

CATALYTIC DESTRUCTION OF TRACE CHLOROBENZENE AND BENZENE OVER NANO-TiO₂-BASED CATALYSTS IN SIMULATING FLUE GAS: EXPERIMENTAL STUDY AND MECHANISM CONSIDERATION

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Introduction

Incineration of municipal and medical waste has become a popular waste treatment method in China due to waste volume reduction resulted and the energy recovery achieved. However, the flue gas from incinerators contains, besides standard combustion by-products (i.e., CO, NO_x, SO_x), considerable amounts of other pollutant, such as heavy metals, and toxic polychlorinated aromatic compounds (e.g., polychlorodibenzo-p-dioxins PCDDs and polychlorodibenzofurans PCDFs, simply as, *dioxins*) are also present. Therefore, feasible and effective technologies should be developed to abate the emissions of dioxins and dioxin-like compounds from incinerators, in order to minimize the environmental and health impacts of waste incineration.

Traditional adsorption on activated carbon knowing as the simplest tail removal method, however merely transfers pollutants from the gas to solid phase. While, catalytic oxidation is comparatively the best method achieving the real destruction of dioxins¹ to CO₂ and H₂O without generation of secondary pollutants²⁻⁴. Vanadium-tungsten catalyst supported on titanium dioxide (V₂O₅-WO₃/TiO₂) catalysts have been recognized as the alternative catalysts with great promising, in consideration of their attractive prices and strong resistance to deactivation caused by chlorine poisoning.

Due to the strong toxicity of dioxins as well as the difficulty of developing stable generation systems, model compounds are used as substitutes for dioxins in most cases. Most laboratory scale experiments

tested the catalysts in the form of powders and evaluated the catalyst activity in the flow stream with simple components^{5,6}, such as mixtures of nitrogen, oxygen and water vapor or O₂-containing helium. However, the compositions of actual combustion flue gas are much more complicated, containing CO, CO₂, HCl, NO_x and SO_x, besides O₂, N₂ and H₂O. Furthermore, monolithic catalysts are more likely applied in the field rather than catalyst powders. Hence, in the present paper, **honeycombed** V₂O₅-WO₃/TiO₂ catalysts were employed to catalytic oxidation of the trace model compounds (1 ppm)-chlorobenzene (CBz) and benzene (Bz) in simulating flue gas, which is quite close to the operation conditions in industrial application.

Materials and methods

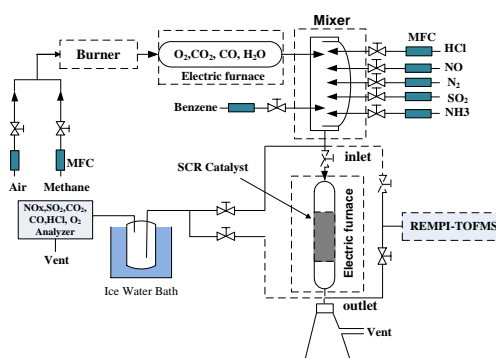


Fig. 1 Schematic diagram of the catalytic experimental set-up

Two conventional honeycombed V₂O₅-WO₃/TiO₂ catalysts (VWT1, 2) with different composition, as well as Nano-TiO₂ supported

V₂O₅/WO₃ catalyst (VWNT) were used in this study (Table 1). Besides, Cu-VWNT and Ce-VWNT were respectively obtained by impregnating⁷ VWNT catalysts into Cu(NO₃)₂·3H₂O or Ce(NO₃)₃·6H₂O aqueous solutions. After that, the impregnated honeycombed catalysts were firstly dried at 80 °C for 16 h and then calcined at 400 °C for 6 h. The exact composition of these proprietary catalysts is not shown because of the business secret, however, “+”

(more than) or “-” (less than) are used to express the relative amount of a catalyst component, using one catalyst VWNT as the standard. Elements dispersion, specific surface area and pore size distribution of those catalysts were obtained respectively using Energy Dispersive X-Ray Spectroscopy (EDX) with an electron microscope (JEOL Model S-4800) and an automated BET and pore analyzer (TRISTAR 3020, Mike Instrument Co., America).

Table 1 Composition of the catalysts tested

Catalyst tab	Main components	V	W	Ti	Ce	Cu
VWT1	V ₂ O ₅ -WO ₃ /TiO ₂	++	+	+	/	/
VWT2	V ₂ O ₅ -WO ₃ /TiO ₂	+++	-	-	/	/
VWNT	V ₂ O ₅ -WO ₃ /Nano-TiO ₂	+	+	+	/	/
Cu-VWNT	CuO-V ₂ O ₅ -WO ₃ /Nano-TiO ₂	+	+	+	/	+
Ce-VWNT	CeO ₂ -V ₂ O ₅ -WO ₃ /Nano-TiO ₂	+	+	+	+	/

Catalytic oxidation tests were carried out on a honeycomb catalyst in tubular quartz reactor. The temperature of the reactor was controlled by an electric furnace (Fig.1). The combustion gas (CO₂, CO, O₂, and H₂O) of a methane burner mixed with HCl (50 ppm), NO (300 ppm), SO₂ (200), NH₃ (270 ppm) and N₂ from gas cylinders was introduced into the reactor to create a simulated incinerator flue gas atmosphere. CBz or Bz (provided by a gas cylinder) was respectively doped (using mass flow controller) into the combustion flue gas to obtain rather low inlet concentration level (1 ppm). The total gas flow rate through the reactor was set as 7 L/min for the gas hourly space velocity (GHSV) of 2000 h⁻¹. Resonance-enhanced multiphoton ionization-Time of flight mass spectrometry (REMPI-TOFMS) was involved to measure the Bz or CBz concentrations at the inlet and outlet of the catalysts in real time. Thus, the catalytic removal efficiency of Bz (η_{Bz}) or CBz (η_{CBz}) can be calculated as:

$$\eta_{CBz} = (1 - [C_{CBz}]_{inlet} / [C_{CBz}]_{outlet}) * 100\% \quad (1)$$

$$\eta_{Bz} = (1 - [C_{Bz}]_{inlet} / [C_{Bz}]_{outlet}) * 100\% \quad (2)$$

where [C_{CBz}]_{inlet} and [C_{Bz}]_{inlet} represent the inlet concentrations of CBz and Bz. The concentrations of CBz and Bz in tail gas are referred as [C_{CBz}]_{outlet} and [C_{Bz}]_{outlet}.

Results and discussion

Evaluation of catalytic activity

Catalytic decomposition of organic compound must undergo three main processes as shown in Fig.2: (1) target organic compounds adsorbing onto the catalyst surface; (2) adsorbed compound destroyed by the active sites; (3) decomposition products desorption. A universal phenomenon observed from the tested catalysts is that rising reaction temperature facilitates the catalytic decomposition of Bz or CBz (as shown in Fig.3-Fig.5). This can be due to the increased collision probability between target compounds and catalyst surface (improves adsorption process) as well as the increased catalytic activity (improves destruction process). The vanadium (V) contents of the tested catalysts decrease as follows: VWT2>VWT1>VWNT, however, the catalytic oxidation activities towards CBz decrease as VWNT>VWT1>VWT2 according to Fig.3. This indicates that the catalytic activities of these catalysts independent of V contents in this study. Not all the VOx present on catalyst surface would be responsible for the catalytic activity⁸. An appropriate support may promote the catalytic activity to a large degree. As revealed in Fig.3,

choosing nano-TiO₂ as the catalyst support shows great advantage in comparison with conventional TiO₂ in this study. The former augments the surface area of the catalyst (165.5 m²g⁻¹) and narrows the pore diameter to 6.56 nm (table 2) which may both benefit the adsorption of CBz.

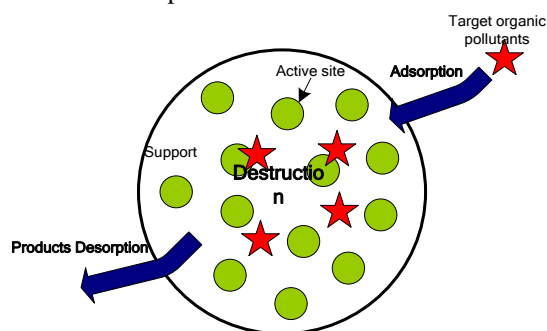


Fig.2 Display of catalytic decomposition process

Table 2 Surface area and average pore diameter of the catalysts

Sample	S _{BET} /(m ² g ⁻¹)	D/nm
VWT1	75	10.6
VWT2	87	11.3
VWNT	165.5	6.56
Ce-VWNT	89	17.1
Cu-VWNT	83	16.4

S_{BET}: BET specific surface area; D: average pore diameter

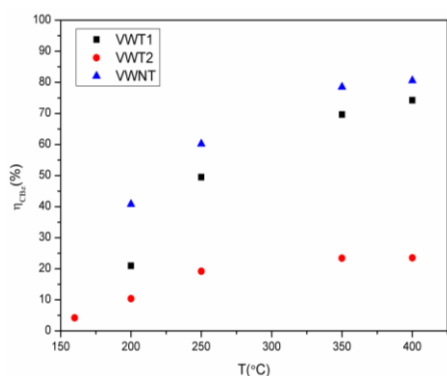


Fig.3 Catalytic oxidation of CBz over VWT1, VWT2 and VWNT

Recently, CuO/CeO₂ catalyst shows great activity in catalytic oxidation of ortho-dichlorobenzene⁹. However, adding CuO and CeO₂ onto the

honeycombed catalysts by wet-impregnating didn't enhance η_{CBz} as expected but lowered it (Fig.4). It ascribes that adding CuO and CeO₂ to VWNT by this method does not build up connections between Cu (or Ce) and catalyst support, however, simply covers the catalyst surface and resulted in the surface area reducing as demonstrated in table 2.

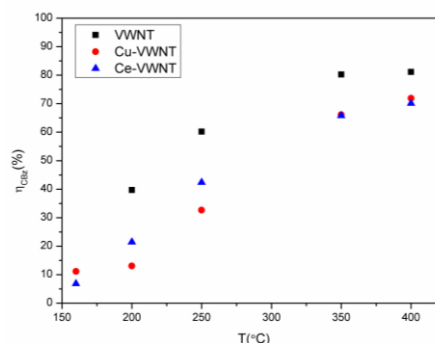


Fig. 4 Effects of Cu- and Ce-modification on the catalytic activity of VWNT

Effect of chlorine substituent on catalysis

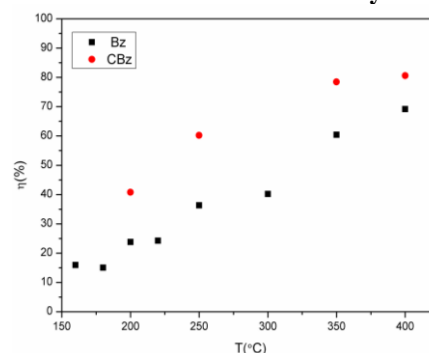


Fig.5 Catalytic oxidation of CBz and Bz over VWNT

Catalytic oxidation of CBz and Bz is conducted respectively to evaluate the effect of chlorine substituent on organic compounds decomposition. According to the results in Fig.5, CBz catalytic decomposition efficiency is higher than that of Bz. It may correspond with the mechanism deduction that the first step of CBz catalytic oxidation over V₂O₅/TiO₂ is nucleophilic substitution¹⁰ between target organic pollutants and active species on catalyst surface, then the destruction process. The C-Cl bond is weaker than C-H bond, thus the former bond is more likely to break up. Therefore, the presence of chlorine substituent on benzene ring

makes the nucleophilic substitution process easier, which contributes higher catalytic decomposition efficiency of CBz than that of Bz over VWNT in this study. The reaction activation energy values (E_a) of CBz and Bz catalytic oxidation are calculated according to the Arrhenius equation¹¹ (eq.(6)) and the hypothesis that the reaction following the first order reaction (shown as eq.(3)~(6))¹².

$$r_b = -kC_o = \frac{dC_o}{dt} \quad (3)$$

$$\ln(1 - \eta_b / 100) = -kt \quad (4)$$

$$k = -\frac{Q}{C_o \times V} \times \ln(1 - \eta_b / 100) \quad (5)$$

$$\ln k = -(E_a / RT) + B \quad (6)$$

Where C_o is the inlet concentration of CBz or Bz, (mol/cm^3); η_b represents the catalytic removal efficiency; Q is the molar velocity (mol/s); k is the reaction rate constant (s^{-1}); R stands for gas constant ($8.314 \text{ J}/\text{K}\cdot\text{mol}$); T is the gas temperature (K) and B is a constant.

The calculation results listed in Table 3 confirm that the chlorine substituent reduces the required E_a evidently, corresponding with the mechanism deduction mentioned above.

Table 3 Activation energy calculation of CBz and Bz removal over VWNT catalyst

Catalyst	Compounds	E_a ($\text{KJ}\cdot\text{mol}^{-1}$)
VWNT	CBz	19.8
	Bz	25.6

Conclusion

Catalytic oxidation of gaseous CBz and Bz over honeycombed catalysts in simulating flue gas was investigated in this paper. Nano- TiO_2 based VWNT catalyst with larger surface area ($165.5 \text{ m}^2/\text{s}^{-1}$) and narrow average pore diameter (6.56 nm) showed stronger catalytic activity toward CBz oxidation than those catalysts using conventional TiO_2 as support. Modifying the honeycombed catalysts with CuO and CeO_2 by wet-impregnating didn't enhance η_{CBz} as expected but lowered it. Besides, the presence of chlorine substituent benefited the catalysis. C-Cl bond in benzene ring was more likely to break up

which makes the nucleophilic substitution process easier. The calculation results of reaction activation energy values confirm the advantage of the chlorine substituent. Moreover, mechanism consideration was also included.

Acknowledgements

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