

DIOXIN FORMATION OVER Pt/Pd CATALYST

Wielosiński G.¹, Grochowalski A.², Machej T.³, Cwiakalski W.⁴

¹ Technical University of Lodz, Faculty of Process and Environmental Engineering, Wolczanska 175, 90-924 Lodz, Poland

² Technical University of Cracow, Department of Chemistry, Warszawska 24, 31-155 Kraków, Poland

³ Institute of Catalysis and Surface Chemistry, Polish Academy of Science, Niezapominajek 1, 30-239 Kraków, Poland

⁴ "EmiPro" Co. Ltd. Wielicka 250, 30-663 Kraków, Poland

Abstract

In the study the results of the research into decomposition of dioxins over Pt/Pd catalyst are presented. The research installation was connected to the hazardous wastes incineration plant. Irrespectively of other scientists it was found that there may occur a secondary dioxin synthesis, probably as a result of the catalytic synthesis of precursors, on such a type of catalyst under technical conditions, particularly in case of flue gases from the process of waste incineration. This finding is of great importance due to the fact that over many years platinum catalysts have been considered to be efficacious in reference to decomposition (oxidation) of chloro-organic compounds.

Introduction

Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzo-furans (PCDFs), referred to as dioxins and furans, are widely regarded as one of the greatest environmental hazards. Waste incineration, especially municipal waste incineration, is considered to be their main emission source to the environment. The investigations on the generation and emission of dioxins, which have been carried out for the last two decades worldwide, have proved unequivocally that there exist many other dioxin emission sources to the environment (both natural emission sources such as forest fires, volcano eruptions, and anthropogenic ones such as, for example, all combustion processes, chemical and metallurgic processes, etc.), whereas as a result of technical advancement in terms of incineration plant construction and the systems of cleaning of flue gases from incineration plant, at present it is not waste incineration which constitutes the main emission source. The Convention concerning Persistent Organic Pollutants, signed on 23 May 2001 in Stockholm in the course of the international conference of governments plenipotentiaries, introduced relevant limitations in production, utilization, export and import of Persistent Organic Pollutants and the strict requirements concerning the evidence and monitoring. One of the most important resolutions resulting from the Stockholm Convention is the obligation for the constant minimization and the final elimination of release of polychlorinated dibenzo-p-dioxins and polychlorinated dibenzofurans (PCDD/Fs), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs).

The methods of the reduction of dioxins emission have been the subject of research of many scientists for a couple of years and in the subject literature one may find a number of reviews concerning this problem¹. In general, the methods of dioxin emission to the atmosphere may be divided into two basic groups:

- primary methods
- secondary methods.

Primary methods are the invasion in the technological process and the creation of such conditions of its course that the quantity of dioxins produced is possibly the smallest². Amongst the secondary methods of reduction of dioxins emission the following methods are of the greatest meaning:

- adsorption on an active carbon (on fixed bed, moving bed or a stream method);
- the catalytic decomposition of dioxins on a catalyst;
- the catalytic filtration method "REMEDIA"
- absorption/adsorption method "ADIOX"
- radiation method (with an electron beam)
- corona discharge method

- adsorption in carbon nanotubes
- nanocatalysis;
- combined methods.

The catalytic method is actually the only known and applied method of reduction of dioxin emission which does not contribute to the occurrence of by-side products and waste.

It is known that on vanadium catalyst deposited on a carrier, which is made of titanium dioxide, there takes place dioxin dechlorination and oxidation and the contribution of those processes – dechlorination and oxidation – is depended upon the composition of the catalyst³. The products of decomposition reaction are carbon dioxide, water and hydrochloride though in particular cases which are accompanied by the application of other catalysts than vanadium-tungsten ones there may appear also other products of the catalytic reaction. The temperature of the process is usually in the range from 200°C to 300°C. The efficacy of dioxin removal using the catalytic methods is equal to 95 – 99%. Numerous industrial applications confirm very high efficiency of the method⁴.

The removal of chloroorganic compounds from flue gases usually takes place on the way of oxidation. In the vast majority the catalysts produced from noble metals, which are more active at the low temperatures than oxide catalysts based on transition metals, are used for this purpose^{5,6}. Catalysts produced from noble metals are characterized by a very high activity⁷. To their drawbacks one may account a relatively high price and instability of work in the conditions of high concentration of hydrochloride and chlorine – the catalysts made of noble metals are frequently prone to contamination and deactivation in the presence of chlorine^{8,9}.

Under laboratory conditions, quite satisfactory results of decomposition of those compounds on the platinum catalyst were obtained with various types of chloroorganic compounds (chlorobenzenes). Nevertheless, it must be underlined that there is a small number of data concerning the possibilities of the utilization of such catalysts under technical conditions.

Methods and Materials

Studies on the catalytic dioxin decomposition were carried out in a specially constructed semi-commercial apparatus, whose most important element was a catalytic reactor with a monolithic catalyst in the form of 150 × 150 × 100 mm cubes. The apparatus was described in detail in the previous work¹⁰⁻¹². A catalyst was made from cordierite with an active layer composed of Palladium and Platinum (50:50) on γ -Al₂O₃ support (Pd/Pt/Al₂O₃). A schematic diagram of the experimental set-up is shown in Fig. 1.

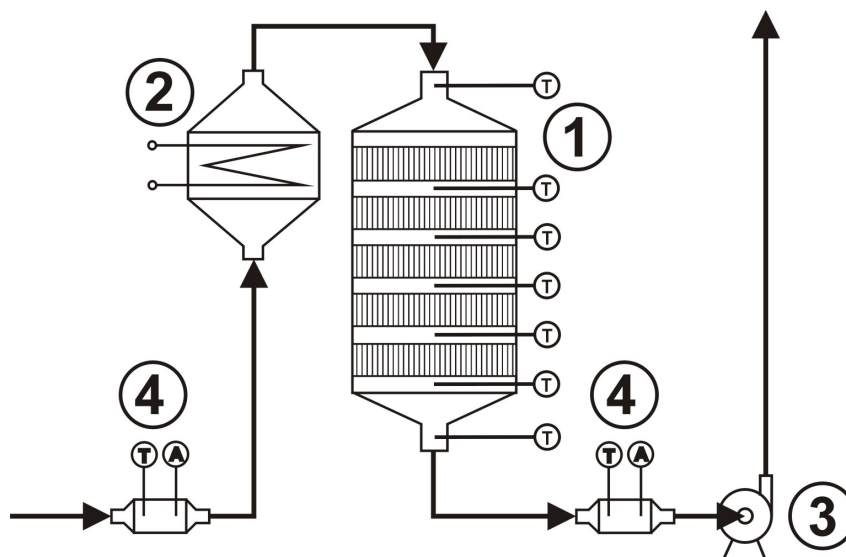


Figure 1. Schematic diagram of the experimental set-up. (1) catalytic reactor, (2) electric heater, (3) fan, (4) point of temperature, pressure, flow rate and concentration control

During the primary tests^{10,12} (with 1,2-dichlorobenzene) no influence of mass transfer processes in the gas phase was reported.

Research on the catalytic decomposition of dioxins was carried out in the installation described above which was connected to a real incineration plant for hazardous wastes of the capacity about 2 500 Mg/year, equipped with a rotary kiln. Investigations were performed on real flue gases using the above presented catalyst. The installation was connected behind the incineration chamber, heat exchanger and flue gas removal system (fabric filters). In that place, the concentration of PCDD/Fs was usually ca. 150–450 ng per m³. The aim of investigations was to determine the effect of temperature and catalyst load (GHSV) on dioxin decomposition efficiency.

Dioxin concentration in flue gases was determined according to EN-1948 standard. The concentration of 17 PCDD/Fs congeners in flue gases at the inlet and outlet from the catalytic reactor was identified, and then the toxicity index TEQ was determined according to the methodology recommended by WHO.

Results and discussion

During the tests with the application of Pd/Pt catalyst it was found that the total quantity of dioxins and furans in the system increases. This would mean that the reactions of dioxin synthesis apart from the decomposition reaction (described in the subject literature many times) also take place on the Pd/Pt catalyst. Those investigations were carried out in 2004 and the moment those results were obtained there were no literature reports that the similar results were attained. On the contrary, a too high number of publications indicated that platinum and palladium may constitute an excellent catalyst for the chloroorganic compounds decomposition. It was the fact that at the end of 2004 the publication by de Jong¹³ appeared which confirmed the results obtained. The scientist carried out the investigations of decomposition of chlorobenzene with the application of a Pt/ γ -Al₂O₃ catalyst and he found that apart from the reaction of chlorobenzene decomposition the reaction of PCDD/Fs synthesis occurs in parallel. The results of the examinations described in the present study and the results obtained by de Jong cast a different light on the possibility of platine catalyst applications to reduce the emission (decomposition, oxidation) of chloroorganic compounds. In the recent years the platinum catalyst was frequently used with success for oxidation of chloroorganic compounds, however, authors of numerous works, obtaining even 80 – 95% of decomposition of the investigated chloroorganic compounds, rather did not realize that the reaction of synthesis of PCDD/Fs took place over the catalyst. Hart¹⁴ has recently taken into consideration the problem of secondary synthesis of dioxins over platinum catalyst. He noticed that concentrations of PCDD/Fs increased even by 1000% while examining the composition of flue gases with catalyst oxidizer, which oxidized the chloroorganic compounds over platinum catalyst.

The dependence of the total quantity of dioxins (expressed in terms of percentage increase in relation to the initial concentration value at the inlet of the reactor) as a function of temperature for various loading of the Pd/Pt catalyst is presented in Figure 2.

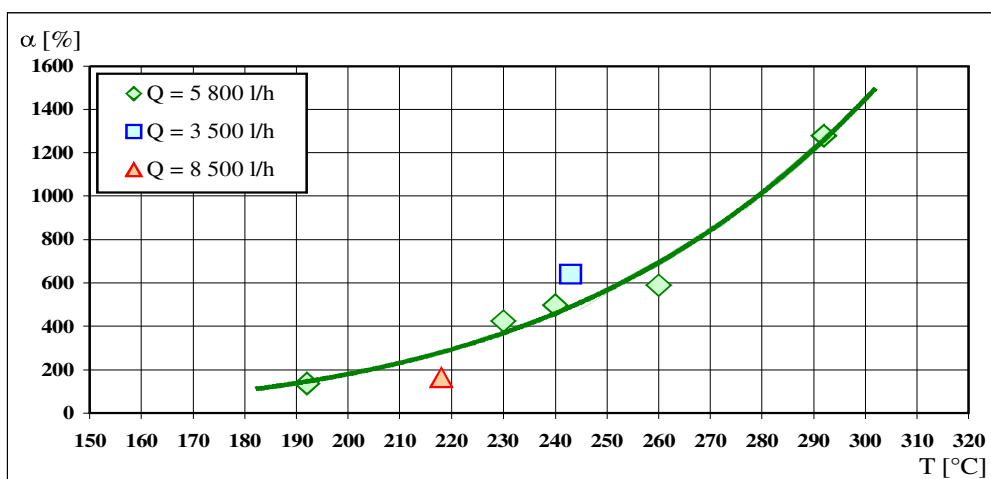


Figure 2. Dependence of the quantity of PCDD/Fs as a function of temperature for various loading of the Pd/Pt catalyst.

Analyzing the obtained results, on the grounds of the whole knowledge in the scope of mechanisms and conditions of dioxin generation, it may be presumed that this is a type of the catalytic synthesis of PCDD/Fs from chlorinated precursors (for example, chlorobenzenes or chlorophenols) carried out at low temperatures with a simultaneous chlorination and de-chlorination of dibenzo-p-dioxin and dibenzofuran particles and that in all probability the catalyst of this reaction is platinum or palladium. Analysing the changes of profiles of congeners (Figure 3) and the increase of the quantity of particular congeners (Figure 4) it may be observed that the highest increase was obtained for six chloro-substituted dibenzo-p-dioxins and five and six chloro-substituted dibenzofurans.

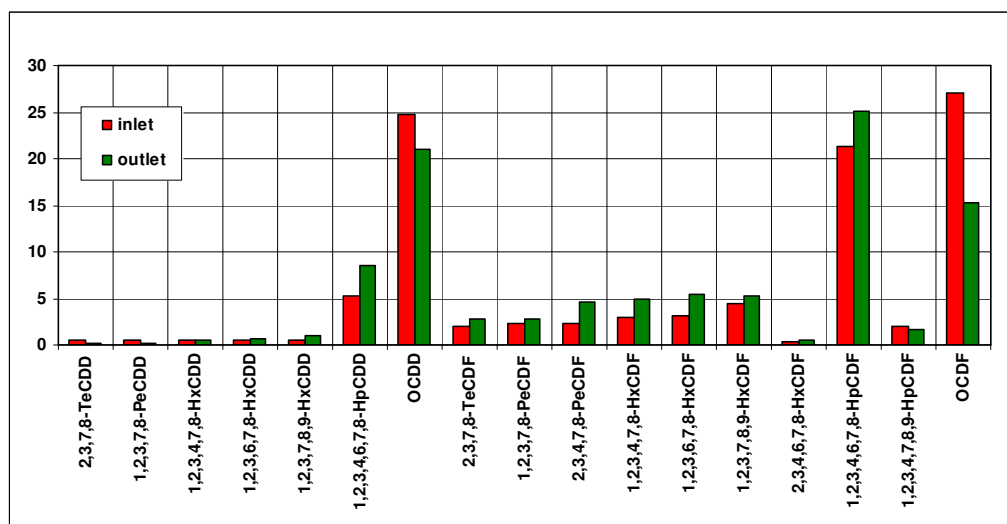


Figure 3. Changes of profiles of congeners PCDD/Fs at the inlet and outlet of the reactor during the reaction over Pd/Pt catalyst.

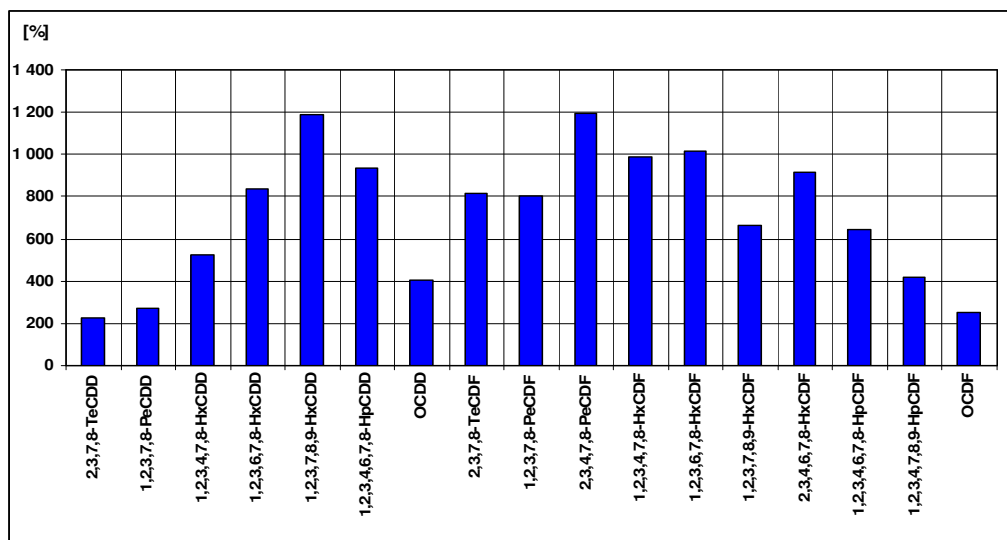


Figure 4. The observed increase of concentrations of particular congeners PCDD/Fs (in [%]) at the inlet and outlet of the reactor during the reaction over the catalyst Pd/ Pt.

In accordance with the literature data it may be expected that in the system higher chlorinated dioxins are produced in the reaction catalysed by certain metals (for instance, copper, zinc, molybdenum, manganese, iron, aluminium or magnesium) but, simultaneously, other metals (e.g. chromium, vanadium, tungsten, cobalt or nickel) catalyse the decomposition of dioxins, which have been generated, or their dechlorination¹⁵. In case of the analyzed catalytic

platinum/palladium system there is lack of information about the influence of those metals on the reaction of synthesis or dechlorination and decomposition of PCDD/Fs. Seemingly, the results of the research presented in this work as well as the results obtained by de Jong¹³ and Hart¹⁴ indicate unequivocally that the secondary synthesis of dioxins may occur over the catalysts made of noble metals (platinum, palladium). Hence, it is essential that they should not be applied for the reduction of emission of chlorinated carbohydrates. This finding is extremely relevant due to the fact that over many years catalysts made of noble metals such as, for example, platinum, have been considered to be exceptionally efficacious with regard to chloroorganic compounds decomposition (oxidation).

References

1. Buekens A. and Huang H. *Journ. Haz. Mat.* 1998;62:1.
2. Wielgosiński G. *Energy Policy (Polityka Energetyczna)* 2003;6:131.
3. Bertinchamps F. Ph. D. Thesis, Universite Catholique de Louvain, Louvain, (Belgium), 2005.
4. Finocchio E., Busca G. and Notaro M. *Appl. Cat. B: Env.* 2006;62:12.
5. Bond G. C. and Sadeghi N. *Journ. Appl. Chem. Biotechn.* 1975;25:241.
6. van den Brink R. W., Mulder P. and Louw R. *Catal. Today* 1999;54:101-106.
7. Corella J., Toledo J. M. and Padilla A. M. *Appl. Cat. B: Env.* 2000;27:243.
8. Spivey J. J. *Ind. Chem. Eng. Res.* 1987;26:2165.
9. Everaert K. and Baeyens J. *Journ. Haz. Mat.* 2004;109:113;
10. Wielgosiński G., Grochowalski A., Machej T., Pająk T. and Cwiąkalski W. *Organohalogen Comp.* 2004;66:1082.
11. Wielgosiński G., Grochowalski A., Machej T., Pająk T. and Cwiąkalski W. *Organohalogen Comp.* 2005;60-65:2242.
12. Wielgosiński G., Grochowalski A., Machej T., Pająk T. and Cwiąkalski W. *Chemosphere* 2007;67:S150-154.
13. de Jong V., Cieplik M. K. and Louw R. *Env. Sci. Technol.* 2004;38:5217.
14. Hart J. R. *Chemosphere* 2008;72:75.
15. Öberg T., Bergbäck B. and Filipsson M. *Chemosphere* 2008;71:1135.