

## Bench-scale Experiment on Catalytic Decomposition of 1,2-Dichlorobenzene by Vanadia-Titania Catalyst

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### Abstract

Catalytic activities of  $V_2O_5/TiO_2$  catalyst were investigated under reaction conditions such as reaction temperature, catalyst size, inlet concentration and space velocity. A 1,2-dichlorobenzene(1,2-DCB) concentrations were measured in front and after of the heated  $V_2O_5/TiO_2$  catalyst bed, and conversion efficiency of 1,2-DCB was determined from its concentration difference. The conversion of 1,2-DCB using a pellet type catalyst in the bench-scale reactor was lower than that with the powder type used in the micro flow-scale reactor. However, when the pellet size was halved, the conversion was similar to that with the powder type catalyst. The highest conversion was shown with an inlet concentration of 100 ppmv, but when the concentration was higher or lower than 100 ppmv, the conversion was found to decrease. Complete conversion was obtained when the GHSV was maintained at below  $10,000\text{ h}^{-1}$ , even at the relatively low temperature of  $250^\circ\text{C}$ . Water vapor inhibited the conversion of 1,2-DCB, which was suspected to be due to the competitive adsorption between the reactant and water for active sites.

**Key Words :**  $V_2O_5/TiO_2$ , 1,2-dichlorobenzene, Catalytic decomposition, PCDDs/PCDFs

### 1. Introduction

Polychlorodibenzo-p-dioxins (PCDDs) and polychloro dibenzofurans (PCDFs) are very harmful, persistent organic pollutants. Due to their toxicity and potential human health effects, many countries have imposed stringent regulations on the emissions of PCDDs/PCDFs. The adsorption of PCDD/F by activated carbon is widely applied in combustion facilities. However, this method merely transfers the toxic pollutants from the gas to a solid phase; as the activated carbon is disposed after use. Therefore, any new techniques should be economically feasible and actually destroy the pollutants.

The catalytic destruction of pollutants to  $CO_2$ ,  $H_2O$  and  $HCl$  is very promising in this context.

Recently, a  $V_2O_5/TiO_2$ -based catalyst, designed for the control of  $NO_x$  emissions by selective catalytic reductions (SCR), has also been considered as an active catalyst for the decomposition of dioxin. Some laboratory experiments have been performed to obtain data on the best catalytic activities<sup>1-6</sup>. Corella et al.<sup>7</sup> compared the catalytic activities of eight different commercial  $V_2O_5-WO_3-TiO_2$  catalysts for the conversion of several chlorinated hydrocarbons, and concluded that such catalysts were ten times more active than noble metal-based catalysts. Graham et al.<sup>8</sup> investigated the role of the V/Ti atomic ratio on the activities of oxide catalysts for the conversion of 265 ppmv of monochlorobenzene. According to these authors, the presence of crystalline vanadia would be needed to convert chlor-

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obenzene at temperatures below 300°C. Total conversion was even achieved at 260°C in a 29,000 h<sup>-1</sup> space velocity. Jones and Ross<sup>9</sup> reported that ethylchloride and mono-chlorobenzene may be totally destroyed at 300-400°C over vanadia supported on different oxides with 0-2% water in the feed. Webber<sup>10</sup> studied the activity of two different commercial V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub>-TiO<sub>2</sub> catalysts in the conversion of PCDD/PCDF, chlorobenzenes and polycyclic aromatic hydrocarbons. PCDD and PCDF are strongly adsorbed but unchanged on the catalyst at temperature below 200°C. Above this temperature, a conversion of 98% of dioxins was found. Conversion of 1 ppm chlorobenzenes was almost total at 300°C with 10% oxygen, 20% water and 5,000h<sup>-1</sup> space velocity. The decomposition of polyaromatic hydrocarbons occurred already 150°C while higher temperatures were needed for mono-aromatic compounds.

However, laboratory data are frequently obtain under conditions quite different from those used in industrial scale application, with one of the main factors being the inlet concentration of the model compound is generally far higher than that found in real flue gases. The gas composition may be different in both oxygen and water contents, as well as for SO<sub>2</sub> and other compounds. Moreover, the catalysts are frequently tested, and the space velocities may be lower than those actually used<sup>11</sup>). Unfortunately, previous many studies have been focused on to obtain the conversion of pollutants by V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst and effects of some reaction conditions in the laboratory-scale. However, with only laboratory-scale test, it is difficult to evaluate effectively the effect of those various reaction parameters.

In this work, the catalytic activity of a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was investigated by using the bench-scale apparatus. A bench-scale experiment was been performed using an entrained flow type apparatus, with a flow rate of 40 L/min, to find suitable operating conditions for industrial scale application. 1,2-dichlorobenzene (1,2-DCB) which is structurally similar to the more toxic 2,4,7,8-tetrachlorodibenzodioxin, was used as a model PCDD/Fs compound<sup>11-13</sup>). The performance of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> in the bench-scale reactor was compared with that obtained on a micro-flow scale. The catalytic conversion for 1,2-DCB were investigated at different

inlet concentrations, space velocities and water vapor compositions. Our study is valuable in the aspect that influence of various reaction parameters on conversion of a chlorinated compounds by V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was investigated in the bench-scale higher 800 times than that in the laboratory-scale experiment.

## 2. Materials and Methods

### 2.1. Catalyst preparation

The catalyst used in this study was prepared using the impregnation procedure. Ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>) was used as the V<sub>2</sub>O<sub>5</sub> precursor. NH<sub>4</sub>VO<sub>3</sub> was resolved in oxalic acid at 40°C and TiO<sub>2</sub> was added into the prepared solution at 80°C with vanadium content of 1-10%. The solution including both NH<sub>4</sub>VO<sub>3</sub> and TiO<sub>2</sub> was dried in vacuum oven at 50°C for 1h after keeping at room temperature for a day. The V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was calcined at 500°C for 3h before use. In the preliminary test, because the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> with vanadium content of 3.5-5.0 wt.% showed higher activity for the degradation of 1,2-DCB, the 3.5 wt.% V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst was used in this work.

### 2.2. Catalytic activity measurements

Fig. 1 shows the experimental apparatus used in this study. The V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalytic activity measurements were conducted in single-pass flow reactor, incorporating the pellet and powder type catalysts. In the micro-flow system, V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> powder was filled into the reactor, with a pellet type catalyst filled into the bench-scale reactor. The flow rate in the micro-flow reactor was only 50 ml/min. The bench-scale experiment was performed with a flow rate of 40 L/min, which was 800 times higher than that in the micro-flow reactor.

The each reactor was vertically set up in the center of an electrical furnace to minimize the channeling effect and any internal diffusion limitations. The reaction temperature was controlled using both a pre-heater and electrical furnace. 1,2-DCB was introduced into the vapor phase using a generator. A stainless saturator containing liquid 1,2-DCB was installed into the gas generator (491MB, Kin-Tek Co. Ltd.). Approximately 200 mL nitrogen was allowed to flow through the saturator,

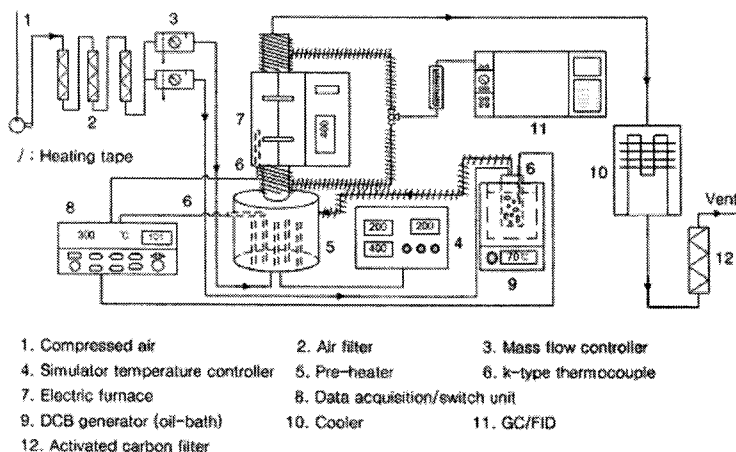


Fig. 1. A schematic diagram of experimental apparatus for the catalytic decomposition of 1,2-DCB.

maintained at 80°C. The saturated 1,2-DCB/N<sub>2</sub> gas was mixed with air. The simulated gas stream was pre-heated, and then introduced into the reactor. Prior to each experiment, the catalyst was pre-treated in air at 400°C for 2h. After stabilization of the temperature and inlet concentration, the activity measurements were initiated by switching the feed stream into the reactor. All the by-pass line and effluent stream temperatures also were kept at 100°C to minimize the condensation of 1,2-DCB and water.

This study conducted the experiments to determine the effect of varying operation parameters. The parameters and ranges of tested parameters were reaction temperature (200–400°C), catalyst pellet size (2.5 mm, 5mm), 1,2-DCB concentration (25–1,200 ppm), space velocity (5,000–18,000 h<sup>-1</sup>), relative humidity (1%, 15%).

### 2.3. Sampling and analysis

The concentration of the organic compounds were measured with an gas chromatography (6000 M, Young-lin Co. Ltd) equipped with an HP-1 column that was equipped with a split/splitless injection and FID detector. The samples were collected from the flowing influent and effluent streams, and they were introduced into the GC injection port with an in-line auto-sampling valve and sampling loop (50 µl). The detailed analytical conditions are described in Table 1. Quantification of the results was done by performing the calibration of

Table 1. Analytical conditions of gas chromatography for 1,2-DCB analysis

Analytical conditions	
Injector temperature	1800°C
Detector temperature	250°C
Oven temperature	100°C
Split ratio	1 : 5
Carrier gas(N <sub>2</sub> )	3 mL
Make up gas(N <sub>2</sub> )	40 mL
Detector(FID)	H <sub>2</sub> 35mL Air 350mL

the 1,2-DCB. The conversion of 1,2-DCB were calculated from the following equation:

$$\text{Conversion of 1,2-DCB (\%)} = \frac{[1,2-DCB]_{inlet} - [1,2-DCB]_{outlet}}{[1,2-DCB]_{inlet}} \times 100$$

## 3. Results and discussion

### 3.1. Comparison of the catalytic activity in the different reactors

The catalytic activities of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> for the decomposition of 1,2-DCB were studied in micro-flow and bench-scale reactors, the results of which are compared in Fig. 2. The experiments were conducted with the same 1,2-DCB inlet concentration, SV and water vapor. The differences between the two reactors were the catalyst type and flow rate.

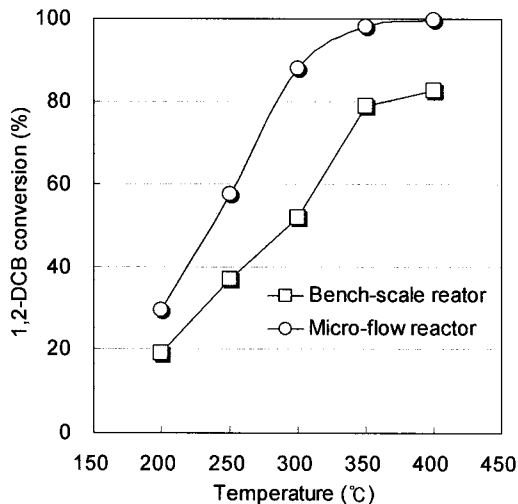


Fig. 2. 1,2-DCB conversion as a function of temperature for the different scale reactors. 1,2 DCB concentration, 250 ppmv, GHSV 18,000 h<sup>-1</sup>, R.H. ca. 15%.

The results showed that the 1,2-DCB conversions obtained in the micro-flow reactor were much higher than that in the bench-scale reactor. The conversion of 1,2-DCB reached nearly 100% in the micro-flow reactor at 350°C, but barely 80% conversion was observed in the bench-scale reactor at the same temperature. The possible reasons for this were attributed to the catalyst size and channeling effect in the catalyst bed.

In order to demonstrate the above assumption, the catalytic activity was investigated by halving the catalyst pellet size. As shown in Fig. 3, when the catalyst size was reduced from 5 to 2.5 mm, the conversion of 1,2-DCB was significantly enhanced, as the effective surface area increases and the channeling effect decreases as the size of the catalyst becomes smaller.

### 3.2. Effect of inlet concentration

The effect of the inlet concentration on the conversion of 1,2-DCB was investigated. Figure 4 shows the conversion of 1,2-DCB by V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> with inlet concentrations of 25, 100, 250 and 1200 ppm, with the highest conversion obtained with 100 ppm at reaction temperatures between 250 and 400°C. However, when the concentration was increased to 250 and 1,200 ppm, or decreased to 25 ppm, the conversions were found to decrease. The decreased conversion with increasing

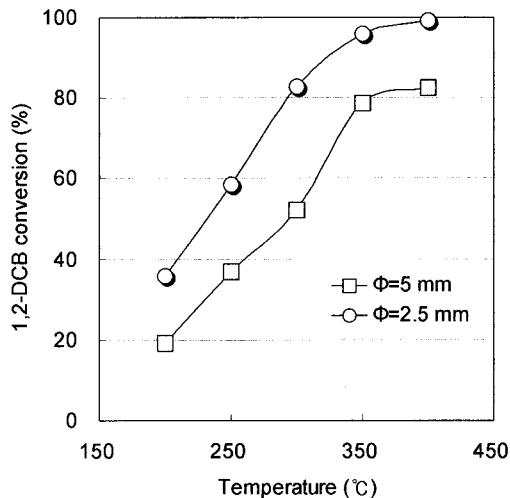


Fig. 3. Effect of pellet type catalyst size. 1,2 DCB concentration, 250 ppmv, GHSV 18,000 h<sup>-1</sup>, R.H. ca. 15%.

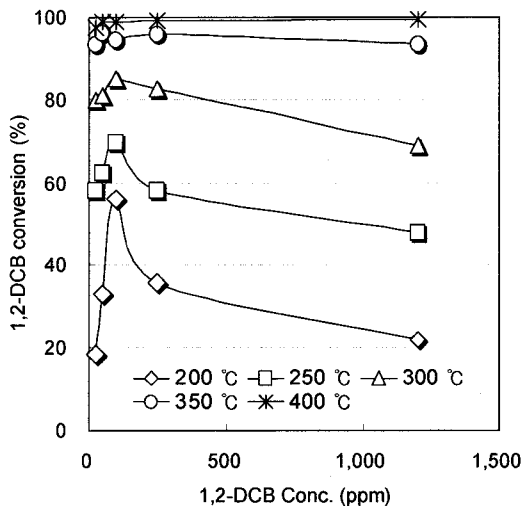


Fig. 4. Effect of 1,2-DCB inlet concentration GHSV 18,000 h<sup>-1</sup>, R.H. ca. 15%, Catalyst size, Φ =2.5 mm.

inlet concentration was attributed to the competition effect between the reactants for the limited active sites on the catalyst.

Conversely, the conversion rate of 1,2 DCB decreased with the concentration 25 ppm, because the mass transfer to the catalyst surface was probably limited. Therefore, because the dioxin concentrations found in flue gases are approximately at the ppb level, this catalyst should be tested for very low dioxin

concentrations.

### 3.3. Effect of space velocity

One of the most important parameters for catalytic reactor design and performance evaluation is the space velocity, which is defined as the volumetric gas flow rate divided by the superficial volume of catalyst. The commercial catalytic processes for the treatment of dioxins via combustion usually require a gas hourly space velocity (GHSV) within the range 8,000~40,000 h<sup>-1</sup> (11).

In this study, experiments were carried out at GHSV ranging from 5,000 h<sup>-1</sup> to 18,000 h<sup>-1</sup>, the results of which are shown in Fig. 5. With GHSV below 10,000 h<sup>-1</sup>, the temperature for the complete conversion of 1,2-DCB was 250°C, but was significantly increased with further increases in the GHSV. The temperature for the complete removal of 1,2-DCB was increased to 400°C when GHSV reached 18,000 h<sup>-1</sup>. From this result, the GHSV should be maintained below 10,000 h<sup>-1</sup> to ensure greater efficiency at 250°C.

### 3.4. Effect of water vapor

The catalytic activity of V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> for the decomposition of 1,2-DCB was investigated in the presence of 1.0 and 15.0% water vapor. The results indicate the presence of water decrease the conversion of 1,2-DCB by around 10% at all of the reaction temperatures tested.

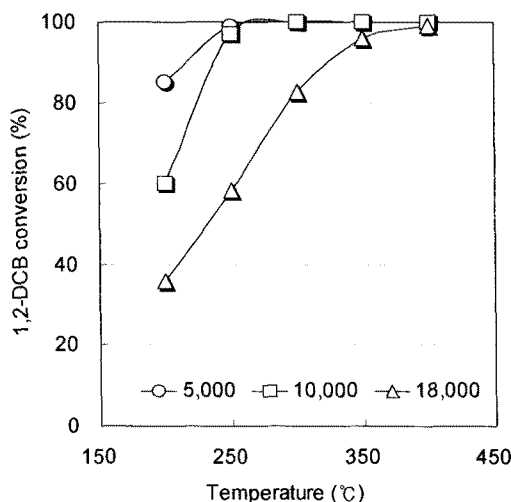


Fig. 5. Effect of the GHSV on the conversion of 1,2-DCB; 250 ppmv, R.H. ca. 15%, Catalyst size,  $\Phi=2.5$  mm.

The reduced conversion of 1,2-DCB was attributed to the competitive adsorption mechanism between 1,2-DCB and water molecules for the active sites on the surface of the V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst.

Lomnicki et. al.<sup>14)</sup> have reported a negative effect of water vapor due to the blocking of a number of the active sites on the catalyst. In the conversion experiment for 2,4,6-trichlorophenol (TCP) using V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst, they found that maximum conversion of TCP was obtained at approximately 10% in the range of water content (0, 10, 40%) tested, and explained for the reason that water competes with TCP for adsorption on the active vanadia sites. They concluded that relatively small amount of water are sufficient for the dechlorination of the surface.

Therefore, our results indicate that the water vapor in the flue gas should be controlled as a key parameter in the catalytic decomposition of dioxin, because water vapor is usually present in significant quantities in the flue gas of most combustion processes.

## 4. Conclusions

For the development of a catalyst for the decomposition of dioxin in waste incinerators, a bench-scale experiment was performed using a V<sub>2</sub>O<sub>5</sub>/TiO<sub>2</sub> catalyst under various reaction conditions.

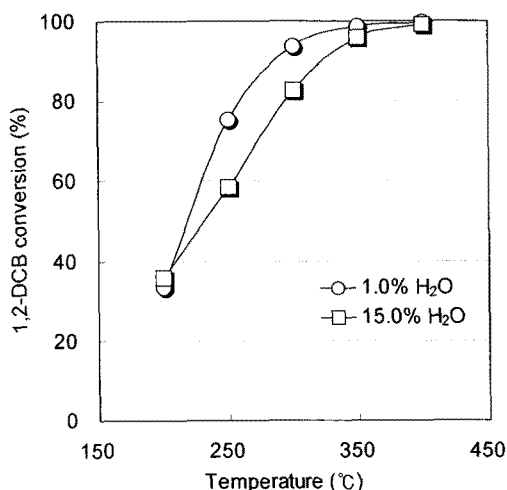


Fig. 6. Effect of water vapor on the conversion of 1,2-DCB; GHSV, 18,000 h<sup>-1</sup>, 1,2-DCB conc. 250 ppmv, Catalyst size,  $\Phi=2.5$  mm.

The conversion of 1,2-DCB by a pellet type catalyst in the bench-scale reactor was lower than that of a powder type catalyst in the micro-flow. However, when the pellet size was halved, the conversion was similar to that obtained with the powder type catalyst. The highest conversion was obtained with an inlet concentration of 100 ppmv, but with a concentration higher or lower than 100 ppmv, the conversion was decreased. It was found that a lower GHSV led to a higher conversion. In particular, when the GHSV was maintained below 10,000 h<sup>-1</sup>, complete conversion was obtained, even at the relatively low temperature of 250°C. Water vapor inhibited the conversion of 1,2-DCB, with the suspected reason being the competitive adsorption between the reactants and water for the active sites on the catalyst surface.

This study presented the information about optimal design parameters required for introduction of catalytic oxidation technology to treat the chlorinated compounds such as dioxin in the combustion flue gases. Future work will focus on the evaluation of catalytic activities for actual dioxin compounds in the pilot-scale reactor.

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