Journal of Thermal Analysis, Vol. 41 (1994) 1529-1534

APPLICATION OF CRTA TO THE STUDY OF MICROPOROSITY BY THERMODESORPTION OF PRE-ADSORBED WATER

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Abstract

Thermodesorption is here considered for its possibility of giving access to the microporosity of adsorbents. The requirements of this application (good separation of successive desorption steps, good control of the desorption pressure and temperature throughout the sample, possibility of a safe kinetic analysis of each step) are here fulfilled by carrying out the thermodesorption in the Controlled transformation Rate Thermal Analysis (CRTA) mode. The method is applied to 4 zeolites (3A, 4A, 5A and 13X) and a well characterized charcoal, from –25 to 325°C, after pre-adsorption of water.

Keywords: activated carbon, CRTA, micropores, thermodesorption, water adsorption, zeolites

Introduction

In porous adsorbents, the micropores (i.e. smaller than 2 nm in width) are those responsible for most of the adsorptive properties of zeolites, activated carbons, clays or oxides (like alumina, magnesia, zirconia etc...). Their quantitative assessment usually involves the use of non-reacting probe molecules, but at least in 3 different ways:

a/ One can derive a useful information from the size of the molecule and amount adsorbed.

b/ One can also analyse the initial part (before monolayer coverage) of the adsorption isotherm by the semi-empirical "α_S" or "*t*" methods, where the adsorptive behaviour of the adsorbent under study is compared with that of a non-porous adsorbent.

c/ One can finally look for the relationship between the adsorbate-adsorbent energy of interaction and the size of the micropore, because of the well-known enhancement of the energy of adsorption in micropores whose width does not

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exceed a few molecular sizes. This former approach can be dealt with by adsorption calorimetry or by immersion calorimetry [1].

All the aforementioned methods rely on the study of states in thermodynamic equilibrium. It follows that none of them is sensitive by principle, to the mechanism of diffusion through the micropores. Nevertheless, diffusion is a highly pore-size dependent phenomenon, which is certainly worth being exploited.

Hence the interest of a kinetical method. Temperature-programmed desorption (TPD) of a porous sample previously saturated with a vapour (for instance water) is probably the simplest and quickest one.

Nevertheless, TPD has mainly been used, until now, to separate, from their different outgassing temperatures, the various gaseous species adsorbed on a solid surface (for instance, that of a catalyst [2]). Quite recently, it was applied to the study of microporous carbons, aluminas or silicas by taking advantage of the enhanced resolution provided by Controlled transformation Rate Thermogravimetry (CR-TG) in the arrangement developed by Paulik and Paulik and called by them "Quasi-Isothermal TG" [3].

Our intention is here to use again Controlled transformation Rate Thermal Analysis (CRTA [4]) but to go two steps further by (i) carefully controlling the desorption pressure throughout the experiment and (ii) drawing kinetic information from the analysis of the curves.

Experimental

CRTA equipment

The equipment used is described in [5] under the name of "Controlled Rate Evolved Gas Detection" (or CR-EGD). It allows to operate in the sole presence of the gas desorbed from the sample and also to control and keep constant the desorption pressure (conveniently selected, with this equipment, within the range from 10^{-2} to 1 mbar).

Samples used

We selected 4 zeolites from Union Carbide (3A, 4A, 5A and 13X) and a moderately activated charcoal (steam activation, 12% burn-off) kindly supplied by CECA S.A. Their main features are reported in Table 1.

Table 1 Properties of adsorbents

Name	Composition	Width of openings /nm	BET-N_2 specific surface area / $m^2 \cdot g^{-1}$	$100 \frac{\Delta m\ (H_2O)}{m_o}$ %
3A	K(Si/Al#1), xH_2O [6]	0.29 [7]	N_2 not accessible	24.2
4A	Na(Si/Al#1), xH_2O [6]	0.38 [7]	N_2 not accessible at 78 K	28.5
5A	Ca(Si/Al#1), xH_2O [6]	0.44 [7]	587 [8]	29.7
13X	Na(Si/Al#1.75), xH_2O [6]	0.80 [7]	657 [8]	36.0
Ceca (12%)	from coal	<2	442 [9]	18.7

Procedure

Approximately 0.5 g of sample is weighed in a pyrex-made adsorption bulb closed with a vacuum stopcock. This is connected to the CR-EGA equipment and brought to 350°C under CRTA conditions, under 10^{-3} mbar. The sample is then cooled down to 30°C and brought in equilibrium with saturating water vapour, during 1 hour. The saturated sample is then cooled down to –25°C, where the Controlled Rate Thermodesorption (CR-TD) experiment is started with a controlled water pressure of $4 \cdot 10^{-2}$ mbar and a controlled rate of desorption of $(2.9 \pm 0.4) \cdot 10^{-4}$ min^{-1} (which means that the desorption is completed in c.a. three days).

Results and discussion

The curves obtained are given in Figs 1 to 3. The water loss on desorption is reported in % of the sample mass (dry sample after preliminary outgassing at 350°C). As early as –22°C sublimation of three-dimensional water adsorbed around the sample, out of the pores, takes place. The interesting information is of course provided for higher temperatures, when the pores are progressively emptied. The results obtained fall into three categories:

1/ Thermodesorption of zeolites 3A, 4A and 13X (cf. Fig. 1). It can be seen that all curves present an inflexion point and that they progressively shift from higher to lower temperatures as the size of the pore-opening increases from c.a. 0.3 nm (3A) to 0.8 nm (13X). The fact that there is an inflexion point but not a vertical drop of the thermodesorption curve indicates that the size of the opening (which is known to be highly uniform throughout each of these samples) is not the only parameter controlling the shape of the curve. Since these experiments were carried out under a constant rate of desorption (isokinetic experiments) this shape can be directly related with the corresponding rate law [10] which happens to be here a diffusion rate law. This is consistent with the results given by Ruthven [7].

2/ Thermodesorption of zeolite 5A (cf. Fig. 2). This zeolite behaves differently, showing now 2 inflexion points (or 2 steps). The second step (above 100°C under the low pressure of $4\cdot10^{-2}$ mbar) is probably due to a special inter-

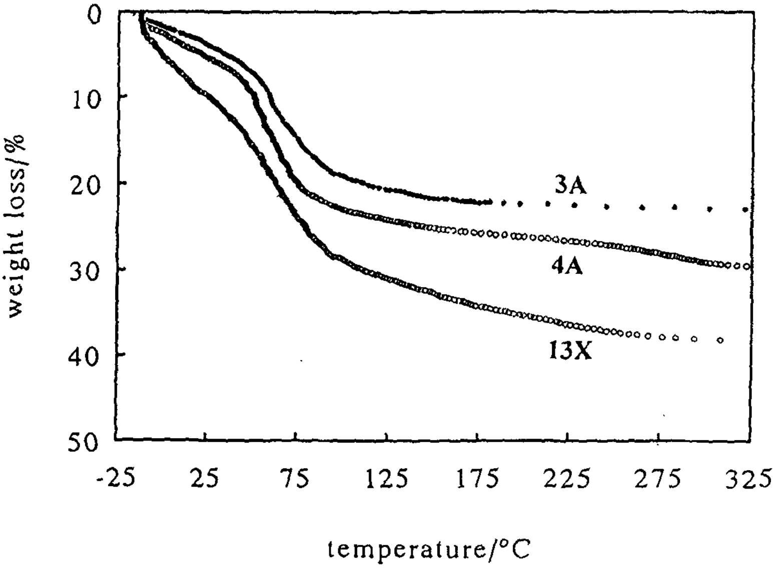

Fig. 1 Controlled Rate Thermodesorption of water preadsorbed on zeolites 3A, 4A and 13X

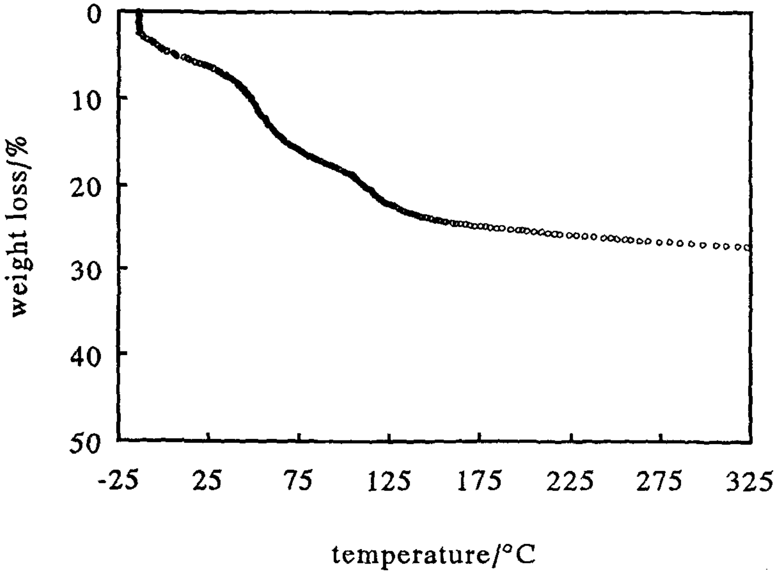

Fig. 2 Controlled Rate Thermodesorption of water preadsorbed on zeolite 5A

action between water and the Ca^{2+} of this zeolite. This is what explains for instance the hydrothermal fragility of calcium faujasites [11]. From the shape of the curve it can be said, here again, that the first step is dominated by a diffusion mechanism.

3/ Thermodesorption of the microporous carbon (Fig. 3). The shape of the curve is here very different: there is a continuity from the sublimation of the external water to the desorption from the micropores. This is probably because this activated charcoal (i) contains micropores in the whole range of widths, from 0.4 to 2 nm [1], (ii) has, like most carbons, a relatively weak affinity for water (explaining an easy desorption, even from the smallest pores) and (iii) has slit-shaped pores (between graphitic, flat, surfaces) which make that diffusion is not any more the rate-limiting phenomenon. Indeed, the shape of the CR-TD curve is consistent with a mechanism controlled by either a 1-order law (F1) or an interface advancement (R2 or R3).

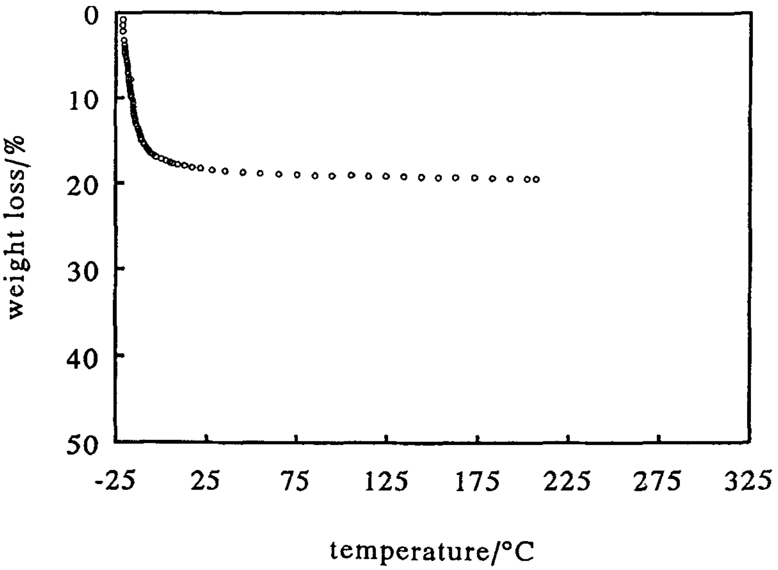

Fig. 3 Controlled Rate Thermodesorption of water preadsorbed on charcoal Ceca (12%)

At this stage we can conclude that the pore-size (cf. for zeolites 3A, 4A, 13X) has a direct influence upon the Constant Rate Thermodesorption curves and that these also carry information about the diffusion process (occurring from the progressive emptying, from outside to inside, of the interconnected cavities of the zeolite structure). These curves are also depending upon any particular interaction between the water molecule and the adsorbent: enhanced interaction with the calcium ions of the 5A zeolite, weakened interaction with the hydrophobic carbon surface. The further step needed to continue this analysis is a new set of experiments making use of a modulated rate of desorption (modulation between two pre-set values) in order to apply the assumptionless rate-jump method [12] for determining the activation energy of the desorption all along the experiment.

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Zusammenfassung — Thermodesorption wird in Erwägung gezogen, um einen möglichen Zugang zur Mikroporösität von Adsorbenten zu erhalten. Die Anforderungen an diese Anwendung (gute Trennung aufeinanderfolgender Desorptionsschritte, gute Kontrollmöglichkeit von Desorptionsdruck und -temperatur innerhalb der gesamten Probe, Möglichkeit einer sicheren kinetischen Analyse jedes Einzelschrittes) werden hier durch die Ausführung der Thermodesorption mittels der CRTA-Methode erfüllt. Diese Methode wurde nach Präadsorption von Wasser zwischen –25 und 325°C an 4 Zeolithen (3A, 4A, 5A und 13X) und einer sehr gut definierten künstlichen Kohle angewendet.