

Catalytic oxidation of gaseous PCDD/Fs with ozone over iron oxide catalysts

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Abstract

Catalytic oxidation of PCDD/Fs (polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans) with ozone (catalytic ozonation) over nano-sized iron oxides (denoted as Fe_xO_y) was carried out at temperature of 120–180 °C. The effects of operating temperature, ozone concentration, space velocity (SV) and water vapor contents on PCDD/F removal and destruction efficiencies via catalytic ozonation were investigated. High activity of the iron oxide catalyst towards PCDD/F decomposition was observed even at low temperatures with the aid of ozone. The PCDD/F removal and destruction efficiencies achieved with Fe_xO_y/O₃ at 180 °C reach 94% and 91%, respectively. In the absence of ozone, the destruction efficiencies of all PCDD/F congeners are below 20% and decrease with increasing chlorination level of PCDD/F congener at lower temperature (120 °C). However, in the presence of ozone, the destruction efficiencies of all PCDD/F congeners are over 80% on Fe_xO_y/O₃ at 180 °C. Higher temperature and ozone addition increase the activity of iron oxide for the decomposition of PCDD/Fs. Additionally, in the presence of 5% water vapor, the destruction efficiency of the PCDD/Fs is above 90% even at lower operating temperature (150 °C). It indicates that the presence of appropriate amount of water vapor enhances the catalytic activity for the decomposition of gas-phase PCDD/Fs.

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1. Introduction

Activated carbon injection (ACI) technology is commonly used to reduce PCDD/F (polychlorinated dibenzo-*p*-dioxins and polychlorinated dibenzofurans) emissions from stationary sources including municipal waste incinerators (MWIs). However, ACI technology only transfers gaseous PCDD/Fs to the solid phase (fly ash) and further treatment is needed for the disposal of fly ash which contains relatively high level of PCDD/Fs. Additionally, ACI may increase the total PCDD/F discharge from muni-

cipal waste incinerators because it brings extra carbon source to the system (Chang and Lin, 2001).

Relevant studies indicate that catalytic process can suppress dioxin formation. Ferric oxide has been tested as a catalyst to oxidize CO and suppress PCDD/F formation in the furnace (Imai et al., 2001; Hung and Lin, 2003). Besides, some catalysts operated at appropriate temperatures also cause complete destruction of PCDD/Fs, resulting in the formation of CO₂, H₂O and HCl (Ide et al., 1996; Liljelind et al., 2001). Noble metals (Pt, Pd and Au) (Becker and Forster, 1997; Scire et al., 2003) and transition metal oxides (CrO_x, MnO_x, VO_x, WO_x and MoO_x) (Krishnamoorthy et al., 2000; Liu et al., 2001; Yim et al., 2002; Cho and Ihm, 2002) catalysts are two major classes used for catalytic oxidation of dioxins or dioxin-like

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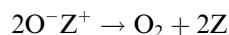
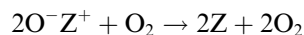
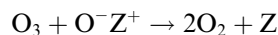
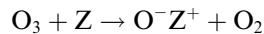
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compounds. However, polychlorinated benzenes are formed as byproducts in the combustion of chlorobenzene on Pt or Pd supported on Al_2O_3 , SiO_2 , $\text{SiO}_2\text{-Al}_2\text{O}_3$, or ZrO_2 (Van den Brink et al., 2000). Moreover, supported noble metal catalysts are deactivated by chlorine. Au/ Fe_2O_3 -Pt/ SnO_2 -Ir/ La_2O_3 catalysts prepared by sequential deposition precipitation showed high activity in the catalytic oxidation of dioxins at low temperature (at 150 °C) (Okumura et al., 2003). However, deactivation of multi-component catalysts by chlorine and byproducts has not been investigated. High cost is the major disadvantage for the use of noble metals in the destruction of dioxins. Bertinchamps et al. (2006) investigated forty different transition metal oxides in the catalytic oxidation of benzene and they found VO_x , CrO_x and MnO_x are the most active catalysts, but $T_{50\%}$ for benzene conversion is still above 250 °C. Previous study of the catalytic destruction of PCDD/Fs on commercial $\text{V}_2\text{O}_5\text{-WO}_3\text{-TiO}_2$ catalysts indicated that PCDDs and PCDFs were mainly adsorbed on the surface of the catalyst at 150 °C and conversion of dioxins was over 95% as the reaction temperature was above 200 °C (Webber et al., 1999).

For the field application, the catalyst reactor was generally located in the tail end configuration to avoid catalyst poisoning. Particulate matter removal is usually achieved with electrostatic precipitator (EP) or baghouse and SO_2 is mostly removed by semi-dry absorption or wet scrubbing. Unfortunately, the flue gas temperature after baghouse was normally between 120 and 180 °C. For the application of these catalysts in the optimum reaction temperature of dioxin destruction, the flue gas must be reheated to over 200 °C prior to entering the catalyst reactor, leading to the dramatic increase of the operating cost. It is essential to develop a new technology which can be operated at lower temperature for effective destruction of PCDD/Fs (<200 °C).

Relevant studies have shown that various organic compounds can be oxidized by hydrogen peroxide (H_2O_2) over heterogeneous catalysts (Watts et al., 1990; Lin and Gurol, 1998); however, those studies are mainly for water pollution control and soil remediation. The application of such processes for gas treatment is still limited. Ozone catalytic oxidation (catalytic ozonation) is an emerging technology which applies ozone as an oxidant in catalytic reactions (Naydenov and Mehandjiev, 1993). Previous studies indicate that the application of ozone can lower the reaction temperature and activation energy for CO (Pettersson et al., 2006) and VOC (*iso*-propanol, benzene, cyclohexane, acetone, and toluene) (Gervasini et al., 1996; Einaga and Futamura, 2005; Xi et al., 2005; Reed et al., 2006; Stoyanova et al., 2006) oxidation on various transition metal oxides, such as Ce, Ni, Co, NiMnO_3 -ilmenite, Mn, Fe, Cu and Ag (Naydenov et al., 1995; Mehandjiev et al., 2001; Einaga and Futamura, 2006; Konova et al., 2006). Naydenov and Mehandjiev (1993) suggested that active oxygen species (O^-) are formed on MnO_x during O_3 decomposition and which are able to oxidize benzene at 10–80 °C.

Konova et al. (2006) proposed the mechanism of catalytic ozone decomposition on the transition metal oxides as follows and reported that the active complex of $\text{O}^-[\text{Co}^{4+}]$ are formed during the reaction of ozone decomposition on $\text{NiO}_x/\text{Al}_2\text{O}_3$, which are capable of oxidizing VOCs at room temperature.



(Z stands for active site of catalyst).

Einaga and Futamura (2004) reported that catalytic oxidation of benzene with ozone over $\text{MnO}_2/\text{Al}_2\text{O}_3$ could be achieved at room temperature (295 K) and water vapor would suppress catalyst deactivation. In another study, Xi et al. (2005) reported that the addition of ozone significantly reduced the oxidative temperature of acetone on $\text{MnO}_x/\text{Al}_2\text{O}_3$. Adsorbed oxygen species formed from ozone decomposition on metal oxides have been shown essential in the course of oxidation process (Naydenov et al., 1995). In situ Raman spectroscopy identified a band at 890 cm^{-1} , which is an adsorbed peroxide species (O_2^{2-}) formed on the manganese oxide from ozone decomposition (Reed et al., 2005).

Study on the oxidation of dioxins in the presence of ozone over catalysts is scarce. Previous studies indicate that iron oxide had high activity in decomposing ozone (Naydenov et al., 1995; Oyama, 2000), besides, nano-sized iron oxide with high surface area has a high catalytic activity for CO oxidation at room temperature (Li et al., 2003; Lin et al., 2005). The aims of this study are to develop a low temperature dioxin destruction technology and to investigate the oxidation behavior of PCDD/Fs over iron oxide catalyst with the addition of ozone. The removal and destruction efficiencies of dioxins achieved at different operating conditions (reaction temperature, ozone concentration, space velocity (SV) and water content) will be discussed.

2. Experimental

2.1. Preparation of the iron oxide catalysts

All reagents used in this study are of analytical grade. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and NH_4OH (Showa, Japan) were used for preparation of iron oxide catalyst with precipitation method as reported previously (Lin et al., 2005). An aqueous solution of iron salt ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, 0.5 M) was slowly added (10 ml/min) to an aqueous solution of NH_4OH (15%) under vigorous stirring. The pH of the mixture was maintained at 11. After 2 h of aging at room temperature, the brown precipitate was filtered and washed several times for the removal of chloride. The obtained solids were dried overnight in an oven at 110 °C. Finally, the catalysts were calcined for 12 h at 180 °C. The iron oxide catalysts

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