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Fuels

A STUDY OF COAL-METAL COMPLEXES BY THERMAL ANALYSIS

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Coal-metal complexes obtained by dynamic sorption of cations from water solution on sulphonated and oxidized coals. Complexes with the following cations were produced: Mg, Ca, Zn, Cd, Ba, Cr, Fe, Co, Ni, Cu, Pb and Ag. DTA curves of sulphonated coal and sulphonated coal-metal complexes are distinct and can be divided into three groups on the basis of shape and peak temperatures, the main influence being the type of chemical bondbetween metal cation and functional group of the coal. For metal complexes with oxidized coal the main exothermic peak shifts either to higher of lower temperatures, depending on the nature of the cations. The presence of metal chemically bound to carboxylic- and sulpho-groups of the coal causes additional thermal effects to appear on the DTA curves.

Keywords: coal-metal complexes

Introduction

Brown coals sulphonated with sulphuric acid or oxidized with nitric acid show very different ion-exchange properties in relation to metal ion [1–3]. Thermal investigations on organic-mineral complexes extracted from soil have proved that metal ions affect temperature and shape of the main exothermic peak at about 300°C related to decomposition of the organic material [3–4].

The aim of this study was to investigate the effect of metal ions present in organic-metal complexes on the thermal decomposition of the organic substance brown coal.

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Experimental

Thermal analysis was carried out on organic-metal complexes resulting from dynamic sorption from water solution of twelve cations on sulphonated and oxidized coals. The original earthy brown coal was sulphonated with concentrated sulphuric acid at 90°C or oxidized with 30% nitric acid at ambient temperature. After sorption the modified coals were washed with distilled water to remove excess salt. Thermal analyses were carried out using a derivatograph (MOM Hungary) at a heating rate of 10 deg·min^{-1}.

Results

Table 1 shows metal contents of the metal-organic complexes produced. The different amounts of metal ions in the metal-organic complexes is a function of differences in chemical affinity between the metal cations and the modified brown coal. The metal ions are bound chemically with functional groups, mainly the carboxylic and sulphonic groups.

DTA curves of the metal-organic complexes obtained from sulphonated brown coal differ significantly from the DTA curve of the metal-free sulphonated brown coal (Figs 1 and 2). There is, however a marked similarity between DTA curves of particular groups of metal-organic complexes, for example in the temperature range 200°–700°C the metal-organic complexes ES–Ca, ES–Zn, ES–Cd, ES–Pb and ES–Ba give similar DTA curves. In this temperature range, a broad exothermic effect with large peaks at 370°–410°C and 500°–520°C can be observed. These two exothermic peaks are separated by a small endothermic effect with a minimum at 470°C. On the DTA curves of ES–Ca and ES–Ba complexes, an additional small endothermic peak at 680°C is present, and at higher temperatures a further large endothermic peak at 850°C for the ES–Ca complex and a smaller peak at 930°C for the ES–Ba sample can be observed. These latter two endotherms are due to decomposition of $CaCO_3$ and $BaCO_3$, respectively. On the DTA curve of the ES–Mg complex there are two exothermic peaks at 410° and 570°C for which no explanation can be given at present.

There is a marked similarity between DTA curves of complexes of sulphonated brown coals with metal ions of group VIII B of the Periodic Tables i.e. Fe, Ni and Co. On DTA curves of these complexes two exothermic peaks are present with maxima at 400° and 460°–480°C for ES–Ni and ES–Co, and at 320° and 380°C for ES–Fe.

The third group of metal-organic complexes is composed of complexes of sulphonated brown coal with Cr^{3+}, Cu^{2+}, Hg^{2+} and Ag^{+}. The main exothermic effect is very broad with a maximum at 400°C (similar to the metal-free sulphonated brown coal). On the DTA curve of the ES–Ag complex an additional weak exothermic peak at 320°C occurs, and for the ES–Hg complex there is a weak exothermic peak at 280°C followed by an endothermic peak at 300°C connected with the thermal decomposition of the ES–Hg sample and evaporation of mercury. This is confirmed by the high weight loss.

Table 1 Charateristics of metal-organic complexes

Symbol of sample	Cation content of sample / $mg \cdot g^{-1}$	Mass loss to 1000°C from TG curves / wt%
ES	0.0	63.7
ES – Mg^{2+}	20.1	62.6
ES – Ca^{2+}	71.1	68.5
ES – Zn^{2+}	120.0	57.5
ES – Cd^{2+}	80.2	47.0
ES – Ba^{2+}	260.6	65.0
ES – Cr^{3+}	43.0	60.0
ES – Fe^{3+}	51.2	76.0
ES – Co^{2+}	52.6	68.9
ES – Ni^{2+}	41.0	63.8
ES – Cu^{2+}	94.0	59.2
ES – Pb^{2+}	331.0	57.0
ES – Ag^{+}	335.0	52.5
ES – Hg^{2+}	–	77.5
EO	0.0	72.5
EO – Mg^{2+}	19.3	66.0
EO – Ca^{2+}	72.0	75.1
EO – Zn^{2+}	119.1	62.5
EO – Cd^{2+}	95.0	68.7
EO – Ba^{2+}	240.1	60.0
EO – Cr^{3+}	27.8	68.7
EO – Fe^{3+}	48.1	76.3
EO – Co^{2+}	48.2	73.8
EO – Ni^{2+}	30.5	70.0
EO – Cu^{2+}	90.0	66.3
EO – Pb^{2+}	340.0	55.0
EO – Hg^{2+}	–	71.2

ES – sulphonated coals
EO – oxidized coals

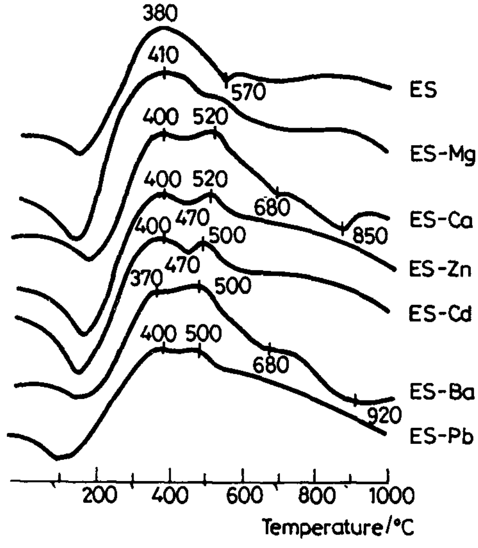

Fig. 1 DTA curves of sulphonated earthy brown coal and its coal – metal complexes

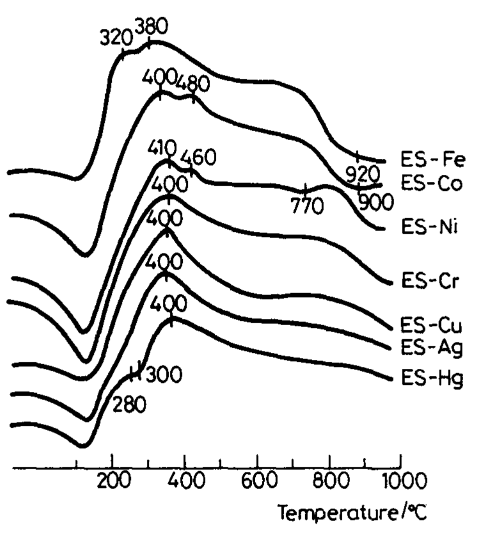

Fig. 2 DTA curves of sulphonated earthy brown coal – metal complexes

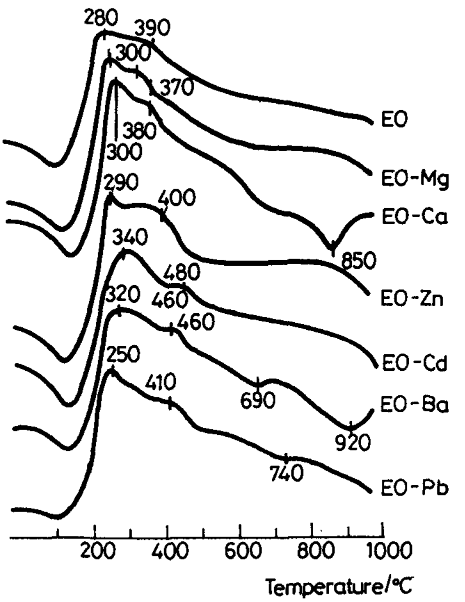

Fig. 3 DTA curves of oxidized earthy brown coal and its coal – metal complexes

Figures 3 and 4 show the DTA curves of metal-organic complexes produced from oxidized earthy brown coal. The first maximum at 280°C characteristic of oxidized brown coal is shifted either to higher or lower temperatures depending on the type of cation, the range being between 250° and 340°C. For the complexes EO–Mg, EO–Ca, EO–Zn, EO–Cd, EO–Ba and EO–Cr this peak either remains at 280°C or shifts lower temperatures. The second peak of the exothermic effect of uncomplexed oxidized coal is weak, but is stronger for the metal-organic complexes. The range of movement for this peak is 360° and 480°C, the biggest shift being for EO–Cd and EO–Ba. These latter complexes are also characterized by endothermic effects at 430° and 460°C. A large endothermic peak can be observed on DTA curves of complexes EO–Ca (850°C), EO–Ba (920°C), EO–Fe (920°C), EO–Co (940°C), EO–Ni (850°C) and EO–Pb (740°C). These effects are related to decomposition of metal carbonates. The DTA curve of EO–Cu is characterized by three maxima at 280°, 330° and 420°C. On the DTA curve of the EO–Hg complex an exothermic effect peaking at 260°C is followed by a weak endothermic peak. These peaks can not be explained at present. The DTA curve of the oxidized coal with three adsorbed cations, EO–Mg, Co, Ni, is very similar to the DTA curve of the EO–Co complex.

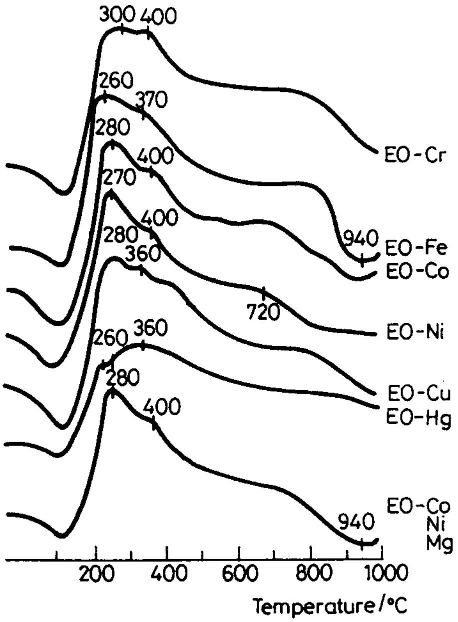

Fig. 4 DTA curves of oxidized earthy brown coal - metal complexes

Weight losses accompanying thermal decomposition of the metal-organic complexes up to 1000°C are generally lower by a number of per cent than weight losses of the metal-free oxidized or sulphonated coals, exceptions being the EO–Ca, EO–Fe, EO–Co, EO–Ni and EO–Hg complexes.

Conclusions

The presence of metals bound chemically to coal components through ion-exchanging functional groups results in the appearance of additional thermal effects on DTA curves. Peak maxima shift to both higher and lower temperatures.

The thermal decomposition of sulphonated coal is retarded by Mg^{2+}, Ca^{2+}, Ba^{2+}, Cd^{2+}, Zn^{2+}, Co^{2+} and Ni^{2+} whereas Cr^{3+}, Cu^{2+}, Hg^{2+} and Ag^{+} have a much less marked effect on thermal decomposition of the organic substance. Cd^{2+} and Ba^{2+} have a pronounced retarding effect on thermal decomposition of the organic substance of oxidized coal.

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Zusammenfassung — Eine Reihe von Kohle-Metall-Komplexen wurde durch dynamische Sorption von Kationen aus wäßrigen Lösungen an sulfonierten und oxidierten Kohlen dargestellt. Dabei wurden Komplexe mit den folgenden Kationen erzeugt: Mg, Ca, Zn, Cd, Be, Cr, Fe, Co, Ni, Cu, Pb und Ag. Die DTA-Kurven für sulfonierte Kohle und sulfonierte Kohle-Metall-Komplexe unterscheiden sich voneinander und können anhand des Kurvenverlaufes und der Peaktemperaturen drei Gruppen zugeordnet werden, wobei der größte Einfluß durch den Typ der chemischen Bindung zwischen Metallkation und den funktionellen Gruppen der Kohle ausgeübt wird. Für Metallkomplexe mit oxidierter Kohle verschiebt sich der größte exotherme Peak in Richtung höherer oder niedrigerer Temperaturen, in Abhängigkeit von der Art des Kations selbst. Die Gegenwart von Metall, welches an der Kohle chemisch über Carbonsäure- und Sulfogruppen gebunden ist, verursacht zusätzliche thermische Effekte, die sich in den DTA-Kurven wiederspiegeln.