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Porosity of solids by temperature programmed desorption of liquids—various heating programs[☆]

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Abstract

Thermogravimetric analysis was applied to the characterization of the porosity of silica gel. The thermal desorption of benzene was investigated by using various heating programs. The influence of desorption conditions on the derived values of the structural parameters of silica gel is discussed. Results from the thermogravimetric method are compared with those obtained from nitrogen adsorption–desorption.

Keywords: Porous structure; Silica gel; Thermal desorption

1. Introduction

Recently, we have applied thermogravimetric analysis to the characterization of the porosity of solids [1–3]. A simple measurement of thermal desorption of liquids is a valuable tool in the investigations of textural properties of silica gels, aluminas [4], activated carbons [5] and porous organic membranes [6]. The experiment consists of measuring the weight loss of the liquid perfectly wetting the porous solid against temperature, $\Delta m = f(T)$. The temperature of desorption may be converted into the pore radius of the evacuated pores R_k by using the Kelvin equation. Thus, from the desorption data of liquids in quasi-isothermal conditions the total pore volumes, mean pore radii and pore size distributions may be calculated.

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The values of the parameters characterizing the porous structure of solids derived from TG data depend on the heating mode of the sample. The aim of the present paper is to compare the textural parameters of porous silica gel obtained from TG data measured by using various heating programs, i.e. linear program, quasi-isothermal program and stepped-isothermal program.

2. Experimental

Silica gel Si-60 (Merck, Germany) was used in the experiment. The fraction 0.1–0.2 mm of silica gel was dried before the experiment by prolonged heating at 180°C. These conditions are sufficient to remove the physically bonded water and the temperature is low enough to avoid removing surface hydroxyl groups.

Benzene (POCh, Poland) puriss grade was carefully dried and stored over 3 Å and 4 Å molecular sieves.

Adsorption/desorption isotherms of nitrogen at –195°C were measured with an automated Sorptomatic 1800 apparatus (Carlo Erba, Italy). Surface areas were calculated from the linear form of the BET equation over the linear range of relative pressure between about 0.05 and 0.4. A value of 16.2 Å²/molecule¹ was used for the cross-sectional area of the nitrogen molecule.

Thermogravimetric measurements of desorption of the liquids were made with a Derivatograph 1500 C (MOM, Hungary), using various heating programs: the quasi-isothermal program (QI-3) at 3 K min⁻¹ heating rate within the linear heating range, the linear heating program (DL-3), and two stepped isothermal programs (SI-3, SI-9).

2.1. Quasi-isothermal program

The main feature of the quasi-isothermal program is a constancy of temperature within the time that the transformation connected with the weight changes takes place in the sample and a fixed weight loss level is exceeded. This heating mode is usually used in the investigations of isothermic processes, for example, decomposition and dehydration. The desorption of liquid from a porous solid is a different type of process that takes place within definite temperature ranges. However, the desorption from pores of different dimensions may be assumed to be the sum of several isothermic processes. Each isothermic process corresponds to desorption from a given group of pores of uniform dimension. Thus, during the desorption experiment carried out under quasi-isothermal conditions, the temperature and heating rate are not constant. If evaporation of the liquid is slow, the fixed weight loss level (in our case 0.5 mg min⁻¹) regulating the run of the program is not exceeded. As a result, the linear increase of temperature within this measurement range is realized. At a certain temperature when intensive evaporation occurs, the above mentioned level is exceeded and quasi-isothermal conditions are established.

¹ Å = 10⁻¹⁰ m.

2.2. Linear program

The linear heating program DL-3 is characterized by a continuous increase in temperature (3 K min^{-1}), independent of the transformations occurring in the sample.

2.3. Stepped isothermal program

The stepped isothermal program is characterized by a constancy of temperature within the fixed time intervals. The time over which temperature remains constant is selected before the experiment. In the experiments presented below, the desorption process of liquid from porous solid was divided into eight steps. The first step consists of the linear heating of the sample within the temperature range from 20 to 79–80°C, i.e. up to the moment when the temperature reaches the boiling point of the liquid (benzene). The evaporation process at the boiling point takes about 20 min. Desorption from the pores consists of six steps. Each is characterized by a fast, small (about 4 K min^{-1}) increase in the initial temperature and then by a constant temperature within the time period earlier programmed. The time intervals of constant temperature in our experiment were 3 min (SI-3) and 9 min (SI-9). The last step of the desorption consists of a continuous increase in temperature until the moment when the adsorbate is completely removed from the pores and the internal surface of the solid, i.e. up to about 150°C.

In the case of the TG experiments, it is very important to keep an atmosphere of saturated vapour above the sample. Therefore, the platinum crucible used in the experiment has a special construction. A schematic diagram of our measurement chamber is shown in Fig. 1. Both parts of the chamber are made of platinum. The sample in the form of paste (wet adsorbent + excess of liquid) is placed in the lower part. During the experiment both parts are tightly closed. The total volume of the chamber is about 0.5 cm^3 . The free space above the liquid is a few mm^3 . Thus, the volume of vapour of the liquid adsorbate exceeds by fifty times the free space filled by air at the beginning of the experiment.

There is a spiral groove 0.1 mm in width on the external surface of the internal part of the chamber to allow vapour removal. A thermocouple is placed in the concave bottom of the chamber so that one can assume that the temperature is measured inside the sample.

3. Results and discussion

In Fig. 2, analyses performed using various heating programs (DL-3, QI-3 and SI-9) are illustrated graphically as the dependence of temperature vs. time, $T = f(t)$. The ranges of constant temperature are clearly visible on curve 1 corresponding to the SI-9 program. In the case of the other two programs, the curves are smooth without separated steps. The desorption curves representing the weight loss against temperature, $\Delta m = f(T)$, for various heating programs are shown in Fig. 3. The shapes of these curves require additional explanation. Segments I of the TG curves represent evapor-

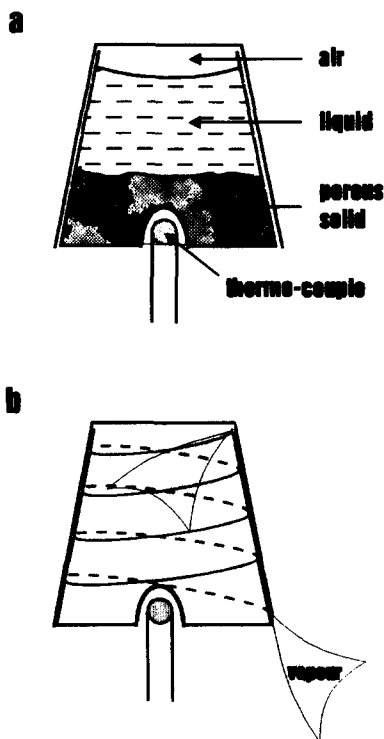


Fig. 1. Sketch of the platinum crucible used in the thermal desorption experiments. (a) Location of the sample (solid + excess of liquid) in the bottom part of the crucible. (b) Path taken by the vapour between the walls of the two parts of the crucible.

ation of the bulk liquid outside the pores of silica. Intensive evaporation at this stage of the process takes place at the boiling point of benzene (80°C). Loss of liquid adsorbate corresponds to the vertical segments on the TG curve. When the first stage of desorption is completed, the temperature increases and starts the desorption from pores. Segments II correspond to desorption of adsorbate condensed within the pores or adsorbed on the walls of the pores and are, therefore, a measure of the total pore volume. As seen, in the case of program SI-3, the decrease in mass of sample within a given time step at the start of desorption from the pores is small and increases progressively as the temperature increases. The opposite is true for program SI-9 for which the steps on the desorption curve become smaller and smaller as the temperature increases. Because the pressure of the saturated vapour depends on the pore dimensions, different groups of pores are evacuated at different temperatures. The emptying of a given group of pores requires appropriate time. When the time of desorption is too short, part of the pore volume remains unevacuated. Liquid remaining inside this group of pores will be desorbed during the next step of desorption. When the time of isothermal desorption is too long, part of the liquid filling other pores evaporates together with the liquid filling a given group of pores. However, the selection of an

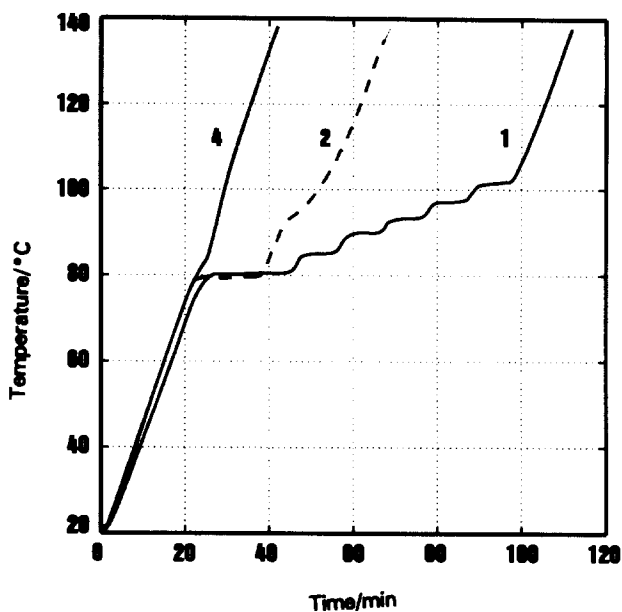


Fig. 2. Dependences of temperature of desorption against time for various heating programs: 1, SI-9; 2, QI-3; and 4, DL-3.

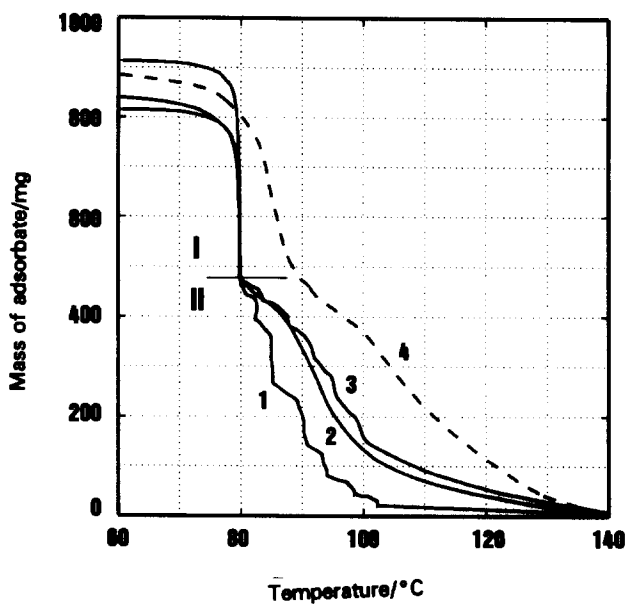


Fig. 3. Desorption curves of benzene from silica gel Si-60 for different heating programs: 1, SI-9; 2, QI-3; 3, SI-3; and 4, DL-3.

appropriate isothermal cycles for a given porous material is difficult in advance. The dotted curve in Fig. 3 represents the results obtained by applying a dynamic heating program with continuously increasing temperature. As can be seen, similar to the case of temperature vs. time dependences, the characteristic points on the desorption curve connected with the textural properties of the solid disappear. The curve is extended along the temperature axis. Curve 2 in Fig. 3 illustrates the desorption of benzene in quasi-isothermal conditions (program QI-3).

Taking into account the Δm values for different heating programs, appropriate volumes of evacuated groups of pores were calculated. The temperatures of desorption for pores of given dimensions were converted into pore radius using the Kelvin equation

$$\ln\left(\frac{p}{p_0}\right) = -\frac{2\gamma V_M}{R_k R T} \quad (1)$$

Eq. (1) gives the relationship between vapour pressure of a liquid over a curved and a flat liquid surface, p and p_0 , respectively; R_k is the radius of the liquid meniscus, γ is the surface tension, V_M is the molar volume of the liquid, and T is the absolute temperature.

When evaporation from a pore occurs, a strongly held monolayer or multilayer film of adsorbate molecules of thickness d remains on the walls. With the usual assumptions that the pores are cylindrical and that the contact angle of liquid with the adsorbed film is zero, R_k becomes equal to the radius of the core. The radius of the pore is given by $R_p = R_k + d$. Unfortunately, standard values of d under the conditions of TG experiments are very difficult to establish unambiguously. Consequently, it is not possible to proceed directly from these data to a pore size distribution but only to a core size distribution. The thickness of the surface film depends on the heating program used in the experiment. However, as we have stated earlier, the effect of surface film may be minimized by choosing an optimal heating program for the TG experiment. The program must be neither too slow nor too fast. If it is too slow, desorption will be too slow and air can mix with the benzene vapour. As a result, weight loss at lower temperatures (large pores) is increased by the mass of adsorbate evaporated from the narrower pores. If the heating program is too fast, the temperature of the sample lags behind the measured temperature (temperature gradient inside the sample). As a result, the radius calculated from the measured temperature by the Kelvin equation is smaller than the actual radius. In the present paper we selected a heating program for which the surface film effect is minimized [3].

After numerical differentiation of the cumulative curves representing the dependences of volume against pore/core radius, $V = f(R)$, the pore/core size distribution (PSD) curves, $\Delta V/\Delta R = f(R)$, were calculated. Because in the case of both SI programs the equilibrium conditions can be assumed only within relatively long isothermal periods, the appropriate pore size distributions are presented in the form of histograms. The values of $\Delta V/\Delta R$ correspond to succeeding isothermal steps. The pore size distributions derived from TG data obtained using the quasi-isothermal program QI-3 and the dynamic linear program DL-3 are shown in Fig. 4. Points represent the PSD derived from data obtained by the nitrogen method. The pore size distribution curve was derived from nitrogen data using the BJH method [7] with corrections to the pore

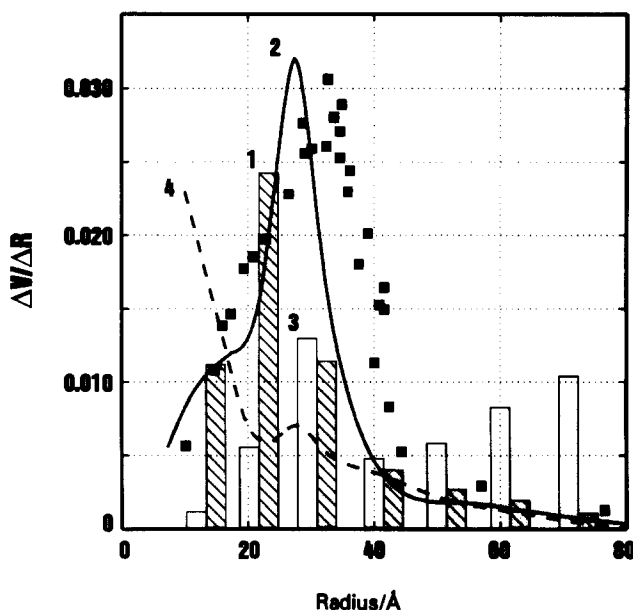


Fig. 4. Pore/core size distribution curves for silica gel Si-60 calculated on the basis of thermogravimetric data from different heating programs: 1, SI-9; 2, QI-3; 3, SI-3; and 4, DL-3. Points represent PSD from the nitrogen method.

radii with respect to the surface film thickness d , where $d = 4.3 \times \sqrt[3]{(-5/\ln(p/p_0))}$. Total pore volumes were estimated taking into account the amount of nitrogen adsorbed at $p/p_0 \cong 1$ [8].

As can be seen, the heating mode of TG analysis influences substantially the shape of the desorption curves and consequently the shape of the pore/core size distribution. Satisfactory agreement occurs in the case of the PSD obtained from the nitrogen method and the TG method for the QI-3 heating program. More or less consistent results were obtained for the stepped isothermal programs. The shape of the PSD and the location of the peak of the distribution curve depends on the range of isothermal cycles.

The presented results illustrate the influence of the conditions of the stepped isothermal experiment on the parameters characterizing the porous structure of the sample.

Numerical values of the total pore volume and the pore radii at the peak of the distribution function are collected in Table 1. As mentioned earlier, the difference in the location of the peak of the PSD derived from TG data in relation to the peak of PSD from the nitrogen method depends strongly on the heating program used in the experiment. The pore radii at the peak of the PSD obtained from the TG method using the QI-3 program and the pore radii from the nitrogen method are close. The total pore volumes derived from the data obtained using various techniques are also in good agreement.

Table 1

Parameters characterizing the porous structure of silica gel Si-60 obtained by using the nitrogen method and using various TG heating programs

Parameters	TG method (programs)				Nitrogen method
	SI-3	SI-9	DL-3	QI-3	
$V_p/(\text{cm}^3 \text{g}^{-1})$	0.69	0.68	0.79	0.65	0.74
$R_{\text{peak}}/\text{Å}$	24	30	–	28	35

In conclusion, one can say that the thermogravimetric technique is useful in investigations of the porosity of solids. Our analysis, based on the Kelvin equation, of the thermogravimetric curves for silica gel wetted with liquid benzene leads to core/pore size distributions curves which are similar, but not identical, in shape to the pore size distribution curves derived by standard procedures from low-temperature nitrogen adsorption/desorption isotherms. The linear heating mode is inadequate in the investigations of the porosity of solids. Mostly appropriate conditions of TG experiment are attained in the case of the quasi-isothermal heating mode. However, the precise experimental conditions should be stated for each experiment with regard to the expected textural properties of the solid and the type of liquid adsorbate.

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