

LOW TEMPERATURE CATALYTIC OXIDATION OF POLYCHLORODIPHENYLS IN WASTE INCINERATION FLUE GAS

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Introduction

Persistent organic pollutants are a class of organic compounds that are persistent, bioaccumulative, long-distance transport and biologically toxic¹. They have slow degradation in the environment, long residence time, semi-volatile and strong lipophilic hydrophobicity². They can be scaled up along the food chain and can migrate in the environment for a long time, which poses a serious threat to organisms, especially human health³. Dioxins are among the most toxic POPs and are among the first 12 POPs to be cut and controlled to be included in the Stockholm Convention⁴. Waste incineration, especially municipal waste incineration, is one of the main sources of dioxins⁵. In China, with the improvement of living standards of residents, the output of municipal waste is increasing year by year. Compared with other two methods of harmless treatment of municipal waste, sanitary landfill and composting, municipal waste incineration(MWI) is rapidly growing due to its huge advantages in volume reducing, harmlessness and resource utilization of waste. As a result, the demand for degradation technology of POPs, especially dioxin, in its flue gas will continue to grow⁶⁻¹⁰.

In this study, PCBs were selected as targets, not only because PCBs are numerous and have high toxicity in MWI flue gas, but also have some similar chemical properties to PCDD/Fs. They are often seen as the indicators of PCDD/Fs. In order to simplify the selection of the optimal catalytic reaction conditions for PCDD/Fs, the catalytic oxidation experiments of PCBs were firstly distributed to explore the optimal conditions, and then the catalytic oxidation of PCDD/Fs were carried out under the optimal conditions. This study mainly explores three factors affecting catalytic oxidation: catalyst, temperature and water vapor.

Materials and methods

Analytical-grade powders of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\gamma\text{-Al}_2\text{O}_3$ were purchased from Shanghai Macklin Biochemical Co., Ltd. Pesticide-grade hexane and toluene were purchased from J. T. Baker Corporation. Aroclor 1254 and CBzs were chosen to investigate the process of PCBs and CBzs decomposition in this study. Native PCB standards, as well as internal PCB standards labeled with $^{13}\text{C}_{12}$ (both in hexane; Wellington Lab.), were used for gas chromatography analysis. All chemicals were used as received, without additional purification

Several mass $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ dissolved in about 20ml deionized water. The obtained aqueous solution was mixed with 20 g of carrier compound, respectively γ - Alumina and ZSM-5 were treated uniformly. The suspension was strongly stirred at room temperature for 12 h. Then it was stirred at 60 °C for 24 h and filtered. The filtered solids were dried overnight at 105 °C. Then it was calcined in tube furnace for 6 h at 450 °C in air atmosphere. The calcined samples were grinded and sieved to ensure that the particle size of the catalyst was in the range of 40-60 mesh. The preparation method of NiO refers to the research of Xia Yunsheng et al. Equal moles of nickel nitrate and oxalic acid are mixed and ground into powder, and the temperature is raised to 400 °C at the heating rate of 1 °C/min, then kept for 4h, and obtained after natural cooling¹¹.

Table 1. Amount of active component in catalyst preparation

Catalyst	Addition of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (g)
a $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$	7.76
b $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$	15.52
c $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$	38.80
a $\text{MnO}_2/\gamma\text{-Al}_2\text{O}_3$	5.77

PCB decomposition experiments were conducted in a tubular furnace system equipped with a silica tube of 500 mm length and 20 mm inner diameter. A ribbon heater was used to maintain the temperature

of the system and drive the gas flow onto the impingers. The catalyst (1 g) was loaded onto the middle position of the furnace, and 1 mL Aroclor 1254 solution (10 $\mu\text{g}\cdot\text{mL}^{-1}$ in hexane) was injected and vaporized at the inlet of the electric furnace. After the decomposition experiments were complete, the nitrogen flow was maintained for another 30 min to cool the furnace down to room temperature. The gas hourly space velocity (GHSV) was maintained at 1400 h^{-1} during the decomposition reaction. The gas-phase decomposition products were dissolved in toluene (100 mL), filled in the impingers. The catalysts were extracted in toluene (200 mL) for 20 h using a Soxhlet apparatus. The extracts were then concentrated to 4 mL volumes in a rotary evaporator at 40 $^{\circ}\text{C}$, followed by column chromatography purification using anhydrous sodium sulfate and silica gel. The volumes of the solutions were further reduced to 100 μL by evaporation under a flow of nitrogen. For these experiments, the reaction time was 30 min, and the gas flow rate was maintained at 50 $\text{mL}\cdot\text{min}^{-1}$.

Result and discussion

Taking PCBs as the target, the effects of catalyst, temperature and steam on the catalytic oxidation of PCBs were studied, and the best catalyst and reaction conditions were selected. Because PCBs have large molecular weight, high boiling point and some residues in the solid phase of the catalyst, the evaluation of the catalytic oxidation effect of PCBs should not only consider the degradation rate and distribution of PCBs homologues, but also investigate the difference of gas-solid distribution and removal rate and degradation rate. The final results are as follows.

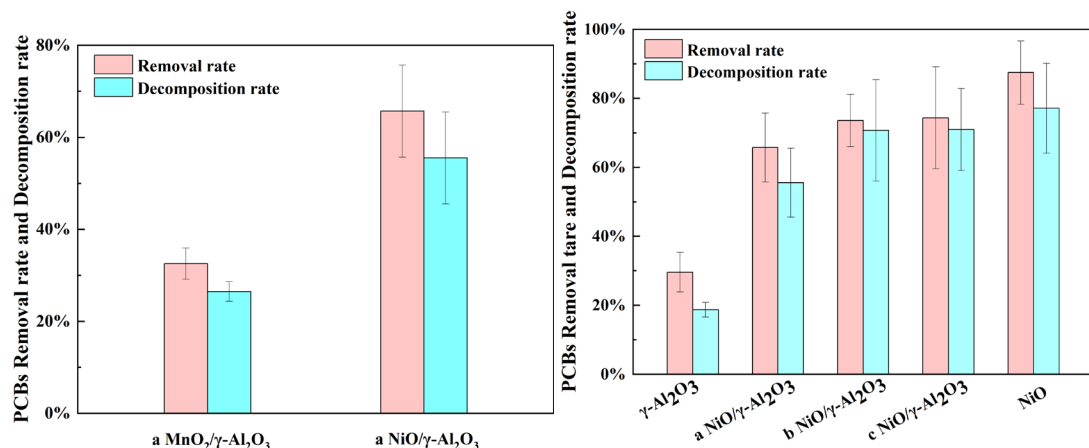


Fig.1 Effect of active components of catalyst on removal rate and decomposition rate of PCBs

The catalytic activity of b $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst for the oxidation of PCBs was the highest. The results show that a $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst has higher catalytic activity, the total removal rate of PCBs is 33.2% higher than that of a $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst, and the total degradation rate is 29.0% higher than that of a catalyst. The analysis of gas-solid distribution of homologues shows that low chlorinated PCBs are more distributed in the solid phase, which can be inferred that high chlorinated PCBs are dechlorinated on the catalyst surface to form low chlorinated PCBs, This part of low chlorinated PCBs did not desorb in time, resulting in more PCBs distributed in the catalyst phase. In the experiment of the influence of the loading rate of the active components on the catalytic oxidation of PCBs, the total removal and degradation rates increased with the increase of the loading rate of the supported $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ catalyst. However, when the loading rate increased from b (13.74%) to c (21.44%), the increase of the removal and degradation rates was very small, and were slightly lower than that of NiO. The total removal rate of PCBs by b $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ is only 0.8% lower than that of c $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$, so b $\text{NiO}/\gamma\text{-Al}_2\text{O}_3$ is an economical and efficient catalyst for POPs catalytic oxidation.

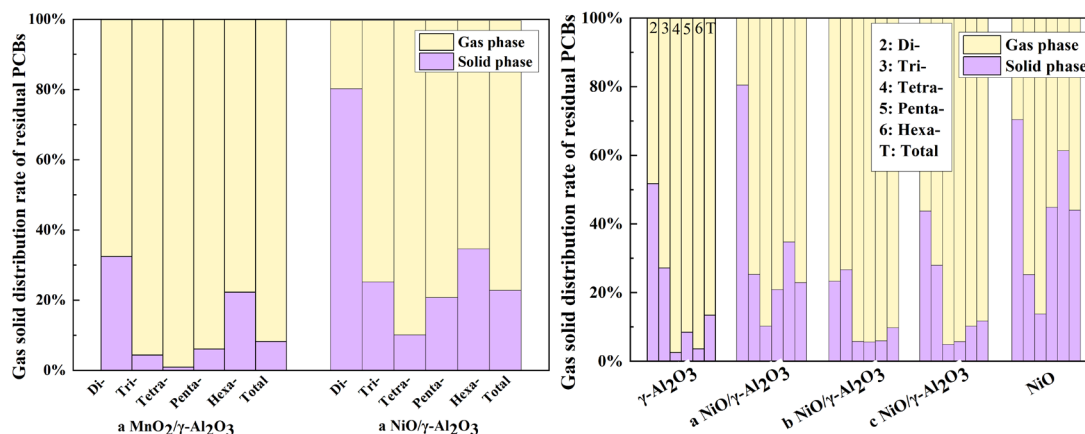


Fig.2 Effect of catalyst active components on gas solid distribution rate of residual PCBs

There is a positive correlation between the catalytic oxidation efficiency of PCBs and temperature, that is, the higher the temperature is, the better the catalytic oxidation effect is. The degradation rate of PCBs was 9.4% at 150 °C and 86.4% at 350 °C. However, the removal rate of PCBs increased from 70.9% to 91.2%, because the adsorption rate of PCBs was higher than the desorption rate and reaction rate at low temperature. A large number of PCBs were adsorbed by catalyst at low temperature, but they were not degraded. This explanation was verified in the gas-solid distribution of residual PCBs. At low temperature, a large number of PCBs exist in the solid phase rather than in the gas phase.

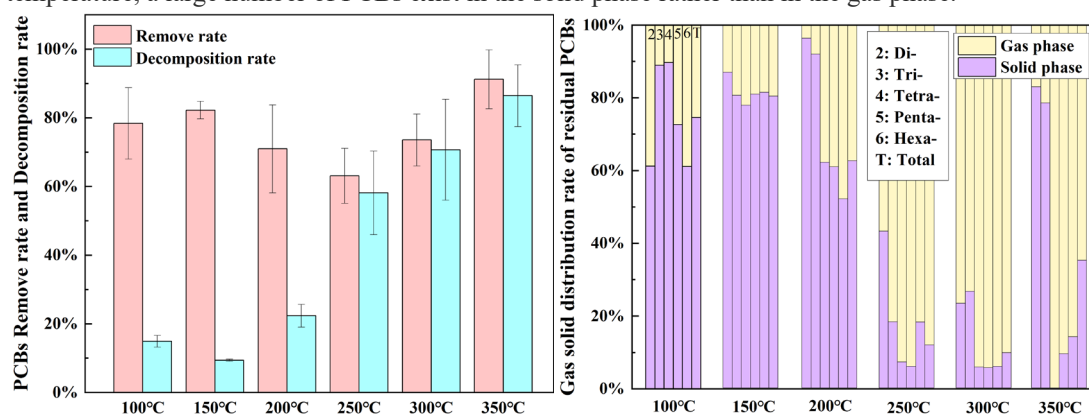


Fig.3 Effect of temperature on decomposition rate and distribution rate of PCBs

When water vapor was added, the catalytic oxidation of PCBs was inhibited, and the higher the content of water vapor, the more obvious the inhibition. The degradation rate of PCBs was 70.7% in dry atmosphere. The degradation rate of PCBs was 51.6% in 5% water vapor and only 34.4% in 10% water vapor. Only 1.1% of PCBs remained in the solid phase when 10% water vapor was introduced, which indicated that when a large amount of water vapor was introduced, H₂O would cover the catalyst surface and occupy the adsorption reaction sites on the catalyst surface, so that PCBs could not contact with the catalyst.

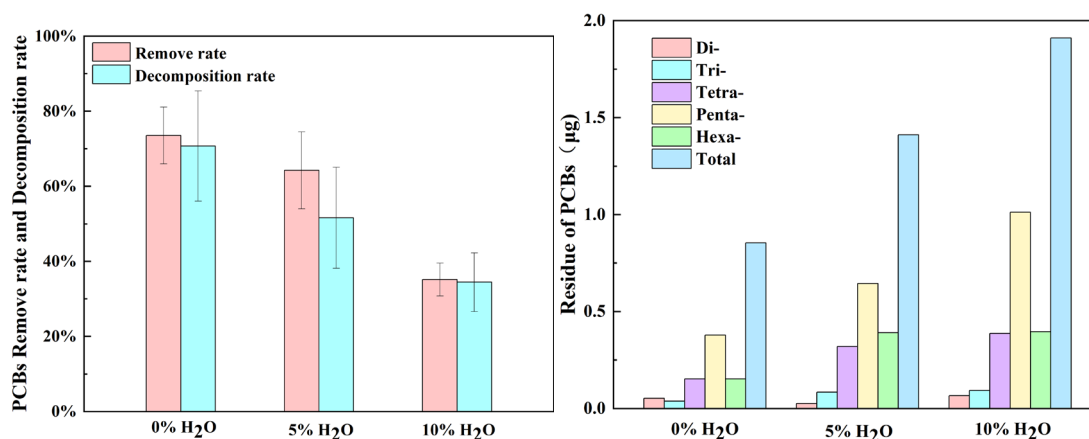


Fig.4 Effect of H₂O on decomposition rate and residue of PCBs

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