDD, PCDF and total TEQ of the model dioxin compound. For example, the efficiency of applying iron oxide on suppressing PCDD/F formation potential was greater than 88% in terms of PCDD/Fs and 95% in TEQ removal in both tests. The most toxic 2,3,7,8-TeCDD (1-TEF = 1) is significantly reduced.

There are several studies on the oxidative characteristics of iron oxide. For example, goethite (α-FeOOH) and hematite (α-Fe₂O₃) were both able to effectively oxidize organic compounds of chlorophenol, chlorobenzene and styrene [34]. When these metallic oxygen compounds were heated at high temperatures with air, the lattice oxygen will be released from the crystal structure as [35]:
The lattice oxygen generated from \( \text{Fe}_2\text{O}_3 \) was a primary means enhancing the oxidation of carbon monoxide [36]. Therefore, it is highly possible that the reason for the increased DE/RE of PCDD/Fs is believed to be the subsequent release of large numbers of lattice oxygen from the structure of iron oxide. Imai et al. [19] further proposed the following mechanisms of goethite catalytic oxidation, involving the atomic [O]:

\[
2\text{Fe}^{2+} + 3\text{O}_2^- \rightarrow 2\text{Fe}^{3+} + 3/2 \text{O}_2 + 4e^-
\]

CONCLUSIONS

In this study, the correlations between PCDD/F formation and chlorine concentrations and gas temperatures in a small size waste solvent incinerator were investigated. A novel catalyst regenerated from ferric iron sludge was used to suppress dioxin formation after the primary combustion reaction. It was found that PCDD/F concentrations are dependent on chloro concentrations in the feed stream of chlorobenzene at 780 °C. PCDD/F concentrations are significantly affected by gas temperature in the presence of catalyst. For example, PCDD/F concentration decreased from 0.78 ng-TEQ/Nm\(^3\) at 580 °C to less than 0.1 ng-TEQ/Nm\(^3\) at or above 750 °C at catalyst dosage 100 g/hr. At 300 g/hr, the DE (> 95% in terms of TEQ) and RE (~ 96% in terms of TEQ) values of a reference dioxin mixture are close, indicating that the mechanism of destroying PCDD/F is likely to be catalytic oxidation and not adsorption. Among the various dioxin congeners, the destruction of the most toxic congener 2,3,7,8-TeCDD is the most effective.

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Discussions of this paper may appear in the discussion section of a future issue. All discussions should be submitted to the Editor-in-chief within six months.

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小型焚化爐利用氧化鐵觸媒催化破壞氯苯及戴奧辛化合物之研究

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關鍵詞：催化劑、含氯化合物、燃燒、戴奧辛、呋喃

摘 要

本研究之主要企圖係在發展出一種可被環境接受並兼具成本效益之技術，以減少小型焚化爐排放戴奧辛之風險。研究內容包括：先將原擬棄棄之含鐵污泥再生製成類似氧化鐵之觸媒材料；次於實際焚化燃燒過程中探討氯苯不同含氯濃度與戴奧辛形成之關係，並評估此再生觸媒添加後破壞氯苯之最佳操作溫度；最後再以戴奧辛標準品直接投入燃燒測試氧化鐵觸媒之破壞去除效率，以及說明其可能之催化氧化機制。污泥再生實驗結果顯示：含鐵污泥經再生轉化後屬於α-Fe₂O₃之氧化鐵型態。氯苯燃焼破壊實驗發現：在未添加觸媒，且定溫燃燒的情況下(一次爐 450°C、二次爐 780°C)，戴奧辛形成濃度與氯苯之含氯量呈線性正比關係，其回歸方程式為 (PCDD/Fs)ₘ = 0.261(Cl)+0.052。此外，在添加一定劑量觸媒(100g/hr)之實驗條件下，當燃燒溫度大於 750°C 時，戴奧辛濃度即從 0.78 降至 0.1 ng-TEQ/Nm³ 符合法規標準。最後再以戴奧辛標準品燃燒測試之結果顯示：在添加 300g/hr 觸媒之幫助下，戴奧辛標準品之破壞效率高達 95% (TEQ)，並接近於 96% (TEQ)之去除效率。此三值之所以如此接近，顯見此氧化鐵觸媒破壞戴奧辛之機制係非由催化氧化效果，而是吸附作用，意即戴奧辛污染物很少殘留在觸媒上，較無二次污染必須處理之問題。同時實驗也發現，在不同戴奧辛同屬物種中，氧化鐵觸媒對於最具毒性之2,3,7,8-TeCDD 之破壞效果最佳。