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A NEW METHOD OF ASSESSING SOLID STATE REACTIVITY ILLUSTRATED BY REFERENCE TO THE CHANGE IN OXIDATION RATE OF ALKALINE AND ACID WASHED CARBONS

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Abstract

In this study gasification in air of activated carbons and carbon blacks is investigated using a simultaneous TG–DTA unit. It is found that a final acid or alkaline treatment can substantially alter their reactivity in the gasification reaction in air. To make a proper assessment of their solid state reactivity with respect to their gasification in air a simple method is advanced which has been used recently in assessing solid state reactivity of other materials. In this method a thermogravimetric (TG) plot is obtained on a reference carbon and then similar TG plots are obtained on the other samples of carbon using identical experimental conditions and the same TG unit. The solid state reactivity is assessed from plots of the α_R (the value of α_R, the extent of the gasification of the reference carbon) against the sample carbons values of the α_S (labeled α_S to denote the value of the various carbon samples). The values of appropriate couples of α_R and α_S at temperatures T_1, T_2, T_3,...T_n allow an α_R–α_S plot to be constructed. If the solid state reactivity of the carbon samples matches exactly that of the reference carbon the result will be a linear plot, showing coincidence of α_S and α_R at all values of α_R. If the solid state reactivity of a carbon sample exceeds that of the reference carbon then the lines plotted will be on one side of the coincidence plot, while if they are less than the carbon reference they will lie on the other side. The results show that treatment of a carbon with alkaline or acid may have a significant effect on the reactivity of the carbon sample which is only partly explained by observable differences in surface area.

Keywords: activated carbons, gasification reaction, TG-DTA

Introduction

Carbons in activated form, i.e. with an appreciable surface area, are generally prepared by chemical activation or by activation in air, CO_2 or water. The general principle is that an incipient surface area can be generated. In practice for activation with air this involves heat treatment around 300–450°C to burn off not more than a few percentage of the initial mass of carbon material. The reaction is:

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$$C + 1/2O_2 \rightarrow CO$$

and

$$C + O_2 \rightarrow CO_2$$

The exact percentage of CO and CO_2 cannot be predicted easily and the reaction is exothermic and this is a drawback in industrial control of activation. Steam activation and carbon dioxide activation's are high temperature processes (850°C) ideally represented by;

$$C + H_2O \rightarrow CO + H_2$$

and

$$C + CO_2 \rightarrow 2CO$$

The high temperature is a disadvantage but the endothermic character means that control of the process is relatively easy. Chemical activation is an easier process normally occurring at relatively low temperatures, but removal of the chemicals poses problems. This is solved in practice by chemical activation with alkali metal salts when the alkali products can be leached out with water. In the above representations the material is portrayed as carbon but carbonaceous products such as wood, coal, etc. are in fact the reactants used. Another factor which in practice seems to have an effect is the treatment the material receives after activation. Simple washing with nitric acid or alkali solution after the preparation has some effect on the activity. In this study a series of activated carbons, some prepared in the laboratory and others supplied by manufactures are examined. The techniques used to assess activity in the present study are the measurement of surface area by nitrogen adsorption and the gasification of the carbon in a simultaneous TG–DTA unit in a dry air atmosphere.

Experimental materials

The materials chosen for this investigation are listed in Table 1. These are given designations A-I. The materials were given an alkaline and also an acid wash. Alkaline washes are indicated by a subscript *B*, and acid wash by subscript A. Thus sample D, acid washed is indicated by D_A, and the alkaline wash is indicated by D_B.

The data is one of almost complete gasification and can be represented by plots of α_S (extent of reaction) going from 0 to 1, *vs.* temperature. By selecting appropriate reference materials they may be compared. The first step is to compare acid and base wash. In all examples a comparison of acid and base rinse shows, that the basic rinse increases reactivity while the acidic rinse decreases reactivity. The acid wash consisted of soaking the sample for five minutes in a solution of 1 *M* HNO_3. The basic wash consisted of soaking the sample for five

Table 1 Investigated samples

	Types of carbon used	Surface area/$m^2 \cdot g^{-1}$ by BET method
(A)	Fisher Scientific Carbon, Decolorizing Neutral Norit	458
(A_B)	Fisher Scientific Carbon, Decolorizing Alkaline Norit A	261
(C)	Aldrich [7440-44-0] Activated Carbon, Norit RO 0.8 pellet Reg trade mark American Norit	393
(D)	Columbian Chemicals Company, Carbon Black, Grade: furnex N-774	29
(E)	Columbian Chemicals Company, Carbon Black, Grade: State X N326	84
(F)	Cabot, Carbon Black, 126 Vulcan 7H N234	
(G)	Cabot, Carbon Black, 42 N550	
(H)	Sample C activated with solid KOH	1843
(I)	Sample A activated with solid KOH	1132

* Samples H and I were chemically activated with KOH, in a limited oxygen atmosphere. This activation was carried out at 850°C

minutes in a solution of 1 *M* aqueous dried in an oven for 2 h, and stored in a dessicator until it was subjected to thermogravimetric analysis.

Equipment

The unit used was the SDT 2960 Simultaneous DTA–TG, supplied by TA instruments. The details of the operational parameters are; heating rate: ramp 10 deg·min^{-1} to 750°C; atmosphere: dry air, flow rate: 30 cm^3/min; sample size: 15–20 mg; crucibles: alumina cup.

Typical TG and DTA data is shown in Figs 1–3, although TG and DTA data is available on all the samples listed in Table 1. The TG/DTA results are summarized in Table 2. All the samples burnt to almost zero residue content with an exothermic reaction. Typical data for the neutral activated carbon C is shown

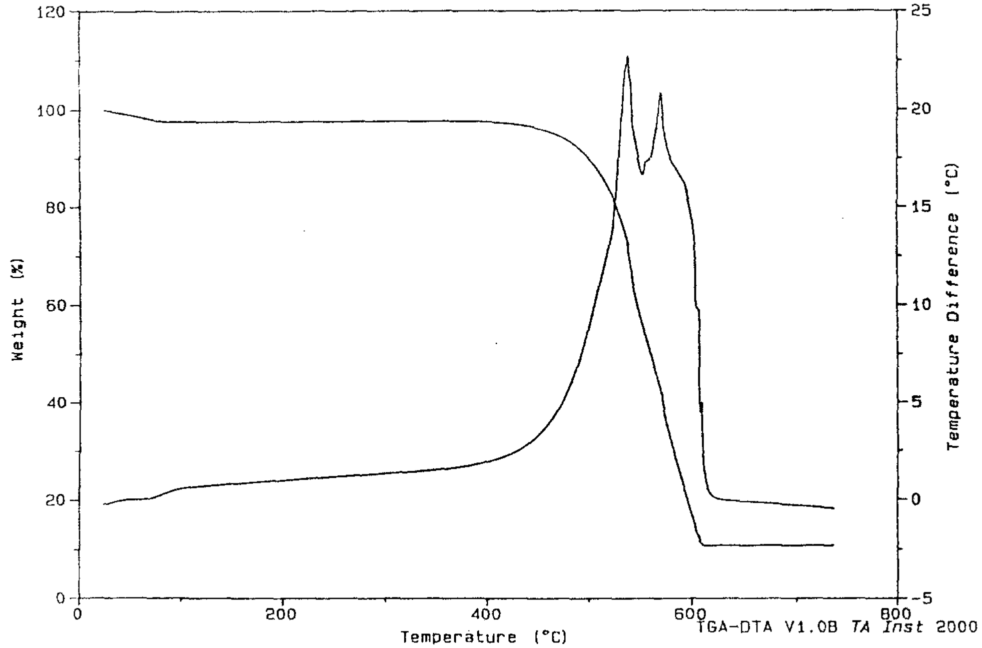

Fig. 1 TG/DTA for the neutral activated sample C

in Fig. 1. The complex nature of exothermic DTA plot is the result of the spontaneity of the process leading to perturbation of the heating rate. Figure 2 shows an acid washed sample of carbon black, (C_A) and Fig. 3 shows a basic rinsed sample (D_B) both undergoing gasification in air. Table 2 summarizes the TG data for the gasification of the untreated carbons in air.

To follow the comparative reactivity of the carbons we have used a new method, which we call the α_S–α_R method. It was demonstrated by Heda [1] and Nair [2] to follow the reactivity of sodium bicarbonate in toothpaste, and limestone and dolomite upon grinding. Here we used it to follow the reactivity

Table 2 The initial decomposition temperature, the peak temperature, the final temperature, and the temperature for $\alpha = 0.5$ for the untreated samples

Sample	T_i	T_p	T_f	$T_{50\%}$
A	415(d)	580(58%w)	620(s)	585
C	385(d)	535(75%w)	620(s)	565
D	460(d)	605(83%w)	715(s)	630
E	400(d)	590(76%w)	650(s)	608
F	365(d)	590(67%w)	650(s)	590
G	470(d)	595(80%w)	690(s)	610
H	354(d)	502(68%w)	724(s)	573
I	321(d)	410(75%w)	690(s)	473

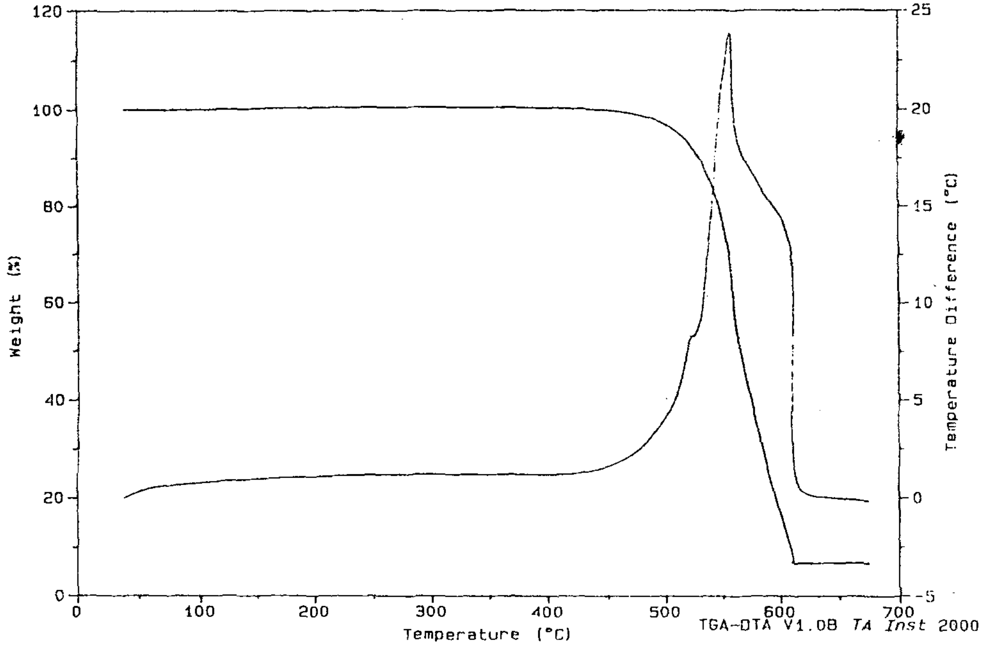

Fig. 2 TG/DTA for the acid washed sample C

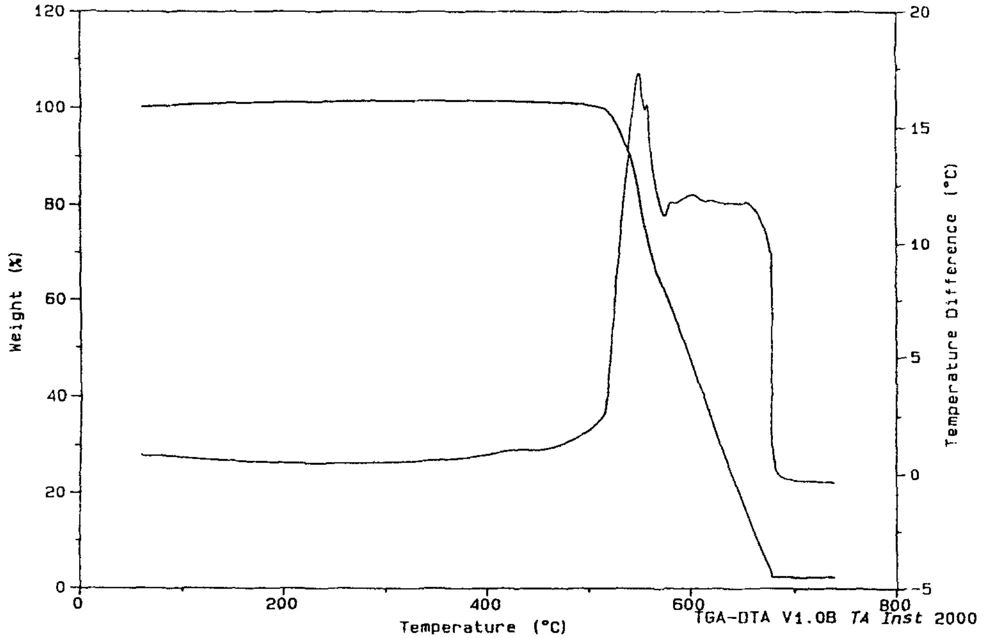

Fig. 3 TG/DTA for the basic washed sample D

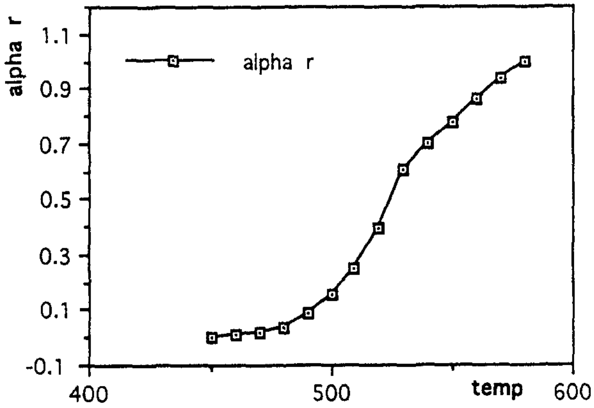

Fig. 4 Untreated carbon black (*r*) *vs.* temperature

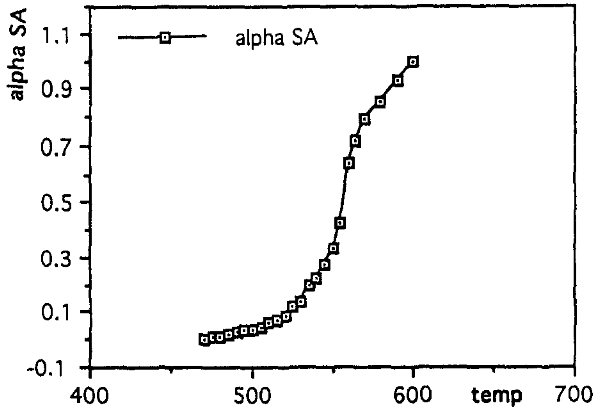

Fig. 5 Acid rinsed sample *vs.* temperature

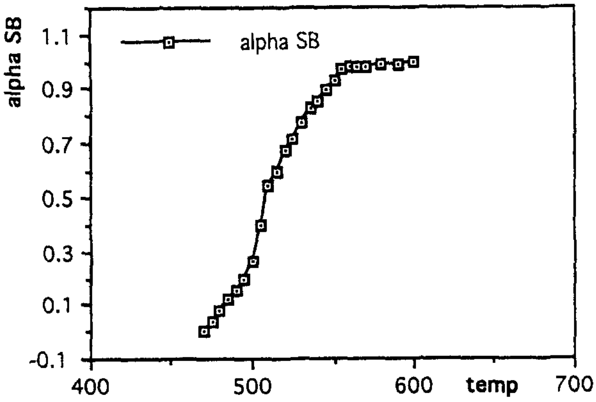

Fig. 6 Base rinsed sample *vs.* temperature

change of carbon blacks subjected to acid and alkali washes. The reactivity changes are seen upon oxidation in air on the TG balance.

If we label the data for the untreated carbon black by the subscript R (for reference), then the subscript SA can be used for the acid treated carbon black and SB for the alkali treated carbon black. We can portray the TG data on the untreated carbon as an α_R-temperature plot (where α_R is the extent of gasification of the untreated carbon) and is shown in Fig. 4, and in Fig. 5 and in Fig. 6 for the acid and base rinsed samples of that carbon.

At any selected temperature, T_i we can abstract from these graphs the values

$$\alpha_{RT1},\ \alpha_{ST1} \text{ and } \alpha_{SBT1}$$

and so on form temp T_2, T_3,...T_n etc. We can then plot α_S values *vs.* α_R value at any desired range of temperatures. This is shown schematically in Fig. 7. Deviations from the coincident line are generally greater for α_R at 0.5, so Table 3 of α_R= 0.5 can be constructed to indicate the relative reactivity of the sample. Value of $(\alpha_S/\alpha_R)>1$ at α_R= 0.5 indicate increased reactivity, while values of

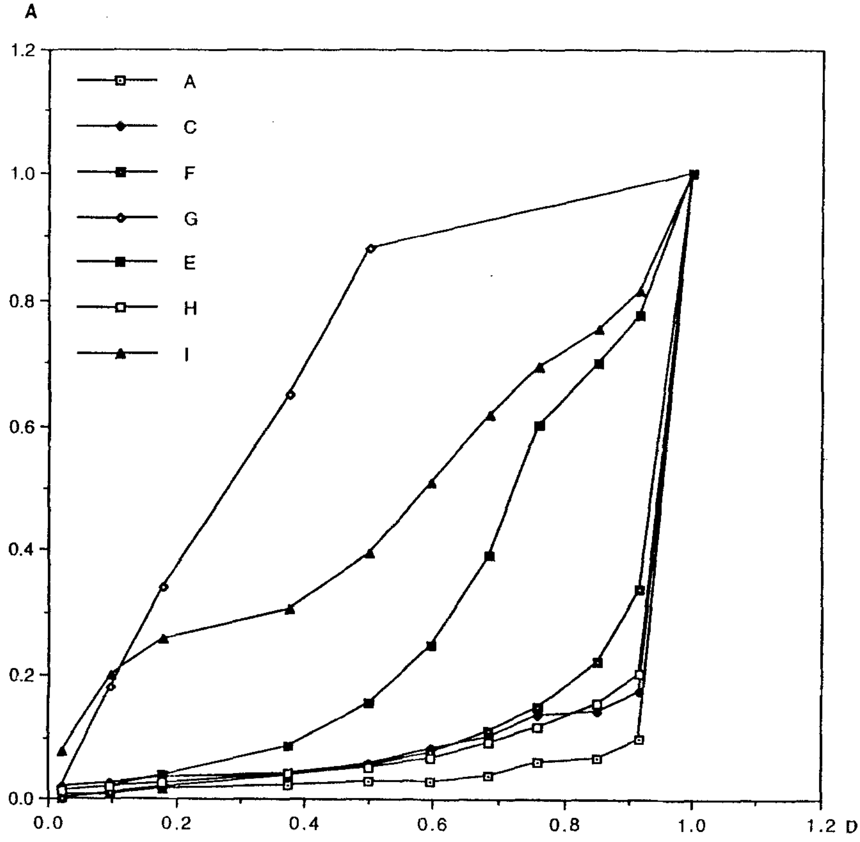

Fig. 7 Untreated samples *vs.* sample D

Table 3 Values of α_s/α_R at α_R= 0.5 for the untreated carbons investigated in this study

Carbon samples	A	B	C	D	E	F	G	H	I
Value of α_s/α_R at α_R= 0.5	0.04	–	0.06	1	0.3	0.2	0.7	0.82	0.1
S.A. /m^2g^{-1}	458	–	393	29	84	126	42	1843	1132

$(\alpha_S/\alpha_R)<1$ indicate reduced reactivity. This simple method overcomes the difficulties of using the more fundamental Arrhenius kinetic parameters of *A*, *E* and *F*(α).

We can first use the method to compare the reactivity of the untreated carbon samples using carbon black sample D as the reference. These plots of α_S against α_R are shown in Fig. 7. From Fig. 7 we can conclude that the sample with the highest surface area have the least amount of reactivity. However, the samples with the extremely high surface areas, produced by chemical activation (H, I), do not seem to follow the trend. This is probably due to the fact that these samples have internal surfaces, which make determination more difficult.

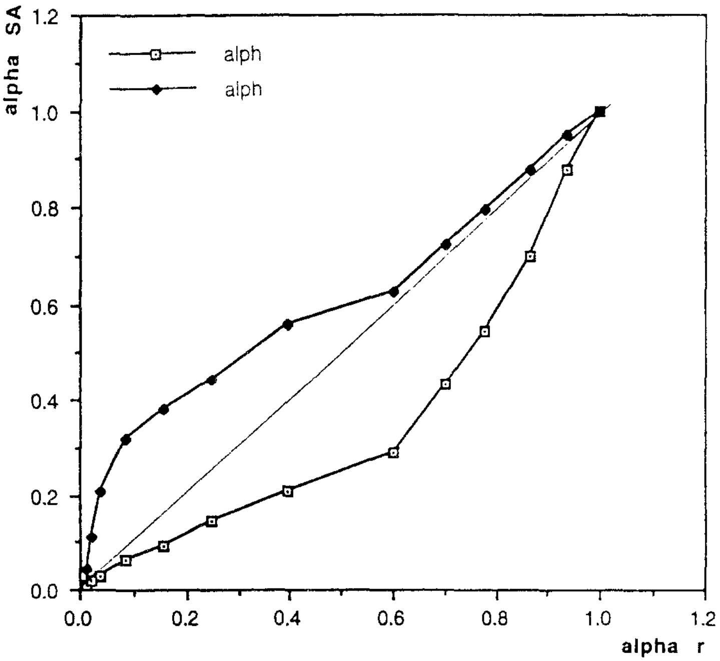

Fig. 8 α_R–α_S plot of sample E

The washing process is done to remove the high amounts of ash produced in the chemical activation of carbon [3]. The literature suggests that this washing be with an acid. However, we investigated the effects of both an acid and alkali washing using the α_R–α_S method. Figures 8, 9, 10 and 11 show this for the

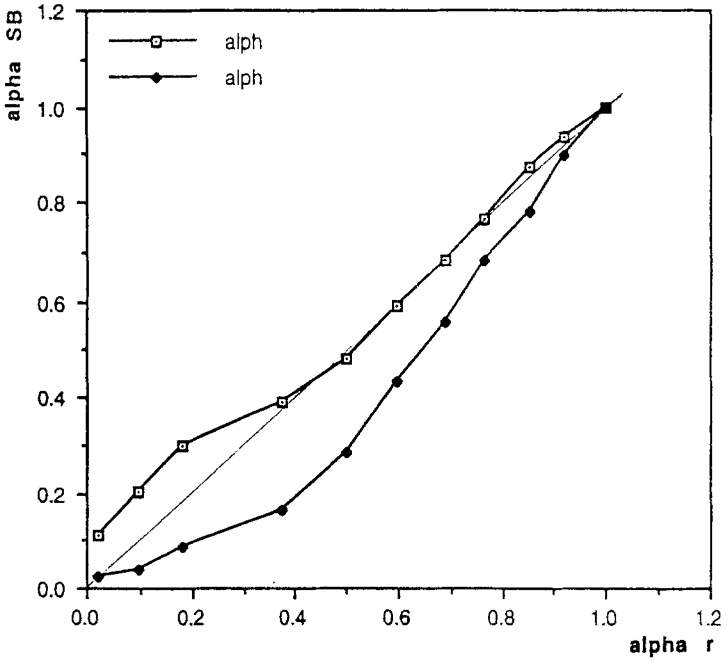

Fig. 9 α_R–α_S plot of sample D

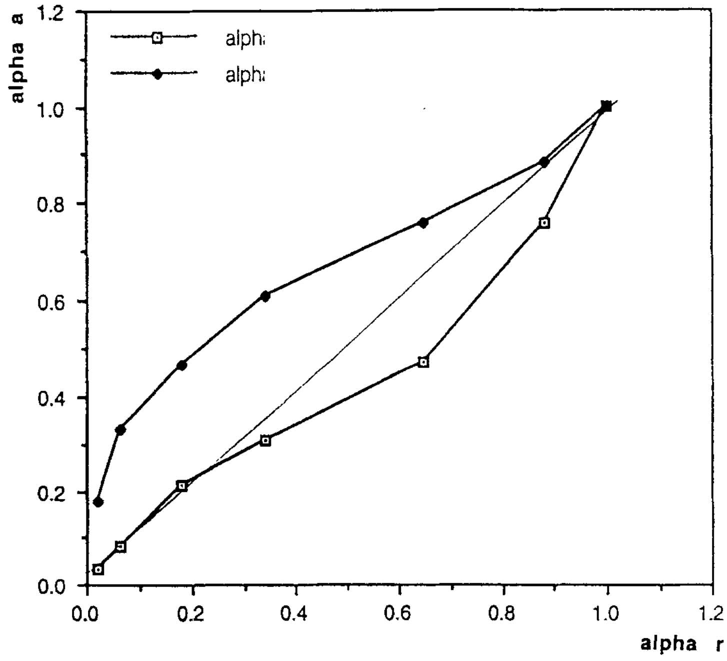

Fig. 10 α_R–α_S plot of sample G

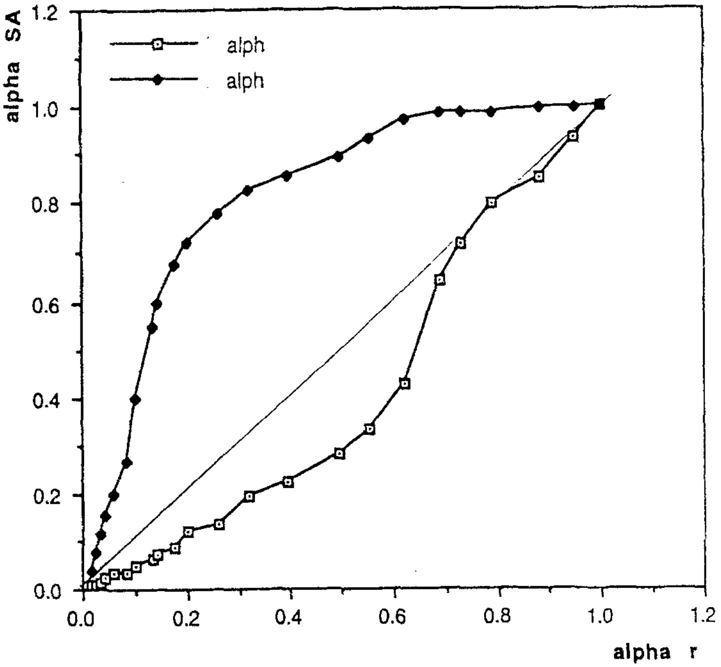

Fig. 11 α_R–α_S plot of sample C

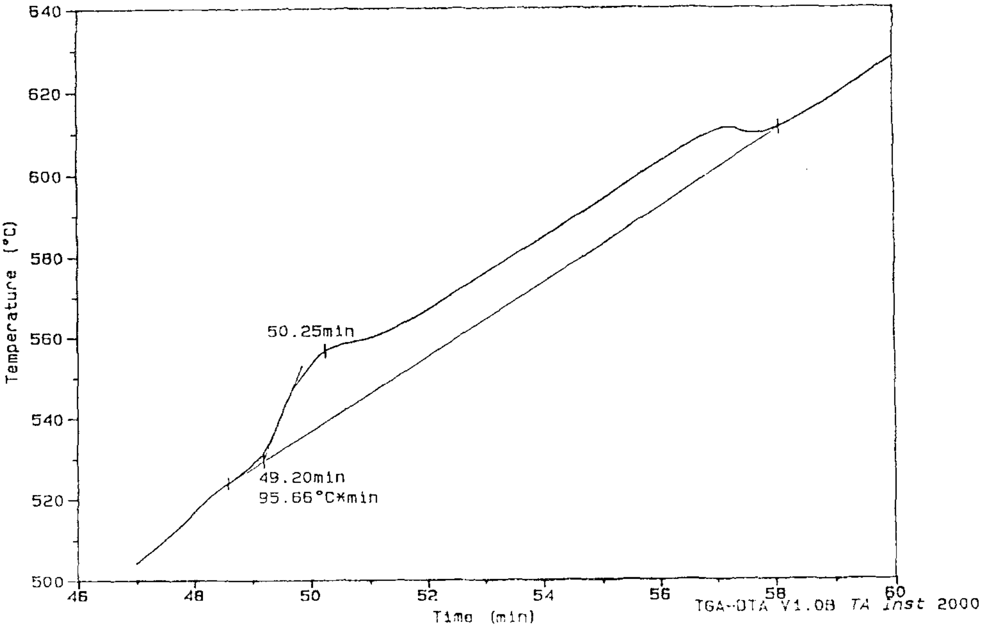

Fig. 12 Temperature *vs.* time plot

samples. Generally, it can be seen that the alkali washed samples are activated while the acid washed samples are less activated than the untreated material.

The complicated nature of the DTA plots needs some consideration. Figure 12 shows a plot of temperature against time for the carbon sample shown in Fig. 11 as a DTA/TG plot. It is apparent that a ΔT signal can be generated from this by noting the perturbation from the projected base line and the actual sample temperature. This ΔT–T signal generated from a single thermocouple reading is reproduced in Fig. 13. It is seen that this signal generated only from the TG data is similar to the DTA signal shown in Fig. 11. The shape of the DTA signal is then a reflection of the event that can be interpreted from the temperature against time plot, namely that once combustion of the carbon had commenced that the temperature then continued to rise at the desired 10 deg·min^{-1} but in a displaced manner. The average extent of the displacement in the example cited being around 10°C in a positive direction because of the exothermic nature of the process, once a steady state has been achieved.

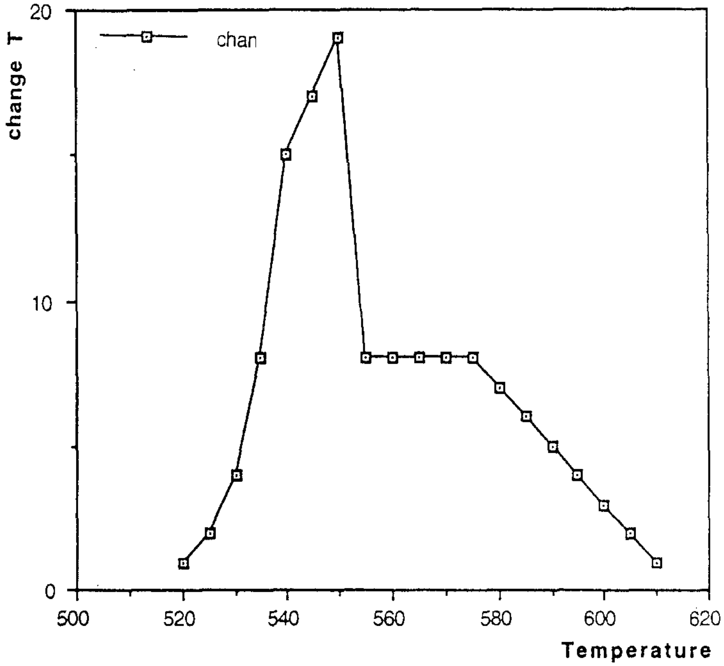

Fig. 13 Reproduction of ΔT–T signal

The KOH activated materials showed an abnormally high BET surface area (Table 1). This is often interpreted as being due to 'super-micro' pores often in the nanometer range where adsorption into the interior with pore filling occurs at low values of P/P_O (<0.3) and is then interpreted in a BET analysis as a surface area. The mechanism for the KOH activation process is unclear or not proven but credence must be given to the possibility of potassium metal being formed. Smisek says, 'with some activation agents, especially potassium and sodium salts, it cannot be excluded that the atoms of the metal temporarily enter the developing carbon lattice and influence the structure of the forming elementary crystallites' [4].

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