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# CATALYTIC OXIDATION OF PCDD/F OVER V2O5-WO3/TIO2: EFFECTS OF BENZENE AND CHLORINATED BENZENES

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## Introduction

V2O5–WO3/TiO2 (VWTi) catalysts are not only applied in selective catalytic reduction (SCR) of NOx, but also have been found effectively destroy chlorinated volatile organic compounds present in gaseous stream as well1,2. Bertinchamps et al. even found the addition of NO, for example, during chlorobenzene oxidation increased the catalyst activity3. However, few researches on the mutual effect between polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/F) and chlorinated benzenes were reported when vanadia based catalysts were utilized in exhaust gases. In this study, a commercial VWTi catalyst was applied and its activity was investigated by degrading PCDD/F (Run 1). Benzene (B, Run 2), chlorobenzene (CB, Run 3), and 1,2-dichlorobenzene (DCB, Run 4), were separately introduced as additive components to study their influence on PCDD/F decomposition.

Materials and methods

The monolith catalyst was carefully crushed and sieved to a 100-200 mesh powder (75-150 μm in diameter). X-ray multi-crystal diffraction shows an anatase structure for the TiO2 phase. The contents of V, W and O, tested by Energy Dispersive Spectroscopy, were 0.41, 14.97 and 51.25 wt. %, respectively. Other important parameters are a BET surface area of 58 m2 g-1, a total pore volume of 0.19 cm3 g-1 and an average pore diameter of 13.02 nm.

Catalytic activity tests were carried out in a reactor with a continuous gas flow system, as Fig. 1 shown. First, the catalyst was loaded into a vertical quartz tube and then installed in an electric furnace. The reaction temperature was monitored by a K-type thermocouple projecting into the catalyst bed at 200±2 °C. The flow rates of mixed gases (N2:O2=89:11) were 500 mL/min. The reaction time of each run is 1 h. The Gas Hourly Space Velocity (GHSV) is 10000 h-1. The concentration of injected B, CB and DCB was separately adjusted to 2000 ppm. The pretreatment procedure of PCDD/F was conducted according to the EPA method 1613. Two parameters were analysed for 136 congeners of PCDD/F. Removal efficiency (RE) and destruction efficiency (DE) were calculated as follows:

RE=(C_in-C_out)/C_in ×100%

DE=(C_in-C_out-C_ads)/C_in ×100%

## Results and discussion

The characteristic of initial PCDD/F

The PCDD/F generating system was stabilized at 200 °C. The average value of three repeatability samples was esteemed to be the initial concentration of PCDD/F. The initial I-TEQ concentration was 5.13 ng I-TEQ Nm-3. T4CDF and P5CDF ranked the dominant mass ratios in generating system. The mass ratios of 17 toxic 2,3,7,8-substituted PCDD/F only accounted for 31.56% in PCDD/F generating system. The reproducibility in the laboratory experiments was very good, proving the reliability of the experimental procedure.

RE and DE Achieved in Run 1

The fresh catalyst showed high removal of PCDD (82.4%) and PCDF (91.97%) in Run 1 (Fig. 2A). The total RE for tetra- to octa-chlorinated PCDD/F was ranged from 62.3 to 99.6%. The RE for the total TEQ was more than 94.2%. However, the DE of PCDD, PCDF, and total I-TEQ were just 50.3%, 77.34% and 81.79%, respectively. The DE was always lower than the RE, which should be ascribed to the adsorption effect of catalyst.

The RE of PCDD or PCDF congeners exhibited an ascending trend with increasing chlorination (Fig. 2B). It was due to the fact that highly chlorinated PCDD and PCDF congeners present lower vapor pressures, lower volatility and higher boiling points compared with lowly chlorinated congeners, which resulted in more easily deposited on the surface of the catalysts. Therefore, the RE of high-chlorinated PCDD and PCDF congeners were higher than the correspondingly low-chlorinated ones.

Lower activity in the decomposition of lowly chlorinated PCDD/F over VWTi catalysts was also observed in this study. The PCDD/F congeners treated with catalyst were converted into the low-chlorinated products via dechlorination4. In addition, higher chlorinated PCDD/F with low volatility is retained on the catalyst surface longer, therefore, increasing the chance of oxidation. This resulted in increasing DE of PCDD/F homologues with increasing chlorination degree.

RE and DE Achieved in Run 2-4

The RE and DE for the oxidation of PCDD/F decrease with the increasing chlorination degree of chlorinated benzenes. The present of B, CB or DCB will increase the competitive adsorption between PCDD/F molecules for active sites on the catalyst surface. The effect of lowering the volatility with increasing substitution resulted in longer residence time on the catalysts, which may lower the RE of PCDD/F when the catalyst provides insufficient active sites.

One key question for assessment of a catalytic oxidation technology involving binary mixtures is whether the more toxic PCDD/F is formed. The results suggest that the DE (-674.2%) surprisingly decreased at the present of DCB (Run 4), with a great formation of T4CDF. Chlorinated benzenes condensation mechanisms may be responsible for less chlorinated PCDF isomer formation. There is an obvious difference between Run 3 and Run 4 (Fig. 2B). There is a great lower chlorinated formation of T4CDD, T4CDF and P5CDF during Run 4. However, except these, some high-chlorinated PCDD/F, such as O8CDD and H7CDF, formed in Run 3. The above phenomenon may indicate a different PCDD/F formation pathway from CB and DCB. However, the catalyzed formation of PCDF from chlorinated benzenes is still little known about the concrete mechanism involved. In part, this is due to the complexity of the catalyst matrix, which effectively obscures the identity of the active catalytic sites. Anyway, the condensation of chlorinated benzenes to PCDF on catalyst surface has to be ascribed to the catalytic activity of metal sites.

In addition, the dechlorination process produced a lot of Cl on the catalyst. The adsorption of Cl on the catalyst via a nucleophilic attack was the reason leading to Cl-poisoning of catalyst. Kinetic studies showed that the main effect of Cl is to block the metal surface, decreasing the number of active sites 5. Furthermore, the strong electronegativity of Cl makes it tend to attract electron from metal atoms or other metal additives, which decreased the electron cloud density on the surface of catalyst and further influence the catalytic oxidation of PCDD/F. Cl also had great mobility. Along with the process of gas migration, Cl would cause the entire bed catalyst poisoning.

## Acknowledgements

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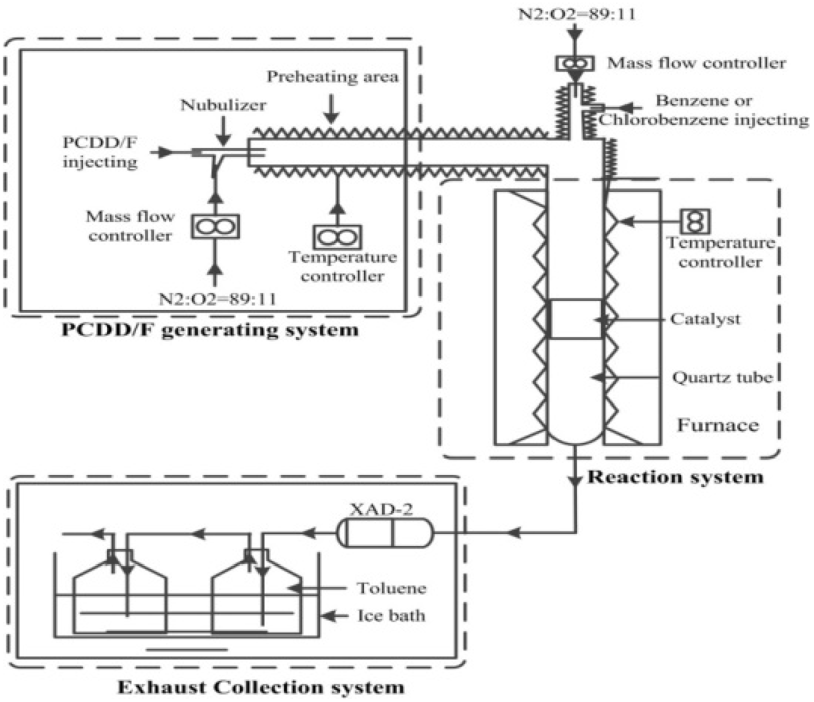

**Figure 1.** Schematic diagram of the experimental apparatus.

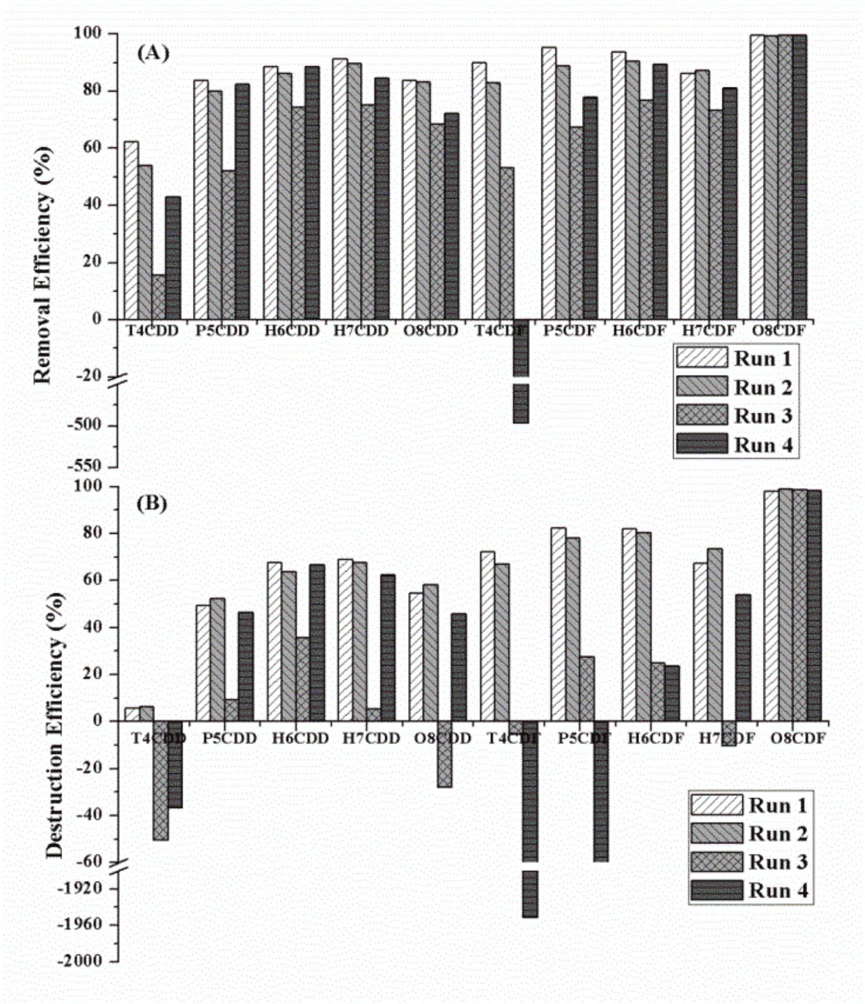

**Figure 2.** RE and DE values of the 136 PCDD and PCDF congeners at different test runs.