A STUDY OF THE ACTIVATION OF CARBON USING SAMPLE CONTROLLED THERMAL ANALYSIS

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Abstract

A constant rate method involving the control of the concentration of evolved CO_2 at a constant level was used to study the air activation of pure and copper-doped carbon prepared from sodium carboxymethylcellulose. Whereas under a linear heating regime, both types of carbon reacted suddenly and quickly with O_2, under constant rate conditions this violent reaction was avoided and oxidation proceeded steadily at a lower temperature until complete burn off of the carbon was achieved. The catalytic effect of the copper on carbon gasification was noted with lower reaction temperatures for both linear heating (380°C compared to 500°C) and for the constant rate experiments (320°C compared to 400°C).
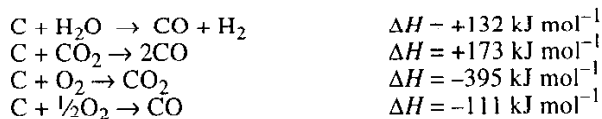
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Introduction

Active carbons are high surface area materials which can be used as adsorbents in fluid filtration processes and as catalyst supports. They are normally manufactured in a two stage process [1] from a carbonaceous precursor, e.g. nutshells, wood pulp or coal. The first stage involves the formation of a low surface area char by thermal decomposition of the precursor in an inert atmosphere. The second stage, where the pore system is developed, leading to surface areas of ca. 1000 $m^2 \, g^{-1}$, utilises carbon oxidation reactions.

Conventionally, mild oxidising atmospheres are used, with steam or CO_2 at temperatures of 800 to 1000°C. The resulting carbon gasification causes a network of interconnecting slit shaped micropores (<2 nm width) to be formed.

Reaction of carbon with either steam or CO_2 is endothermic [2] whereas with oxygen, the reactions are exothermic:

$$C + H_2O \rightarrow CO + H_2 \qquad \Delta H - +132 \text{ kJ mol}^{-1}$$
$$C + CO_2 \rightarrow 2CO \qquad \Delta H = +173 \text{ kJ mol}^{-1}$$
$$C + O_2 \rightarrow CO_2 \qquad \Delta H = -395 \text{ kJ mol}^{-1}$$
$$C + \tfrac{1}{2}O_2 \rightarrow CO \qquad \Delta H = -111 \text{ kJ mol}^{-1}$$

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The gasification reactions of carbon with oxygen can therefore be difficult to control [1] although they occur at much lower temperatures (around 350 to 500°C) than the steam/CO$_2$ reactions. This lack of control can result in overheating and excessive burn off, giving a non-uniform product.

It is well known that group VIII metals catalyse carbon gasification [3]. The presence of copper has been shown to lower reaction temperatures of both the thermal decomposition of cellulose and the subsequent activation of the char thus formed [4]. It has been suggested that the reaction of graphite with copper proceeds by an oxygen transfer mechanism [5] involving repeated oxidation/reduction of the Cu/CuO surface.

Sample Controlled Thermal Analysis (SCTA) is the generic name given to a broad family of techniques where the heating rate is altered as some function of the rate of a physical or chemical change undergone by the sample. Of particular relevance to this work is the Constant, or Controlled Rate Thermal Analysis (CRTA) technique developed by Rouquerol [6]. In CRTA the heating rate is altered in any manner, including cooling, necessary to maintain a constant rate of reaction. CRTA has been demonstrated to provide more uniform reaction conditions leading to greater resolution and improved kinetic information [7]. CRTA has also been shown to have an effect on the properties, such as surface area, of materials produced under these conditions [8, 9].

In this paper we demonstrate that CRTA techniques can be extended to the study of the gasification of both doped and undoped carbons in air by eliminating the problems caused by exothermic runaway.

Experimental

Materials

The carbons used in this study were prepared from the sodium salt of carboxymethylcellulose (Whatman, grade CM32, small ion exchange capacity: 1 meq g^{-1}). Sodium carboxymethylcellulose (Na-CMC, 50 g) was stirred with sodium hydroxide solution (0.5 M, 750 cm^3) for 30 min. It was filtered, washed with deionised water until the pH was neutral, then stirred for a further 30 min with dilute HCl (0.5 M, 750 cm^3) before filtering and washing again as described. The acid wash was repeated to give carboxymethyl cellulose (CMC) which was then filtered and washed with deionised water.

The prepared CMC was then divided into two equal portions. The first half was dried overnight at 100°C and then charred at 400°C under flowing nitrogen (BOC, O$_2$ free, 100 cm^3 min^{-1}) for 4 h.

The second portion of CMC was used to prepare copper-doped cellulose (Cu–CMC) by ion exchange. The CMC was stirred for 30 min with sodium hydroxide solution (0.5 M, 375 cm^3), filtered and washed as described above. The Na–CMC was then stirred into deionised water (400 cm^3) and a solution of CuSO$_4$·5H$_2$O (3.0 g) in deionised water (30 cm^3) was slowly added. This amount was equivalent to the total exchange capacity of the Na–CMC. After stirring overnight, the blue Cu–CMC was

filtered, washed, dried and then charred as above. After charring, atomic absorption spectroscopy showed the copper content to be 9.5%.

The carbons were finally ground in a mortar and pestle and sieved to obtain the 125–250 μm fraction and 5 mg samples were used in the activation experiments.

Apparatus

We have previously described an apparatus, a modified form of which was developed for this study, for performing a variety of SCTA techniques using evolved gas analysis to monitor the rate of reaction [10]. The apparatus, whose operation is shown schematically in Fig. 1, comprises a water-cooled tube furnace (model 761, Stanton Redcroft) in which is situated in a 6 mm diameter silica tube containing the sample. Evolved gases from the sample are passed, via a heated capillary and bypass interface, to a quadrupole mass spectrometer (model HPR20, Hiden Analytical) set to monitor the mass/charge fragments corresponding to oxygen and carbon dioxide. These values are transferred to an IBM compatible 166 MHz pentium PC (Viglen) running SCTA software developed by the authors. The data is processed and the furnace temperature altered as necessary via a temperature programmer (818P, Eurotherm) interfaced to the computer by a RS232C serial connection.
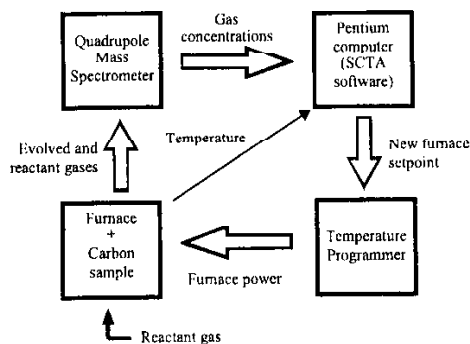

Fig. 1 Schematic diagram of operation of SCTA carbon activation apparatus

In all the experiments the capillary and bypass interface was adjusted so that mass spectrometer operated at a pressure of 1×10^{-6} Torr. This caused air to be drawn through the sample, via a molecular sieve to remove moisture, at a flow rate of approximately 20 cm^3 min^{-1}.

The linear heating experiments used a heating rate of 10 to 600°C for the Cu–CMC carbon, and 700°C for CMC carbon. In the CRTA oxidation experiments the set rate of CO_2 production approximately corresponded to a rate of carbon consumption of 0.04 mg min^{-1}. Heating rates were in the range −10 to +10°C min^{-1} to maximum temperatures as for the linear heating experiments.

Results and discussion

In Figs 2 to 5, the CO_2, O_2 and temperature profiles are marked a, b and c, respectively.

Linear heating

Figure 2 shows the oxidation of CMC carbon. Initially, there is a short period of low O_2 uptake/CO_2 evolution, but at 500°C the reaction accelerates dramatically as seen by the rapid rise in the CO_2 level and the corresponding fall in the O_2 level. Complete burn off occurs within about 2 min of the start of the reaction.
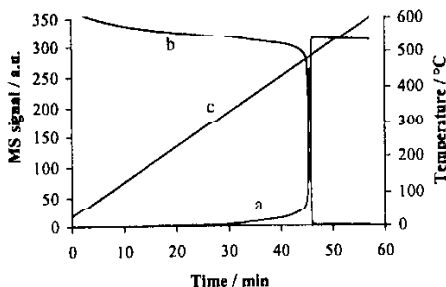

Fig. 2 Oxidation of CMC carbon at 10°C min^{-1} in flowing air: a – carbon dioxide, b – oxygen, c – temperature

The catalytic effect of the copper on the oxidation process of the Cu–CMC carbon sample can be seen in Fig. 3. The maximum rate of O_2 uptake/CO_2 evolution is at 380°C and total burn off has been achieved by 450°C. The peaks are broader than for the pure carbon (Fig. 2) possibly due to other reactions involving carbothermal reduction of surface copper oxides.
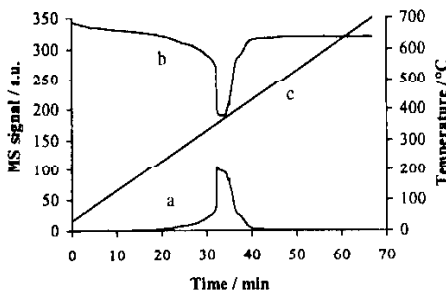

Fig. 3 Oxidation of Cu–CMC carbon at 10°C min^{-1} in flowing air: a – carbon dioxide, b – oxygen, c – temperature

Constant rate

The effect of CRTA conditions on the oxidation of the CMC carbon is shown in Fig. 4. The low reaction rate, as revealed by the low CO_2 level, completely avoids the sudden violent reaction of the pure carbon at 500°C seen in the corresponding linear heating experiment. The O_2 level is correspondingly steady and complete burn off of the carbon is achieved under controlled conditions. In this experiment the heating rate starts at 10°C min^{-1} but slows during the oxidation to maintain a constant reaction rate eventually reaching a minimum of approximately 1°C min^{-1}. It becomes negative very briefly towards the end of the process in response to a small increase in the CO_2 level (and corresponding decrease in the O_2 level) which has been attributed [11] to final fragmentation of the carbon grains. After the carbon has been consumed the CO_2 level falls to zero and the heating rate returns to 10°C min^{-1} for the reminder of the experiment.
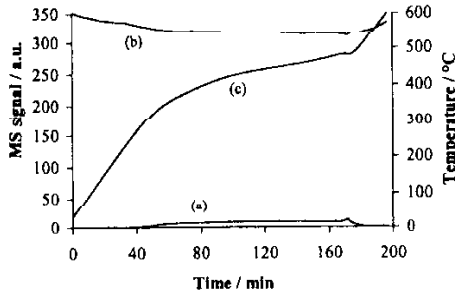

Fig. 4 Oxidation of CMC carbon in flowing air under CRTA conditions: a – carbon dioxide, b – oxygen, c – temperature

The results for the oxidation of the Cu–CMC carbon using CRTA are shown in Fig. 5. Again, the entire process proceeds in a controlled manner unlike the corresponding linear heating experiment. There is also evidence of the final fragmenta-
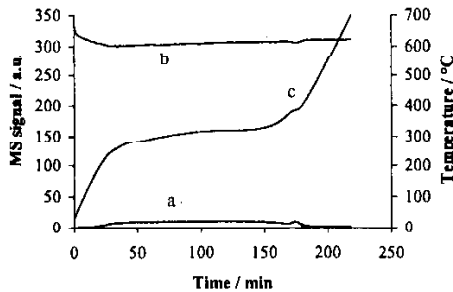

Fig. 5 Oxidation of Cu–CMC carbon in flowing air under CRTA conditions: a – carbon dioxide, b – oxygen, c – temperature

tion of the carbon grains towards the end of the reaction seen with the undoped CMC carbon (Fig. 4). Although the CO_2 and O_2 profiles for the two experiments appear very similar, slight differences can be seen between the temperature profiles. Initially, the heating rate starts at 10°C min^{-1} and again slows to maintain a constant reaction rate. However, half way through the process the temperature becomes virtually isothermal at 320°C and only rises towards the very end when the burn off is nearly complete. Generally, the gasification of the copper-doped carbon takes place at both a lower and more constant temperature.
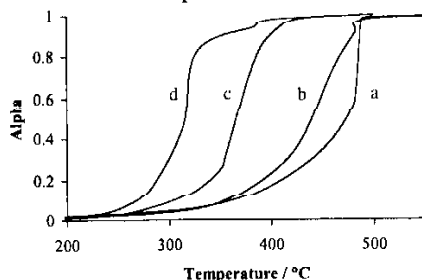

Fig. 6 Alpha *vs.* temperature profiles for the oxidation of CMC carbon and Cu–CMC carbon: a – CMC carbon: linear heating, b – CMC carbon: CRTA, c – Cu–CMC carbon: linear heating, d – Cu–CMC carbon: CRTA

The α-plots (extent of reaction) for all samples plotted as a function of temperature are shown in Fig. 6. These clearly demonstrate the effect on the reaction temperature of both the heating regime and the presence of copper. Two important features are apparent from these results. Firstly, the temperature at which the bulk of the reaction proceeds is lower for the experiments under CRTA conditions (profiles b and d) than for the corresponding linear heating experiments (profiles a and c). Secondly, in both the linear heating and CRTA experiments the temperature of the Cu–CMC carbon gasification reactions (profiles c and d) is lower than for either of the CMC carbon experiments (profiles a and b), demonstrating the effectiveness of copper as a catalyst for carbon gasification.

Conclusions

It has been shown that carbon gasification in air under linear heating gives a rapid release of CO_2 at 500°C. This reaction temperature is lowered to 380°C in the presence of copper, showing the catalytic effect of the metal. However, this reaction can be controlled at a very low rate by using a CR method involving the monitoring of the CO_2 concentration and forcing the furnace to heat or cool to keep this CO_2 level constant. In this way, the reaction proceeds steadily over a longer period of time, at lower temperature.

Future work will involve modifying the equipment to handle carbon samples in the range 300 to 500 mg, thus allowing the effect of the rate and duration of oxida-

tion on the total surface area and porosity of the carbons to be investigated. The potential for carbon activation at a constant temperature by means of controlling the partial pressure of oxygen to maintain a constant oxidation rate will also be investigated.

The CRTA method has potential advantages in the manufacture of activated carbons in air, which could yield reproducible products of pre-determined pore structure and surface area. It also may find applications in the regeneration of both carbon adsorbent beds and coked supported metal catalysts where the lower reaction temperatures under which CRTA experiments typically proceed could provide an additional benefit of reduced metal particle sintering.

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