

**Multiphase Catalytic Hydrodehalogenation: A New PCDD/PCDF  
Detoxification Method**

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**Introduction**

A novel catalytic multiphase system consisting of a hydrocarbon solvent and an aqueous phase, catalyzed by a supported metal catalyst (Pt or Pd) and a phase-transfer (PT) agent as a promoter allows the rapid and efficient hydrodehalogenation of various polyhalogenated aromatics<sup>1-3</sup>. The method affords the quantitative yields of reduction products in extremely mild conditions: hydrogen at atmospheric pressure and 50 °C temperature.

This multiphase system has been recently shown to be a promising environmentally friendly tool for the selective removal of halogen and/or the reduction of other functional groups such as carbonyl group and phenyl ring. The selectivity can be easily controlled by varying such simple reaction conditions as the nature of a supported metal (Pd or Pt) or phase-transfer (PT) catalyst or their ratio<sup>4</sup>, the composition and acidity of the aqueous phase<sup>5</sup>, etc. The examples of polyhalobenzenes<sup>1</sup>, *p*-chloroacetophenone<sup>6</sup>, *p*-chloropropiophenone<sup>3,4,5</sup>, acetophenone<sup>6</sup>, etc. using various supported metal catalysts<sup>1</sup>, PT agents<sup>1,4</sup>, and hydrogen sources<sup>5</sup> have been studied.

The mechanistic conclusions suggest<sup>5</sup> that a PT agent form a third liquid phase over the surface of a metal supported catalyst, therefore modifying the reacting surface by changing the geometry of the substrate sorption complexes on the solid Pt/C (Pd/C) surface. This new catalytic phase is especially effective for dehalogenation since in the absence of PT agent the halogen removal is strongly suppressed.

This work places the specific emphasis on the application of this multiphase system to the degradation of persistent organic pollutants. The applicability of this mild technique to the dechlorination of polychlorinated biphenyls (PCBs)<sup>1</sup> and toxic congeners of polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs), collected from a municipal solid waste incinerator (MSWI) is demonstrated.

**Methods and materials**

The hydrodehalogenation technique was performed using a three-necked water-coated reactor thermostated at 50 °C loaded with 10 ml of substrate solution in isooctane, Aliquat 336 (tricaprylmethylammonium chloride) (0.26 mmol), Pt/C or Pd/C catalyst (0.021 mmol of Pt or Pd), and 5.7 ml of 1% aqueous KOH solution. The reaction mixture was bubbled with hydrogen at 5 ml/min flow rate and magnetically stirred at 1000 rpm.

For 2,4,8-trichlorodibenzofuran (commercial reagent from Aldrich), the reaction was started with 0.07 M of substrate in 10 ml of isooctane. The reaction course was followed by GC and the products were analyzed by GC-MS. Both 5% Pt and 10% Pd supported catalysts were used. The results are reported in Fig. 1.

# EMISSION CONTROLS, ABATEMENT TECHNOLOGIES AND REMEDICATION - POSTERS

Under the same conditions using Pd/C, but starting from the initial concentrations reported in Table 2 the reaction was performed for PCDDs/Fs, concentrated samples of which were collected from a MSWI (fly ash extract). High-resolution GC/MS (HR GC/MS) analyses were performed for the determination of PCDD/F concentrations and the procedures assigned by the US Environment Protection Agency (EPA) for the treatment and concentrating of PCDD/F samples were used. The results are reported in Table 2.

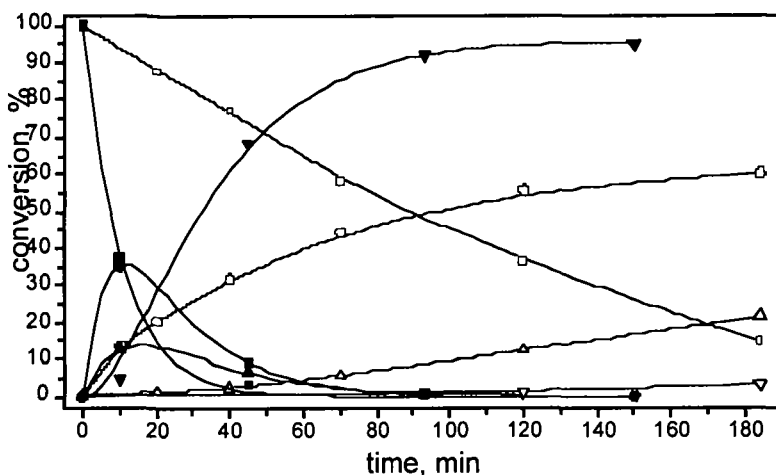
The hydrodehalogenation of PCB mixtures<sup>2</sup> (Arochlor 1254) was conducted starting from 35 000 ppm of PCB in 7 ml of isoctane, 0.2 mmol of Aliquat 336, 0.015 mmol of Pd (5% Pd/C), and 4 ml of 50% KOH solution. The results are reported in Table 1.

## Results and Discussion

The results show that the reaction affords the quantitative yields of reduction products in very short times not much depending on the type of polychlorinated aromatics.

**Table 1.** Hydrodechlorination of PCBs under Multiphase Conditions over Pd/C.

entry	Aliquat 336	time (h)	products (% of yield)
1	yes	3.0	biphenyl (99) is the only reaction product
2	no	3.0	biphenyl (54)



**Figure 1.** Hydrodechlorination of 2,4,8-trichlorodibenzofuran over Pd/C (solid symbols) and Pt/C (open symbols) in multiphase conditions.  $\square, \triangle$ : 2,4,8-trichlorodibenzofuran;  $\circ, \delta$ : dichloro isomers;  $\triangle, p$ : monochloro isomers;  $q, s$ : dibenzofuran.

The hydrodechlorination of PCBs (Table 1) affords the fully dechlorinated product in 99% yield in three hrs over the Pd/C catalyst. It does not much differ from the results obtained for polychlorobenzenes<sup>1</sup>. Remarkably, the role of PT agent is quite substantial in this case: only 54% conversion to biphenyl is observed in the time studied if no Aliquat 336 is used.

The hydrodechlorination conditions have been initially probed on the example of non-toxic 2,4,8-trichlorodibenzofuran (TCDF). The kinetic profiles (Fig. 1) show the consecutive removal of all aromatic chlorines with apparently equal rates and with observed first-order kinetics. In case of the Pd-catalyzed reaction, the complete conversion to DF is achieved in about 1.5 hrs. The use of Pd/C appears to be much more effective comparing to Pt/C where only minor amount of full

# EMISSION CONTROLS, ABATEMENT TECHNOLOGIES AND REMEDATION - POSTERS

dechlorination products is observed in the time studied. The Pd/C is also the catalyst of choice for the dechlorination of PCBs and halobenzenes<sup>1,2</sup>. On the other hand, Pt/C more favors the reduction of phenyl ring<sup>6</sup>, which appears to be another useful PCDD/F degradation technique.

**Table 2.** Hydrogenation of PCDD/PCDF Samples Under Multiphase Conditions over the Pd/C Catalyst. Concentrations are Reported in pg/ml Units.

PCDD/PCDF	0 min	20 min	60 min	185 min	390 min
2,3,7,8-TCDD	10	12	3	1	< 1
1,2,3,7,8-PCDD	56	11	3	1	< 1
1,2,3,4,7,8-HCDD	105	2	< 2	< 2	< 2
1,2,3,6,7,8-HCDD	638	8	4	2	< 2
1,2,3,7,8,9-HCDD	351	13	6	3	< 2
1,2,3,4,6,7,8-HpCDD	3181	10	9	< 3	< 3
1,2,3,4,6,7,8,9-OCDD	4193	13	15	< 5	< 5
2,3,7,8-TCDF	69	1	1	< 1	< 1
1,2,3,7,8-PCDF	89	< 1	1	< 1	< 1
2,3,4,7,8-PCDF	263	2	2	1	< 1
1,2,3,4,7,8-HCDF	746	3	3	2	< 2
1,2,3,6,7,8-HCDF	421	< 2	2	< 2	< 2
2,3,4,6,7,8-HCDF	718	3	4	2	< 2
1,2,3,7,8,9-HCDF	59	< 2	< 2	< 2	< 2
1,2,3,4,6,7,8-HpCDF	2284	6	6	< 3	< 3
1,2,3,4,7,8,9-HpCDF	330	< 3	< 3	< 3	< 3
1,2,3,4,6,7,8,9-OCDF	1735	< 5	< 5	< 5	< 5
Total I-TEQ* (pgTEQ/ml)	549	21.8	7.7	2.9	—

Note: «<» reports the concentration under the determination limit; \* International Toxic Equivalent.

A mixture of PCDD/PCDF congeners containing 17 toxic ones and their non-toxic isomers, obtained by the extraction from MSWI fly ash has been tested for dechlorination under the same reaction conditions over Pd/C. The results reported in Table 2 show the change in the PCDD/PCDF concentrations in the organic phase vs. the reaction time. There is a sharp decrease (about two orders of magnitude) observed in the concentrations of all PCDD/F in the first 20 min. The concentrations of all PCDD/F become undetectable by HR GC/MS after 5.5 hrs of reaction. Nevertheless, there is no such a sudden fall for the concentration of the most toxic 2,3,7,8-TCDD congener, which is also assumed most thermodynamically stable among the others<sup>8</sup> and is formed during the dechlorination of higher chlorinated congeners. However, 2,3,7,8-TCDD is initially present in a very low amount, and only some slight increase in its concentration is observed in the beginning. Further, it is dechlorinated as well. On the other hand, there is no such behavior for 2,3,7,8-PCDF, which reacts rapidly from the very beginning. The majority of other PCDD/F congeners are dechlorinated with apparently equal rates though there should also be some increase in the rates for highly chlorinated congeners because they are not formed during the dechlorination of the others.

The sharp concentration decrease in the beginning of the reaction along with the equal dechlorination rates for the majority of PCDDs/PCDFs suggest that the reaction preferably proceeds in a mass-transfer mode. Respecting a high excess of Pd/C over the PCDD/F amount there should be a strong adsorption of PCDDs/Fs over the surface of Pd/C in the beginning of the reaction. It explains the sharp initial decrease in the PCDD/F concentrations and their comparable dechlorination rates, because the reaction is probably controlled by the adsorption-desorption of PCDDs/Fs and not by their intrinsic dechlorination rates which are presumably higher in this case since the reaction rate should be dependent on the Pd/C-substrate ratio.

# EMISSION CONTROLS, ABATEMENT TECHNOLOGIES AND REMEDIAATION - POSTERS

Unfortunately, the results do not directly show whether PCDDs/Fs are more or less reactive comparing to 2,4,8-TCDF, PCB or polychlorobenzenes since the hydrogenation of PCDD/F samples was performed using a huge excess of Pd/C and Aliquat 336 over the substrate concentration. Nevertheless, there is not likely to be any pronounced difference between the dechlorination rates for the toxic PCDD/F congeners and for 2,4,8-TCDF.

## Conclusion

The reported new multiphase hydrodehalogenation conditions were successfully probed for the degradation of various polychlorinated aromatics including such hazardous POPs as PCBs and PCDDs/Fs. The results show the complete dechlorination of all 17 toxic PCDD/F congeners and PCB mixtures in short reaction times and under very mild reaction conditions. The dechlorination rates for different PCDD/F congeners do not much differ during the reaction course that suggests that the reaction is probably controlled by the adsorption processes.

The investigation of the adsorption contribution in the catalytic hydrodechlorination of PCDDs/Fs is presently in progress. The results promise to estimate the extent of PCDD/F adsorption in the conditions studied and to tell whether the reaction proceeds as well with regard to those PCDDs/Fs, which are sorbed over Pd/C surface and are not detected in the organic phase.

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