Journal of Thermal Analysis, Vol. 52 (1998) 345-353

STUDY OF THE EVOLUTION OF CARBON DIOXIDE FROM ACTIVE CARBON BY A THRESHOLD TEMPERATURE-PROGRAMMED DESORPTION METHOD

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(Received December 22, 1997)

Abstract

A particular Temperature-Programmed Desorption (TPD) method, called 'Intermittent TPD', has been applied to the decomposition of oxygen groups naturally present at the surface of a microporous active carbon. It is shown that this method provides more information on the kinetics of the thermal decomposition of these species than the classical TPD technique. The main result is that the decomposition of these oxygen groups occurs in at least 7 distinct stages which have been characterized by their apparent activation energy and the corresponding frequency factor. The present study underlines the usefulness of ITPD for studying the rate of desorption of gases from powdered samples with a strongly heterogeneous surface.

Keywords: active carbon, Intermittent TPD, oxygen groups, TPD

Introduction

Temperature-programmed desorption (TPD) is a well-known technique for studying the desorption kinetics of neutral molecules from the surface of solid materials. The basic equations used to interpret TPD spectra under high vacuum have been developed by Carter [1] and Redhead [2]. Since then, many efforts have been made to design methods for calculating the kinetic parameters, i.e., the activation energy of desorption and the so-called frequency factor, from the TPD peaks [3–8]. These methods allow, in principle, the kinetic parameters to be determined from the position and the shape of the TPD peaks obtained under various experimental conditions. These conditions include free readsorption [6] and possible transport phenomena in the pores [7, 8]. The proposed models are convenient to interpret experiments carried out either under vacuum or in a stream of an inert gas.

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1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

Nevertheless, Soler and Garcia [9] have shown that methods based on the shape of the TPD peaks can give ambiguous results because they require a precision in experimental data that can be hardly achieved. In these circumstances, a right solution should be to use a threshold method, like that proposed by Habenshaben *et al.* [10]. A threshold method uses the very onset of the TPD (recorded with a high sensitivity by the desorbed gas detector) in a threshold region where the population of the adsorbed species may be considered as constant. The validity of threshold methods has been discussed in a review by Zhdanov [11].

A general expression for the rate r of desorption (or decomposition) of a superficial species is

$$r = -\frac{d\theta}{dt} = A(\theta)f(\theta)\exp(-E(\theta)/RT), \tag{1}$$

with

$$\theta = \frac{N}{N_o} \tag{2}$$

where N is the current population of the species involved in the desorption, N_o is the population of the adsorption sites for these species, $A(\theta)$ is the frequency factor, $E(\theta)$ is the apparent activation energy of desorption, R is the gas constant, T is the absolute temperature and $f(\theta)$ is a function of θ.

The function $f(\theta)$ is equal, for instance, to θ for a simple decomposition process of first kinetic order without readsorption. In this case A is expected to be close to 10^{13} s^{-1}. Explicit expressions for $f(\theta)$ have been proposed for various desorption mechanisms [5]. The principle of threshold methods relies on the fact than Eq. (1) reduces to

$$r = A'\exp(-E/RT), \tag{3}$$

with A' constant, when the variation of θ is negligible. This expression allows E to be determined from a mere Arrhenius plot. Threshold methods have been frequently used to interpret TPD experiments of light molecules from well defined metallic surfaces [12].

Intermittent temperature-programmed desorption (ITPD) is a particular threshold method which uses a saw-tooth heating program in order to obtain a set of TPD onsets for a sequence of decreasing surface coverages [13]. It has been successfully applied to the desorption of oxygen from powdered metallic oxides [14, 15], of carbon dioxide from calcium oxide [16], and of ammonia from zeolites [17] or alumina [18].

This work presents an attempt to use ITPD in the rather difficult case of the desorption of carbon dioxide resulting from the decomposition of the numerous oxygen surface species, commonly found at the surface of active carbons [19].

The study of these groups is of interest in research on active carbons used as adsorbents or catalysts [19, 20]. This paper shows the use of ITPD to get an insight into such a complex system.

Experimental

We studied a commercial activated carbon named 'Charbon Végétal Activé' from 'Prolabo'. Its surface area, obtained by applying the BET method to the isotherm of nitrogen physisorption at 77 K, is 1070 $m^2 g^{-1}$. Such a high value is not surprising with active carbons which are highly porous materials.

The apparatus used to perform TPD runs is depicted in Fig. 1. The sample of carbon is located in a quartz bulb of a few cm^3 at the centre of a tubular furnace equipped with a linear heating system. This bulb may be connected with a vacuum line ($P=10^{-4}$ Pa) or with a mass spectrometer (AEI MS 10) through a needle valve. The mass spectrometer (MS) is set to mass m/e=44 amu to detect carbon dioxide selectively. The pressure of carbon dioxide in the sample holder remains lower than 10^{-3} Pa during the desorption. Thus, the accumulation rate of carbon dioxide in the sample holder is much lower than the desorption rate. Under these conditions, the MS response is proportional to the desorption rate of CO_2. The response time of this system is a few seconds.

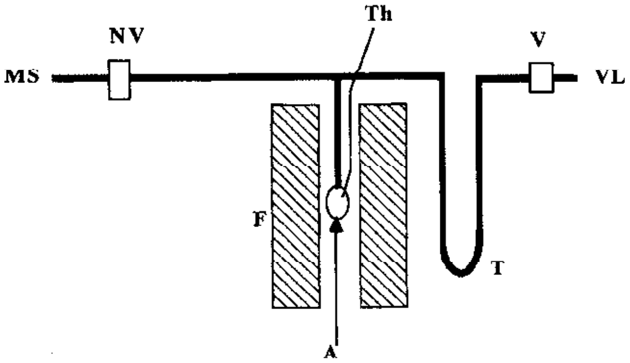

Fig. 1 Scheme of the TPD setup. A – quartz bulb containing the sample of active carbon; Th – type K thermocouple; F – furnace; VL – vacuum line; NV – needle valve; V – vacuum valve; MS – mass spectrometer; T – liquid nitrogen trap

All the temperature-programmed runs were carried out at a heating rate of 5 K min^{-1}. In the case of ITPD, a series of partial desorptions was obtained by means of a saw-tooth heating program composed of temperature rises at 5 K min^{-1} separated by temperature drops until no desorption was detected. Thresholds at quasi constant population of the adsorbed species were thus obtained at the beginning of every partial desorption. Two ITPD studies have been carried out. The first one was carried out with a 100 mg sample. In this case, the sample holder was isolated from the vacuum line of the desorption set-up and the vacuum above the carbon was maintained by the pumping system of the MS. The second one was carried out with 760 mg of carbon, the sample holder being connected to both the vacuum line of the desorption set-up and the MS. The complete TPD was carried out with a mass of carbon of 116 mg under the same experimental conditions as the second ITPD.

Results

Figure 2 shows the complete TPD spectrum of CO_2 between 300 and 1100 K. It exhibits two main broad peaks at 440 and 830 K and several shoulders. This spectrum illustrates that, as expected from carbon surface chemistry, the decomposition of oxygen groups into CO_2 is a strongly heterogeneous process. The total amount of CO_2 desorbed is about 180 micromole/g of carbon.

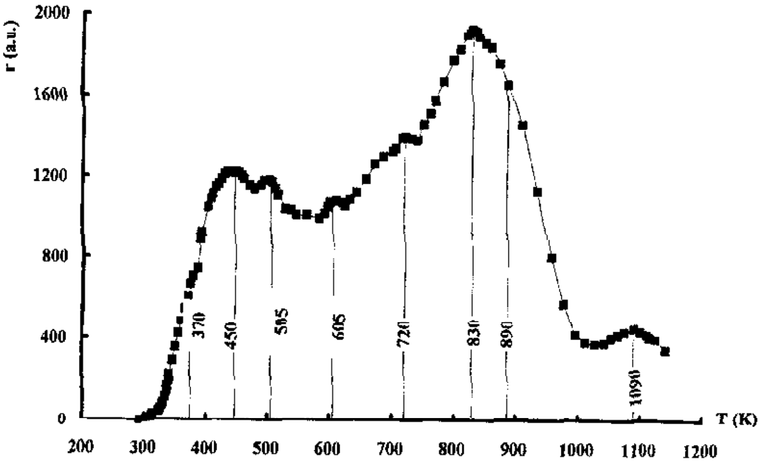

Fig. 2 Complete TPD of CO_2

Figure 3 shows how the CO_2 spectrum, as presented in Fig. 2, has been sliced into more than forty partial TPD's by the saw-tooth heating program.

Arrhenius transforms of these curves are presented in Fig. 4. It is seen that most of the transforms have an S shape with a linear part around the inflection point. Theoretically, by application of Eq. (1) at constant surface population, straight lines were expected in the lower part of the curves. In our case, curves with upward concavity were observed. This discrepancy is explained by a slight reconstruction of oxygen groups with a low energy of decomposition. This phenomenon, which occurs during the cooling of the sample between two successive

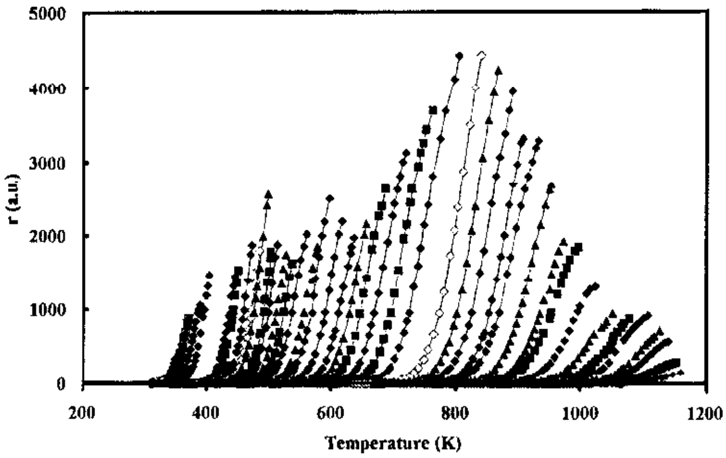

Fig. 3 Successive partial TPD's obtained by means of a saw-tooth heating program (First ITPD)

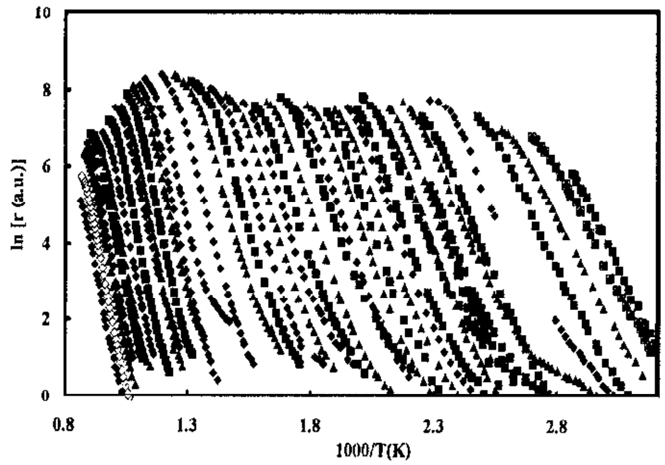

Fig. 4 Arrhenius transforms of the partial TPD's presented in Fig. 3

partial TPD's, may be due to a readsorption of CO_2 or a transformation of oxygen groups at the surface of carbon. Thus the lower part of the curves in Fig. 4 cannot be used to estimate the desorption activation energy of CO_2. On the other hand, the upper part of the curves in Fig. 4 cannot be used for this purpose either, because the population of the decomposing species is not constant in this region. In other words, the downward concavity of the curves shows that the threshold under which the population of the species is quasi constant is overpast. Consequently, the activation energies have been estimated from the greatest slopes of the S-shaped curves, i.e., at their point of inflection.

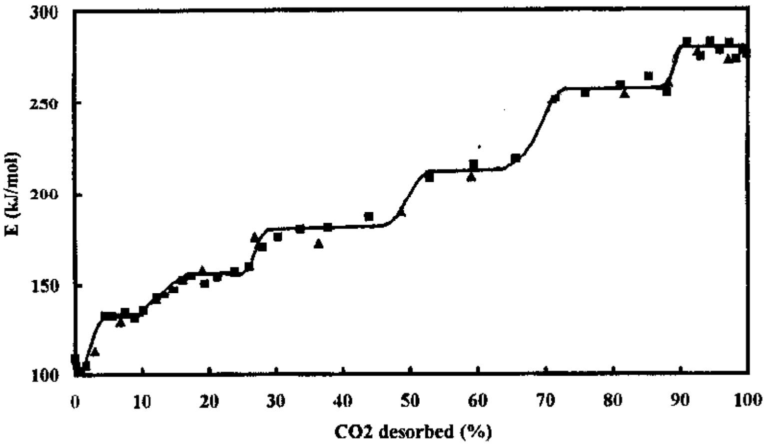

Fig. 5 Variation of the apparent activation energy of desorption *vs.* the total amount of CO_2 desorbed from carbon surface. (■) First ITPD; (▲) Second ITPD

Figure 5 shows the apparent activation energy E *vs.* the fraction of the total amount of CO_2 evolved from the beginning of the first partial desorption at 300 K. It is seen that this curve exhibits plateaux which correspond to various CO_2-producing chemical reactions with a definite energy of activation. During the ITPD process, species with a lower activation energy decompose before those with a higher activation energy. This means that the surface is progressively depleted of the oxygen species with an increasing activation energy of decomposition.

The straight part of Arrhenius transforms allows the order of magnitude of the frequency factor A to be assessed using Eq. (1) written in the following form at a fixed value of θ,

$$\ln(A_\theta/r_\theta) = -\ln(f_\theta) + E_\theta/(RT) \tag{4}$$

with

$$r = -\frac{dN}{N_0 dt}, \tag{5}$$

and assuming that the order of magnitude of f_θ is 1 when the concerned species is half-decomposed, i.e., for the points at the middle of the plateaux in Fig. 5. The values obtained for E and A are listed in Table 1.

Discussion

In principle, the ITPD method has to provide apparent activation energies that are independent of the number of partial temperature-programmed desorptions

Table 1 Kinetic parameters for the various steps of CO_2 desorption

E/kJ mol^{-1}	105	134	156	180	218	260	281
A/s^{-1}	10^{12}	10^{12}	10^{11}	10^{10}	10^{10}	10^{11}	10^{10}
%CO_2	0–3	3–14	14–28	28–50	50–70	70–89	89–100

E: apparent activation energy of desorption; A: order of magnitude of the frequency factor. %CO_2: percentage range of CO_2 desorbed for the various desorption steps.

used. The second ITPD experiment, for which the complete TPD spectrum was sliced into 14 partial desorptions, instead of the forty ones employed previously, has given the Arrhenius transforms presented in Fig. 6. It is seen that the points obtained fit the curve in Fig. 5. Obviously, this number of partial desorptions was not sufficient in this case to detect the presence of the plateaux. Apart from that, this result shows that our results are reproducible in spite of the difficulties due to the lack of linearity of the Arrhenius transforms at lower desorption rates, as explained above.

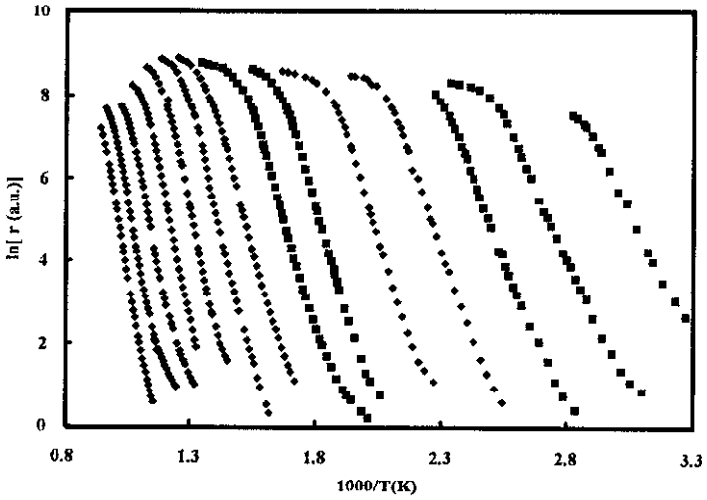

Fig. 6 Arrhenius transforms of the partial TPD's composing the second ITPD

It is interesting to go back to the complete TPD (Fig. 2) to verify that ITPD results may explain the main features of the complete spectrum. In the particular case of a process of first kinetic order, for which $f(\theta)=\theta$ in Eq. (1), the following equation holds at the maximum of the TPD peak [2],

$$\frac{E}{RT^2}=\frac{A}{\beta}\exp\left(-\frac{E}{RT}\right) \tag{6}$$

where β represents the heating rate.

This expression holds only approximately for some other desorption kinetics including the possibility of readsorption [6]. Equation (6) has been used to calculate the apparent energies of desorption E from the temperatures of the maxima and shoulders of the complete TPD, using the value of A obtained by ITPD (Table 1). The result is presented in Table 2. It can be stated that there is an overall agreement between the values of E obtained by the two methods if one considers that Eq. (6) is probably an approximate one in the present case. These results are supported by more recent ones we obtained by ITPD with another active carbon sample [21]. Thus it can be concluded that the results of ITPD are consistent with those of the complete TPD.

Table 2 Temperatures of the main peaks and shoulders in the complete TPD presented in Fig. 1 and values of E calculated by Eq. (6) using the value A given in the first line

A/s^{-1}	10^{12}	10^{12}	10^{12}	10^{11}	10^{10}	10^{10}	10^{11}	10^{10}
T/K	370	450	505	605	720	830	950	1090
E/kJ mol^{-1}	100	121	147	159	176	209	255	260

The results obtained illustrate the usefulness of the threshold TPD methods which allow the number of desorption steps to be determined and characterized by the apparent activation energy of desorption. This result should be, in principle, accessible through deconvolution of the complete desorption spectrum. Nevertheless, this deconvolution needs models for the kinetics of desorption that are much more detailed than the general models used in this paper. Moreover, it has been shown that determining both E and A in the case of heterogeneous surfaces would require a precision in experimental data far beyond the experimental possibilities [9]. Thus it seems that, in the difficult case of strongly heterogeneous surface processes, it is easier to overcome experimentally the problem by using a threshold method.

The difficulties of deconvolution of TPD spectra are even greater in the case of a microporous solid if one admits that readsorption is possible. In this case the rate of transport phenomena intervenes in the desorption kinetics. It has been shown in a study of the desorption of ammonia from zeolite that the threshold methods may be used in this case [17].

The conclusion is that threshold differential methods, and in particular ITPD which allows the surface coverage to be controlled for each threshold, are interesting not only in the case of desorption of small molecules from well-characterized metallic surfaces, but also with powdered samples. The method of ITPD supplies interesting results in one of the most complicated cases, i.e., the thermal decomposition of superficial oxygen species at the surface of a microporous active carbon. This first attempt to apply ITPD to a commercial active carbon that we studied as received, revealed several steps of decomposition of the oxygen groups which decompose into CO_2. This may constitute a progress toward the identification of these species.

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