Fly Ash of MWI as a Reagent and Catalyst for the Formation of Micropollutants: Oxidation of Particulate Carbon Monitored by Simultaneous Thermal Analysis-Mass Spectrometry and Differential Scanning Calorimetry

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Introduction

Fly ash of municipal waste incinerators (MWI) has been shown to act as a reagent as well as a catalyst in formation and destruction of halogenated micropollutants like PCDD/F in the temperature range of 300 - 500°C. Fly ash has been shown to act as an efficient chlorinating agent of aromatic compounds (1), adsorbed chlorophenols are transferred into PCDD by Ullmann type reactions (2) and stereoselective bromine/chlorine exchange reactions have been observed (3). De-novo synthesis of PCDD/F from fly ash particulate carbon have been studied in detail (4). The destruction of adsorbed PCDD/F at higher temperatures by the activity of this matrix is now used as a detoxification method (5).

These heterogenous reactions are generally studied by methods of trace analysis. Recently we have applied a method of surface FTIR-spectroscopy to follow the reaction of bromobenzene with Cu as a model for PCDD formation (6). Now we have applied the methods of thermal analysis (TA) (7) such as differential scanning calorimetry (DSC) and thermal analysis/mass spectrometry (TA/MS) to follow some of the known reactions. In the following we will describe the reaction of particulate carbon in the temperature range of 300 - 500°C in air.

Experimental

The simultaneous TA/MS analysis system consists of a Netzsch STA 429 and a Balzers QMG 420 quadrupole mass spectrometer. Two specially arranged ceramic tubes were used to achieve the pressure drop from ambient pressure to high vacuum, to permit the simultaneous recording of the mass spectra (8). The heating rate applied was 10 K/min in air atmosphere.

The DSC measurements were performed with a Netzsch DSC 200 Differential Scanning Calorimeter in air atmosphere. The applied heating rate was 10 K/min, the measuring range from 30 - 510°C. Oxidized fly ash without carbon was used as a reference material.

Fly ash was taken from a MWI plant of Munich North. It was purified from organic contaminates by extraction with toluene in a Soxhlet apparatus. It contained the standard composition of the elements with a particulate carbon content of 1-2%. Charcoal DeguSorb A and soot 101 both from Degussa were used.

Results and Discussion

The effect of oxidative processes of the particulate carbon as a part of fly ash has been studied by addition of charcoal and soot.

The DSC-curve of fly ash is shown in Fig. 1.

The peak at 100°C can be explained by the evaporation of water from the fly ash. The second peak at 420°C is due to the oxidation of the fly ash particulate carbon in the presence of air.
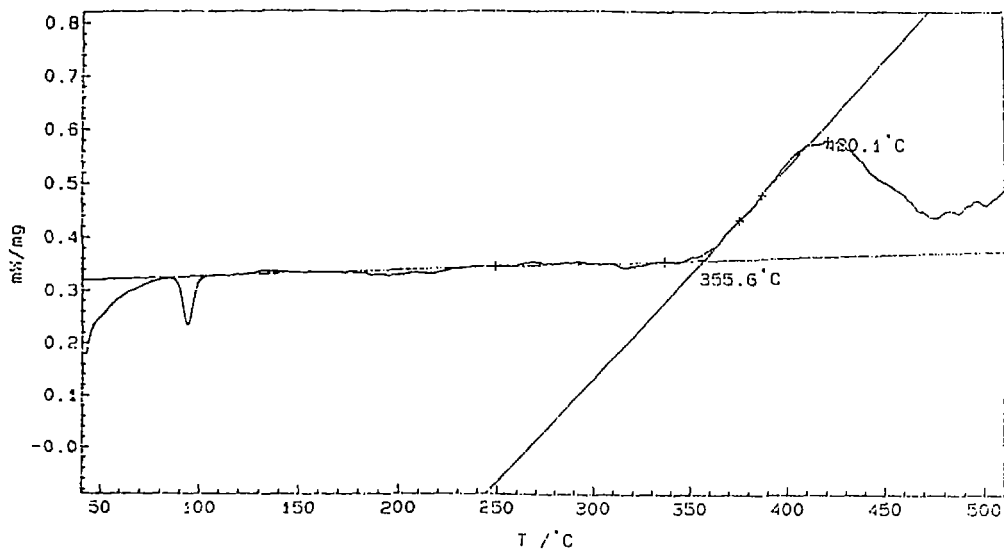

Fig. 1. DSC-curve for purified fly ash

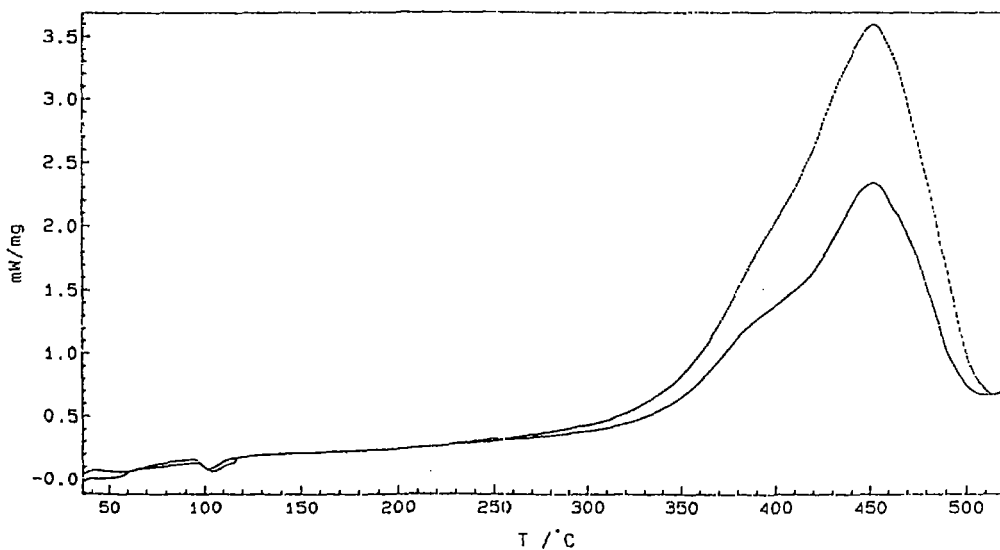The effect of addition of carbon as charcoal is shown in Fig. 2.

Fig. 2. DSC curves for fly ash with 5 and 10 % added charcoal, respectively

Fig. 2 shows two oxidation peaks for fly ash with 5% charcoal at 450°C and 10% charcoal at 458°C, respectively. For pure charcoal we observed the oxidation peak at 500°C.

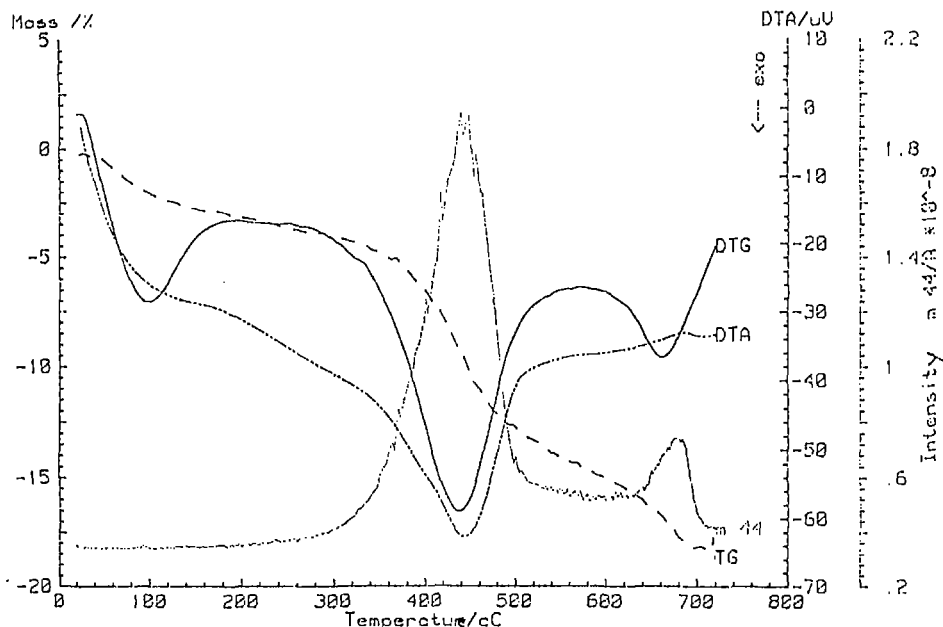The results of TA/MS measurement of fly ash with 5% charcoal are shown in Fig. 3.

Fig. 3 . Thermal analysis curves for fly ash with 5% charcoal and the total ion current intensity of CO_2 (m/z=44)

The first DTG-peak at 100°C is due to loss of water from the fly ash. The DTA-curve shows at 450°C an exothermic effect corresponding to a weight loss shown in the DTG-curve. At the same temperature we observe an emission of CO_2 (m/z=44). This is confirming our finding from the DSC-analysis (Fig. 2), that charcoal is oxidized at 450°C in the presence of fly ash. At 680°C occurs a further oxidation process leading to CO_2 emission. This peak has been observed at the STA/MS-analysis of pure charcoal too.

The results of DSC and TA/MS measurements are summarized in Table 1 and 2.

Table 1: DSC values for the investigated materials

	T_o (°C)	T_p (°C)
fly ash	362 *	425 *
charcoal	431 *	500 *
fly ash with 5% charcoal	338 *	450 *
fly ash with 10% charcoal	355 *	458 *
fly ash with 10% soot	486	> 500
soot	> 500	> 500

	T_0(°C)	T_p(°C)
silica with 5% charcoal	424 *	503 *
silica with 5% CuCl$_2$ and 5% charcoal	-------	434 *

T_0 - extrapolated onset temperature (9)   * - average value of 3 measurements
T_p - maximum peak temperature

Table 2: TA/MS values for the investigated materials

TA/MS			
	T_0 (CO$_2$-curve)	T_p (CO$_2$-curve)	T_0 (DTA)
fly ash	313°C	425°C	434°C
charcoal	408°C	492°C	491°C
fly ash with 5% charcoal	330°C	445°C	446°C
fly ash with 10% charcoal	341°C	445°C	445°C
fly ash with 10% soot	459°C	507°C	509°C
Soot	539°C	644°C	647°C
silica with 5% charcoal	410°C	500°C	495°C
silica with 5% CuCl$_2$ and 5% charcoal	260°C	405°C	380°C

The two modifications of particulate carbon, charcoal and soot, show a distinct different thermal behaviour. Charcaol is much easier to oxidize than soot. Under these conditions pure graphite shows no thermal effect: no oxidation is observed until a temperature of 800°C. The presence of fly ash has a dramatic effect on the thermal behaviour of charcoal and soot: the oxidation of these materials occurs at a temperature nearly 100°C lower compared to pure materials demonstrating the catalytic activity cf this matrix. An analogous effect can be observed at the presence of copper (II) chloride. A similar study of the reactions of aryl halide on fly ash is under way.

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