

## “Relevance of PCDD/PCDF Formation for the Evaluation of POPs Destruction Technologies - PCB destruction over a TiO<sub>2</sub>-Based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> Catalyst”

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### Introduction

Persistent Organic Pollutants (POPs) pose a serious threat to public health and the environment. The Stockholm Convention on POPs<sup>1)</sup> has selected 12 POPs (“The dirty dozen”) to be reduced and/or eliminated within the next two decades. PCBs are one group of POPs of major concern. Although their production has ceased worldwide, PCBs are still present in storages and remain in large quantities in electrical transformers and capacitors, as hydraulic fluids in coal mining or soil and sediment contaminant.

The current base line remediation technology for PCBs is incineration. However, temperatures of more than 1100°C are required for their safe destruction, which demand state of the art hazardous waste incineration facilities. These technologies are available only in a few highly industrialized countries. Therefore, during the last two decades several alternative non-combustion technologies have been proposed for PCB/POPs destruction.

The TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst has been applied for more than 10 years for the destruction of PCDDs/PCDFs and PCBs in off-gas from municipal waste incinerators<sup>2,4)</sup>. At higher temperatures, the catalyst can also be used for POPs (and VOC) destruction. In this respect Hagenmaier investigated different oxidation catalysts for PCB destruction efficiency and found superior destruction properties for the TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst<sup>4)</sup>.

PCB destruction exhibits a special challenge because they are PCDF precursors and can easily be oxidised into the more toxic PCDFs (Figure 2). Therefore, the formation of PCDDs/PCDFs during destruction of PCBs (POPs) is one important criterion for the evaluation of a PCB (POPs) destruction technology<sup>5)</sup>. The relevance of PCDF formation during destruction of PCBs was demonstrated e.g. for the supercritical water oxidation technology (SCWO), a technology listed in the highest rank of non-combustion technologies from the United Nations Environmental Programme (UNEP) and the United Nations Industrial Development Organization (UNIDO), where PCDFs were formed in the %-range<sup>6)</sup>.

Therefore the present study evaluates the relevance of PCDF formation during catalytic destruction of PCBs on a TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst. The study aims to give an example of how an assessment of PCDF formation as a function of operation conditions for PCB (POPs) destruction might be performed for the evaluation of a PCB (POPs) destruction technology. Further, the results demonstrate that for the catalytic oxidation over TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst, the problem of PCDF formation can be overcome.

## Materials and Methods

**Catalyst.** A commercial catalyst ( $V_2O_5$ - $WO_3$  on  $TiO_2$  basis) was used which was developed especially for the simultaneous destruction of PCDDs/PCDFs and nitrogen oxides. According to the manufacturer, the specific surface area of the catalyst was between 60 and 75  $m^2/g$  and the pore volume was above 25  $ccm/g$ .

**Chemicals.** The PCB mixture used in this study included a Clophen A 30 sample and transformer oil corresponding to Clophen A 60. For the experiments, these PCB mixtures were combined to get a homogeneous homologue distribution of diCB to heptaCB. The mixture also contained measurable amounts of octaCB and nonaCB. The PCDFs, generally present in the ppm levels in commercial mixtures<sup>7)</sup>, were separated from the PCB on an alumina column before application of the mixtures to avoid their interference with PCDFs that may form during the experiments.

**Flow-stream experiments.** The honeycomb catalysts were crushed and sieved. The particle size of the resulting flakes were about 0.6mm x 1mm x 1mm. Approximately 5 g of the catalyst was placed in the quartz tube (13 mm internal diameter) of a flow reactor. Before closing the reactor, the PCB mixture (1000  $\mu g$  - 10000  $\mu g$ ) was applied to silica and placed in the evaporating zone. After the reactor reached a set temperature, the gas flow (10% $O_2$ , 70% $N_2$ , 20% $H_2O$ ) was started. The volumetric flow through the catalyst bed corresponded to a space velocity (SV) of 5000 1/h. The flow rate was regulated using mass flow controllers (Shinagawa Seiki, Japan). When equilibrium was reached, the experiment was started by heating the evaporation zone for 10 minutes and continuing the flow for 30 minutes or 120 minutes, respectively.

**Extraction.** The catalysts were extracted for 12 hours by Soxhlet extraction with toluene. The glass tubes after the catalyst were rinsed with toluene. These rinses were combined with the toluene in the washing bottle (Impinger). The toluene in the washing bottle and the extracts of the catalysts were analysed separately.

**Clean-up, GC/MS analysis and quantification** were described previously<sup>6)</sup>.

**Calculation of removal efficiency and destruction efficiency.** All removal and destruction efficiencies were calculated based on TEQ (WHO 1998).

Removal efficiency ( $RE_{TEQ}$ ) describes the ability of the catalyst to remove PCBs from the gas stream and was calculated as:  $((PCB)_{inlet} - (PCB)_{outlet}) / (PCB)_{inlet}$ .

Destruction efficiency ( $DE_{TEQ}$ ) describes the ability of the catalyst to destroy PCBs during the experimental time and was calculated as:  $((PCB)_{inlet} - [(PCB)_{outlet} + (PCB)_{on\ cat}]) / (PCB)_{inlet}$ .

The PCB recovery in the impinger was calculated as:  $Recovery_{impinger} = 100 - RE$ .

The PCB recovery on the catalyst was calculated as:  $Recovery_{catalyst} = (PCB)_{on\ catalyst} / (PCB)_{inlet}$ .

The PCDFs formed in the experiments were also converted to TEQ and for evaluation of DE and RE calculated to the TEQ of PCBs initially present.

## Results and discussion

### Removal efficiency and destruction efficiency of PCBs

The catalyst was tested for the destruction efficiency of PCBs during flow experiments in the temperature range of 200-400°C. The catalyst showed a removal efficiency of more than 99% in the entire temperature range tested (Figure 1A). However it was discovered that at a temperature of 200°C, a considerable amount of the  $PCB_{TEQ}$  (12.0 %) were adsorbed on the catalyst after the 30-minute experiment (Figure 1B). Therefore, the destruction efficiency of PCBs ( $PCB\ DE_{TEQ}$ ) was below 88%. On the other hand, no PCBs were adsorbed on the catalyst in the experiments at 250°C

and higher temperatures. Hence, for a temperature above 250°C the PCB  $DE_{TEQ}$  corresponded to the PCB  $RE_{TEQ}$ .

# REMEDATION METHODS AND CONTROL TECHNIQUES

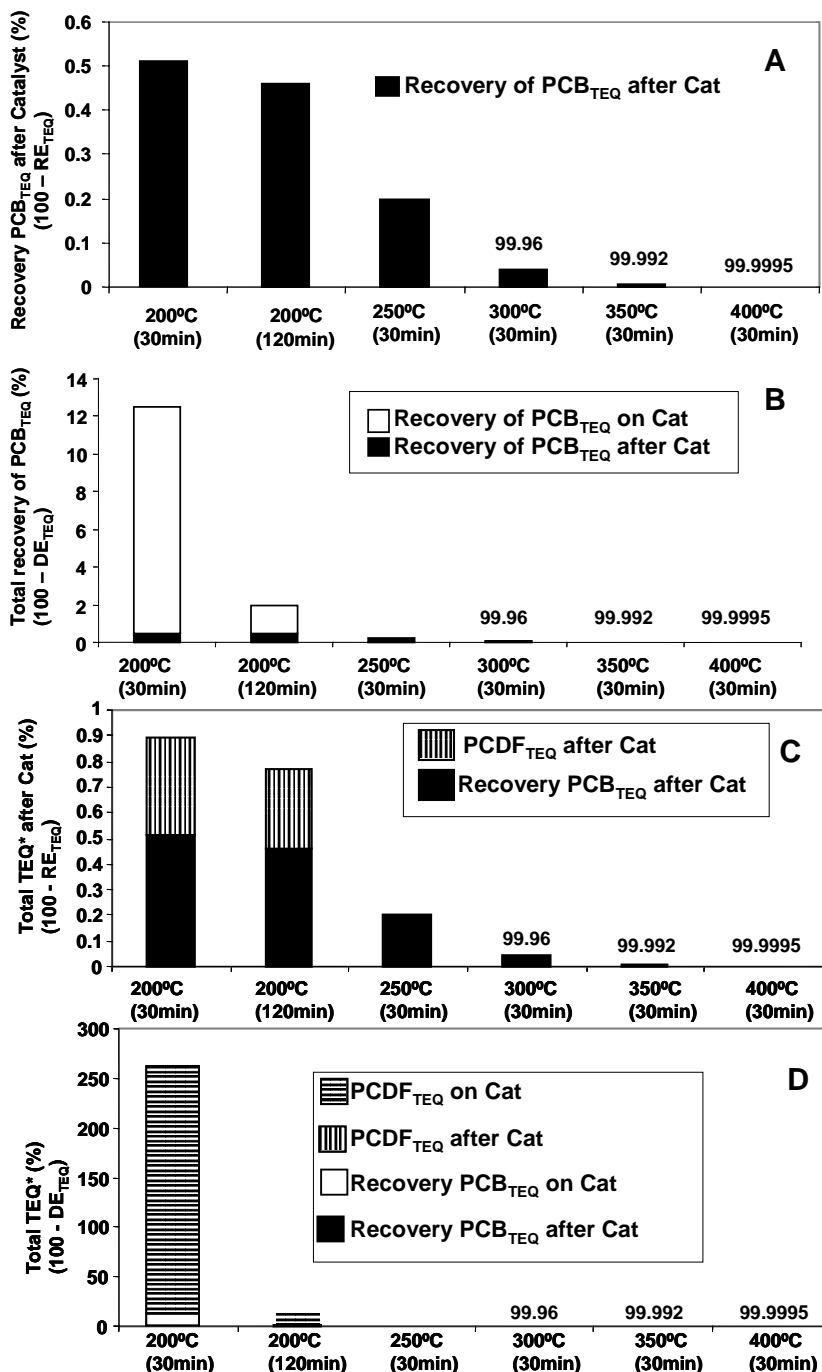


Figure 1: PCB RE<sub>TEQ</sub>, (A) PCB DE<sub>TEQ</sub>, (B) Total RE<sub>TEQ</sub> (C) and Total DE<sub>TEQ</sub> (D) of PCB destruction on TiO<sub>2</sub>-Based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> (space velocity (SV) 5000 h<sup>-1</sup>)

**Removal efficiency and destruction efficiency of total TEQ (PCB and PCDD/PCDF)**

One key question for the assessment of a PCB/POPs destruction technology is whether the more toxic PCDD/PCDFs are formed and under which conditions and applications their potential conversion to PCDFs has no relevance<sup>5)</sup>. The conversion of PCBs to PCDFs demands only the insertion of an oxygen (ether-bridge; compare Figure 2; which is discussed further below), a process which is generally observed during thermal oxidation of PCBs in the presence of air<sup>8,9)</sup>. The impact of PCDD/PCDFs can easily be included into the RE/DE calculations when including the TEQ of PCDD/PCDFs formed and recalculating it to the TEQ of the initial PCBs (a practice which should be generally requested for PCB destruction applications).

In the present study, PCDF<sup>[1]</sup> were detected in the off-gas of the catalyst in the experiments conducted at 200°C (Figure 1C). The concentrations of PCDFs (based on TEQ) were comparable with the TEQ concentration of emitted PCBs, and the RE efficiency based on total TEQ decreased slightly but still was more than 99% (Figure 1C).

However, when analysing the catalyst it was found that at 200°C a considerable amount of PCDFs was formed and adsorbed on the catalyst surface. The TEQ of these PCDFs was higher compared to that of the starting PCB (Figure 1D). Hence, the total DE<sub>TEQ</sub> would have been negative (ca. –160%) while for the calculation based on total RE<sub>TEQ</sub>, the efficiency would still be more than 99% (Figure 1C).

When prolonging the reaction time at 200°C to 120 min, considerable smaller concentrations of PCDFs were detected on the catalyst and resulted in a total DE<sub>TEQ</sub> of 88% (Figure 1D). In this experiment the concentration of PCDFs and PCBs in the off-gas of the catalyst were comparable with the concentration at the 30 min experiment and the total RE<sub>TEQ</sub> was still higher than 99% (Figure 1C). This demonstrates that the PCDFs formed in the early stage of PCB destruction at 200°C remain mainly adsorbed on the catalyst and are destroyed at prolonged reaction time.

At a temperature of 250°C and above, no PCDFs were detected on the catalyst (Figure 1D) or in the off-gas of the catalyst (Figure 1C). Hence, the formation of PCDF has no relevance in the temperature range proposed for the destruction of PCBs/POPs. The DE<sub>TEQ</sub> reached more than 99.995% at 300°C and more than 99.9999% at 400°C. The results are in agreement with the study of Hagenmaier<sup>4)</sup>, who reported a PCB destruction efficiency of more than 99.99% at 400°C.

***Mechanistic aspects of PCB degradation and PCDF formation***

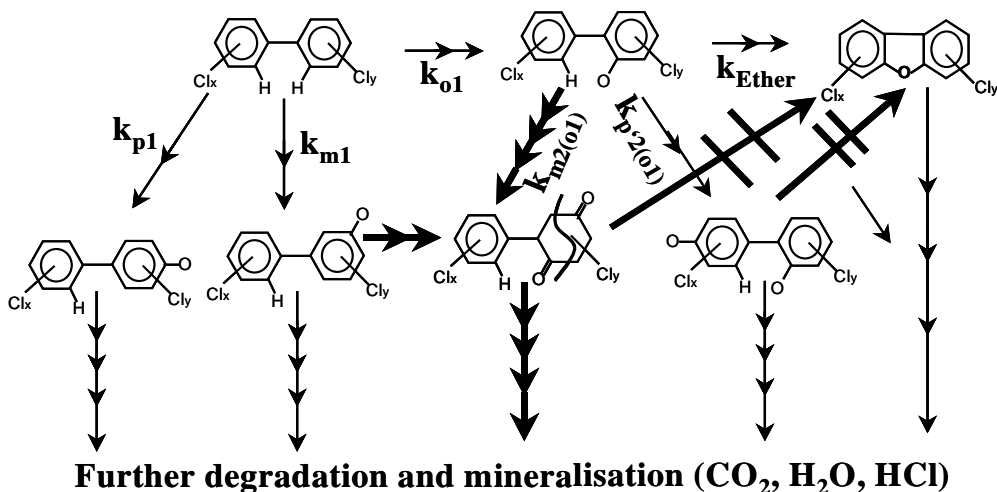
For the transformation of PCBs into PCDFs two hydrogen (or one hydrogen and one chlorine)<sup>10)</sup> have to be substituted and two oxygen-carbon bonds have to form (Figure 2). This demands at least two reaction steps: I) Oxidation in one of the ortho positions and then II) The formation of the ether-bridge closure to the dibenzofuran (Figure 2). If in the first step the oxidation occurs at meta- or para-position, a further formation of PCDF is prohibited and other degradation pathways take place. The reason for the low conversion rates in ppm range on the catalyst at 200°C (while the conversion rates in air<sup>8)</sup> and SCWO<sup>6)</sup> can reach up to 25% and 7%, respectively) and absence of conversion at temperatures above 250°C can not be explained with these alternative substitution positions in the first oxidation step but have to be explained mainly with the second oxidation step and the ether bridge formation.

As can be derived from the long retention times of PCBs on the catalyst at 200°C, the rates for the first oxidative attack ( $k_{\text{ortho(o)}}$ ;  $k_{\text{meta(m)}}$  and  $k_{\text{para(p)}}$ ) on the aromatic ring at 200°C are in the minutes

[1] PCDD were not detected in any of the experiments of PCB destruction on the TiO<sub>2</sub>-Based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst.

(to hour) range. In the second step the oxidation can then take place either at the same ring as the first oxidation or at the second non-oxidized aromatic ring (Figure 2). It can be assumed that the rates for an oxidative attack on the second non-oxidized aromatic ring are comparable with the rates of the oxidation of the non-oxidized PCB. However, the oxidative attack on the same ring as the first oxygen attack seems much faster (in the second or even sub-second range). This is supported by the finding that no hydroxylated PCBs were detected on the catalyst at 200°C and above (and only in sub ppm range at 150°C). The sensitivity of hydroxylated aromatic rings towards oxidative destruction by TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> is further demonstrated by the high destruction rates of chlorinated chlorophenols on SCR catalysts compared to chlorinate benzenes<sup>15</sup>. Therefore the second oxidation and main degradation pathway proceeds via a second oxidation step in the same ring as the first oxidation and can then not result in a conversion to PCDFs (Figure 2) since the formation of the ether bridge to form PCDFs requires the second oxidation step to take place at the second aromatic ring.

The differences in transformation yields of PCBs to PCDFs on TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> compared to the oxidation with only oxygen in the supercritical water oxidation<sup>6</sup>) or in air<sup>8</sup>) indicate that the degradation pathways are different for these oxidative destruction methods. The transformation of PCBs in SCWO (up to 450°C) and air around 550°C in the % range indicates that under these conditions the second oxidative attack on the second aromatic ring (including the option of PCDF formation) is in the same order of magnitude as the initial oxidation step of the PCB.



**Figure 2: Simplified oxidative degradation pathways of PCBs**

In the opinion of the author, the investigation of degradation pathways in respect to potential PCDD/PCDF formation is one important (pre-) evaluation for the risk assessment of an oxidative (and reductive<sup>[2]</sup>) PCB (POPs) destruction technology.

<sup>[2]</sup>high concentration of PCDF can be formed during PCB destruction under reductive conditions in presence of alkaline<sup>[1]</sup>.

### Conclusions

This risk of PCDF formation during PCB destruction is minimal for catalytic oxidation on a TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalyst even for low temperatures used for catalytic off-gas cleaning for PCDD, PCDF, PCB and NO<sub>x</sub> (200-300°C). At 200°C the PCBs were decomposed only slowly. A considerable amount of PCBs remain adsorbed on the catalyst and are destroyed at prolonged reaction times. Therefore, a destruction efficiency of more than 99% can also be achieved at temperatures around 200°C sufficient for e.g. off-gas cleaning in MWI.

Above 300°C deep oxidation occurred without detection of by-products. The oxidation catalyst in this temperature window is a true sink for POPs and chlorinated VOC due to complete mineralization of the compounds resulting in CO<sub>2</sub>, H<sub>2</sub>O and HCl<sup>4)</sup>.

In a survey of UNEP, a destruction efficiency of >99.9999% is recommended<sup>12)</sup>. From the laboratory test, temperatures below 300°C are not sufficient to reach this aim. However, the catalytic test at 400°C reached a destruction efficiency of more than 99.9999% and therefore this temperature region seems appropriate for practical application of PCB (POPs) destruction over TiO<sub>2</sub>-based V<sub>2</sub>O<sub>5</sub>-WO<sub>3</sub> catalysts.

In addition, the experiments at 200°C demonstrate that the evaluation of PCB (POPs) destruction technologies have to be based on destruction efficiency (DE) and not on removal efficiency (RE) (compare Figure 1A and 1B). Further it demonstrates the necessity not to limit the evaluation of a PCB (POPs) destruction technology/application on the PCB (POPs) destruction efficiencies but to include the analysis of PCDDs/PCDFs in off-gas and solids and base the evaluation on overall toxicity (DE<sub>TEQ</sub>; compare Figures 1B and 1D). This shows that all residues of PCB (POPs) destruction processes have to be monitored for PCDD/PCDF (and other toxics).

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