The dechlorination of OCDD and OCDF on an alumina support.

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INTRODUCTION

De-novo synthesis is an important reaction pathway in the formation of polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) during municipal waste incineration[1,2]. Model experiments with fly ash have shown that reaction time, temperature, copper catalyst- and oxygen concentration are important parameters in PCDD/PCDF formation[2,3,4,5,6,7]. Also model supports, like alumina and Mg-Al-silicate, are studied in PCDD/PCDF formation from particulate organic carbon[1,8,9]. The acidity of the alumina support is an important parameter in the formation of PCDDs and PCDFs[8].

In absence of oxygen a dechlorination reaction is observed. In earlier experiments, alumina seems to be an important dechlorination agent[8].

Recently we have looked into the influence of the acidity of the alumina support on the dechlorination of OCDD and OCDF. Some results are presented in this paper.

EXPERIMENTAL

Alumina was impregnated with a solution of 2 μg/g OCDD and OCDF in hexane and the hexane was evaporated. The impregnated alumina was heated at 275°C in a glass tube at a flow of 16 ml/min nitrogen for 30 min, as described before[8]. After the flow tube all volatile organic substances were collected in a cold trap filled with hexane and cooled with ice. The various reaction conditions are described in table 1, each experiment was performed three times.

The pH of the alumina support was measured by suspending 1g in 30 ml water, heating for 10 min, filtration and determining the pH of the filtrate with a pH meter.

Extraction, clean up and GC/MS analysis

After adding a solution of ^{13}C labeled PCDDs and PCDFs as internal standard, the sample was soxhlet-extracted with toluene. The extract was purified by using acid, base and silver nitrate modified silica gel, and aluminum oxide. After preparative HPLC the PCDDs and PCDFs were identified and quantified with GC-MSD. This have been described before[8].

Table 1 experiments

No	support	OCDD & OCDF	reaction time, temperature and gas flow rate
1	5 g alkaline alumina (pH=8.9)	2 μg/g OCDD 2 μg/g OCDF	30 min; 275°C; 16 ml/min
2	5 g neutral alumina (pH=5.7)	2 μg/g OCDD 2 μg/g OCDF	30 min; 275°C; 16 ml/min
3	5 g acid alumina (pH=4.6)	2 μg/g OCDD 2 μg/g OCDF	30 min; 275°C; 16 ml/min
4	5 g alkaline alumina (pH=8.9)	2 μg/g OCDD 2 μg/g OCDF	30 min; 275°C; 16 ml/min with water

RESULTS AND DISCUSSION

In two blank experiments (extraction and clean up of ^{13}C labeled PCDDs and PCDFs) only trace amounts of OCDD and OCDF were found (<0.8 ng/g and <0.4 ng/g resp). No PCDDs and PCDFs were found in the cold trap.

In table 2 a comparison is made between the degree of dechlorination of OCDD and OCDF and the acidity of the alumina support. OCDD and OCDF were dechlorinated very fast to lower chlorinated congeners. Besides OCDD and OCDF only trace amounts of hexa and hepta chlorinated congeners were found. This indicates that the dechlorination of OCDD/OCDF to H_7CDD/H_7CDF is rate limiting and the dechlorination of H_7CDD and H_7CDF to lower chlorinated congeners proceeds with a faster rate.

The dechlorination of OCDD on alkaline alumina is faster than on neutral alumina. Although the experiment with acid alumina was only performed once, we can conclude that the dechlorination of OCDD on acid alumina takes place at a lower rate than on alkaline alumina but at a higher rate than on neutral alumina. The dechlorination of OCDF on alkaline alumina is as fast as on neutral alumina. The dechlorination of OCDF on acid alumina is lower.

Earlier we reported[8] the formation of PCDDs and PCDFs from particulate organic carbon via de-novo synthesis on different kinds of alumina. Acid alumina gave a greater amount of PCDDs and PCDFs than neutral and alkaline alumina. No significant difference was observed between the amount of PCDDs and PCDFs formed on neutral and alkaline alumina. With respect to the results of the dechlorination study described above, the greater amount of PCDFs in the de-novo synthesis on an acidic alumina support can be explained by a low dechlorinaton rate of OCDF.

Table 2 The amount of PCDDs and PCDFs found after heating the starting material with 2 μg/g OCDD and OCDF (ng/g).

exp. No.	1		2		3		4	
congener	alkaline alumina	SD %	neutral alumina	SD %	acid alumina	SD %	alkaline with water	SD %
H_6CDD								
1,2,4,6,7,9- 1,2,4,6,8,9- 1,2,3,4,6,8-	n.d.		0.37	28#	n.d.		n.d.	
1,2,3,6,7,9- 1,2,3,6,8,9-	n.d.		0.23	0.4#	n.d.		n.d.	
H_7CDD								
1,2,3,4,6,7,9-	0.38	31	8.5	43	2.9	21	0.14	16
1,2,3,4,6,7,8-	0.38	31	3.4	39	n.d.		0.13	24
OCDD	8.4	15	416	17	145	*	4.9	12
H_6CDF								
1,2,4,6,7,8-	n.d.		0.11	12#	n.d.		n.d.	
H_7CDF								
1,2,3,4,6,7,8-	0.13	33	0.97	42	0.84	32	0.052	23
OCDF	1.3	8.9	1.1	15	3.5	10	1.2	14

n.d.= not detected (detection limit = 0.06 ng/g).
* single experiment # performed twice

The influence of the acidity of the alumina support on the formation of PCDDs by de-novo synthesis and the dechlorination of OCDD is not as clear as for the PCDFs. Because of the slow dechlorination of OCDD on neutral alumina with regard to alkaline and acid alumina, other processes have to play an important role in PCDD formation .

In the presence of water no significant change in the dechlorination rate of OCDD and OCDF was observed. Therefore, the earlier reported[8] shift in the formation of PCDDs and PCDFs via de-novo synthesis towards higher chlorinated congeners in the presence of water can not be explained by a lower dechlorination rate.

CONCLUSIONS

The dechlorination rate of OCDD on alkaline alumina is high in comparison with that on neutral alumina.
The dechlorination rate of OCDF on acid alumina is low in comparison with neutral and alkaline alumina.

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