

DECOMPOSITION OF GASEOUS 1,2-DICHLOROBENZENE ON V₂O₅-WO₃/TiO₂ CATALYST FILMS: RESEARCH OF SYNERGISTIC EFFECT OF MULTIPLE PATHWAYS

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Introduction

Waste incineration is expanding rapidly in China for the last 20 years because of its attractive ability to reduce solid waste volume and recover the energy. However, poor combustion and inadequate flue gas treatment aggravates the emission of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs), in brief, dioxins. The concentration of dioxins in raw flue gas varies in wide ranges, i.e. 5–30 ng TEQ/Nm³ [1] and far higher than the stringent emission limit of the European Union (0.1 ng TEQ/Nm³). Their adsorption on activated carbon now [2] just transfers dioxins from gas to solid residues and additional treatment is still needed to decontaminate the used activated carbon. So some tail control technologies, such as thermal catalysis and photocatalysis have been proposed to destroy the dioxins more completely.

V₂O₅-TiO₂ catalysts are well-known efficient catalysts for the total oxidation of various air pollutants including aromatics, chlorinated aromatics, furans and dioxins [3]. The addition of WO₃ in the formulation is reported to enhance the catalytic activity in the abatement of VOC like chlorobenzene [4] and benzene [5]. V₂O₅-WO₃/TiO₂ (VWTi) catalyst is usually regarded as thermal catalyst, however, in another opinion, the TiO₂ component in it may also make it interact with the UV-irradiation because the photocatalysis using TiO₂ has been proved to destroy dioxins[6], and V₂O₅-WO₃/TiO₂ catalyst may also be applied as a modified photocatalyst. Thus if heat and UV-irradiation are both applied on V₂O₅-WO₃/TiO₂, photocatalysis and thermal catalysis may produce coupling and improving the degradation efficiency of dioxins.

Strong toxicity of dioxins and its difficulty to develop stable generation systems have restricted the direct application of dioxins in lab-scale tests. In this paper, gaseous 1,2-dichlorobenzene (1,2-DCBz) was studied as model compound for dioxins, due to it an important precursor of dioxin, its high toxicity and delicate manipulation in laboratories[7]. Besides, ozone was added in the reaction system as it was reported to enhance catalytic decomposition of organic compounds [8].

Thus, the aim of present paper is researching the synergetic effects of UV-irradiation, photocatalysis, thermal catalysis and oxidation by ozone in the decomposition of 1,2-DCBz on the V₂O₅-WO₃/TiO₂ catalyst films. Moreover, the resistance time of the gas was also evaluated. The simulated flue gas(10% O₂, 90% N₂) was used and its temperature was controlled to 160 °C to simulate the atmosphere of the flue gas in actual incinerator plant.

Materials and methods

All reagents, such as 1,2-DCBz, ethylalcohol and potassium iodide, were analytical grade. High purity nitrogen (>99.999%) and air were used as dry carrier gas. All were used without further purification.

The V₂O₅-WO₃/TiO₂ catalyst was prepared by sol-gel method and the particles were coated on the reactor as the deposition method described in [9]. The catalyst were exposed onto the UV-irradiated inner wall of the quartz reactor. The reactor was designed like a tunnel with below dimensions: length, external diameter and internal diameter are 250 mm, 28mm and 22mm, respectively (shown in Fig.1). The wall of the "tunnel" was hollowed so the gas can be in and out the reactor and contact with the catalyst. The "hollowed" volume V was 190 cm³. A 200W mercury lamp (dominant wavelength 365 nm) was positioned in the center of reactor as ultraviolet light source. The light intensity reaching the catalyst surface, measured by a UV-radiometer, was 10.8 mW/cm².

A thermostatic bubbler was employed to generate gaseous suitable 1,2-DCBz concentrations in the carrier gas stream (nitrogen). The resulting stream was then led to the reactor, after diluted by the simulated flue gas, and mixed by a static gas mixer. Mass flow meters were used to regulate the flow rates of the gas streams. The

control of the reactor temperature was in 2 cases: when the UV lamp was on, as it produced a lot of heat, the gas temperature could reach about 110°C (ambient temperature was about 20°C), if it was cooled by an air fan, the temperature was about 70°C and if part of it was wrapped in foil, the temperature can be about 165°C; When the lamp was off, the reactor temperature was maintained about 160°C (marked as T) by heating tape, wrapping around the reactor closely. Experiments started when the 1,2-DCBz generator, reactor and 2 tail gas absorption bottles were connected together. The absorption bottles were in ice-bath and filled with 100 ml ethylalcohol to absorb any 1,2-DCBz remaining in the tail gas after the reaction. Quantitative analysis of 1,2-DCBz concentrations was proceeded by gas chromatography(GC).



Fig.1 The schematic diagram of the quartz reactor

Results and discussion

The Removal Efficiency (RE) of 1,2-DCB was defined as Eq. (1):

$$RE = (C_{\text{inlet}} - C_{\text{outlet}}) / C_{\text{inlet}} \times 100\% \quad (1)$$

Where C_{inlet} (ppm) and C_{outlet} (ppm) were the inlet and the outlet concentration of 1,2-DCBz in tail gas, respectively.

From the volumetric flow rate of reactant gas Q_g and the internal volume of the reactor V , the residence time t_r of reactant gas inside the reactor at 160°C can be calculated, which was about 3.6s.

As shown in Fig.2, when the resistance time t_r was set to 3.6s, the average RE 1,2-DCB during an hour was just about 4% on VWTi catalyst in the simulated flue gas of 160°C. Then the 200W UV lamp was turned on, at the same time, a fan was used to cool the reactor making gas temperature decreased to 70°C, the RE obtained increased to 16%. In this case, the temperature was so low that thermal catalysis on VWTi was thought not working, the degradation of the organic was all through the photocatalysis path. When temperature was revived to 160°C, RE jumped to about 46%, which was far higher than the sum of individual contributions of thermal catalysis and photocatalysis, which means, two degradation paths coupled (Couple 1). However, the coupling RE still seemed low, thus ozone was added in the reaction system to assist improve it.

As expected, when an ozone dosage of 190ppm ($C_{\text{ozone inlet}}$) was led in the reactor from its inlet, RE of 1,2-DCB was dramatically improved. Compared with RE of ozone free, combined use of VWTi and ozone removed 98% of 1,2-DCB (shown in Fig.3), which was also higher than the sum of separated REs of VWTi (4%) and Ozone (49%) implying that the synergetic effect occurred in the process (Couple 2). If the UV joined in, the amazing RE of 99% can be got which was bigger than the value of RE (4%) through VWTi plus RE (76%) through UV/ozone or RE (49%) through ozone plus RE through VWTi/UV (46%), that means, another couple took place (Couple 3).

By doubling the flow rate of the gas steam, t_r was reduced from 3.6s to 1.8s, REs through VWTi/ozone and VWTi/UV/ozone did not decrease, actually, they were still above 98% (shown in Fig.4). On one hand, the ozone may be excessive for the 1,2-DCB because at this time C_{inlet} was just half of the previous as the flow rate of gas steam increased; On the other hand, it indicated that the ozone assisted reaction was so fast that the reaction time of 1.8s on VWTi was enough for 1,2-DCB to be degraded fully.

The actual dosage of ozone in the reaction was monitored (shown in Fig.5) by using a bottle of potassium

iodide solution to adsorb any ozone in the tail gas after the reaction. Although ozone decomposed violently when the temperature was above 100°C, the difference of dosage of different reaction conditions was clearly observed that a lower RE corresponded to a lower dosage of ozone (referred to Fig.3), then an apparent positive correlation between the RE of 1,2-DCB and the dosage of ozone could be acquired.

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