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In celebration of the 60^{th} birthday of Dr. Andrew K. Galwey

A THERMOANALYTICAL STUDY OF THE FORMATION AND ACTIVATION OF NOVEL COPPER-CARBON CATALYSTS

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Abstract

Simultaneous DSC-TG and DTA-TG were used to investigate the calatytic effect of the metal on the thermal decomposition of a cellulose matrix containing small copper particles. The techniques were also used to demonstrate the effect of the metal particles on the subsequent activation of the carbon matrix, a process which develops the pore structure necessary to expose the metal particles to the gas phase. Temperature programmed desorption was used to study the initial mass loss found on activation. To quantify the catalytic effect of the copper particles on the activation process an estimate was made of the activation energy of the catalysed and uncatalysed reactions. The work gives valuable information on the processes involved in the preparation of a new range of metal-carbon catalysts.

Keywords: catalysts, cellulose pyrolysis, DTA-TG, DSC-TG, kinetics, metal-carbon catalysts

Introduction

Metal-carbon catalysts find considerable industrial use. Traditional methods of preparation, which effectively result in the deposition of small metal particles in the pores of a pre-formed, high surface-area carbon, have certain limitations. Many of these disadvantages can be overcome by adopting a new preparative technique, the thermal decomposition of a novel copper(0) cellulose material which is prepared by the reduction of a copper(II) cellulose complex. The new catalysts contain a much higher metal loading which can be tailored to requirements. Furthermore, the metal can be exchanged, either completely, or partially, to give a wide variety of single or mixed metal-carbon catalysts [1].

The thermal decomposition of the copper(0) cellulose produces an array of small copper particles dispersed throughout a carbon matrix. The catalysts are

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made by activating the carbon component of the material to open up a pore structure which exposes the copper particles to the gas phase [2]. This is achieved by a mild oxidation treatment, similar to that used to manufacture activated charcoal, which involves heating in an atmosphere containing a controlled amount of water vapour. Both the thermal decomposition reactions and the subsequent activation process have been widely studied in pure cellulose, and are modified by the presence of additives. Our work shows that similar catalytic effects are found with the copper(0) cellulose materials. This is particularly important for two reasons. Firstly, the reduced temperature found in both processes limits the amount of sintering of the copper. Secondly, the copper facilitates the formation of the pore network which is important if the metal is to be accessible to the gas phase.

The two processes, decomposition of the precursor and activation of the product, are clearly vital to the production of the copper-carbon catalysts, and to the other catalyst systems derived from them [1]. A study of the catalytic role of copper in the preparation of these materials is therefore of considerable interest.

Review of previous work and its relation to the current research

Cellulose is made up of long chains of glucose units which exist in the cyclic form, and has an average relative molecular mass of ca. 500,000. It is generally accepted that the two main reactions in the pyrolysis of cellulose are:

a) dehydration at a temperature of about 520 K to give 'anhydrocellulose' and

b) depolymerisation to give 1,6-anhydro-β-D-Glucopyranose, (levoglucosan, Fig. 1) at temperatures above 520 K.

These reactions are to some extent competitive, although the dehydration is faster at low temperatures and the depolymerisation predominates at higher temperatures. Subsequent reactions include the decomposition of the anhydrocellulose to give a carbonaceous material and the breakdown of levoglucosan with the production of a complex mixture of volatile species.

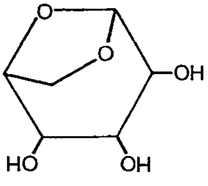

Fig. 1 Structure of levoglucosan

Several groups [3–6] have used thermal analysis to investigate the pyrolysis of cellulose. Dollimore and Hoath [3] concluded that the atmosphere, (air or nitrogen) had little effect on the decomposition itself, but the volatile products were oxidised in air, with flaming combustion. The main decomposition showed a mass loss beginning at 510 K, reaching a maximum rate at 590–630 K depending on the atmosphere used. They also showed [4] that up to a temperature of 530 K, few changes occurred, as monitored by infrared spectroscopy, but above this water was lost with a concomitant increase in unsaturated groups.

Jain *et al.* [5] studied the thermal degradation of cellulose, using DTA and TG, and attributed the DTA endotherm in nitrogen at 620–640 K to the formation of levoglucosan, water, carbon dioxide and carbon monoxide.

Kosik *et al.* [6] also found that, up to 520 K, the only volatile product was water, produced by the dehydration of the cellulose chain and that, at higher temperatures, depolymerisation occurred. TG and GC-MS were used to follow the reactions.

The processes involved in the formation of carbons by the thermal decomposition of cellulose can be influenced by the presence of suitable additives. For example, Tang and Eickner [7] and Brunner and Roberts [8] in their investigations of the decomposition of cellulose and the effect of catalysts on carbon yield concluded that dehydration catalysts such as Lewis acids and bases increased the dehydration rate of cellulose. At high temperatures, where normally depolymerisation would predominate, they found that the presence of the catalyst increased the relative rate of dehydration, leading to an increased car-bon yield. The stability of the dehydrated cellulose char (carbon) was attributed to the degree of aromaticity and conjugation which resulted from the increased loss of water due to the effects of the catalyst.

Tang and Neill [9] and Morterra and Low [10] investigated cellulose combustion in the presence of potassium hydrogen carbonate (a flame retardant). Tang and Neill showed that the combustion reaction was distributed over a wider temperature range with a correspondingly lower maximum intensity. Morterra and Low used IR spectroscopy to ascertain the temperature range at which the cellulose structure vanished, and showed that it was lower (500 K) than that obtained in the absence of the salt (580 K).

Kaur *et al.* [11] used TA and MS to study the thermal decomposition of cellulose phosphate-transition metal complexes. They found that the rates of dehydration and carbon formation were enhanced compared to those of cellulose itself. Furthermore, the formation of volatile products was reduced. It was suggested that in-situ formation of polyphosphoric acid, which is a dehydration catalyst, increased the amount of stable carbon formed.

The starting material used in our work is neither pure cellulose nor a simple physical mixture of a metal salt and cellulose. It is derived from a copper(II) cellulose complex which we believe has the structure shown in Fig. 2, where the copper(II) ions are complexed to deprotonated glucose units of different polysaccharide chains [1]. Reduction of these ions in-situ, using an alkaline hydrazine solution, yields small copper particles, of mean diameter 17 nm, dispersed throughout the bulk of a cellulose matrix. Accordingly, it is to be expected that a catalytic effect of the metal on the decomposition and activation processes will occur, but the effect may not be identical to that produced by simple additives.

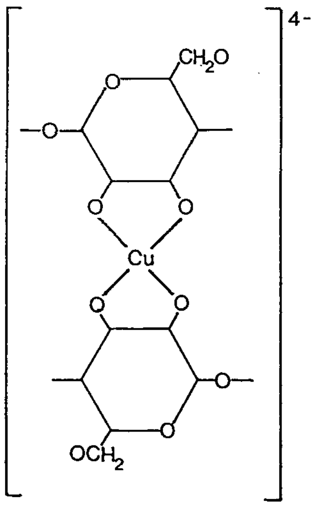

Fig. 2 Structure of the copper(II) complex with deprotonated cellulose

Kinetic studies: estimation of the effect of the copper as a catalyst on the activation energy of carbon gasification

This method relies on the determination of the reaction rate (rate of change of amount of reactant) from DTG curves. The normal DTG data, $(dw/dT)/T$, can be recalculated in terms of the rate of mass change with time against temperature, i.e. $(dw/dt)/T$, to give the rate of reaction directly, in arbitrary units, as a function of temperature. Furthermore, the analysis is simplified since, when comparing a reaction in the presence and absence of a catalyst, the same mechanism, and hence kinetic dependence, can be assumed.

There is a major problem which invalidates much of the work on kinetic analysis using rising temperature techniques. Unless stringent precautions are taken to reduce the temperature and concentration gradients across the sample, which arise from the dynamic nature of the technique, or to eliminate them by extrapolating to zero heating rate, the temperature of the sample and the gas phase composition are indeterminate. The problem is exacerbated in conventional TG because of the difficulties in measuring the sample temperature with a remote thermocouple. Even in simultaneous DSC-TG, where there is good thermal contact between the sample and the thermocouple, the temperature gradients between them can be sufficiently large to give temperature errors which can be significant, where kinetic analysis is concerned, unless rigorous calibration is undertaken. However, when establishing the effects of a catalyst, these factors will be similar for both materials, if run under identical conditions. Then, provided the values are accepted as relative, the effects of the catalyst can be quantified as outlined below.

It seems reasonable to assume that the reaction rates for carbon and for copper-carbon are dependent on the same function of the carbon 'concentration', $f(c)$, as essentially the same process is occurring in both samples. The rate equations for the two materials can be expressed as

$$\text{rate}_1 = k_1 f(c) \text{ and } \text{rate}_2 = k_2 f(c)$$

where k is the rate constant and $f(c)$ is the (unknown) function of the amount of reactant.

The temperature dependence of the rate constant is given by the Arrhenius equation

$$k = A\,\mathrm{e}^{-E/RT}$$

where A is the pre-exponential factor and E is the activation energy.

Combining these two expressions gives the general equation

$$\text{rate} = A\,\mathrm{e}^{-E/RT} \cdot f(c)$$

Applying this equation to the two processes and taking the natural logarithms gives

$$\ln(\text{rate}_1) = \ln A - E_1/RT + \ln f(c) \qquad \text{(i)}$$

$$\ln(\text{rate}_2) = \ln A - E_2/RT + \ln f(c) \qquad \text{(ii)}$$

At equal rates, these can be combined to give

$$E_1/RT_1 = E_2/RT_2 \text{ and hence } T_2/T_1 = E_2/E_1 = \text{constant.}$$

Thus, the magnitude of the catalytic effect can be quantified in terms of the ratio of the temperatures required to give equal reaction rates. The analysis assumes that the pre-exponential factors are the same for both materials, but this is a reasonable approximation, in view of the similarity of the chemical processes involved. Bearing in mind the provisos mentioned above, the relative value (i.e. the ratio) of activation energies of the carbon gasification process, calculated in this way, can be compared with that of the activation energies determined from the slope of plots of ln $(\mathrm{d}w/\mathrm{d}t)$ *vs.* $1/T$ (Eqs (i) and (ii)).

Experimental

Materials

Copper(0) cellulose films were prepared as described previously [1]. To avoid oxidation of the finely divided copper particles, the films were stored under de-oxygenated water. It is very difficult to dry them completely, and handle them subsequently, without causing surface oxidation at least. For this reason the samples used were always damp.

Apparatus

The thermal decomposition of the copper(0) cellulose complex was studied by simultaneous DSC-TG, using a Stanton-Redcroft STA 625 which incorporates a heat flux DSC head within the sample holder of the thermobalance. It is limited to a maximum temperature of approximately 870 K. The damp samples (10 mg) were heated at 10 $\mathrm{deg\cdot min^{-1}}$ under flowing nitrogen (BOC, oxygen free, 30 $\mathrm{cm^3\cdot min^{-1}}$) to 673K. The thermally inert reference material used was calcined alumina. Comparison was made between the curves found for copper(0) cellulose and cellulose itself, in the form from which the copper(II) cellulose complex was originally made (Whatman No. 1 filter paper).

The gasification of carbon was studied using a Stanton-Redcroft STA 1500 simultaneous DTA-TG thermal analyser. Samples (10 mg) of carbon (formed from cellulose) and copper(0) carbon were heated at 10 $\mathrm{deg\cdot min^{-1}}$ to 1720 K in a controlled atmosphere of nitrogen/water vapour. The latter was achieved by passing the nitrogen at 30 $\mathrm{cm^3\cdot min^{-1}}$ through a saturator containing de-oxygenated water in a thermostatted water bath at 298 K. To quantify the amount of water used in the activation stage, the empty equipment was connected via a gas sampling valve to a gas chromatograph (Pye 204) for analysis of the gas stream. Data collection and processing were by on-line microcomputer. The sample injection volume was 49 μl, and standard injections of 0.5 μl of water (1% in ethanol) were used for the calibration. The water concentration in the carrier gas flow was $3.06 \pm 6\times10^{-2}$ mmol·cm^{-3} ($5.5\times10^{-2} \pm 1\times10^{-3}$ mg·cm^{-3}). This ensured that during the thermal activation study, the amount of water used was more than that necessary for complete oxidation of the carbon.

Temperature programmed desorption

Samples (1.0 g) were placed between quartz wool plugs in a borosilicate glass tube and heated at 10 deg·min^{-1} to 423 K under flowing helium (20 cm^3·min^{-1}). As mentioned above, it was not possible to dry the samples rigorously to avoid oxidation of the copper. The effluent gas line was linked via a jet separator to a mass spectrometer (VG Micromass 601). The temperature and the signal corresponding to m/e 18 were monitored using the mass spectrometer in peak select mode, together with a 16-bit ADC (Comark) and microcomputer (BBC Master).

Kinetic studies: estimation of the effect of the copper as a catalyst on the activation energy of carbon gasification

The thermogravimetric curves for both carbon and copper-carbon were differentiated with respect to time to give $(dw/dt)/T$ plots for the carbon gasification reaction. From these curves, the reaction rates, normalised for the mass of carbon, were determined from the magnitude of the DTG signal above the baseline and the temperatures corresponding to these values were noted.

Results

Thermal analysis of drying and decomposition

The DSC and TG results are shown in Figs 3 and 4 respectively for the cellulose and copper(0) cellulose. Both DSC curves showed an initial endothermic process, the onset of which coincided with the start of heating, with a peak minimum at approximately 320 K in both curves (Table 1). The return to baseline was slow and the associated TG curves registered a slow 5–10% mass loss. This was thought to be due to the loss of physically bound water as both samples were damp, for reasons described above.

The onset of the decomposition reaction of the copper(0) cellulose material occurred approximately 50 K lower, at 545 K, than the pure cellulose, as shown by the major DSC endotherms. Peak minima were at 633 K for cellulose, but at

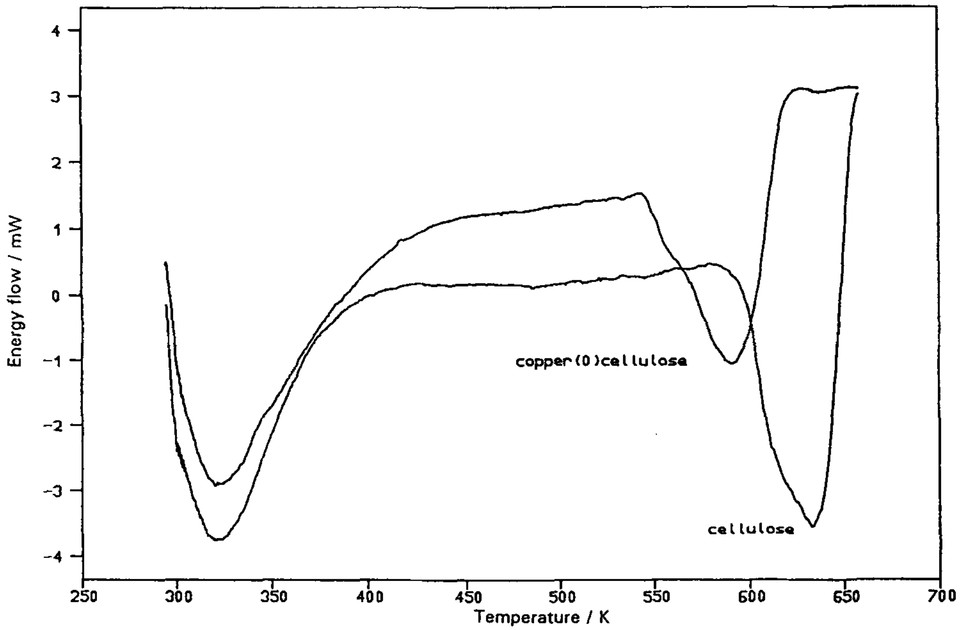

Fig. 3 DSC curves for cellulose and copper(0) cellulose pyrolysis

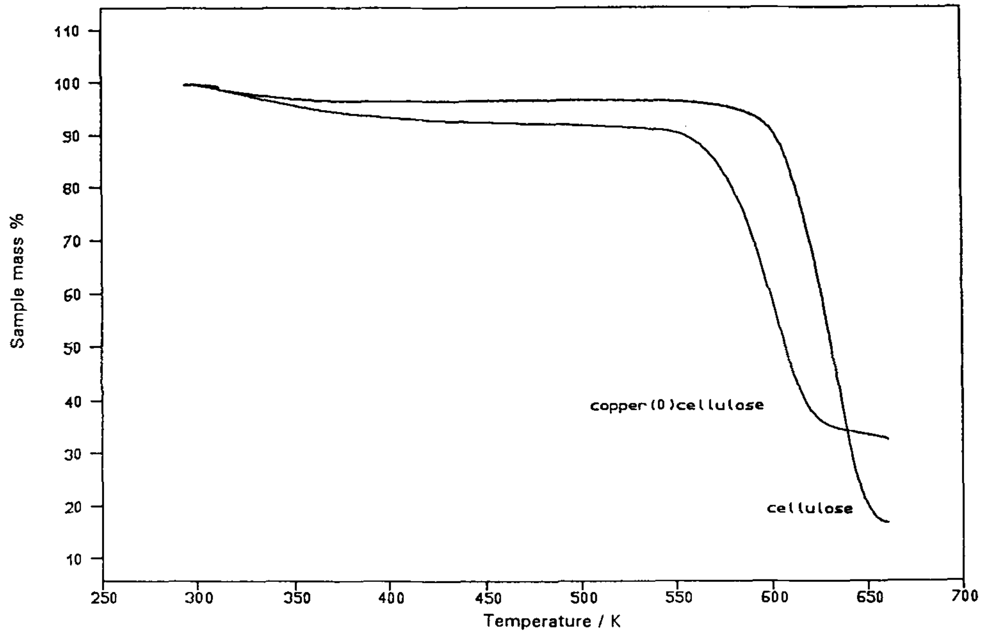

Fig. 4 TG curves for cellulose and copper(0) cellulose pyrolysis

591 K for copper(0) cellulose. Both showed signs of a shoulder on the low temperature side of the endotherm, indicating two overlapping reactions. The DSC results are summarised in Table 1.

Table 1 Temperatures recorded by DSC-TG for pyrolysis of pure cellulose and copper(0) cellulose

Thermal event		Temperature/K	
		Cellulose	Copper(0) cellulose
loss of physically	peak onset	ambient	ambient
bound water	peak minimum	323	323
decomposition	peak onset	593	545
	peak shoulder	612	556
	peak minimum	633	591

The catalytic effect of the copper particles on the decomposition of cellulose is clearly shown by the lowering of the decomposition temperature of copper(0) cellulose compared with pure cellulose. Examination of the TG curves reveals that the decomposition of the copper(0) cellulose occurs over a wider range of temperature. It seems to be a more complex process, to judge by the shapes of the DSC traces. In particular, the shoulder on the low temperature side of the endotherm is much more pronounced, while that for the pure cellulose is barely discernible.

Table 2 Temperatures recorded by DTA-TG for the activation of pure carbon and the copper-carbon composite material

Thermal event	Temperature/K	
	Carbon	Copper-carbon
activation onset	1030	803
peak shoulder	1106	995
peak minimum	1307	1129

Thermal analysis of activation

The DTA curves from the simultaneous DTA-TG activation experiments for both samples were corrected for baseline drift and are shown in Fig. 5. A small exotherm at approximately 650 K was found for the copper-carbon. In comparing the magnitude of the DTA and TG changes, it should be remembered that the copper-carbon contains only half the carbon compared to the material pre-

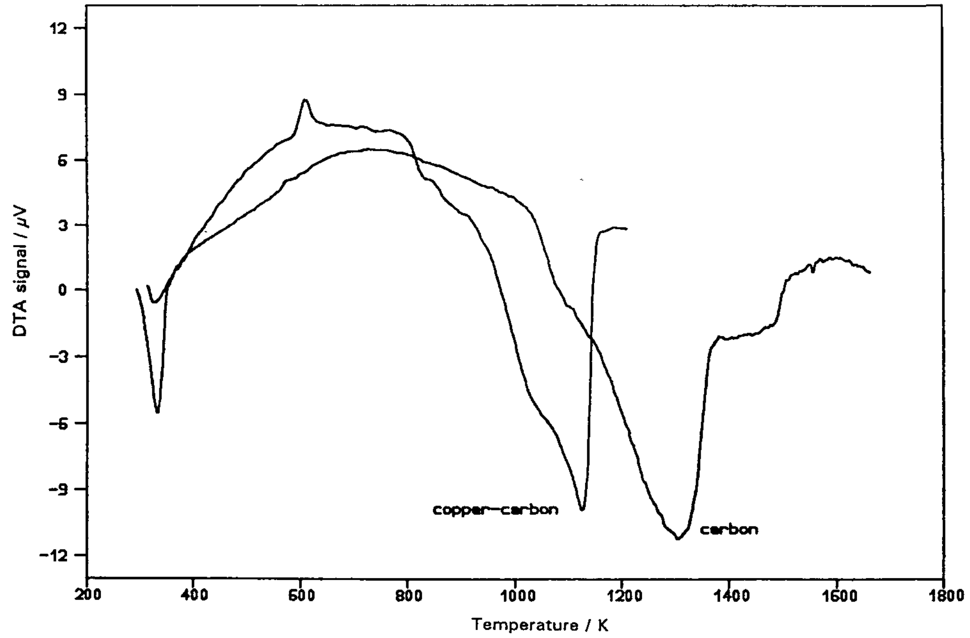

Fig. 5 DTA curves for carbon and copper-carbon activation

pared from pure cellulose. Both samples had an initial water uptake equivalent to approximately 2% of their mass. As the temperature increased, this adsorbed water was then steadily lost, giving rise to an endotherm. Details are given in Table 2.

It is clear that the activation process, i.e. the oxidation of the carbon by water vapour, is catalysed by the presence of the copper particles, as judged by the DTA onset temperatures shown in Table 2. The TG onset temperatures from the curves shown in Fig. 6 demonstrate similar trends. The TG results show that oxidation went to completion in these experiments. The lower mass loss for the copper-carbon reflects the fact that only 50% of the original material was carbon.

Temperature programmed desorption study of water from carbon

A typical temperature programmed desorption curve is shown in Fig. 7. Water evolution was first detected at about 313 K, the peak maximum occurring at 385 K. At 423 K, no further water was evolved and the sample was therefore assumed to be completely dried at this temperature. The TPD results confirm that the initial mass loss and the associated endotherm observed in the DTA-TG experiments are due to the loss of water.

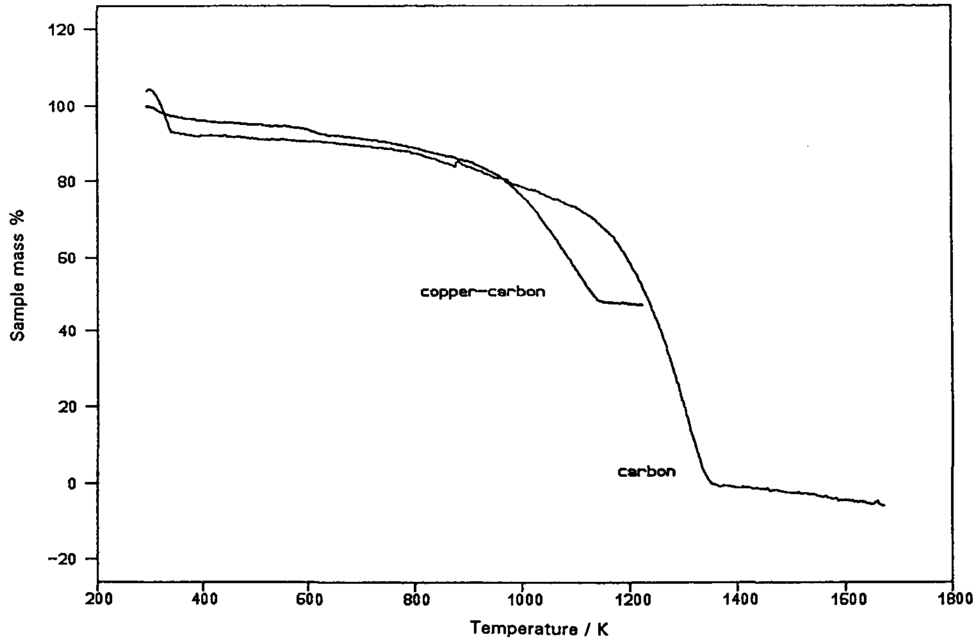

Fig. 6 TG curves for carbon and copper-carbon activation

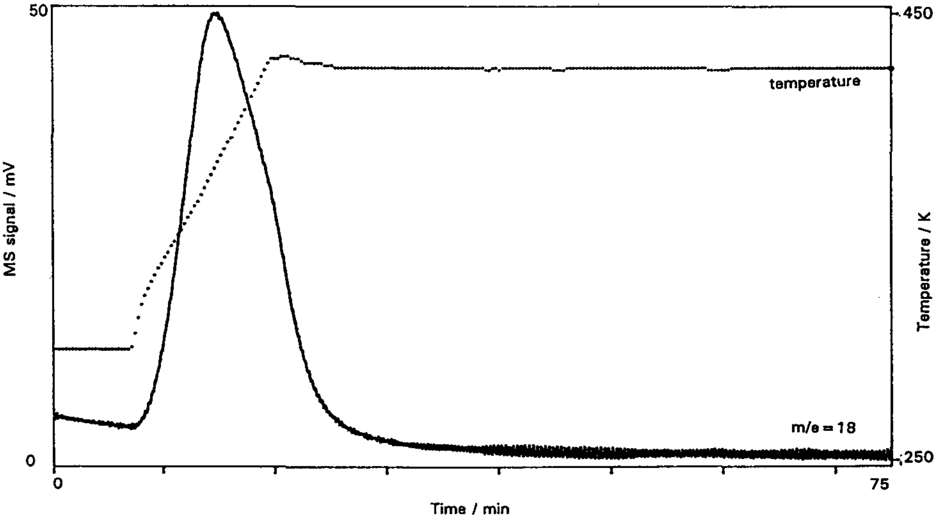

Fig. 7 MS data for thermal desorption of water from carbon

Kinetic studies: estimation of the effect of the copper as a catalyst on the activation energy of carbon gasification

The ratio of the activation energies of the catalysed and uncatalysed reactions was determined as described above and found to be 0.82. From the plots of ln (dw/dt) *vs.* $1/T$ an estimate was made of the absolute values of activation energy for the two samples. For carbon, the activation energy was 116 $kJ \cdot mol^{-1}$ and for copper-carbon it was 96 $kJ \cdot mol^{-1}$.

Discussion

The low temperature endotherms found for the cellulose and the copper(0) cellulose samples were suspected to be due to the loss of physically adsorbed water, since it was not possible to dry the samples fully without incurring some oxidation of the metal component. The temperature at which these events were found was consistent with the loss of water.

The simultaneous DSC-TG results showed that the major mass loss, at temperatures above 540 K in the charring (carbon forming) process, was associated with endothermic reactions in both samples. These have been shown by other workers [1–4] to be due to 'chemical' dehydration (responsible for the low temperature shoulder) and depolymerisation of the cellulose molecule, with the formation of volatile organics, e.g., levoglucosan.

It was evident from the lower reaction temperatures found for the copper(0) cellulose that the copper had a significant catalytic effect on the decomposition of the cellulose. Copper is not conventionally used as a dehydration catalyst for compounds containing OH groups, e.g., alcohols are dehydrogenated over copper, but dehydrated over alumina. However, copper is used in the hydration of acrylonitrile. From the results here it would appear that both dehydration and depolymerisation of cellulose are catalysed by copper. Alternatively, if dehydration is necessary before depolymerisation can proceed, catalysis of the former reaction only would facilitate depolymerisation at lower temperatures. The more pronounced shoulder found in the DSC curve of the copper(0) cellulose suggests that the dehydration reaction is certainly influenced by the presence of the copper particles. This is consistent with the so-called 'chemical activation' of pure carbons, in which an internal pore structure leading to high surface areas is developed by incorporating a dehydrating agent such as zinc chloride or phosphoric acid into the cellulosic precursor. Dehydration/activation then proceeds at temperatures of 670–870K in the absence of air.

Physical activation, where carbon is removed using a gaseous oxidising agent, e.g., steam or carbon dioxide, is very slow below 1070 K, but it has been shown [12, 13] that the presence of certain transition metals catalyses carbon gasification. Using temperature programmed reaction techniques with on-line mass spectrometry [2]), we have demonstrated that the presence of copper in our composite material causes a significant reduction in the temperature of activation. This conclusion is supported by our DSC and DTA results, which give a more exact measurement of the temperatures involved because of the good thermal contact between the thermocouple and the sample. In the TPR apparatus used previously, the thermocouple was placed outside the borosilicate glass tube which contained the sample, and gave only an approximate indication of sample temprature.

The activation energies calculated here confirm our earlier qualitative results showing that copper acts as a catalyst in carbon gasification. The activation energy is lowered by approximately 20 $\mathrm{kJ \cdot mol^{-1}}$.

Temperature programmed techniques are not ideal for measuring activation energies. The traditional interpretation of activation energy in the context of solid state reactions is questionable since the concept of concentration cannot be applied in the same sense as in homogeneous systems. Solid state processes are complicated by problems of mass transfer and the energetics of the interfaces involved. It is perhaps more accurate to regard such activation energies as empirical temperature coefficients of the reaction. Our aim was to confirm the catalytic effect of the copper particles on the activation process and to quantify its relative magnitude with and without the presence of a catalyst. As a check, we determined the ratio of the activation energies from equations (i) and (ii) above and this value (0.82) was in reasonable agreement with the ratio of the separate values (96/116 = 0.83).

The apparently small decrease in activation energy found should be interpreted with some care. In conventional heterogeneous catalysis, much larger activation energy differences are required to increase the reaction rate, or lower the temperature of reaction significantly. This is because of the greatly decreased pre-exponential factors which arise because the reaction is limited to the surface of the solid where the concentrations of reacting species are considerably decreased compared to a similar reaction occurring homogeneously.

The catalytic effect of the copper on the oxidation of the carbon is important because it provides a mechanism for the formation of the pore network which is responsible for exposing the copper particles in the bulk of the carbon matrix to the gas phase. Oxidation is initiated at the interface between the carbon matrix and a surface copper particle and proceeds preferentially along the turbostratic spaces until a second copper particle is reached. The catalytic reaction then ensures that the reaction continues at the copper surface, thus creating an annular sphere around the copper particle. At various points across the external surface of this sphere, further embryonic micropores are created, as before, and these pores penetrate the carbon matrix further, until another copper particle is reached and the process is repeated.

A secondary advantage is that the reduced activation temperature limits the possibility of sintering of the copper particles. This is not a serious problem, as far as the particles in the carbon matrix are concerned, since they are trapped in their annular cages. However, the surface particles are more prone to sintering and a reduction in temperature of activation is therefore desirable.

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Zusammenfassung — Mittels simultaner DSC-TG und DTA-TG wurde der katalytische Effekt des Metalles auf die thermische Zersetzung einer Zellulosematrix mit einem Gehalt an kleinen Kupferpartikeln untersucht. Diese Techniken wurden ebenfalls verwendet, um den Einfluß der Metallpartikel auf die anschließende Aktivierung der Kohlenstoffmatrix zu zeigen, bei dem die Porenstruktur gebildet wird, die notwendig ist, um das Metall in die Gasphase freizusetzen. Zur Untersuchung des anfänglichen Massenverlustes bei der Aktivierung wurde eine temperaturprogrammierte Desorption durchgeführt. Um den katalytischen Effekt der Kupferpartikel auf den Aktivierungsprozeß zu quantifizieren, wurde eine Schätzung der Aktivierungsenergie von katalysierter und unkatalysierter Reaktion angestellt. Diese Arbeit lieferte wertvolle Informationen über den Prozeß bei der Herstellung einer neuen Reihe von Metall-Kohlenstoff-Katalysatoren.