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THERMAL DECOMPOSITION OF METAL-DOPED CARBONS

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Abstract

The effects of different concentrations of metals (Ni, Cu, Cd, Zn) on the reactivity of carbon towards air were studied by means of TG and DTA. It was observed that these metals are capable of decreasing the ignition temperature and increasing the mass loss. Activation energies calculated by Horowitz's method revealed that these metals promote the combustion of active carbon.

Keywords: combustion, metal-doped carbons, thermal study

Introduction

The combustion of carbonaceous materials is one of the most ancient chemical reactions utilized by mankind. The accelerating effects of impurities on the combustion have also been known for a long time. Most natural carbonaceous materials usually contain appreciable amounts of inorganic impurities, that generally increase, but occasionally decrease the reactivity of the carbon. During the past decade, analyses of kinetic measurements of the effects of different catalysts on the combustion of carbons have once again proliferated in the literature [1, 2]. The precise mechanisms of the catalysis of the oxidation of carbons and graphite remain unknown, due to their complex and extremely variable structures. Thermal analysis, and especially the combined application of TG and DTA, although an old technique, is now proving useful in interpretations of the individual steps involved in catalyzed gasification reactions [3–5]. Through measurement of the rate of evolution of the gaseous oxidation products when doped carbons are heated in oxygen at linearly increasing temperature, the activities of a range of catalytic additives can be compared and estimates of apparent activation energies can be obtained [6–8].

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Experimental

Active carbon was supplied by Merck (Calatog No. 2184). It was washed several times by immersion in distilled water until there was no change in the *pH*. The divalent metal chlorides used were supplied by Merck with purities better than 99%.

For doping of active carbon, a predetermined amount of metal chloride was magnetically stirred in 200 ml of distilled water, and 10 g of active carbon was added to the mixture. The mixture was stirred for 8 h at 373 K until a slurry was formed, which was then dried under vacuum at 353 K for 3 h. The dried samples were next heated at 735 K for 7 h under a nitrogen atmosphere. A blank carbon sample was also prepared by using the same treatment, except that distilled water was used in place of metal chloride solution.

For measurement of metal concentration, 1 g of the sample was thoroughly stirred with 0.1 *N* perchloric acid for 4 h at room temperature. The total amount of the metal in the solution was then determined by atomic absorption spectrophotometry (Zeiss, Model FMD 47).

The metal-doped carbon samples are designated by the formula M_x–C, where *M* stands for Ni, Cu, Cd and Zn and *x* represents the number of moles of metal per 100 g of active carbon.

The effect of temperature on the carbon samples was studied by using a Shimadzu thermal analyzer (TGA-31). A known amount of dehydrated powdered carbon sample was placed in a crucible and suspended in a quartz tube capable of controlling the atmosphere of gases inside the system. The sample was heated at a ramping rate of 10 deg·min^{-1} to a temperature of 600°C under a constant flow of air. For DTA measurements, weighed amounts (6.00 mg) of the dehydrated powder sample and of reference substance (inert alumina, Al_2O_3) were placed in two separate platinum cells and transferred onto the dumbbell-type detector. The sample and reference materials were then heated together, at a ramping rate of 10 deg·min^{-1} under a constant flow of air.

Results and discussion

In an attempt to unravel the mechanism of the catalytic process, the effects of metal chlorides on the reactivity of carbon towards air were studied by means of separate TG and DTA techniques under controlled conditions. The thermal analytical curves of dehydrated active carbon and carbon samples containing different concentrations of copper are given in Fig. 1. The TG measurements for active carbon show that the weight loss is initiated at around 250°C and accelerated in the temperature range 450–500°C. The TG curves for metal-doped carbons exhibit a similar single step of decomposition, which accelerated in the temperature range 420–460°C. From an analysis of the TG curves for metal-

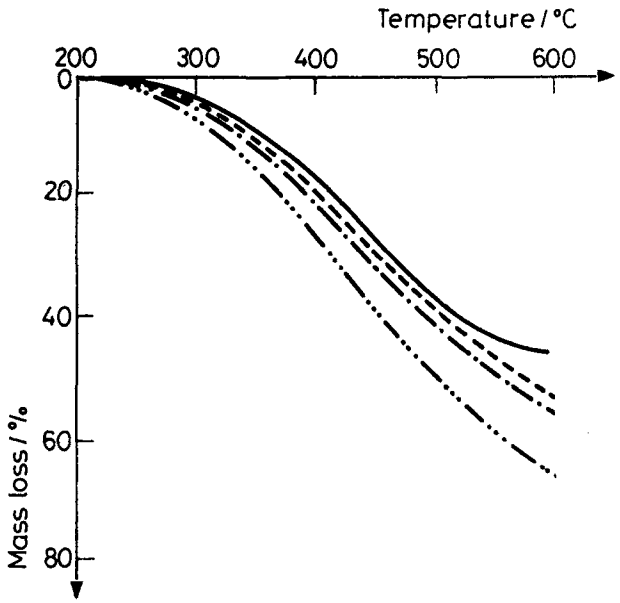

Fig. 1 TG curve for active carbon (—); $Cu_{0.0158}$-C (---); $Cu_{0.0291}$-C (—·—); $Cu_{0.0535}$-C (—·····)

Table 1 Thermal data for metal doped carbons

No.	Sample	Ignition temp./ °C	Weight loss/ %	Act. energy, *E*/ kJ·mol^{-1}	*P* (max)/ °C
1.	Carbon	252	43	86.1 ± 7.6	480
2.	$Ni_{0.0169}$–C	235	48	74.4 ± 5.1	482
3.	$Ni_{0.0348}$–C	225	51	69.6 ± 4.6	475
4.	$Ni_{0.0578}$–C	220	54	64.6 ± 4.1	468
5.	$Ni_{0.0775}$–C	217	57	55.4 ± 4.5	465
6.	$Cu_{0.0158}$–C	230	55	68.8 ± 6.8	472
7.	$Cu_{0.0291}$–C	224	59	59.3 ± 4.3	465
8.	$Cu_{0.0535}$–C	210	71	51.9 ± 6.5	440
9.	$Zn_{0.0149}$–C	240	45	76.5 ± 7.8	476
10.	$Zn_{0.0297}$–C	236	49	70.3 ± 7.4	473
11.	$Zn_{0.0532}$–C	226	53	66.5 ± 6.1	468
12.	$Cd_{0.0168}$–C	240	51	78.9 ± 6.7	477
13.	$Cd_{0.0295}$–C	235	55	69.4 ± 5.4	473
14.	$Cd_{0.0356}$–C	228	58	60.1 ± 6.8	467

doped carbons, it was observed that the transition metals used for doping increase the reactivity of carbon towards air and progressively decrease the ignition temperature at which the combustion of active carbon is initiated. The ignition temperature, the activation energy and the total mass loss are given in Table 1. From these data, it can be seen that the transition metals (Ni, Cu, Cd, Zn) are able to decrease the ignition temperature and increase the percentage loss in mass. For example, the ignition temperature of active carbon is 250°C, while for copper-doped carbons this value decreases with increase of the metal concentration in the carbon lattice. It was found that copper-doped carbon samples had an ignition temperature 20–40 deg lower than that of the parent active carbon. Similar behavior was observed for the (Ni, Cd and Zn systems, but these metals exhibit only modest catalytic effects on the carbon – air reactivity (Table 1).

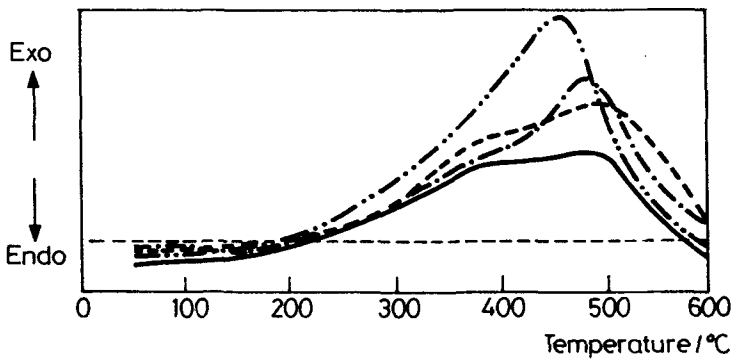

Fig. 2 DTA curves for active carbon (—); $Cu_{0.0158}$-C (---); $Cu_{0.0291}$-C (— — —); $Cu_{0.0535}$-C (—·—·—)

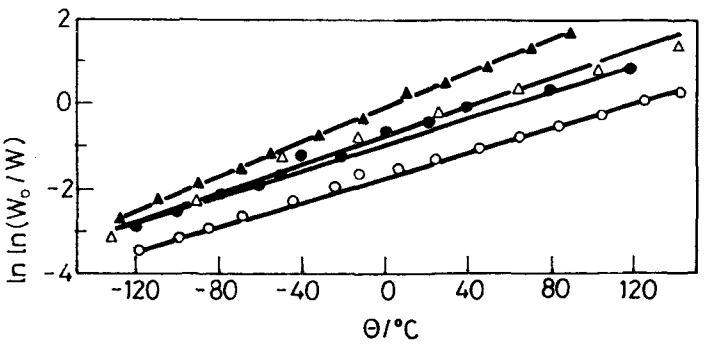

Fig. 3 Plots of ln ln W_0/W *vs.* θ for active carbon (▲); $Ni_{0.0169}$-C; (Δ) $Ni_{0.0348}$-C; (•) $Ni_{0.0578}$-C (o)

The effects of different amounts of metal on the combustion were also investigated by using DTA. DTA curves for active carbon and copper-doped carbons

are given in Fig. 2. It can be seen that the exotherm in the DTA curve of the original carbon sample changes its position and intensity with change of the metal concentration in the carbon lattice. Analysis of the data in Table 1 reveals that in the presence of transition metals, the temperature of the exothermic combustion reaction decreases. For example, in the case of active carbon, the main exotherm occurs at 480°C while for copper-doped carbons this temperature was 10–40 deg lower than that for the parent active carbon. Other systems also decrease the temperature, but the effect is not so pronounced.

Kinetic parameters were calculated in order to study the effects of metal doping on the thermal decomposition of carbon. The activation energy for the combustion of carbon was determined by the method of Horowitz *et al.* [9]. Plots of ln ln W_o/W *vs.* θ are given in Fig. 3, where W is the mass remaining, W_o is the initial mass and $\theta = (T-T_s)$. These plots yielded the straight lines from which the apparent energy of activation was calculated. The activation energy for the combustion of active carbon was found to be 86.1±7.6 kJ·mol^{-1}, which is in good agreement with the value observed by other workers [10, 11]. From the data, it can be seen that the values of activation energies for metal-doped carbons are apparently low; the catalytic effect of copper is highest, the other metals being relatively less active, as observed by Otto *et al.* [12]. They showed that additives such as Ni, Zn and K_2CO_3 had little effect on the activation energy for the combustion of either charcoal or graphite.

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Zusammenfassung — Mittels TG und DTA wurden die Einflüsse verschiedener Konzentrationen von Metallen (Ni, Cu, Cd, Zn) auf die Reaktivität von Kohlenstoff gegenüber Luft untersucht. Es wurde beobachtet, daß diese Metalle die Fähigkeit besitzen, die Zündungstemperatur herabzusetzen und den Gewichtsverlust zu erhöhen. Berechnungen der Aktivierungsenergien nach der Methode von Horowitz lassen erkennen, daß diese Metalle die Verbrennung von Aktivkohle fördern.