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INFLUENCE OF CARBON MORPHOLOGY AND VARIOUS METAL CATALYSTS ON THE DE-NOVO-SYNTHESIS OF PCDD/F

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Abstract:

Different kinds of carbon matrices and metal catalysts were investigated concerning their PCDD/F formation potential. Carbon types with incorporated oxygen in their matrices show a completely different isomer distribution pattern compared to those that have a degenerated graphitic structure. AlCl_3 acts as a catalyst for the selective formation of dioxins with the so-called „2,6-pattern“ during thermal treatment with activated charcoal.

Keywords:

PCDD/F, PCB, PCBz, PCPh, de-novo-synthesis, „2,6 - pattern“

Introduction:

In the last years lots of model experiments were performed in order to get more information about the formation mechanism of PCDD/F and related compounds in real combustion systems. For that purpose either fly ashes from MWI or synthetic fly ash mixtures with added catalysts and carbon sources were used.

Flyash itself represents a very complex matrix that makes it more complicated to distinguish between various effects of formation/destruction and the influence of different metal catalysts. On the other hand the addition of activated charcoal to synthetic fly ash mixtures does not display the real situation in combustion processes. Carbon is at least partially emitted as soot resulting from the gas-phase condensation of acetylene radicals or similiar precursor radicals/1/. Soot particles can be described by a degenerated graphitic structure with a low content of oxygen containing groups. Activated charcoal has also a graphitic structure but may have besides polar functional groups on its surface also preformed dioxin- and furan structures in the matrix that can be released during thermal treatment. To study these influences different carbon matrices (activated charcoal, soot, graphite, wood, lignite, fullerenes) were chosen for model experiments.

Various metal catalysts are known to promote the formation of PCDD/F and related compounds. Cu and Fe can act as Deacon catalysts in the formation of $\text{Cl}_2/2/$. In addition Cu is able to catalyze Ullmann condensation reactions as well as the transfer of chloride to the carbon surface/3,4/. In a series of model experiments CuCl_2 , FeCl_3 and AlCl_3 were

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investigated concerning differences in their catalytic activity. The catalytic activity of AlCl_3 wasn't examined until now but it may play an interesting role as a catalyst during aluminum recycling processes where we could observe a typical „2,6-pattern“ of PCDD/5/.

Experiments:

The thermal treatment of model mixtures was performed in a vertical glass tube with a frit at the bottom in an upward gas stream of technical air. Before reaching the reaction zone the gas stream was passed through a washing bottle with distilled water. The volatile reaction products were trapped in a toluene-filled washing bottle followed by a tube with XAD-resin.

For comparative studies a unique composition of the reaction mixtures was used, the relation of C:Cl:Me was 21:3:1. The reaction times varied between 5min. and 2h and the reaction temperatures between 300°C and 500°C. Following mixtures were annealed:

CuCl_2 : graphite, soot, fullerenes (mixture of $\text{C}_{60}+5\%\text{C}_{70}$), wood, activated charcoal;

FeCl_3 : activated charcoal;

AlCl_3 : graphite, soot, lignite (opencast mine Schleenhain, Saxony), wood, activated charcoal.

The treated mixtures and the content of the washing bottle were analyzed for PCDD/F, PCB, PCBz and PCPh. After a 48h soxhlet extraction an aliquot of the extract was used for analyses of PCBz and PCPh without further clean-up. For the determination of PCDD/F and PCB the remaining extract was subjected to column chromatography (alumina, silica, acid/base silica).

The GC/MS measurements were performed with a HP 5890 GC / HP 5971 MSD. A DB5ms (30m x 0.25mm x 0.25 μm) and a RTX 2330 (60m x 0.25mm x 0.1 μm) were used as capillary columns.

Results and Discussion:

Carbon matrices:

The thermal treatment with AlCl_3 and different carbon sources doesn't lead to a unique homologue and isomer distribution. If a matrix with a graphitic structure is used none/only a few hepta- and octachlorinated dioxins and furans could be detected whereas the existence of incorporated oxygen containing groups in the carbon matrix leads to a completely different isomer pattern. A dominance of the so-called „2,6“ - PCDD isomers was observed which is known to be the result of a gas phase condensation of chlorophenols. This isomer pattern is more emphasized in the reaction with activated charcoal but also to be found in reactions with lignite and wood. A possible explanation for that phenomenon may be the release of (chloro)-phenol molecules during thermal degradation of these matrices. It can be assumed that AlCl_3 catalyses the condensation of chlorophenols similar to a mechanism proposed by Voncina /6/. Other chlorinated compounds (PCB, PCBz, PCPh) show a tendency to lower chlorinated congeners.

During thermal treatment with CuCl_2 mainly higher chlorinated congeners are formed. That may be explained by a preferred chlorination of the carbon surface followed by a release of the chlororganic compounds and subsequent dechlorination of the higher chlorinated congeners. But in addition a similar mechanism to that of AlCl_3 cannot be excluded because in short-time

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experiments (5min) as well as in experiments with a low Cu - concentration a domination of the „2,6“ - PCDD was observed. These isomers were destructed with increasing annealing time and Cu - concentration. These findings are in agreement with similiar results published in literature /7,8/.

The analysis of PCB, PCBz and PCPh shows again a preference of higher chlorinated congeners.

Temperature:

The influence of temperature was studied while annealing activated charcoal and soot with CuCl_2 at 300°C and 500°C. It is known that the process of oxidative degradation is accompanied by the formation of PCDD/F /9/. It was observed that the oxidative degradation of activated charcoal occurs at 300°C whereas the degradation of soot is shifted to higher temperatures. The higher thermal stability of soot may be the reason for that.

Metal catalysts:

It could be proved that CuCl_2 is the strongest catalyst of the de-novo-synthesis. But also the influence of AlCl_3 on oxygen containing matrices cannot be ignored. A comparison of the isomer profiles points to similiarities and differences in the activity of the single catalysts during formation of furans and dioxins. While the isomer profiles of dioxins in the reactions of CuCl_2 and FeCl_3 correlate well the isomer distribution of furans in the reactions of AlCl_3 and CuCl_2 shows a good agreement. These observations can only be explained by a different mechanism of activity of the single catalysts concerning dioxins and furans.

Summary and Conclusions:

An attempt was made to distinguish between various effects that can occur during thermal processes.

It could be shown that the type of carbon matrix and different catalysts influence the isomer distribution as well as the homologue profile considerably. AlCl_3 can act as a catalyst in the condensation of (chloro)phenols. The release of these precursor compounds and also the release of chlorinated dioxins and furans is a function of temperature and matrix. The temperature optimum of the de-novo-synthesis is also related to the carbon matrix.

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