

## On the Dual Role of Metal Catalysts in the De-novo-Synthesis of Organochlorine Compounds on Fly Ash from Municipal Waste Incinerators

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### 1. Introduction

The formation of polychlorinated dibenzodioxins (PCDD) and -dibenzofurans (PCDF) on fly ash in the temperature range between 250 and 400°C has been recognized as a relevant source in municipal waste incineration. Detailed investigations of the influence of different parameters were carried out by a series of research groups on the mechanism of the reaction and its significance for the incineration process. The state of the art has been reviewed recently <sup>1)</sup>. Besides chlorophenols <sup>2)</sup>, according to our investigations residual carbon of the fly ash reacts as precursor material with inorganic chloride, leading to the production of substantial concentrations of PCDD/PCDF. It could be proven experimentally that metal ions in the ash, primarily Cu<sup>2+</sup> ions, but also Fe<sup>3+</sup>, were an important partner acting apparently as catalyst. For the elucidation of the mechanism fly ash as well as model mixtures with different compositions were used. It could be established that the reaction is not restricted to the synthesis of PCDD/PCDF but that also a great variety of other aromatic chlorocompounds is formed such as chlorobenzenes, -phenols, -biphenyls, -naphthalenes etc., including mixed chloro-bromo- and polybromospecies. <sup>3,4)</sup> Based on experimental evidence the de-novo-synthesis was postulated to proceed in two steps: the transfer of chloride (halide) to the macromolecular structure of the residual carbon, catalyzed by metal ions, e.g. Cu<sup>2+</sup>, followed by an oxidative degradation of the carbon, primarily to CO<sub>2</sub>, with the release of aromatic halogen compounds as side products at a yield of 10<sup>-3</sup> to 10<sup>-4</sup> relative to carbon oxidized. <sup>5)</sup> Also in this step the catalytic action of metal ions is relevant; by the presence of metal ions the oxidation temperature of the carbon, normally around 500°C, is decreased to the low temperature range of ca. 300°C. <sup>6,7)</sup> Since the two steps are completely different chemical reactions, also different metal ions may be involved in the individual steps. In order to differentiate the two reactions, experiments were performed in nitrogen and in air separately. An attempt was made to correlate the formation of total organochlorine with the change of the valency of copper, and the release of organochlorine compounds with the oxidation step.

### 2. Experimental

Model mixtures were prepared to contain 4.4% CuCl<sub>2</sub>·2H<sub>2</sub>O, 4.4%KCl, and 3.5% charcoal (Merck). The samples were heated in a vertical quartz tube on a frit in an upward gas stream with a flow of 50 ml/min., corresponding to a velocity of 10.2 cm/min. The gas stream was passed through two washing bottles in series containing toluene. Further details are described elsewhere. <sup>7)</sup> For the differentiation of the chlorination and oxidation process the sample was first annealed in nitrogen for a specific time, then cooled down under nitrogen. Ca. 50% of the sample was withdrawn from the apparatus for

# SOUR I

analysis, and stored under nitrogen. The remaining fraction was heated in an airstream (50 ml/min), containing 150 mg water/l. The experimental parameters for the two steps (gas phase composition, temperature, reaction time) are included in the results in table I.

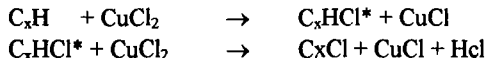
The annealed residue and the content of the washing bottle was analyzed for PCDD/PCDF, chlorobenzenes and chlorophenols by standard GC-MS procedures. Additionally the concentration of total organic carbon (TOC) was determined using a Ströhlein analyzer (C-MAT 550 C). The total organic chlorine (TOCl) was determined using a modification of AOX-procedure, as described in <sup>8)</sup>. The thermal behaviour of the annealed samples was investigated by differential scanning analysis (DSC 404, Fa. Netzsch) in the temperature range from 20 to 700°C at a heating rate of 4°C/min. as described in <sup>6)</sup>.

XPS-measurements: The concentration of the Cu<sup>2+</sup> species was determined by X-ray photo-spectroscopy using an ESCA spectrometer PHI5600ci. (Al K, Xray). In order to overcome electrostatic effect on the surface a beam of low energy electrons (0.1 eV) was applied. Due to the peak broadening a separate determination of Cu<sup>+</sup> and Cu<sup>2+</sup> was not possible. Therefore the rest concentration of the Cu<sup>2+</sup> species was measured via the shake-up lines, allowing a clear identification of the chemical state of the element and its concentration.

### 3. Results and Discussion

From the number of experiments only a fraction of the data is given and discussed here. It is demonstrated that with the designed experiments the two reaction steps may be differentiated:

a.) Transfer of Chloride with the Formation of C-Cl-Bonds: As discussed earlier <sup>5)</sup> in the transfer of chloride via the catalytic action of copper(II) the metal species is a reduced according:



where C<sub>x</sub>H stands for the residual carbon. For the formation of one C-Cl bond two CuCl<sub>2</sub> are needed. In this reaction Cu(II) is converted to Cu(I). The molar ratio of Cu<sup>2+</sup> /C is ca. 1/10 and so sufficiently high to produce a measureable yield of organic chlorine if carried out in nitrogen. Correlated with this a decrease of the Cu<sup>2+</sup> concentration must be within the range of detection. Since with this step no oxidative degradation occurs no change of the concentration of the organic carbon should be expected and the release of volatile organochlorine compounds to be low. Data from the experiments in nitrogen are presented in table I, marked as the experiments with „A“.

The carbon concentrations in the thermally treated samples were found to in the range of 3.5 to 3.9 % indicating that no oxidation did occur. The blank value for the total organic chlorine in the original mixture was 80 µg/g. By the thermal treatment at 300°C a concentration of ca. 300 µg/g TOCl was produced already during the first 20 min. No further increase could be achieved by longer reaction times. So the transfer of chloride seems to proceed fast

The concentrations of the PCDD vary between 20 and 70 ng/g, those of the PCDF are in the range of 300 ng/g, whereas the chlorobenzenes approach concentrations of 3000 to 4700 µg/g. These relatively low concentrations are probably blank values, considering the concentrations after annealing in air (see below).

The results of the XPS measurements are presented in fig. 1. Shown are the peaks for the Cu<sub>2p</sub>3/2 lines and the shake-up lines. The untreated model mixture with 4.4% CuCl<sub>2</sub> is represented by spectrum (1). The spectrum after the thermal treatment in nitrogen is (1A). The quantitative evaluation of the two peak areas of the shake-up lines indicates that the Cu<sup>2+</sup> concentration decreased to 1,45%, i.e. only 33% of the initial Cu<sup>2+</sup> concentration is left after the annealing in nitrogen.

Table 1. Data from the annealing of model mixtures in nitrogen (experiments A), followed by oxidation in air (experiments B)

sample #	gas phase	temp. °C	time min.	concentration				
				TOCl µg/g	PCDD ng/g	PCDF ng/g	PCIBz ng/g	PCIPh ng/g
3A	N <sub>2</sub>	300	20	315	19	290	2300	1300
3B	air	300	60	990	23800	38100	103000	1100
4A	N <sub>2</sub>	300	40	290	67	330	2800	1100
4B	air	300	60	920	25300	38000	42000	960
1A	N <sub>2</sub>	300	60	320	20	300	2900	590
1B	air	300	60	750	34000	43300	152000	1100
5A	N <sub>2</sub>	250	60	200	20	77	860	1200
5B	air	300	60	980	14000	21000	40000	950
2A	N <sub>2</sub>	350	60	330	40	200	4700	400
2B	air	350	60	250	27000	65300	95000	450

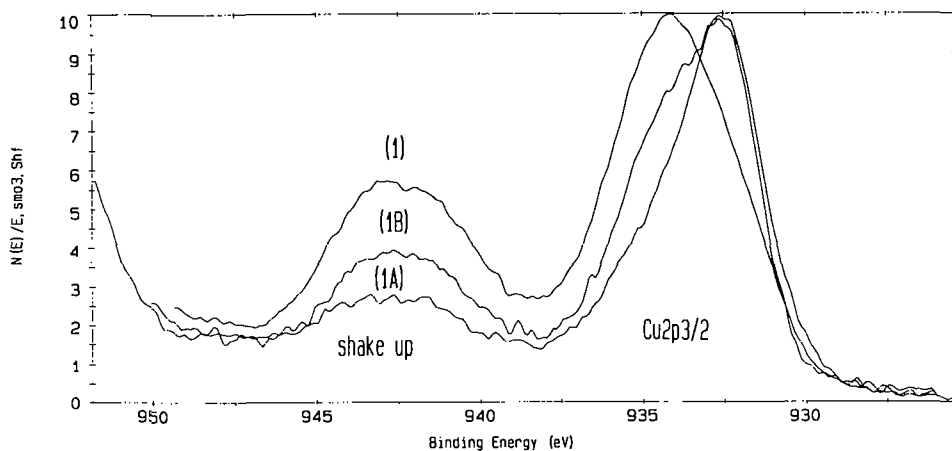


Fig. 1: XPS-spectra of the Cu species in the annealed samples. (1) initial mixture, (1A) sample after treatment in nitrogen at 300°C, (1B) sample after additional oxidation at 300°C in air.

### b.) Oxidation of the pretreated samples in air.

After the initial thermal treatment in nitrogen, the samples were heated in air at 300°C, with the exception of sample 2 which was annealed at 350°C. The data are given in table 1. The experiments are marked with B. The annealing results in a decrease of the organic carbon to less than 0.5%. The samples exhibit a color change from dark gray/black to whitish-yellow.

The nitrogen annealed specimen were also investigated by differential scanning calorimetry. The results are presented in fig. 2., including the measurement of the original model mixture. The model mixture is characterized by two exothermal peaks at 300 and 387 °C indicating the oxidation of the carbon species. Charcoal as itself without metal additives has a peak temperature of ca 500°C. The

# SOUR I

presence of 4.4% copper chloride leads to a decrease to 300°C. This has been demonstrated earlier<sup>6,7)</sup>. The additional thermal treatment in nitrogen results in a further decrease of the peak temperature to 255°C, with an on-set temperature as low as ca. 200°C. This effect is independent on the temperature of the preceding treatment (300-350°C).

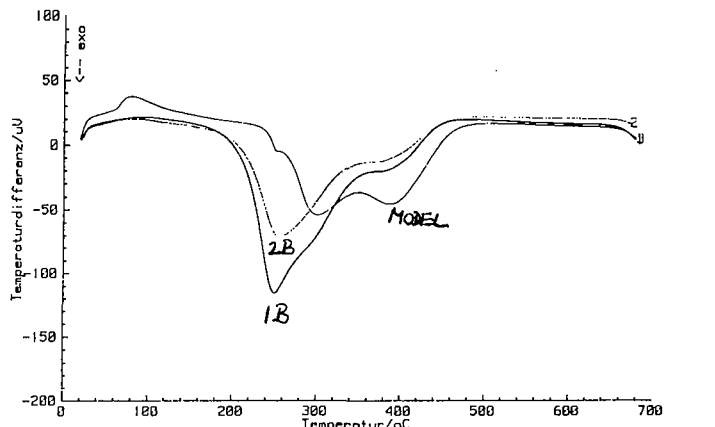


Fig.: 2 Differential scanning calorimetry measurements of the model mixtures pretreated at 300 and 350°C in nitrogen

In summary the following facts are noteworthy:

- After the heating in nitrogen the total organic chlorine of the sample was increased from 80 μg/g (blank) to ca. 300 μg/g. The additional thermal treatment results in concentrations of 800-900 μg/g TOX. Apparently the formation of C-Cl bonds in nitrogen was interrupted due to the deficiency of Cu(II). On annealing in air the Cu(I) species was again oxidized. This is obvious from fig 1, where the intensity of the shake up line for Cu<sup>2+</sup> (1B) is increased compared to (1A). So the Cu<sup>2+</sup> could further participate in the chloride transfer. The quantitative evaluation shows that the Cu<sup>2+</sup> species increased to 66%, relative to the initial concentration. This fact demonstrates the necessity of the metal catalyst to undergo redox reactions in order to be restored again in its activity to promote the chloride transfer. This in analogy to reactions quite known in organic chemistry, as summarized by D.C. Nonhebel<sup>9)</sup>: Under heterogeneous conditions copper halides react with aromatic compounds such as benzenes, chlorobenzenes, phenols, anthracen to give the corresponding halogen compounds. For the reaction it is essential that solid copper halide is present. It is concluded that the aromatic system is complexed at the surface of the copper(II) halide.
- Additional investigations with Cu(II)-smectite demonstrated that with aromatic compounds radical cations of the aromatic species are formed by single electron transfer to the metal cation. Electron spin resonance, infra red-, ultraviolet-visible- and resonance Raman spectroscopic studies demonstrated the intervention of aromatic molecules as intermediates in these reactions;<sup>10)</sup> the only difference to our system is the macromolecular structure of the educt.:
- The oxidative treatment at 300°C leads to a burst of polychlorinated aromatics: PCDD are released in quantities of 24 to 34 μg/g, the corresponding PCDF range from 38 to 43 μg/g. The major congener groups with the PCDD are the OCDD (81%), H7CDD (17%), with the PCDF the OCDF present ca 70% and the H7CDF ca 20% of the sum. Tetra- and pentachloro species are found in fractions < 5%. The polychloro benzenes are even in the range from 40 to 150 μg/g, whereas the concentrations of chlorophenols resemble rather those of the sample treated in nitrogen.

## 4. Conclusions

Attempts were made to differentiate the reaction steps important for the de-novo-synthesis of organochlorine compounds on fly ash, viz. the transfer of chloride to the carbon structure and the oxidative degradation followed by the release of volatiles.

The catalytic action of Cu(II) in the system Mg-silicate-KCl-carbon involves two processes

- the transfer of chloride to the carbon macrostructure with the formation of carbon-chlorine bonds. In this step the aromatic system reacts with Cu(II)Cl<sub>2</sub> with the transfer of halogen to the aromatic structure and formation of a radical. In the next stage breaking of a C-H bond occurs, followed by loss of hydrogen halide. In this process another CuCl<sub>2</sub> is involved. The result is the reduction of two molecules of CuCl<sub>2</sub> with formation of Cu(I). Under inert conditions with the depletion of Cu(II) the reaction stops, depending on the ratio Cu(II)/carbon. For the reaction to continue, Cu(I) must be oxidized and fed back into the redox process.
- the oxidative degradation of the carbon structure: For the release of chlorinated aromatic structures the oxidative break-down of the macrostructure to volatile compounds is essential. By the presence of metal ions the oxidation temperature is decreased from ca. 500°C to the range of 250-350°C. The efficiency of different metals in this process is different. Cu(II), especially Cu(II)halides, are the most potent catalysts.
- The proposed mechanism in which the metal ions exhibit a dual role must be extended to include other species such as Fe(III). With respect to fly ash with its unique composition, also a combination of different metal species may be considered.
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## 5. References

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