

ENHANCEMENT OF GASEOUS PCDD/F REMOVAL OVER MANGANESE OXIDE VIA OZONE INJECTION

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Introduction

Manganese oxide (MnO_x) catalyst has been shown as one of the most active metal oxides for oxidation of chlorinated organic compounds and has a high activity in the decomposition of ozone¹. However, the total oxidation of chlorobenzene by MnO_x catalyst takes place at about 400 °C². Catalytic oxidation with ozone is a promising technology which applies the synergistic effect of transition metal oxide and ozone. It can lower the reaction temperature and activation energy for catalytic oxidation of volatile organic compounds (VOCs)³. Study on the oxidation of dioxins in the presence of ozone over MnO_x is scarce. In this paper, the enhancement of gaseous PCDD/Fs (polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans) oxidation over manganese oxide catalyst via ozone injection was investigated.

Materials and Methods

Preparation of the manganese oxide catalysts

Manganese oxide catalysts were prepared with precipitation method. An aqueous solution of manganese salt ($Mn(NO_3)_3 \cdot 4H_2O$, 0.5M) was slowly added (10 ml/min) to an aqueous solution of NH_4OH (28%) 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 impurities. The obtained solids were dried at 110 °C overnight and calcined at 300 °C for 4 h. The specific surface area of the catalyst was determined by the BET method using low temperature (-197 °C) N_2 -sorption in a Micromeritics ASAP 2010. The surface area of MnO_x is measured as 53.0 m²/g.

Dioxins oxidation reaction testing

The dioxin oxidation reaction was investigated in a fixed-bed reactor which was made of a glass tube with the inner diameter of 16 mm. The catalytic bed was composed of 1.0 g of catalyst selected with the fraction 40-60 mesh (0.42-0.25 mm) and diluted in 9.0 g of inactive SiO_2 with particle size in the range of 30-50 mesh (0.59-0.297 mm). Ozone was synthesized from dry air with Triogen laboratory ozone generator (LAB2B). The inlet ozone concentration of the reactor was controlled to be 100 ppm. Ozone concentrations were measured with an ozone analyzer (Ozomat GM-6000-OEM). In this study, a stable dioxin-containing gas stream generating system was constructed. The system consists of a PCDD/F stock solution injector, temperature-controller, evaporator and a set of mass flow controllers. The total gas flow rate was controlled at 3.0 l/min (balanced with air). The inlet PCDD/F concentration was 2.0 ng-TEQ/Nm³ and the space velocity (SV) was controlled at 20,000 h⁻¹. The fresh catalyst is used in each run to eliminate possible contamination. The duration of each run was set as one hour.

PCDD/F sampling and analysis

The PCDD/Fs in the outlet gas stream of the reactor and on the catalysts, respectively, are collected and analyzed. The vapor-phase sample was collected by XAD-2 resin. They were then spiked with known amounts of USEPA Method 23 internal standard solution. Thereafter, the XAD-2 and solid (on catalysts) samples were Soxhlet extracted with toluene for twenty-four hours. The toluene extract was then concentrated to about 1ml by rotary evaporation and was replaced by 5.0 ml hexane for pretreatment process. Having been treated with conc. sulfuric acid, the sample was then subjected to a series of clean-up 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 seventeen 2,3,7,8-substituted

PCDD/F congeners with high resolution gas chromatography (Hewlett Packard 6890 plus) / high resolution mass spectrometer (JEOL JMS-700) equipped with a fused silica capillary column DB-5 MS (60m x 0.25 mm x 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.

Results and Discussion

1. Reactivity results

Fig. 1 presents the destruction and removal efficiencies of PCDD/Fs within the temperature range (120-180 $^{\circ}\text{C}$) achieved with ozone alone, MnO_x , and MnO_x/O_3 , respectively. For three series of experimental tests, the removal and destruction efficiencies of PCDD/Fs increased with increasing temperature. However, the removal and destruction efficiencies of PCDD/Fs achieved with MnO_x was 85% and 25%, respectively at 180 $^{\circ}\text{C}$. It indicated that more than half of the dioxins just adsorbed on the surface of the solids with MnO_x . It indicates that the activity of MnO_x itself for the decomposition of PCDD/F is not high enough. In the absence of the catalyst, the conversion of PCDD/Fs achieved with addition of 100 ppm O_3 was between 15 and 31% at the temperature range of 120 to 180 $^{\circ}\text{C}$. It indicates that ozone is a stronger oxidizing agent than oxygen, however, its oxidizing power is not high enough to effectively destroy dioxin completely.

At 180 $^{\circ}\text{C}$, the removal and destruction efficiencies of PCDD/Fs achieved with 100 ppm ozone over MnO_x were 94% and 88%, respectively. It indicates that the activity of MnO_x for the decomposition of PCDD/F significantly increases with ozone addition. Previous studies show that manganese oxide has a high activity for ozone decomposition due to its different oxidation states⁴. Decomposition of ozone on MnO_x leads to the formation of atomic oxygen on the oxide surface and which may be a strong oxidizing agent⁵. Einaga and Futamura identified a band at 890 cm^{-1} by in-situ Raman spectroscopy which is a peroxide species (O_2^{2-}) formed on the manganese oxide from ozone decomposition at the temperature between 30 and 100 $^{\circ}\text{C}$ ⁶. The enhancement may be due to two reasons. One is that free-radical species derived from thermal ozone decomposition at higher temperature react with dioxins homogeneously. The other one may be due to the active oxygen species formed during the decomposition of ozone on MnO_x catalyst and further react with gaseous dioxin molecules. Both homogeneous and heterogeneous reaction mechanisms may be present at the same time in the temperature range of 120-180 $^{\circ}\text{C}$. Furthermore, ozone is a powerful oxidant and may oxidize the intermediates and reduce surface poisoning.

2. Destruction and removal efficiencies of dioxin congeners over MnO_x with or without ozone

Fig. 2 shows that in the absence of ozone, the destruction efficiencies of most PCDD and PCDF congeners were very low (below 20%) with MnO_x at 120 $^{\circ}\text{C}$ and most congeners just adhered to the catalysts. The destruction efficiencies of PCDD and PCDF congeners decreased with increasing chlorination level of PCDD/F congeners. It may be attributed to the fact that the structures of highly chlorinated PCDD/F congeners are more stable thermally and difficult to decompose. With the increase of the operating temperature, the increasing rate of destruction efficiencies of lowly chlorinated PCDD and PCDF congeners is significantly larger than that of highly chlorinated congeners.

A remarkable increase in destruction efficiencies of lowly chlorinated PCDD and PCDF congeners over MnO_x catalyst was observed with the addition of ozone to the feeding gas stream at 120 $^{\circ}\text{C}$. However, the destruction efficiencies of highly chlorinated PCDD and PCDF congeners were still low. It indicates that the promotional effect of ozone on the oxidation of lowly chlorinated congeners over MnO_x is significant at lower temperature. The destruction efficiencies of highly chlorinated PCDD and PCDF congeners increase with increasing temperature. It may be attributed the fact that the higher temperature leads to more active oxygen species being produced and which can oxidize dioxins effectively. The removal and destruction efficiencies of all PCDD and PCDF congeners were over 90% and 80%, respectively, at 180 $^{\circ}\text{C}$.

Experimental results indicate that MnO_x catalysts can be applied for the destruction of PCDD/Fs in the presence of ozone at 180 $^{\circ}\text{C}$. However, due to the relatively low dioxin concentration in the gas streams investigated, it is difficult to obtain the information on the intermediate compounds on the catalyst surface and carbon balance. These studies will be further investigated in the future.

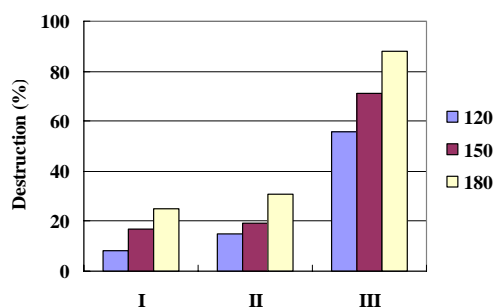
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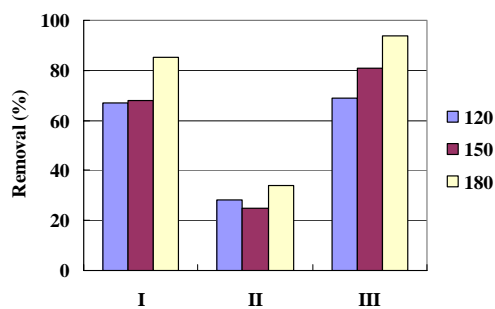
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(a) Destruction efficiencies of PCDD/Fs (%)



(b) Removal efficiencies of PCDD/Fs (%)



I: MnO_x (1.0 g MnO_x catalyst, 9.0 g SiO₂)

II: Ozone (100 ppm O₃, 10 g SiO₂)

III: MnO_x/O₃ (1.0 g MnO_x catalyst, 9.0 g SiO₂, 100 ppm O₃)

Fig. 1. The removal and destruction efficiencies of PCDD/Fs versus operating temperatures.

(SV = 20,000 h⁻¹, inlet PCDD/Fs = 2.0 ng-TEQ/Nm³).

*Removal efficiency (%) = $[\text{PCDD/F}_{\text{inflow}} - \text{PCDD/F}_{\text{outflow}}] / \text{PCDD/F}_{\text{inflow}} \times 100$

**Destruction efficiency (%) = $[\text{PCDD/F}_{\text{inflow}} - \text{PCDD/F}_{\text{outflow}} - \text{PCDD/F}_{\text{on catalyst}}] / \text{PCDD/F}_{\text{inflow}} \times 100$

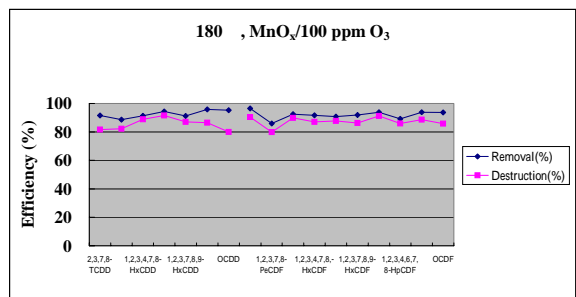
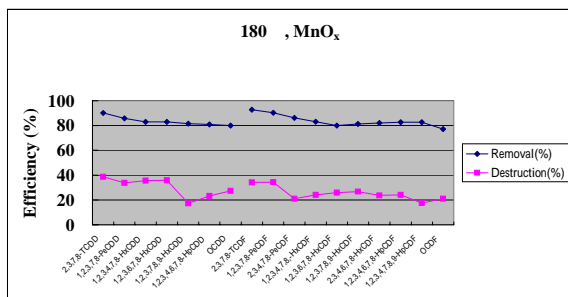
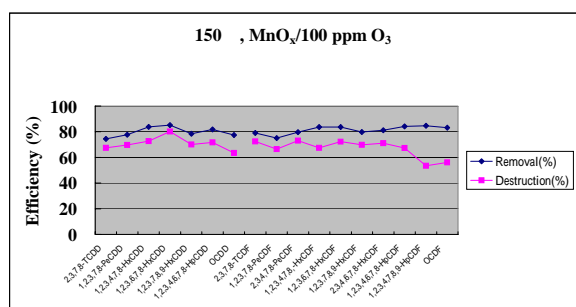
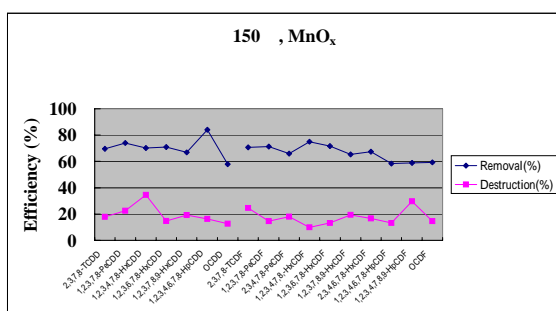
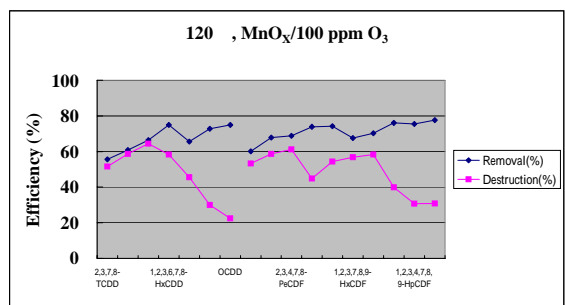
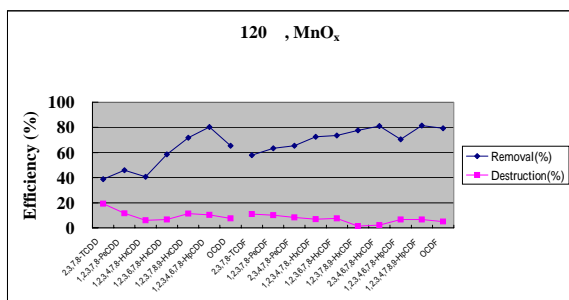


Fig. 2. The removal and destruction efficiencies of PCDD and PCDF congeners.

(SV = 20,000 h⁻¹, O₃ = 100 ppm, inlet PCDD/Fs = 2.0 ng-TEQ/Nm³).