

## CATALYTIC DESTRUCTION OF DIOXINS OVER GOLD-DEPOSITED METAL OXIDES

Osamu Kajikawa, \*Xiang-sheng Wang, Takeshi Tabata, Osamu Okada

Osaka Gas Co., Ltd., Osaka 541-0046, Japan

\*Kansai Research Institute, Kyoto 600-8813, Japan

### Introduction

The treatment of gaseous emissions containing volatile organic compounds as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) has been of increasing concern in recent years. Thermal incineration, catalytic oxidation and adsorption are commonly used for removing these pollutants. Among them, catalytic oxidation is an energy efficient and economical way of destroying gaseous organic emissions if catalytic reactor operates at significantly lower temperatures and shorter residence time than thermal incineration and requires smaller reactors made of less expensive materials. So far, several kind of catalysts such as  $\text{TiO}_2\text{-V}_2\text{O}_5\text{-WO}_3$  [1], Pt supported on a carries based on Si and Ti [2], chromium oxide or a boehmite supported platinum [3] and related techniques for the treatment of gaseous emissions containing dioxins have been reported. However, the operation temperature for these catalysts are usually above  $300^\circ\text{C}$ , and re-heating of gaseous emissions is required because the temperature of gaseous emissions from the waste heat boiler or air pollution control unit such as electrostatic precipitator or bag filter is usually below  $200^\circ\text{C}$ [4]. For this reason, these catalysts are not enough efficient from the energy saving perspective.

For the object of lowering reaction temperature, Au-deposited  $\text{Fe}_2\text{O}_3\text{-La}_2\text{O}_3$  catalyst has been developed by the authors. It was reported that fine dispersed gold catalyst shows activity for CO oxidation even at  $-70^\circ\text{C}$ . However, a few work has been carried out on oxidative decomposition of halogenated hydrocarbons with gold catalyst. In previous paper, we have reported the decomposition behavior of chlorinated phenol over Au-deposited  $\text{Fe}_2\text{O}_3\text{-La}_2\text{O}_3$  catalyst. In this work, activity of Au-deposited  $\text{Fe}_2\text{O}_3\text{-La}_2\text{O}_3$  catalyst for destruction of dioxins has been examined and the result shows that PCDDs and PCDFs can be destructed at temperature of  $140^\circ\text{C}$ .

### Material and Methods

Au-deposited  $\text{Fe}_2\text{O}_3\text{-La}_2\text{O}_3$  catalyst was prepared by coprecipitation method from the mixed aqueous solution of chloroauric acid, and metal nitrates according to the procedure described as follows. The mixed aqueous solution containing chloroauric acid and metal nitrates was titrated with a aqueous solution of 5%  $\text{NaCO}_3$  to a given pH at which all metal ions will educe in forms of

metal hydroxide from the mixed aqueous solution under stirring at room temperature. The precipitate was washed, vacuum dried, and calcined in air at 450°C for 4 hr. The composition of the catalyst finally obtained was adjusted to Au:La:Fe=5:27:63 in atomic ratio by changing the concentrations of chloroauric acid and metal nitrates in the starting solution. Specific surface area of catalyst obtained finally was determined to be 45m<sup>2</sup>/g by a BET single point method by using a Quantasorb Jr. analyzer.

Measurements of catalytic activity for destruction of standard dioxin reagent were carried out in a small fixed-bed continuous flow reaction unit as shown in Fig. 1, with 2.0g of catalyst that had passed through 70- and 120-mesh sieves, diluted with an inert quartz sand (average diameter 0.3mm) of 8.0g. 170ng of standard dioxin reagent containing seventeen types of PCDD and PCDF isomers, which concentration of each isomer is 0.1ng/ml in hexane, was poured into the catalyst filling zone at room temperature. And then, the reactor was heated to a given temperature with a air flow rate of 1,000ml/min through a pre-heating zone and maintained at that temperature for 4hr to allow destruction of dioxins adsorbed previously over catalyst. While reactor returned to room temperature, catalyst and XAD-2 resin was taken out from the reaction unit, respectively. Residual dioxin on catalyst and dioxin trapped by XAD-2 resin were abstracted by toluene solvent and the amounts and isomer distribution of residual dioxin on catalyst and dioxin trapped by XAD-2 resin were determined by a standard procedures for analysis and calculation methods of dioxin concentration enacted by the Ministry of Public Welfare of Japan. The catalytic destruction of dioxins was calculated according to following equation.

$$Destruction(\%) = \left\{ 1 - \frac{W_{ad} + W_{pass}}{W_{in}} \right\} \times 100$$

Where,  $W_{ad}$ : Amount of dioxin adsorbed on catalyst after reaction.

$W_{pass}$ : Amount of dioxin trapped on XAD-2 resin during reaction.

$W_{in}$ : Amount of dioxin added to the catalyst filling zone before reaction.

### Results and Discussion

The activity of Au-deposited Fe<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> catalyst for destruction of dioxin reagent was measured at temperatures of 140°C, 170°C and 200°C respectively, and the results were shown in Fig. 2 and Fig. 3. Fig.2 shows the destruction of PCDDs and PCDFs and decrease of total toxicity equivalency quantity (TEQ) against reaction temperature. The catalytic activity was observed even at 140°C, and the activity increased with temperature. 100% destruction was achieved while temperature is above 170°C. From this result, it can be concluded that the temperature for completed destruction of dioxin with Au-deposited Fe<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> catalyst is quite low as compared with these catalyst previously reported such as Pt supported on a carries based on Si and Ti,

$V_2O_5$ - $TiO_2$ - $WO_3$  catalyst etc. which usually shows activity for destruction of dioxin above 300°C.

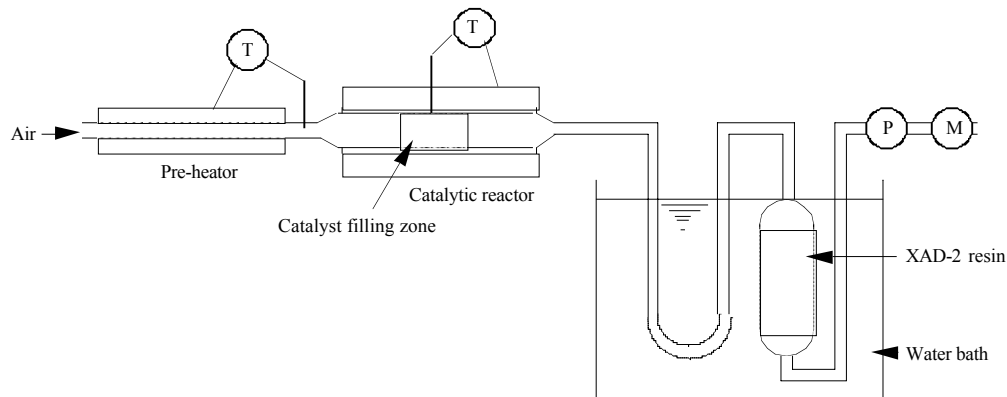


Fig. 1 Fixed-bed Continuous Flow Reaction Unit for Catalytic Activity Measurement

Fig. 3 shows the destruction of each dioxin isomer at different temperature. It can be seen that destruction of various dioxin are different from each other at a given temperature. Isomers of PCDD or PCDF with higher molecular weight such as 1,2,3,4,6,7,8,9- $O_8$ CDD, 1,2,3,4,6,7,8- $H_7$ CDF and 1,2,3,4,6,7,8,9- $O_8$ CDF are difficult to decompose relatively to those with lower molecular weight, in particularly at low temperature. It is inferred that the higher melting point and higher adsorption force on catalyst of such dioxin with higher molecular weight are the reason for their lower destruction. Because dioxin molecules were previously adsorbed on the surface of catalyst, an enough desorption energy, that is a higher temperature would be needed for mobilization of dioxin molecules to active site of catalyst. That is, even through such temperature of 140°C may be enough for completed destruction of all PCDD and PCDF isomers, in our experimental method, a temperature higher than 140°C will be required for mobilization of such dioxin molecules with high molecular weight to active site of catalyst

## Acknowledgements

Environmental Science Research Institute of Miura Kogyo Ltd., who participated in the catalytic activity measurement and dioxin concentration analysis, is acknowledged.

## References

1. Y. Idle, K. Kashiwabara, S. Okuda, T. Mori and M. Hara, Chemosphere, Vol. 32, No. 1, 189-198(1996).
2. J. J. Spivy, Ind. Eng.Chem. Res., 1987, 26, 2165-2180.
3. U.S.P 3,972,979 and U.S.P 4,053,557

4. G. C. Bond and N. Sadeghi, J. Appl. Chem. Biotechnol., 1975, 25, 241-248.

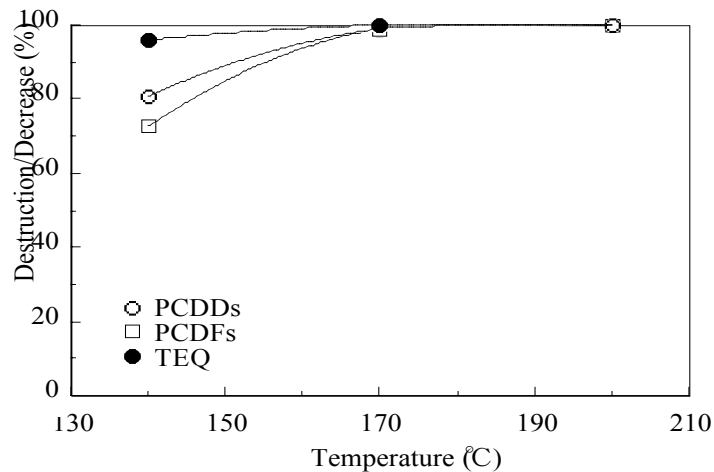


Fig. 2 Dependences of PCDDs/PCDFs Destruction and TEQ Decrease with Temperature.

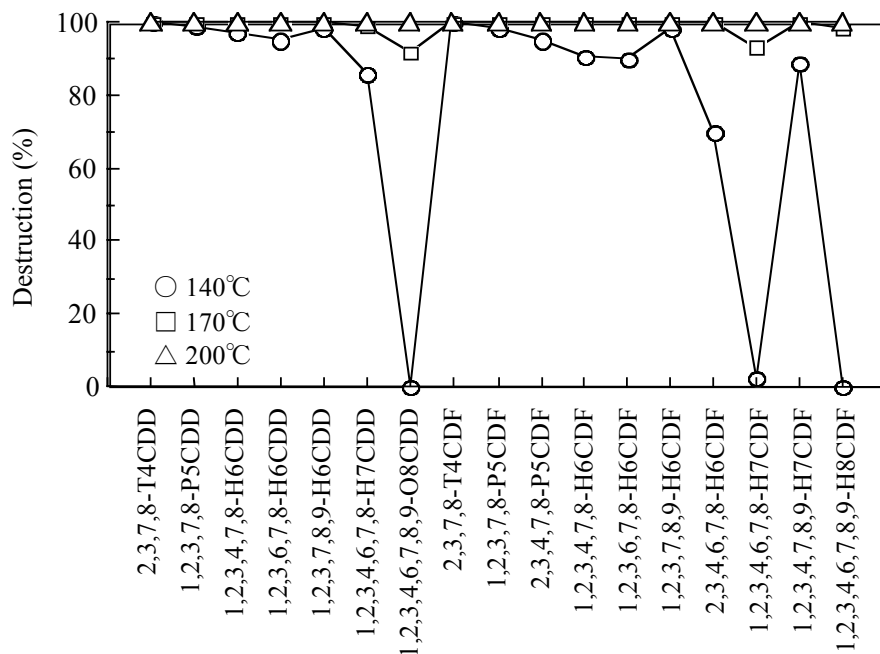


Fig.3 Destructions of Various PCDD and PCDF Isomers at Different Temperature.