

CATALYTIC OXIDATION OF HIGH CONCENTRATION PCDD/Fs OVER THE MIXTURE OF V₂O₅-WO₃/TiO₂ AND ACTIVATED CARBON

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Introduction:

Catalytic oxidation was not only useful for NO_x removal but also for the oxidised of PCDD/Fs over V₂O₅-WO₃/TiO₂ catalyst via selective catalytic reduction (SCR)¹. For PCDFs and PCDDs, removal efficiency increased from approximately 80% to >98% as temperature increases from 100 °C to 230 °C. At 100 °C removal was by adsorption and by 230 °C it was entirely via destruction². At temperatures below 200 °C, the oxidizing potential of V₂O₅-WO₃ was obviously not sufficient to decompose polychlorinated aromatic compounds effectively³. Hence, ozone, coupled with the transition metal oxides (iron or manganese oxide), has ever been investigated to oxidize PCDD/Fs at low temperature (120-180 °C)⁴. Activated carbon (AC) has been extensively studied as an adsorbent for the removal of volatile organic compounds (VOCs) as its porous characteristic and large BET surface area⁵⁻⁶. In fact, the temperature of the flue gas, which was fallen to 140-180 °C after the bag-filter, couldn't supply an optimal reaction temperature for V₂O₅-based catalyst. In this study, V₂O₅-WO₃/TiO₂ catalyst and AC would be combined to enhance the oxidation activity and adsorption abilities for the removal of high concentration PCDD/Fs at low temperature (160 °C). The effects of oxygen content, ozone and ratios of catalyst and AC were investigated on the degradation of high concentration PCDD/Fs.

Materials and methods:

In this study, a commercial honeycomb structured catalyst (V₂O₅-WO₃/TiO₂, Zhejiang Sanlong Catalyst Co., Ltd., China) was used. The anatase-TiO₂ phase was detected by X-ray multocrystal diffraction (XRD, PANalytical-X'Pert PRO, Holland). The contents of V, W and O, tested by Energy Dispersive Spectroscopy (EDS, EDAX-GENESIS4000, USA), were 0.75 wt.%, 6.08 wt.% and 37.78 wt.% respectively. The BET surface area, determined by N₂-Physisorption (Quanta Chrome, USA), was 93 m²/g. Two commercial ACs are also used, one based on lignite (AC-1) with BET surface area of 374.9 m²/g, and the other one on coconut shell (AC-2) with BET surface area of 715.8 m²/g.

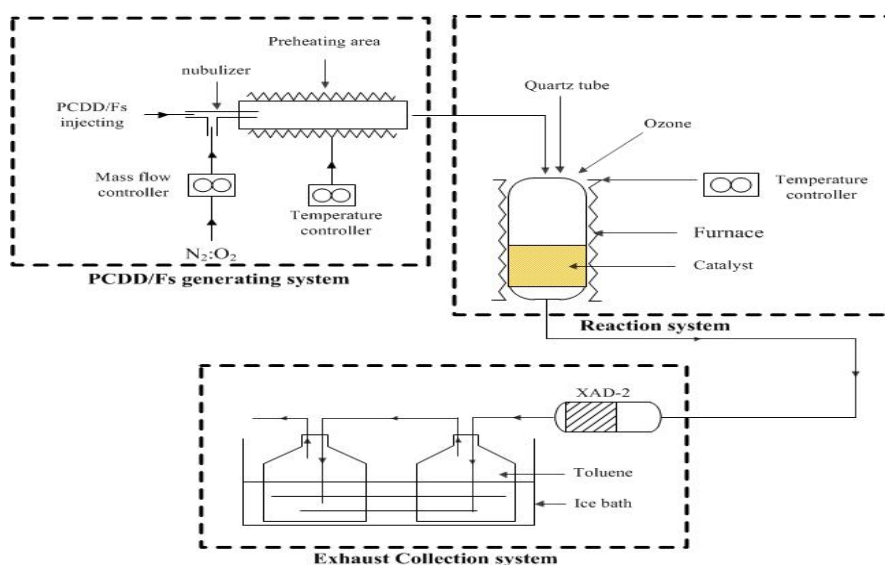


Fig.1 Diagrammatic of the experimental apparatus.

A PCDD/Fs generating system would supply stable and continuous flow of vapour phase PCDD/Fs congeners. This system mainly includes a gas flowmeter, a temperature controller, a quartz tube preheater, and an injector/nebulizer of PCDD/Fs solution. The PCDD/Fs solution was extracted (Soxhlet extraction) from fly ash of medical waste incinerator, then pretreated to purify and concentrated. Adding solvent (nonane) to the concentrated solution was allowed to obtain suitable injection liquors. Carrier gas (N₂:O₂ = 9:1), mixing atomized PCDD/Fs, was heated in the preheater at a certain rate (0.5-2 L min⁻¹); then, a dioxins stream with a certain concentration was discharged stably.

The experiment was conducted using a vertical quartz tube with heating system at 160 °C as shown in Fig. 1. The initial concentration of PCDD/Fs was 9.80 ng I-TEQ/m³, which was the average value of three repeated experiments. A tailored filter cartridge placed in tube contains 1.0 g reactant (the mixture of catalyst and AC) and 4.0 g SiO₂ (sifted to 50 mesh). The corresponding Gas Hourly Space Velocity (GHSV) is 8000 h⁻¹. The sampling time during each run was one hour. After each run the reactor was cleaned with toluene. PCDD/Fs contained in the exhaust (collected by XAD-2 polymeric resin and a toluene absorber bottle), the tailored filter and cleaning fluid of reactor walls (Soxhlet Extracted by toluene for 24 h) all were analysed. In this study, two parameters were analysed for only 17 toxic congeners of PCDD/Fs. Removal efficiency and destruction efficiency, referred to as “RE”, “DE” for short, were calculated as follows:

$$RE = (PCDD/Fs_{inlet} - PCDD/Fs_{exhaust}) \div PCDD/Fs_{inlet}$$

$$DE = (PCDD/Fs_{inlet} - PCDD/Fs_{exhaust} - PCDD/Fs_{cata+tube}) \div PCDD/Fs_{inlet}$$

Results and discussion:

1. The effect of ratios of catalyst and AC on the PCDD/Fs degradation

In order to enhance the adsorption ability at low temperature (160 °C) with oxygen (N₂:O₂ = 9:1 in volume), two kinds of AC (AC-1, AC-2) was mechanically mixed with catalyst (M-1, M-2, respectively) to destroy high concentration PCDD/Fs (9.80 ng I-TEQ/m³). The effects of three different ratios of the mixture (AC: Catalyst = 4:1, 3:2, 1:1, respectively) were investigated in this study. RE and DE value is only 73.6% and 52.2% without AC, as shown in Fig.2. For the M-1 mixture, almost no change has happened for RE values at the ratios of 4:1 and 3:2 (decreased from 91.6% to 90.8%). When the ratio decreases to 1:1, only 87.7% PCDD/Fs have been removed. The maximum of DE value is 79.0% with the ratio of 1:1 while the minimum is 75.5% with the ratio of 3:2. For the M-2 mixture, RE value decreases from 94.3% to 91.0% and DE value increases from 63.7% to 71.1% as the ratios of the mixture decrease from 4:1 to 1:1.

The results show adding AC is beneficial to promote the removal and degradation of PCDD/Fs. The adsorption capacity of M-2 mixture is stronger than that of M-1 mixture as the larger specific surface area and richer porous structure of AC-2. However, more PCDD/Fs are destroyed by M-1 mixture compared with M-2. It's due to PCDD/Fs molecules adsorbed by AC-2 couldn't easily desorb to react with catalyst as the stronger adsorption capacity of AC-2.

2. The effect of oxygen content on the PCDD/Fs degradation

In this study, three different oxygen contents (0%, 10%, 20%) have been researched to observe the effect of PCDD/Fs degradation over the mixture (ratio of AC and catalytic is 3:2) at 160 °C. As fig.3 shown, for the M-1 mixture, RE and DE value obviously increase (RE: 74.2%, 90.8%, 92.1%; DE: 27.4%, 75.5% 82.2%) with oxygen contents increased (0%, 10%, 20%). However, RE and DE values are basically lower for the M-2 mixture due to the stronger adsorption capacity of AC-2.

As the DE values show, oxygen has a significantly effect on the decomposition of PCDD/Fs. Relevant study

shows VO_x is considered as the active ingredient of vanadium–tungsten oxidation catalysts. The active lattice atoms of oxygen V^{5+}O_x oxidize pollutants on the catalyst surface so that V^{5+}O_x is reduced to V^{4+}O_x ; then, in the present of oxygen re-oxidation occurs to V^{5+}O_x ⁷. As the oxygen content increases, the conversion rate of V^{4+}O_x to higher oxide is faster and then more PCDD/Fs congeners will be destroyed. Attractively, more than 15% PCDD/Fs is still destroyed when no oxygen is introduced. It's maybe due to the lattice oxygen existed in the catalyst.

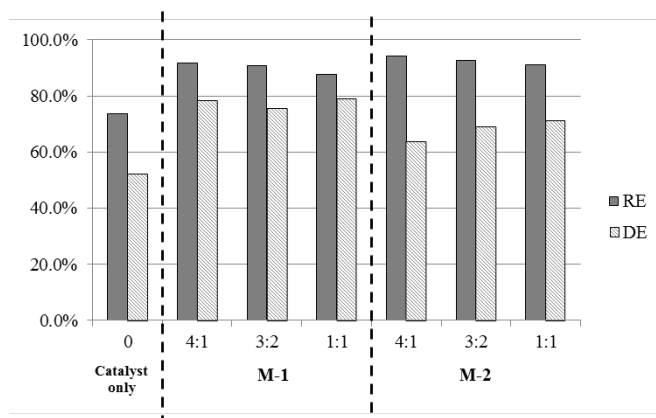


Fig.2. The effects of different ratios of the mixture on the degradation of PCDD/Fs.

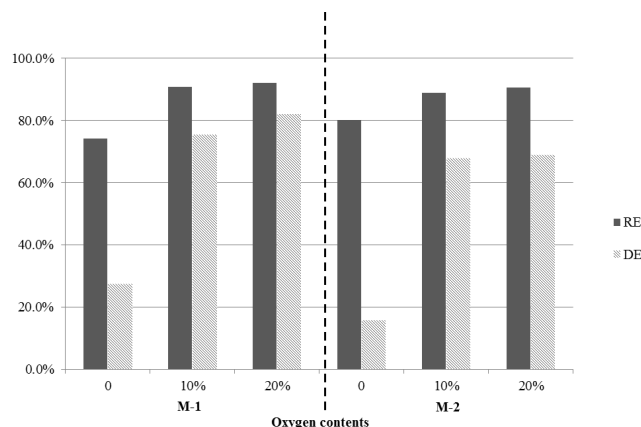


Fig.3. The effects of oxygen content on the degradation of PCDD/Fs.

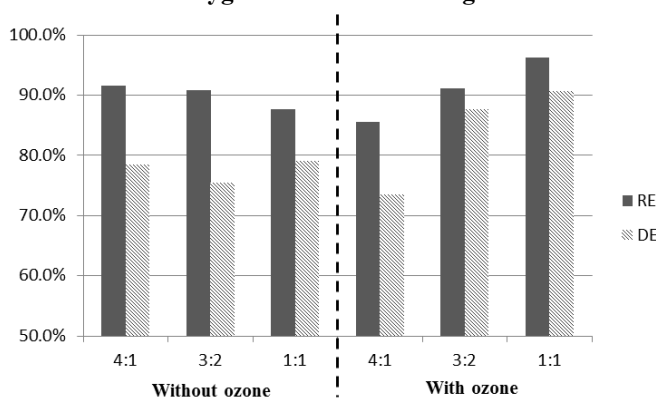


Fig.4. The effect of ozone on the degradation of PCDD/Fs.

3. The effect of ozone on the degradation of PCDD/Fs

In order to enhance the oxidizing capacity of the M-1 mixture at 160 °C, ozone (200 mg m⁻³) was introduced into the reaction. RE and DE values obviously increase with ozone present except for the ratio of 4:1, which means that ozone plays a more important role on catalytic oxidation than AC adsorption. After the reaction, a dark brown flock appeared at the bottom of the toluene absorber bottle. At the ratio of 4:1, large amount of the flock are generated due to the reaction of AC and ozone, thus, RE and DE values are even lower (RE: 85.6%, DE: 73.5%) in the presence of ozone. However, with the catalyst content increased, almost no dark brown flock is produced, thus, more PCDD/Fs congeners are removed and destroyed (RE: 91.2%, 96.3%, DE: 87.6%, 90.6% at the ratio of 3:2, 1:1, respectively), as fig. 4 shown.

Relevant study shows, ozone can decompose to form active oxygen species such as superoxide (O⁻) and peroxide (O²⁻) species, which would make a great contribution to PCDD/Fs oxidation⁸. Also, oxygen content in the reaction atmosphere increases to nearly 40% as the ozone decomposition. It is proposed that the free-radical species derived from thermal ozone decomposition react with dioxins homogeneously and the active oxygen species formed during the decomposition of ozone on Fe_xO_y catalyst and further react with gaseous dioxin molecules⁹.

Acknowledgements:

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