

DSC AND TA/MS STUDIES ON FORMATION AND DECOMPOSITION OF POLYCHLORINATED DIBENZO-*p*-DIOXINES AND DIBENZOFURANES
Fly ash as reagent and catalyst; oxidation of particulate carbon

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The effect of oxydation of particulate carbon as a part of fly ash has been studied by mean of differential scanning calorimetry (DSC) and simultaneous thermal analysis/mass spectrometry (TA/MS). The results from different carbon modifications added to fly ash were discussed and compared to those of the pure samples.

Keywords: catalyst, DSC, fly ash, oxidation of particulate carbon, polychlorinated dibenzo-*p*-dioxines and dibenzo-furanes, TA/MS

Introduction

Fly ash of municipal waste incinerators (MWI) has been shown to act as a reagent and catalyst in formation and decomposition of halogenated micropollutants like PCDD and PCDF in the temperature range of 300^o to 500^oC. These heterogeneous reactions are generally studied by methods of surface- and trace analysis. Recently we have applied differential scanning calorimetry (DSC) and simultaneous thermal analysis/mass spectrometry (TA/MS) to follow some of the known reactions. In the following the reaction of particulate carbon in the temperature range up to 500^oC in air is described.

Results and discussion

The effect of oxidation of particulate carbon as a part of fly ash has been studied by addition of charcoal and soot. As it can be seen from the DSC curves of fly ash with 5 and 10% charcoal added (Fig. 1), the oxidation of charcoal occurs at about 450° to 460°C (T_p).

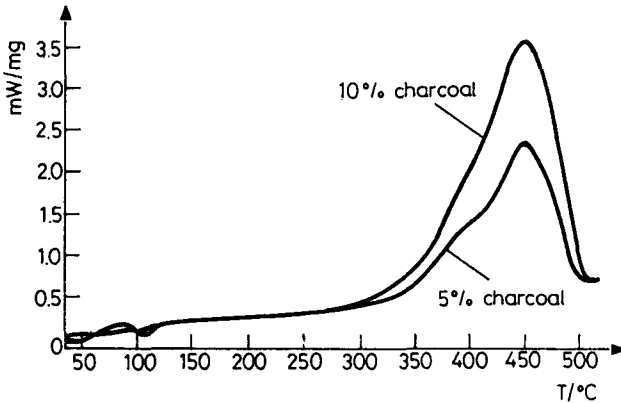


Fig. 1 DSC curves of fly ash with 5 and 10% charcoal added

The TA/MS measurement of fly ash with 5% charcoal added (Fig. 2) shows a first weight loss at about 100°C (DTG-peak) due to the loss of moisture from the fly ash. The second weight loss with the DTG-peak at about 450°C is related to a strong exothermic effect (DTA-peak at 450°C). From the simultaneous mass spectrometric investigations we observe an emission of CO₂ (m/z 44) at the same

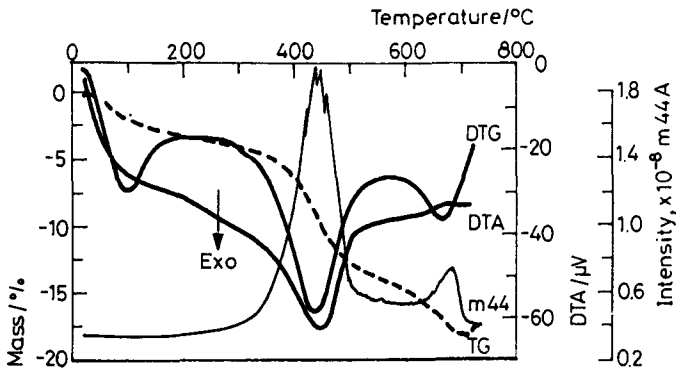


Fig. 2 Thermal analysis and CO₂ emission curves from fly ash with 5% charcoal added

temperature. This is confirming our results from DSC analysis. Charcoal is oxidised at about 450°C in the presence of fly ash. The results (T_e : extrapolated onset, T_p : maximum peak temperature) of the TA/MS measurements of all sample (charcoal and soot) are listed in Table 1.

Table 1 TA/MS values of the investigated samples

| Samples | T_e (CO ₂ curve) | T_p (CO ₂ curve) | T_e (DTA) |
|--|-------------------------------|-------------------------------|-------------|
| | | | |
| fly ash | 313 | 425 | 434 |
| charcoal | 408 | 492 | 491 |
| soot | 539 | 644 | 647 |
| fly ash with 5% charcoal | 330 | 445 | 446 |
| fly ash with 10% charcoal | 341 | 445 | 445 |
| fly ash with 10% soot | 459 | 507 | 509 |
| silica with 5% charcoal | 410 | 500 | 495 |
| silica with 5% CuCl ₂ , 5% charcoal | 260 | 405 | 380 |

Conclusions

The two modifications of particulate carbon, charcoal and soot, show a different thermal behaviour. Charcoal is much easier to oxidize than soot. Under the same conditions pure graphite will not be oxidized up to a temperature of 800°C. The presence of fly ash has a drastic effect on the thermal behaviour of charcoal and soot. The oxidation occurs at nearly 100°C lower, compared with the pure samples (Table 1). This demonstrates the catalytic effect of the matrix 'fly ash'.

An analogous effect can be observed at the presence of copper(II) chloride as a model of fly ash.

Zusammenfassung — Mittels DSC und Thermoanalyse/Massenspektrometrie wurde der Effekt der Oxidation von Kohlenstoff als Teil von Flugasche untersucht. Die durch Zusatz verschiedener Kohlenstoffarten zu Flugasche erhaltenen Ergebnisse wurden diskutiert und mit denen von reinen Proben verglichen.