

IGNITION TEMPERATURES OF CARBON SAMPLES CONTAINING METAL OXIDE CATALYSTS BY A DTA METHOD

D. DOLLIMORE, L. F. JONES

Department of Chemistry and Applied Chemistry, University of Salford, Lancs. M5 4WT (England)

T. NICKLIN

The Chief Scientist's Department, The North-Western Gas Board, Stretford, Manchester (England)

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ABSTRACT

The variation of the ignition temperature of a carbon black impregnated with various amounts of manganese oxide and uranium oxide has been measured by a DTA method. The technique allows a rapid assessment to be made of sample reactivity and only small amounts (approximately 5 mg) are required. Correlation of sample reactivity by ignition temperature measurement and isothermal weight-loss data is shown.

INTRODUCTION

It is well known that the presence of metal oxide impurities in carbon increases its ease of reaction with oxygen. Increases in reactivity with increasing impurity content can be conveniently followed by measurement of the lowering of ignition temperature of the samples.

The method employed by several workers¹⁻³ consisted essentially of heating the sample in a flowing air stream at a constantly increasing rate. A single thermocouple placed in the sample was used to record the ignition temperature by observation of a sudden rise in sample temperature. Measurements were estimated to be reproducible to within about 10 K.

The present paper describes a rapid, convenient method for determination of ignition temperatures using only small quantities of material.

EXPERIMENTAL

Materials

The carbon used in this study was Spheron 9, a non-porous carbon black. Portions of the carbon were impregnated with uranyl nitrate and manganous nitrate and then thermally decomposed to the metal oxides. Two series of samples containing various amounts of uranium and manganese were thus prepared, designated "U" series and "M" series respectively. Details of the impregnation procedure and analysis for the metal oxides have been described previously⁴.

Ignition temperatures

Ignition temperatures were measured using a Netzsch low temperature DTA unit with Ni/Ni-Cr thermocouples. To increase the accuracy of sample temperature measurement and also to locate the onset of exothermicity more precisely, the sample thermocouple and differential thermocouples were connected to a Solartron modular data logger unit capable of measuring emf to within 0.01 mV. Alternate measurements of sample temperature and differential temperature were made every two seconds when nearing the ignition temperature. The results were recorded on punched tape in the data logger and recovered as an emf reading using a Friden flexowriter.

After a series of preliminary experiments, the most satisfactory results were obtained by using a standard DDK head with open alumina cups. The sample cup was charged with a thin layer (approximately 5 mg) of sample while the reference cup was used empty, as shown in Fig. 1. A constant flow of dry air at a nominal rate of 50 ml min^{-1} was passed through the outer sheath and over the sample. A heating rate of 25 K min^{-1} was used throughout.

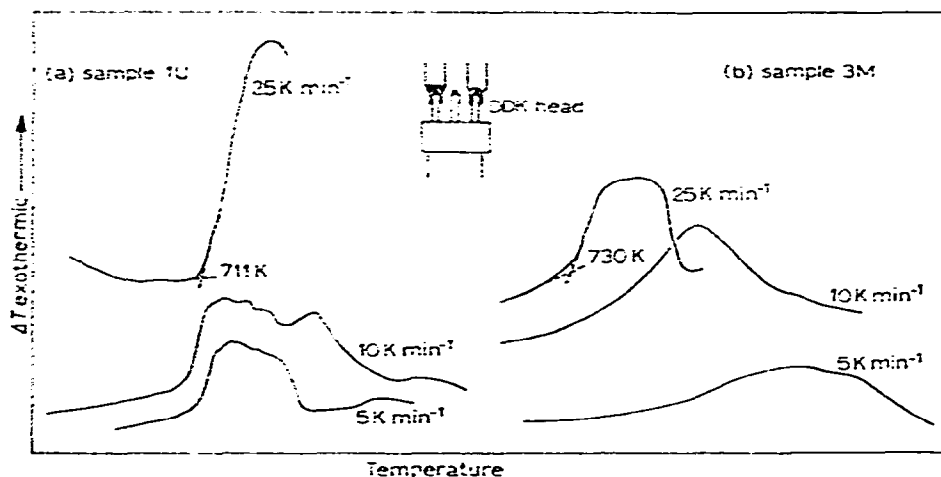


Fig. 1. Effect of heating rate on (a) highly-impregnated samples and (b) less-impregnated samples.

Thermogravimetry

The reactivity of each sample was determined at a series of temperatures in the range 600–900 K by measurement of the rate of oxidation under isothermal conditions. The experimental details have been given previously⁴.

RESULTS

Two criteria were used in selection of the optimum conditions for determination of ignition temperatures: (i) The sharpness of the onset of exothermicity, and (ii) the reproducibility of the results.

Initial experiments were conducted using conventional qualitative heads with air flowing (a) through the bulk of the sample and (b) through the outer sheath and

over the surface of the sample. The effects of sample size, dilution with inert materials, heating rate and type of DTA head were investigated. It was found that the best results were obtained from the second of these procedures, the first procedure giving very broad exotherms with marked baseline drift. Dilution of the sample with inert material (calcined alumina) caused no improvement in the sharpness of peak onset.

The sharpest exotherms were obtained using the DDK head. Large samples produced marked baseline drift while smaller samples produced satisfactory baselines. The most critical parameter affecting the sharpness of the peak onsets was the heating rate, as shown in Figs. 1a and 1b. The sharpness was increased substantially by the use of high heating rates but in practice a rate of 25 K min^{-1} was used since above this value the reproducibility was impaired. The amount of catalytic impurity present also strikingly affected the sharpness, as shown in Figs. 1a and 1b. Highly impregnated samples gave sharp exotherms with heating rates as low as 5 K min^{-1} but the least-impregnated samples gave very broad exotherms at this heating rate.

TABLE I
IGNITION TEMPERATURES AT 25 K min^{-1}

Sample	<i>g. atom metal per 100 g sample ($\times 10^3$)</i>	Ignition temp. (K)	Reproducibility (K)
SPHERON 9	—	868	12
1M ^a	7.28	703	4
2M	3.26	709	6
3M	1.34	730	6
4M	0.48	768	10
1U ^b	15.8	711	4
2U	8.07	736	5
3U	2.76	798	6
4U	2.07	806	8
5U	1.19	818	10

^aM = manganese-impregnated samples. ^bU = uranium-impregnated samples.

Table I shows the results obtained for each impregnated sample with an estimate of the reproducibility. Each result is the average of three determinations. The ignition temperature was taken as the extrapolated onset of the exothermic peak.

Thermogravimetry

The variation of oxidation rate with temperature for the manganese impregnated samples is shown in Fig. 2. The uranium impregnated series showed a similar variation. These could be shown to obey the Arrhenius equation in the form $k = Ae^{-E/RT}$ with two distinct linear regions of differing activation energy⁴. Values of oxidation rate were interpolated from the linear regions of the Arrhenius plots.

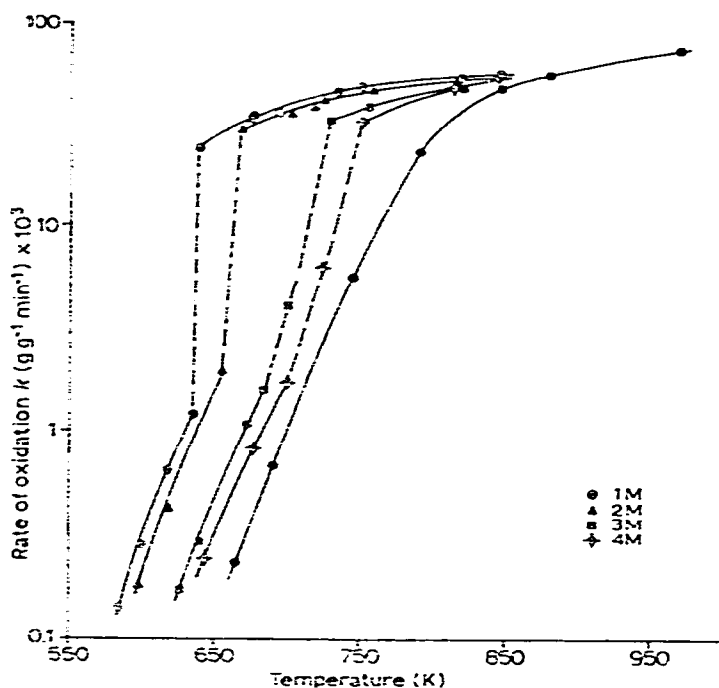


Fig. 2. Rate of oxidation as a function of temperature (manganese series).

DISCUSSION

Comparison of a series of samples such as those used in this study can only be made if the conditions discussed earlier concerning reproducibility of the results and sharpness of the exotherms can be met. The preliminary trials in this study showed that the measured ignition temperature of any sample apparently increased with heating rate. It would be desirable to take the lowest measured value of ignition temperature as the most meaningful but, as discussed earlier, this would lead to a high degree of uncertainty in those samples containing small amounts of catalytic impurity. It was therefore considered preferable to use the results at 25 K min^{-1} since these are more meaningful on a comparative basis.

The results shown in Table I compare favourably with those obtained by other workers¹⁻³, where the maximum reproducibility was estimated at 10K. In addition, quantities as small as 2-3 mg have been used with the present method with no significant difference in results.

Comparison of reactivity by TG and DTA

Each sample exhibited two distinct temperature zones, as shown in Fig. 2, in accordance with the postulates of Walker *et al.*⁵. Reaction in the low temperature zone was governed by the chemical reactivity of the sample whereas reaction in the high temperature zone was controlled by gaseous diffusion⁴. The reactivity of each

sample as measured by ignition temperatures, T_i , was compared with the reactivity from the TG data using three criteria:

- (i) The temperature at which diffusion-controlled reaction commenced (T_d).
- (ii) The temperature at which a constant rate of oxidation was obtained in the chemically-controlled zone (T_k).
- (iii) The rate of oxidation at constant temperature in the chemically-controlled zone (k_T).

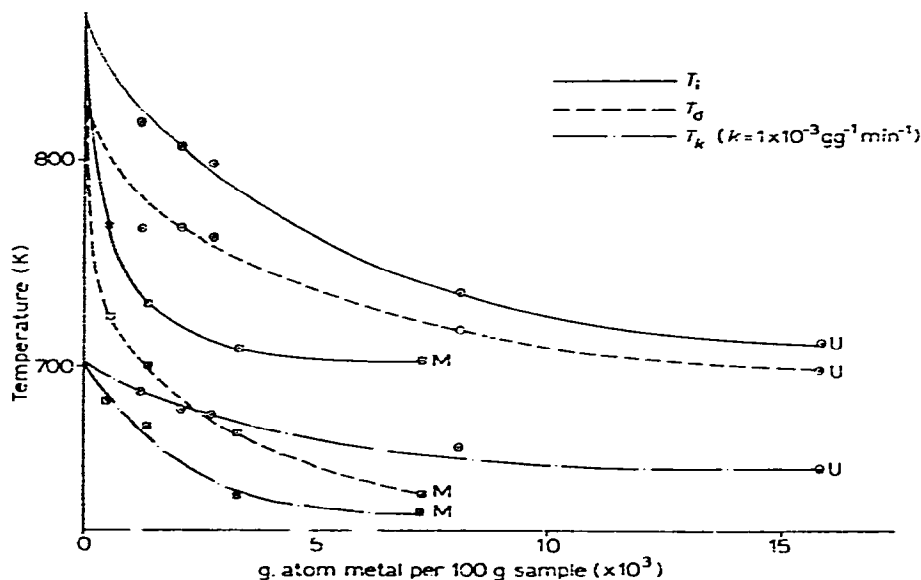


Fig. 3. Comparison of sample reactivity by three criteria.

Figure 3 shows that T_i , T_d and T_k all follow the same trend with increasing catalyst concentration. It was expected that the T_d value for any sample would be near the corresponding T_i value since both are a measure of the onset of rapid oxidation. For the U series, T_d values were lower than T_i values by about 15–35 K while the M series showed no such constant difference. Trends in T_k showed a similar variation.

Figure 4 shows a comparison of sample reactivity as measured by the rate of oxidation at constant temperature, k_T , and the lowering of ignition temperature, ΔT_i , as a function of catalyst concentration. It is clear from these plots that reactivity as measured by T_i values can be used to predict trends in oxidation rate from isothermal weight-loss data.

To determine the relationship between reactivity as measured by DTA and TG, plots were constructed of ΔT_i as a function of both $1/T_k$ and k_T . Both plots showed identical variation, as expected. The plots of ΔT_i against $1/T_k$ are shown in Fig. 5. The U series showed a linear variation while the M series showed a distinct curvature. The data for both series did not lie on a common line as would be expected if ΔT_i was a function of the sample reactivity only. It appears, therefore, that ΔT_i depends also on the nature of the catalytic impurity present.

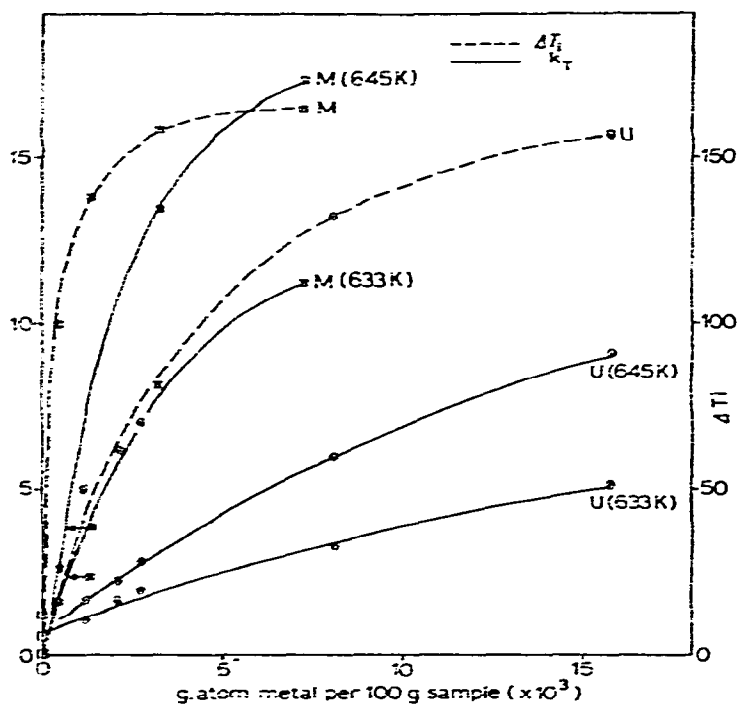


Fig. 4. Sample reactivity by DTA and TG as a function of catalyst concentration.

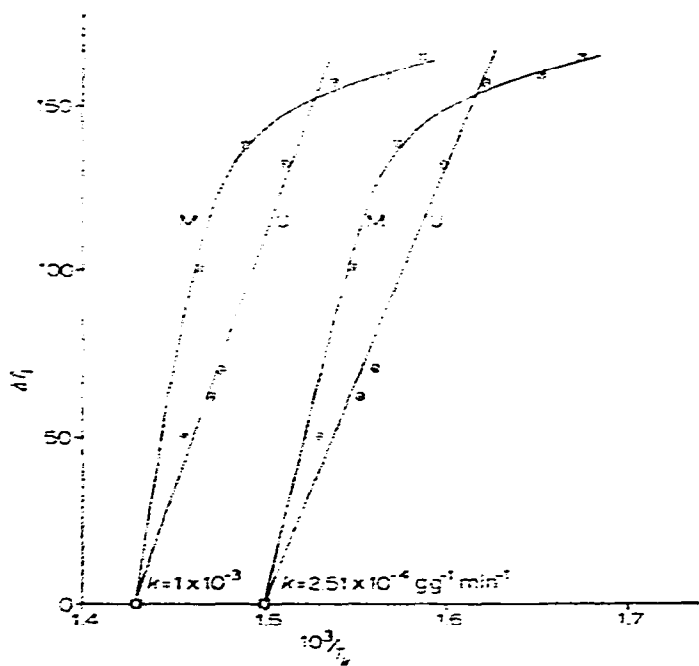


Fig. 5. Relationship between sample reactivity from DTA and TG.

CONCLUSIONS

The ignition temperature method is useful for rapid assessment of sample reactivity. With the present method, only small quantities of material (≤ 5 mg) are required. Comparison of the results with isothermal weight-loss data suggests that trends in the lowering of ignition temperature depend on the nature of the catalytic impurity as well as the increases in reactivity produced.

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