Journal of Thermal Analysis, Vol. 45 (1995) 999-1007

POROUS STRUCTURE OF MIXED SILICA SAMPLES BY THERMOGRAVIMETRIC METHOD

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Abstract

Thermogravimetric analysis was applied to the characterization of the porosity of silica gels. Results from thermogravimetric method are compared with those obtained from the nitrogen method. The consistency of the parameters characterizing the porous structure of silica gels derived from the data of various methods is satisfactory.

Keywords: mixed silica, porous structure, TG

Introduction

In a previous paper attention was drawn to the application of thermogravimetric analysis to the characterization of the porosity of a series of solids [1–5]. The measurements of the weight loss of wet porous solid samples *vs.* temperature give characteristic desorption curves $\Delta m = f(T)$. Benzene, aliphatic hydrocarbons, alcohols were used as the wetting liquids. From the desorption data the total pore volumes and pore size distribution curves for the investigated materials were calculated. The results derived from TG data are in good agreement with those from low temperature adsorption/desorption isotherms of nitrogen. In the present paper the efficiency of the method was tested for mixed samples of silica gels showing bimodal type of pore size distribution function. The silica gels selected as our model porous materials are a group of well characterized adsorbents used as a support in column liquid chromatography. The characterization of the physical features of these materials reported elsewhere indicates that they have a large specific surface areas, a large total pore volumes and are stable when exposed to most organic solvents. Moreover, all these adsorbents do not contain micropores.

Experimental

The silica gels Si-40, Si-60 and Si-100 (Merck, Germany) were used in the experiment. Mixed samples Si-40/Si-60, Si-40/Si-100 and Si-60/Si-100 were

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prepared gravimetrically at the proportion 1:1. Silicas were dried before experiment by prolonged heating at 180°C. These conditions are sufficient to remove the physically bonded water and temperature is low enough to avoid removing surface hydroxyl groups.

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

The physical characterization data for single silicas have been previously reported [2]. For mixed silica samples the adsorption/desorption isotherms of nitrogen at −195°C were measured with 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 to 0.4. A value of 16.2 Å/molecule was used for the cross sectional area of the nitrogen molecule.

Thermogravimetric measurements of desorption of the liquids were made with Derivatograph C (MOM, Hungary). The samples, in the form of paste, were prepared by adding excess of liquid adsorbate to the dry adsorbent and placed in the platinum crucible of a spiral type. The quasi-isothermal program of 3 deg·min^{-1} heating rate within the linear heating range was used in the experiments.

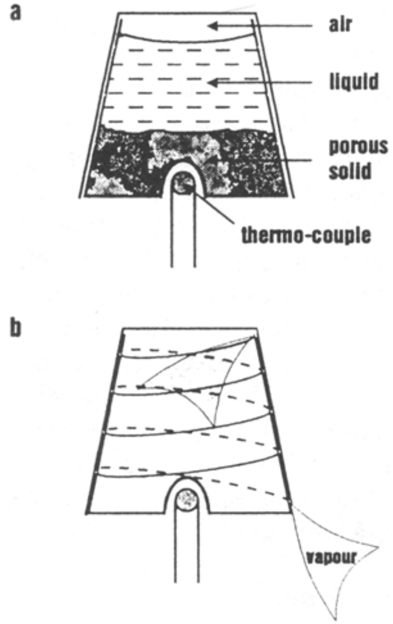

Fig. 1 Diagram of platinum crucible used in thermal desorption experiments. a) location of the sample (solid+excess of liquid) in the bottom part of the crucible; b) pathway of vapour between the walls of both parts of the crucible

During the desorption experiment carried at quasi-isothermal conditions the temperature and the heating rate are not constant. If evaporation of liquid is slow, the fixed weight loss level (in our case 0.5 mg/min) regulating the run of the program is not exceeded. As a result, the linear increase of temperature within this measurement range is realized. At the certain temperature when intensive evaporation occurs the above mentioned level is exceeded and quasi-isothermal conditions are established. The sharp evaporation of liquid takes place at the boiling point of the liquid out of pores or at temperature for which the pressure of the saturated vapours above the liquid meniscus in the pore becomes equal to atmospheric pressure. Thus, it is very important to keep an atmosphere of saturated vapours above the sample. In this connection, the platinum crucible which we use in the experiment is of special construction. The schematic picture presenting our measurement chamber is shown in Fig. 1.

Both parts of the chamber are made of platinum. The sample (wet adsorbent+excess of liquid) is placed in the lower part. During the experiment both parts are tightly closed. Total volume of the chamber is about 0.5 cm^3. Free space above the liquid is about few mm^3. Thus, the volume of vapours of the liquid adsorbate exceeds about fifty times the free space filled by air at the beginning of the experiment.

On the external surface of the internal part of the chamber the spiral groove of 0.1 mm width is made to make the vapour removal possible. Thermo-couple is placed in the concave bottom of the chamber so one can assume that temperature is measured inside the sample.

Results and discussion

Thermal desorption curves representing the weight loss of sample (loss of benzene) against temperature $\Delta m=f(T)$ for all investigated silicas are reported in Fig. 2. The curves were normalized to mass of 1 g of dry adsorbent. The shape of these curves shows several segments and inflection points which may be ascribed to succeeding stages of the desorption process.

The upper parts of the desorption curves represent the bulk liquid outside the pore structure of the adsorbent. Evaporation on this stage of the process takes place at the boiling temperature of liquid (perpendicular segments).

The bottom parts (dark shaded area) correspond to desorption of capillary condensed liquid within the pores, together with the adsorbed film on the walls of the pores, and is therefore a measure of the total pore volume. Points (a) indicate the end of desorption of the bulk liquid. Points (b) indicate beginning of intensive desorption from pores. On the lower segments of the desorption curves one can observe clearly visible the inflection points (open circles). Above and below these points the curves are steepest. Thus, one can assume

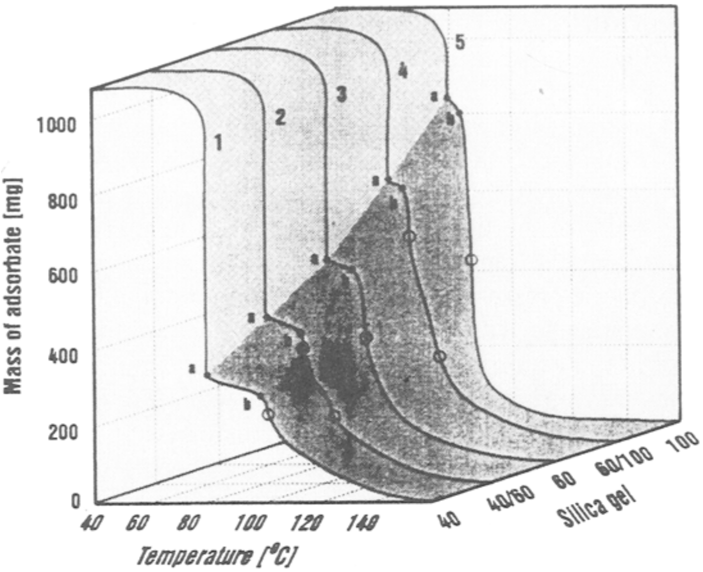

Fig. 2 Desorption curves of benzene from silica samples: 1 – Si-40; 2 – Si-40/60; 3 – Si-60; 4 – Si-60/100 and 5 – Si-100. Points (a) – the end of desorption of the bulk liquid; Points (b) – beginning of desorption from mesopores. Circles – inflection points corresponding to desorption from the pores constituting the highest share in the total pore volume. Dark shaded area – desorption from pores

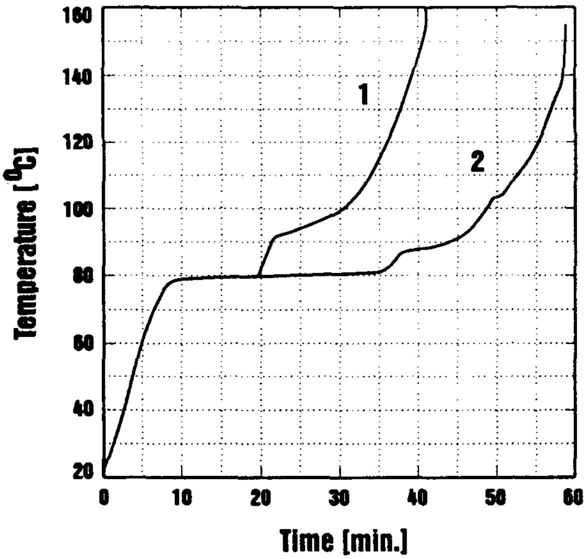

Fig. 3 Dependencies of temperature of desorption against time for silica gel Si-100 (1) and mixed silica sample Si-40/100 (2)

that the region directly on the left and right side of these points represents the amount of liquid desorbed from the pores of highest share in total pore volume.

Figure 3 shows, for illustrative purpose, the dependencies of the temperature against time for two choosen silica samples: Si-100 and Si-40/Si-100. The shape of these curves is very similar to the dependencies $\Delta m = f(T)$ and confirms the quasi-isothermal conditions when intensive desorption takes place.

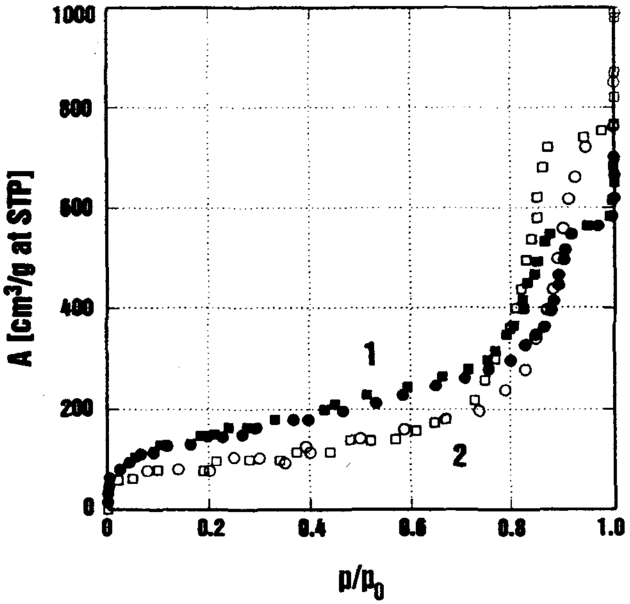

Fig. 4 Nitrogen adsorption/desorption isotherms at – 195°C for silica gels: 1 – Si-40/100, 2 – Si-100. Circles – adsorption, squares – desorption

In the case of silica gel Si-40 (Fig. 2) the desorption branch of the TG curve is extended along the temperature axis. When the pore radii increases (samples Si-60 and Si-100), the temperature range corresponding to desorption from pores becomes smaller and smaller. In the case of mixed silica samples two inflection points on TG desorption curves are present. Depending on the amount of a given silica type in the sample, the increase or decrease of the appropriate segment on these curves is observed. The slight slope of the desorption curves directly above boiling point of benzene represents desorption from wider mesopores and macropores.

In order to calculate the pore size distribution curves, the experimental curves $\Delta m = f(T)$ were transformed into the dependence of volume loss *vs.* pore radius $V = f(R)$ by using the Kelvin equation:

$$\ln\left(\frac{p}{p_o}\right) = -\frac{2\gamma}{R_k}\cdot\frac{V_M}{RT} \qquad (1)$$

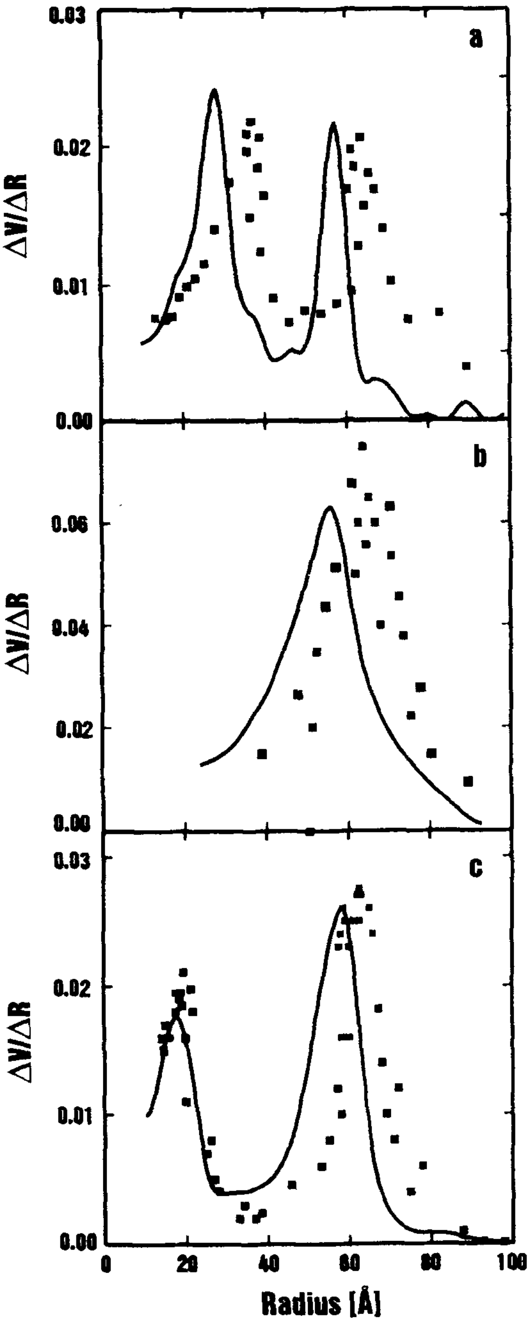

Fig. 5 Pore/core size distribution curves (PSD) for silica gels: a – Si-60/100, b – Si-100 and c – Si-40/100. Solid lines – PSD from TG method. Points – PSD from nitrogen method

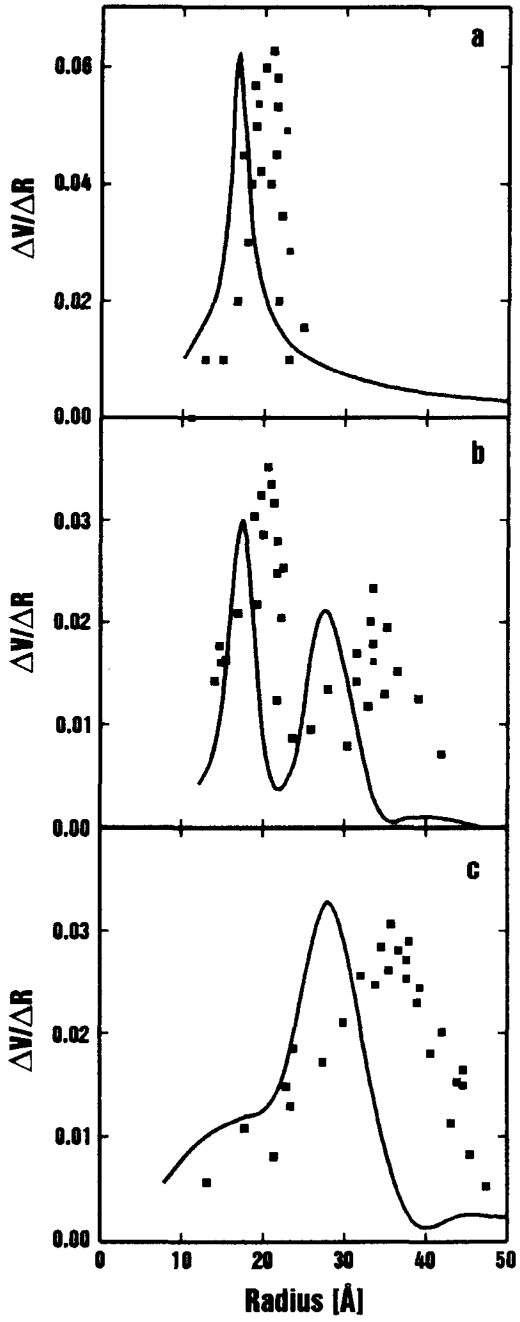

Fig. 6 Pore/core size distribution curves (PSD) for silica gels: a – Si-40, b – Si-40/60 and c – Si-60. Solid lines – PSD from TG method. Points – PSD from nitrogen method

Equation (1) gives the relationship between vapour pressure of a liquid over a curved and flat liquid surface p and p_o, 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.

It should be noted that when evaporation from a pore occurs a strongly held monolayer or multilayer film of adsorbate molecules of thickness d, remains on the walls of pore. 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 $R_p=R_k+d$. The thickness of the surface film depends on the heating program used in the experiment. As it was mentioned earlier, the program must be neither too slow nor too fast. If is too slow, desorption will be too slow and air can mix with benzene vapour. As a result, weight loss at lower temperatures 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 was used appropriate selected heating program for which surface film effect is minimized [3].

Pore/core size distribution curves (PSD), $\Delta V/\Delta R=f(R)$ for investigated silicas were calculated in the manner describer earlier [4].

In Fig. 4 for illustrative purposes, the adsorption/desorption isotherms of nitrogen for the silicas Si-100 and Si-40/Si-100 at –195°C are shown. Pore radii and pore size distributions were derived from the desorption branches of the nitrogen isotherms. The calculations were performed using the BJH method [6] with correction of the pore radii in respect of surface film thickness d, where $d=4.3\cdot\sqrt[3]{-5/\ln p/p_o}$. Total pore volumes were estimated from desorption isotherms at $p/p_o\cong 1$ [7].

Numerical values of the parameters characterizing the pore structure of the investigated samples are collected in Table 1. The data derived from nitrogen isotherms show a decrease of specific surface area and increase of pore volume in the order Si-40, Si-40/Si-60, Si-60, Si-60/Si-100, Si-100. Pore size distributions for these samples from nitrogen method (points) are shown in Figs 5–6. For the convenience of the reader the data for single silica samples are also included. Solid lines in Figs 5–6 represent PSD calculated on the basis of TG data.

It should be noted that the mixed samples of silica gel contain the mesopores in the wide size range. As is seen, the PSD determined by nitrogen method for Si-40 and Si-100 silica gel do not overlap i.e. these silicas do not contain the pores of the same dimensions. However, in the case of Si-60 and Si-100 PSD partially overlap. Very similar textural characterization was obtained by using

TG method either in the case of single silica samples (homogeneous PSD) or mixed silica samples (bimodal PSD).

Table 1 Parameters characterizing porous structure of silica gels obtained by using nitrogen and TG methods

Sample	TG method		Nitrogen method	
	R^{TG}_{peak} /Å	V^{TG}_{p} /cm^3·g^{-1}	$R^{N_2}_{peak}$ /Å	$V^{N_2}_{p}$ /cm^3·g^{-1}
Si-40	18	0.44	21	0.52
Si-40/Si-60	18, 27	0.53	20, 35	0.64
Si-60	28	0.65	35	0.74
Si-60/Si-100	28, 56	0.81	34, 63	0.87
Si-100	56	0.97	64	1.10

Taking into account, the amount of liquid adsorbate desorbed above its boiling point the total pore volumes were calculated. As is seen in Table 1 the total pore volumes determined by using TG and nitrogen method for the same sample of silica are close together.

Summing up, one can state that temperature programmed desorption of liquids is a convenient method to characterize of the porosity of solids. Presented results confirms the high efficiency of TG method in a wide range of mesopores.

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Zusammenfassung — Zur Charakterisierung der Porösität von Silikagelen wurde die thermogravimetrische Analyse angewendet. Ergebnisse thermogravimetrischer Methoden wurden mit denen aus der Stickstoffmethode verglichen. Dabei wurde eine zufriedenstellende Übereinstimmung der anhand der Daten aus verschiedenen Methoden gewonnenen Parameter festgestellt, die die poröse Struktur von Silikagelen beschreiben.