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Low temperature constant rate thermodesorption as a tool to characterise porous solids

V. Chevrot[a], P.L. Llewellyn[a,*], F. Rouquerol[a], J. Godlewski[b], J. Rouquerol[a]

[a]*Laboratoire de Matériaux Divisés, Revetements et Electrocéramiques (MADIREL), CNRS — Université de Provence, 26 rue du 141 RIA, 13331 Marseille Cedex 3, France*

[b]*CEA Cadarache, DRN-DEC-SH2C, B.P. No. 1, 13108 Saint-Paul-lez-Durance, France*

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Abstract

An apparatus is described allowing the study of controlled rate thermodesorption (CRTD) in the temperature range from 163 to 473 K and in the residual pressure region around 10^{-3} mbar. This apparatus is designed with the aim to increase the sensitivity in the estimation of the specific surface area with respect to traditional adsorption experiments. The thermodesorption of water from a model mesoporous MCM-41 sample is studied using this apparatus. The thermodesorption curve obtained is related to the mesopore size distribution via an expression based on the Kelvin law. These results compare well with those obtained by adsorption gravimetry of water at 303 K on the same MCM-41 sample. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Temperature programmed desorption (TPD) traditionally consists of linearly increasing the temperature of a sample pre-adsorbed with a liquid or vapour (ammonia, *n*-nonane, water, ...) and measuring the temperature at which the vapour desorbs. Initially, such experiments were used to determine an energy of desorption [1] and thus to characterise specific surface sites. However, it is also possible to determine a number of other properties of the sample such as surface coverage, micropore volume and even an estimation of the micropore size (TPD of nonane [2]) etc... However, if several adsorption processes occur, these may overlap, thus, requiring increased resolution. Non-linear temperature programmes can be applied to TPD experiments, which would seem to partially overcome this problem [3]. Nevertheless, in such experiments where a predetermined heating profile is used, the level of control and reproducibility is limited due to the pressure gradients that are generated within the sample.

A direct feedback from the sample, which can be used to generate the heating profile during the experiment, is a means to overcome these problems of reproducibility. This solution is proposed by the various methods of sample controlled thermal analysis (SCTA) [4]. The quasi-isothermal heating mode proposed by the Paulik brothers' [5], used for the thermodesorption of liquids [6–10] is one way to increase the resolution of traditional TPD experiments. The quasi-isothermal heating mode is one that starts with a linear temperature rise. The differential mass loss is

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[*] Corresponding author. Fax: +33-495-132-074.
E-mail address: pllew@ctm.cnrs-mrs.fr (P.L. Llewellyn)

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calculated with time and when this increases above a certain pre-set value, an isothermal plateau is maintained. When the differential mass loss with time descends below a second pre-set value, a linear increase in temperature again takes over. Such experiments have been used to estimate the pore volume and mesopore mean width of a range of porous samples including silicas [6,9,10] and carbons [10].

Although quasi-isothermal thermodesorption leads to an increased resolution with respect to standard TPD, several limitations can be observed. For small amounts of a given porosity, the quasi-isothermal programme is not at its optimum [10]. Thus, for the evaluation of microporosity and adsorbed surface species, the same resolution is obtained as with a linear heating programme [10]. Furthermore, this technique is theoretically limited to the saturated vapour pressure of the pre-adsorbed liquid. Although, different forms of sample cell can be used which seem to permit different pressures above the sample [11], this pressure is not measured and more importantly, not controlled.

Another manner to use SCTA that was proposed by Rouquerol is in the form of 'controlled transformation rate thermal analysis' [4,12]. In its most simple form, the rate of gases evolved from a sample, undergoing a thermal transformation, is kept constant with time [12]. Both the rate of gas loss and the residual pressure above the sample can be tuned in such a way as to minimise any pressure and temperature gradients within a sample. This again leads to an increased resolution of the experiments allowing the separation of various different steps.

Controlled rate thermal analysis (CRTA) has been used for the study of thermodesorption of water from various zeolites [13] as well as from heterogeneous surfaces [14,15]. Here, a residual pressure above the sample of the order of 10^{-2} mbar was used which is sufficient to estimate the micropore volume. Even though the temperature at which the experiments were started was around 248 K, this is not sufficient to retain physisorbed water within mesopores. Two solutions are possible: the first is to drastically increase the residual pressure above the sample; the second is to decrease the initial temperature at which the experiments start.

The aim of the present study is to describe a SCTA apparatus that has been adapted to study the controlled rate thermodesorption (CRTD) of pure liquids at a temperature starting from 163 K. The motivation behind this project was to increase the resolution of surface area determination with respect to traditional adsorption experiments (gravimetry and manometry). This especially, for the case of bulk samples which are unable to be loaded into an adsorption sample cell. Thus, the measurement of mass (gravimetry) or pressure (manometry) is substituted by a measurement of time in the CRTD experiments.

The pressure range in which the experiments can be carried out is from 10^{-4} to 5 mbar. This allows the study of the thermodesorption of water at a rate of water loss as low as 0.02 mg h^{-1}. Thus, for an experiment that lasts 1 h that corresponds to the loss of 0.02 mg of water, assuming an equivalent surface area of 0.11 nm^2 for one water molecule, an equivalent surface area of 0.07 m^2 can be measured in the sample cell itself.

To verify this set up and experimental method, the present study presents results pertaining to a mesoporous model test sample, MCM-41. The details of calculations, relating the curve of temperature increase with time, to the average mesopore width are then given. These results are compared to those obtained from nitrogen and water adsorption data.

2. Apparatus

The CRTD apparatus used in the present study is schematised in Fig. 1. The sample is placed into a cell which itself is fitted to a conventional CRTA apparatus such as that described in [4]. The furnace used for these experiments is placed onto a liquid nitrogen Dewar. Inside the Dewar, the electrical resistance maintains a constant boiling of liquid nitrogen. The vapour thus produced passes through a spiral tube within the furnace assuring constant cooling down to a minimum temperature of 163 K. The furnace resistance is connected to a PID control [4], whilst the sample temperature is measured via a Platinum 100 thermometer. This apparatus permits a temperature interval from 163 to 473 K to be explored.

The maximum time taken for an experiment depends on the amount of liquid nitrogen in the Dewar. The current set up, with the 25 l reservoir allows experiments to be carried out for up to 20 h.

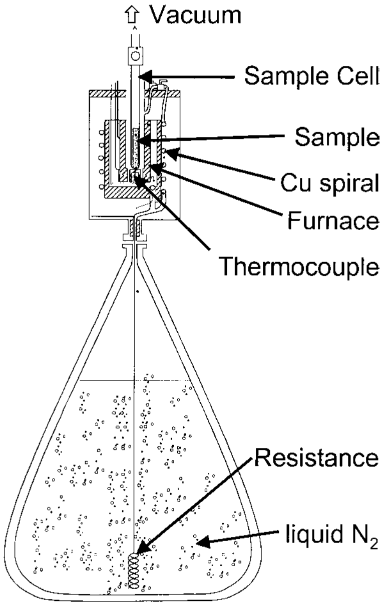

Fig. 1. Schematic diagram of the CRTD apparatus used in the present study.

3. Experimental

3.1. MCM-41 sample

The MCM-41 sample was obtained using a synthesis procedure based on that presented in [16]. An aqueous solution was made containing pyrogenic silica, waterglass, tetramethyl ammonium bromide. To this was added hexadecyltrimethylammonium bromide ($C_{16}TABr$) as a micelle builder. The solution was poured into an autoclave that was then placed into an oven at a crystallisation temperature of 373 K for 72 h. We chose to use a relatively high temperature synthesis in order to have materials more resistant to degradation by water than materials produced at room temperature.

The resultant synthesis mixture was then filtered and thoroughly washed with water. The solid material obtained was calcined, to eliminate the residual water and organic material, by heating from room temperature by 1 K min^{-1} to a final temperature of 823 K which was maintained for 4 h.

3.2. Outgassing and pre-adsorption

Prior to any experiments, around 50 mg of sample was pre-weighed into the sample cell. The sample was outgassed via CRTA at a constant residual pressure of 2×10^{-3} mbar up to a final temperature of 623 K. The outgassed sample was then placed into a thermostated bath at 293 K and open into contact with doubly distilled water at a temperature of 291 K. This ensured a p/p^0 of water at 0.95. The sample was thus left to pre-adsorb under these conditions for a minimum of 16 h.

3.3. Experimental procedure

The pre-adsorbed sample was placed into the furnace shown in Fig. 1 before being rapidly cooled down to a minimum temperature of 193 K. At this point, the vacuum line was opened and the sample was pumped down to a pressure of 2×10^{-4} mbar. Previous experiments have shown that the sample cell adsorbs a certain quantity of water that desorbs at around 204 K. The initial part of the experiment thus heats under CRTA conditions to remove this excess. It is interesting to note that the silica sample cells age with time. This is highlighted by the increase in time needed to remove this excess. Care was thus taken not to use the cells once this ageing started. A future development would be to treat the cell to be more resistant to ageing as well as to limit the amount of water adsorption on the cell's surface.

The sample is then heated under CRTA conditions under a constant residual pressure of 2×10^{-3} mbar. Curves of the increase in temperature with time are thus obtained. Prior calibration curves for the loss of water under the same experimental conditions permit the time scale to be converted to mass loss. In the present study, a rate of mass loss of water of 0.16 mg h^{-1} was used.

This rate of mass loss is calibrated during a separate experiment for the dehydroxylation of gibbsite under the same experimental conditions as the CRTD experiment. Around 1 g of sample is heated and the mass loss is calculated at different points of the thermal transformation. For the lowest rates of water loss 0.02 mg h^{-1}, this calibration took over 4 weeks.

3.4. Adsorption isotherms

As a comparison to the results obtained by thermodesorption, water adsorption gravimetry at 296 K and nitrogen adsorption manometry at 77 K were carried out. The apparatus used for water adsorption is described elsewhere [17] and is based on a continuous introduction of water vapour. Nitrogen adsorption was carried out using a point by point procedure on a commercial apparatus (Omnisorp 100, Coulter, France).

4. Results

Fig. 2 represents the curves of mass loss with increasing temperature for the MCM-41 used in this study. This curve can be split into two main parts. The initial part, up to point A, corresponds to the loss of water from the external surface of the sample as well as excess condensed water from the surface of the sample cell. This was previously confirmed in a blank experiment.

Thermodesorption from the sample proper starts from point A with a small increase in temperature from 204 to 209 K. For the calculations that follow, the amount of water desorbed from point A up to the end of the experiment is normed between 0 and 1, and is termed *Alpha* (cf. Figs. 5 and 6).

The following step which occurs in this step up to a temperature of around −40°C corresponds to the majority of water loss. This can be logically attributed to water loss from the mesoporosity. It is interesting to note that this step is not isothermal which may highlight a small pore size distribution.

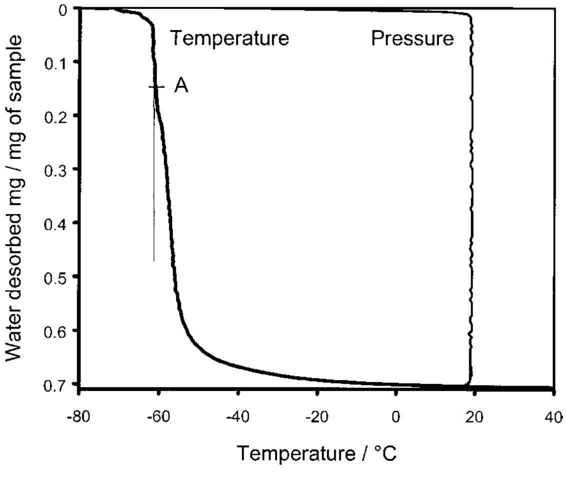

Fig. 2. CRTD curve for the desorption of water from MCM-41.

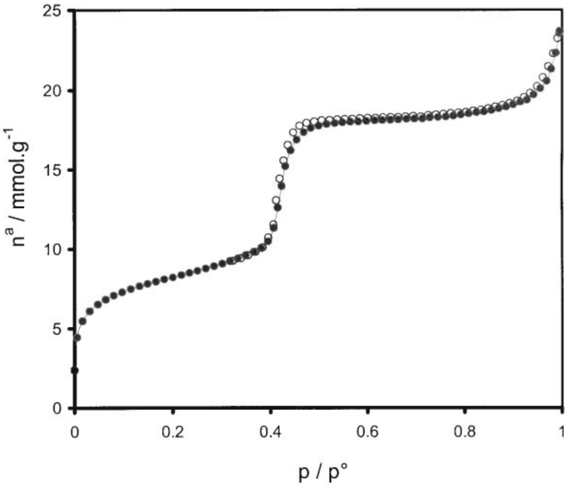

Fig. 3. Nitrogen isotherm at 77 K obtained with MCM-41.

The adsorption–desorption isotherms for the MCM-41 sample are shown in Fig. 3 for nitrogen at 77 K and Fig. 4 for water at 298 K. Whilst, for the adsorption of nitrogen, an isotherm of distinct Type IV character is observed, the water isotherm has more Type V character [18]. The capillary condensation steps are observed at p/p^0=0.44 for nitrogen and p/p^0=0.58 for water. It can be seen in both cases that this condensation step is not completely vertical, indicating the distribution in pore size for this sample. This is in concordance with the thermodesorption result shown in Fig. 1.

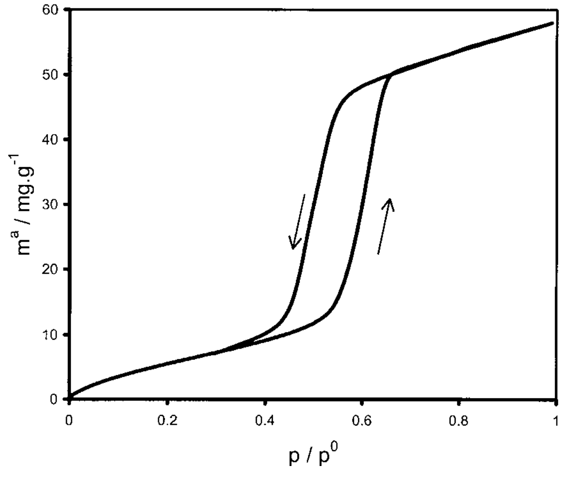

Fig. 4. Water isotherm at 298 K obtained with MCM-41.

The desorption branch of the nitrogen isotherm shows very little hysteresis which can be explained by the lack of thermodynamic stability of the nitrogen meniscus below $p/p^0=0.42$ at 77 K. The desorption branch of the water isotherm, however, shows a distinct hysteresis loop which closes to the adsorption branch above the limiting relative pressure of 0.28 for water at this temperature. From this, it is possible to consider that the Kelvin law can be used to characterise the results obtained with water.

5. Calculations

5.1. Adsorption potential curve

One of the simplest calculations relates the adsorption potential to the pressure via the expression [19]

$$A = -RT\ln\left(\frac{p}{p^0}\right) \tag{1}$$

This type of expression has been well exploited by Staszczuk [20] where, p is the vapour pressure above the sample, p^0 the saturated vapour pressure, T the absolute temperature and R the ideal gas constant. As in the present study, p is maintained constant, an expression for p^0 with temperature therefore needs to be found. Such an expression is described below. An example of such a curve of adsorption potential is given in Fig. 5.

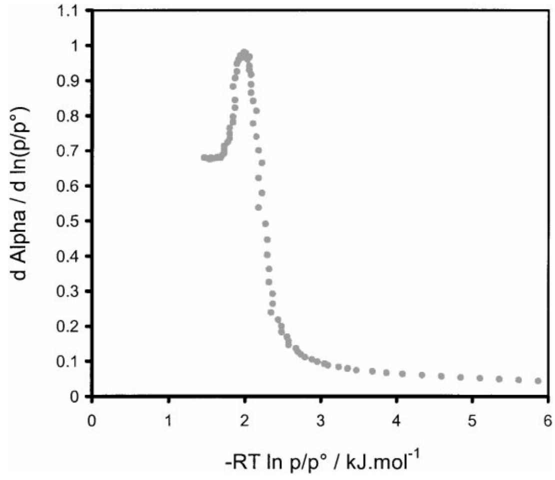

Fig. 5. Potential energy curve obtained for the CRTD of water from MCM-41.

It can be seen that only a single peak is observed as would be expected for a sample containing only mesopores. It is possible to exploit the results from such a potential curve using expressions such as those recently put forward by Villiéras et al. [15]. In cases where enhanced adsorption interactions occur, such as desorption from micropores or chemisorption, this approach seems extremely interesting.

In the present study, it is logical to relate this potential energy curve to the pore radius of the MCM-41 sample. This is described as follows.

5.2. Relation between the adsorption potential curve and the pore size distribution

In the present case, for the thermodesorption of a capillary condensate liquid, we have chosen to use the Kelvin law for the estimation of the pore size [21,22]. This law assumes thermodynamic equilibrium. To verify thermodynamic equilibrium, a number of experiments can be carried out at different rates. In the current case, a second experiment (not shown here) was carried out at a much lower rate of 0.06 mg h^{-1} to verify that the resultant temperature curves overlap.

The results highlighted above show that for the given example, the Kelvin law may be used to treat the results. Traditionally, the Kelvin law is written in the form

$$\ln\left(\frac{p}{p^0}\right) = -\frac{2\gamma}{r_K}\frac{v^l}{RT} \tag{2}$$

where γ is the surface tension of the liquid, v^l the molar volume of the capillary condensate and r_K the average pore radius of the meniscus or Kelvin radius. Again, p is maintained constant, whereas, p^0, v^l and γ vary with temperature T (in K). Tables for each of these variables as a function of temperature can be found [23]. After plotting the values of $\ln(p/p^0)$, v^l and γ in these tables as a function of $1/T$, various fits were obtained which are described as follows.

We have used an expression for $\ln(p/p^0)$ assuming back extrapolation to temperatures below 193 K. For the pre-set pressure value at which the thermodesorption experiment was carried out (2×10^{-3} mbar), the following expression has been used:

$$\ln\left(\frac{p}{p^0}\right) = \frac{238743.416}{T^2} + \frac{3697.501}{T} - 23.373 \tag{3}$$

The variation of the surface tension γ (in mN m^{-1}), with temperature was also fitted to data in [23] and has been expressed as follows:

$$\gamma = \frac{2990880834.5}{T^3} - \frac{36560128.13}{T^2} + \frac{157960.29}{T} - 159.39 \tag{4}$$

whereas, v^1 (in cm^3 mol^{-1}) can be expressed as M/ρ, where the variation of density, ρ (in g cm^{-3}) with temperature was obtained in [23] and fitted via the expression

$$\rho = \frac{10751322.945}{T^3} - \frac{153002.11}{T^2} + \frac{685.59}{T} + 0.013 \tag{5}$$

In the present case where a cylindrical pore geometry is assumed, the pore radius r_p, is obtained using the following expression: $r_p = r_K \cos\theta + t$. Here, one considers that the liquid wets perfectly the solid then $\cos\theta = 1$. Therefore, $r_p = r_K + t$. The thickness of adsorbed film 't' does not desorb with the capillary condensate. This thickness varies with p/p^0 and, therefore, also with temperature T. For a silica sample, Naono and Hakuman [24] studied the variation of water thickness on a silica sample as a function of p/p^0. From this study, an expression to fit the variation of t (in nm) with p/p^0 is given by

$$t = 0.0044\left[\ln\left(\frac{p}{p^0}\right)\right]^4 + 0.046\left[\ln\left(\frac{p}{p^0}\right)\right]^3 + 0.1792\left[\ln\left(\frac{p}{p^0}\right)\right]^2 + 0.3397\left[\ln\left(\frac{p}{p^0}\right)\right] + 0.321 \tag{6}$$

Introducing the expression for $\ln(p/p^0)$ in Eq. (3) leads to the relationship of t as a function of T.

After first converting the time to mass loss after calibration experiments, it is possible to plot mass loss as a function of temperature. Each temperature can be converted to a value of r_K. The curve of mass loss as a function of r_K is then derived. Finally, using $r_p = r_K + t$, it is possible to obtain results in the form of the curve presented in Fig. 6a.

The pore size distribution curves obtained from water thermodesorption and using the BJH treatment of the water desorption data are compared in Fig. 6. Table 1 shows a comparison of the results of average pore width and pore volume obtained from these curves. Taking into account the large differences in experimental conditions of temperature, pressure and

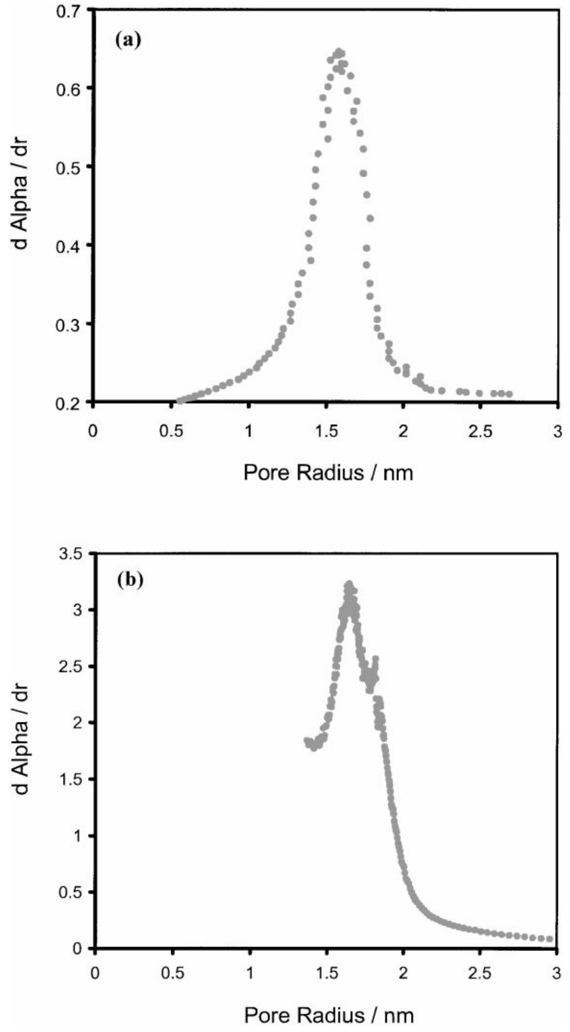

Fig. 6. Pore size distribution obtained from (a) treatment of the CRTD curve of water desorption from MCM-41, and (b) BJH treatment of the water adsorption data obtained with the same sample.

Table 1
Comparison of pore width and pore volume obtained from CRTD and from the water desorption isotherm

	Pore radius (nm)	Pore volume (cm g^{-1})
CRTD of water	1.58	0.51
Water isotherm at 303 K	1.65	0.52

protocol a surprisingly good correlation is obtained for these treatments.

It should be noted, however, that a number of assumptions and back extrapolations are made in the mathematical treatments proposed. For example, the evolution of the adsorbed film thickness '*t*' with relative pressure should be varied for each sample of different chemical nature. Furthermore, one should also use the appropriate expression for other pore geometry's. Finally, the use of a pure silica, model mesoporous MCM-41 sample with a cylindrical pore system permits a number of these assumptions to be valid in the present case.

6. Conclusions — perspectives

CRTD is a tool that can be used to characterise porous solids, permitting an increased resolution and sensitivity with respect to traditional TPD experiments. It is, thus, possible to study very low surface areas and small quantities of sample. The use of a special set up allows the CRTD experiments to be carried out at temperatures from 163 K. Relatively simple calculations can be made from the CRTD curves, such as the distinction of adsorption sites and different pore volumes. After verification of thermodynamic conditions, the Kelvin law can be used to calculate the mesopore width.

The utility of such an apparatus is to study very low surface areas, well below those currently accessible via other methods. This is especially the case for bulky samples (tubes, electrodes, ...) which cannot be packed into a normal adsorption cell.

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