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The influence of polarity of liquids on the parameters characterising the porosity of silica gels estimated by thermogravimetric analysis

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Abstract

Thermogravimetric analysis was applied to the characterisation of the porosity of silica gel. Thermal desorption of liquids from silicas for column chromatography was measured. Water and *n*-hexane were used as liquid adsorbates. Pore size distribution curves of silica gels were determined on the basis of thermogravimetric curves using Kelvin equation. The resulting distributions and total pore volumes were compared with those obtained from the nitrogen method. The influence of polarity of adsorptives on the porosity parameters of silica gels and on the shape of pore size distribution curves is discussed.

Keywords: Polarity; Porosity; Thermogravimetric analysis

1. Introduction

The work reported here was carried out as a part of a long-term study of application of thermogravimetric analysis to characterisation of mesoporous solids. Two oldest techniques which are used for quantifying porosity are a gas/vapour adsorption and mercury porosimetry [1]. The newer techniques for pore structure investigations include nuclear magnetic resonance (NMR) [2], small angle scattering of X-rays (SAXS) and neutrons (SANS) [3,4] or thermoporometry [5]. Another empirical approach for assessment of mesoporosity is thermogravimetric method [6–8].

The recording of the weight loss against temperature for adsorbed species starting from their boiling point gives the isobars of desorption. The wet solid at a given temperature is in contact with the saturated vapour of adsorbate. Initially, the solid is wetted with some excess of liquid adsorbate and pores are totally filled. For temperatures below boiling point evaporation only takes place. At the boiling point the excess of liquid out of pores is evacuated. Next starts desorption from pores of different dimensions and finally desorption from internal surface.

Thus, the temperature desorption process is analogous to the desorption under isothermal conditions when we control the pressure. Temperature of evaporation is dependent on the pore dimensions. The lower the radii of pores the higher temperature is required for their evacuation.

The method described in this paper is a succeeding one, like adsorption or thermoporometry, depending on the curvature of the interface within narrow capillaries of solid. In all these methods the radius of liquid meniscus represents the radius of a core of pore. In the temperature programmed desorption after evacuation

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of the core, there remains on the pore walls a liquid film, which does not take place in desorption at a given temperature. The thickness of this film is a function of the temperature and it diminishes when temperature increases.

In the case of thermoporometry the number of molecular layers of benzene which do not take place in the phase transformation is equal to 3.5 (i.e. 1.33 nm). For water, the thickness of surface film corresponds to 2.5 layers (i.e. 0.8 nm) [9]. Surface films of comparable sizes are probably formed during evacuation of the pore cores in the TG experiment.

For porous solids characterised by a wide range of pore dimensions, the amount of liquid desorbed at higher temperatures, when cores of narrow pores are evacuated, is enhanced by the amount of liquid coming from the thinning of the surface film in pores of larger dimensions. The aim of the present paper is to illustrate the effect of the thinning of the surface film on the desorption curves and, consequently, on the pore size distribution (PSD) derived from these curves.

Thermal desorption results are discussed for silica gels Si-40 and Si-100 containing small and large mesopores, respectively, and for a mixed sample.

We used in TG experiments a Hungarian Derivatograph, which is equipped with the so-called quasi-isothermal (QI) program [10]. The QI program regulates automatically the heating rate according to transformations of the sample. During intensive evaporation resulting in high weight loss values, exceeding fixed weight loss level, the isothermal conditions are established. During small changes of mass, linear heating is realised. Desorption is measured in platinum crucibles with two tightly closed parts where liquid vapour is in contact with the external atmosphere through a small row between these parts [10]. Thus, one can assume that, above the sample, the self-generated atmosphere of the saturated vapour is present.

2. Experimental

Silica gels Si-40 and Si-100 (Merck, Germany) and their mixture Si-40/Si-100 were used in the experiments. The silica samples were dried before experiment by prolonged heating at 180°C in vacuum. These conditions are sufficient to remove the physically bound water.

Water and *n*-hexane were used as wetting liquids. Thermodesorption experiments were made with Derivatograph C (MOM, Hungary) using the QI program at the heating rate of 3°/min within the linear heating range. The samples in the form of paste were prepared by adding an excess of liquid adsorbate to the dry adsorbent and were placed in a conical platinum crucible. Prior to experiment the silica gels were outgassed to facilitate the penetration of liquid adsorbate into pores.

The adsorption/desorption isotherms of nitrogen at −195°C were measured with an automated apparatus ASAP 2010 (Micromeritics, USA). The specific surface areas S_{BET} were calculated from the linear form of the BET equation taking the cross-sectional area of the nitrogen molecule to be 16.2×10^{-20} m^2. PSDs were calculated in the standard manner by using BJH method [11].

3. Results and discussion

The adsorption/desorption isotherms of nitrogen onto silica gels Si-40, Si-100 and Si-40/100 are shown in Fig. 1. For both Si-40 and Si-40/100 samples, a

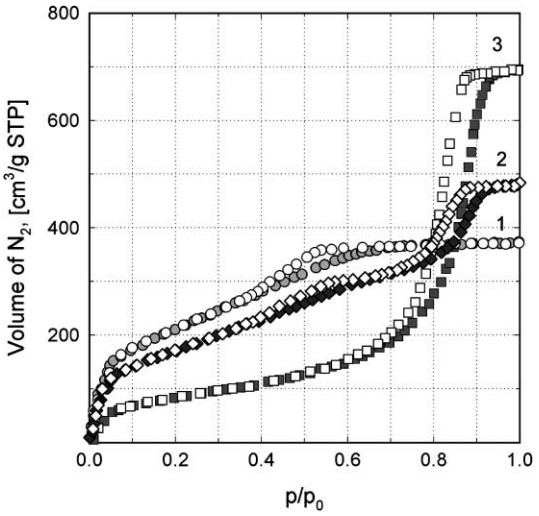

Fig. 1. Nitrogen adsorption/desorption isotherms at −195°C for silica gels. (1): Si-40; (2): Si-40/100; (3): Si-100; filled points: adsorption; open points: desorption.

rapid linear increase in nitrogen adsorption at low relative pressures is followed by a less steep linear increase in a relative pressure range 0.1–0.6 (Si-40) and 0.1–0.8 (Si-40/100). A steep increase appears again for Si-100 and Si-40/100 within a range of $p/p_0 = 0.8$–0.9, which is due to capillary condensation in the mesopore system. In the case of Si-40/100, one can observe two steps and two hysteresis loops. It is interesting to note that sorption isotherms for the mixed silica sample are a simply sum of the isotherms for pure silicas Si-40 and Si-100, taking into account appropriate amounts of these silicas in the mixed sample. The additivity of nitrogen adsorption for a given p/p_0 is a result of the maintenance of equilibrium conditions within measuring range. The presence of a surface film of thickness depending on the adsorbate and quasi-equilibrium conditions used in the thermogravimetric experiment causes the interpretation of thermal desorption curves to be more complicated.

Fig. 2 shows TG curves for the investigated silica samples and two different adsorbates: water and *n*-hexane. Both desorption curves for Si-40 sample are extended along the temperature axis. For mixed Si-40/100 sample, two steps on desorption curves are observed. These steps may be ascribed to desorption from groups of pores giving the greatest contribution to the total pore volume. The step at lower temperatures corresponds to desorption from Si-100 sample and that at higher temperature to desorption from Si-40 sample. Perpendicular segments on the TG curves for temperatures corresponding to the boiling point of *n*-hexane and water represent the evaporation of the excess of liquid out of pores. At lower temperatures below boiling point only slow evaporation occurs.

Figs. 3 and 4 show the desorption curves for the mixed silica sample. Each curve 1 originates from the experiment whereas curve 2 has been obtained by summation of the amounts of liquid desorbed at a given temperature from pure silicas Si-40 and Si-100, accounting for the relative mass contributions of both samples.

The presented results clearly demonstrate the different desorption conditions and the surface film effect in the case of pure silica gels and their mixture. In the latter case, the evacuation of pores is accompanied by thinning of the surface film in the whole temperature range. Thus, desorption at higher temperatures from Si-40 sample is enhanced by the amount of liquid

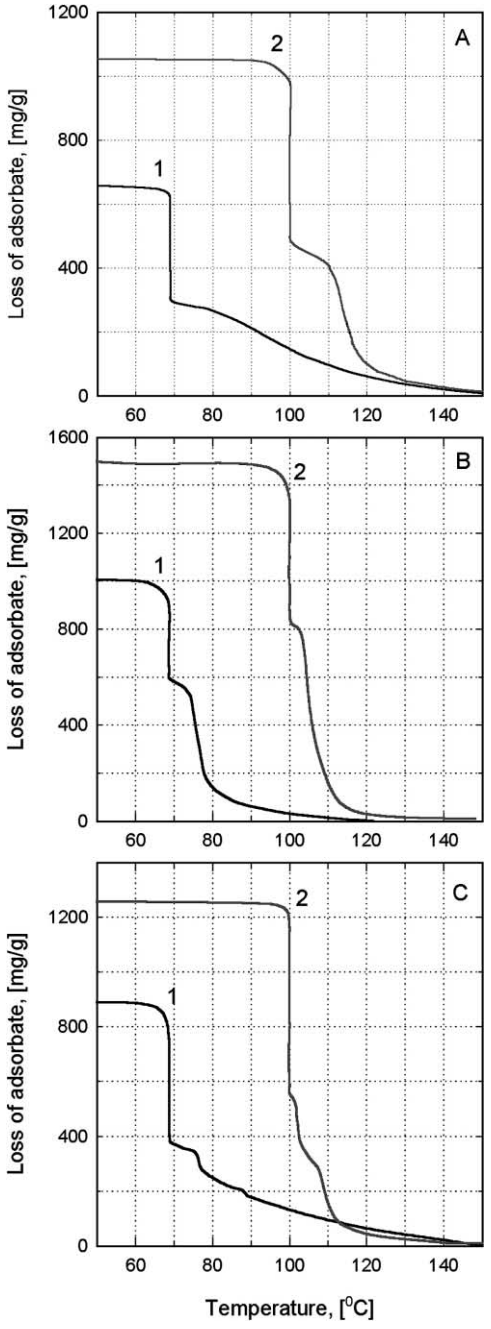

Fig. 2. Thermodesorption curves of *n*-hexane (1) and water (2) onto silica gels: Si-40 (A), Si-100 (B) and Si-40/100 (C).

arising from desorption of the surface film from both Si-40 and Si-100 silica gels. Due to absence of larger pores in Si-40 sample, the desorption curve in the

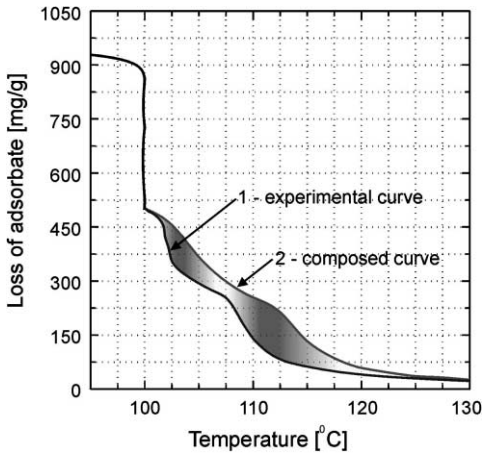

Fig. 3. Thermodesorption curves of water onto mixed Si-40/100 silica sample.

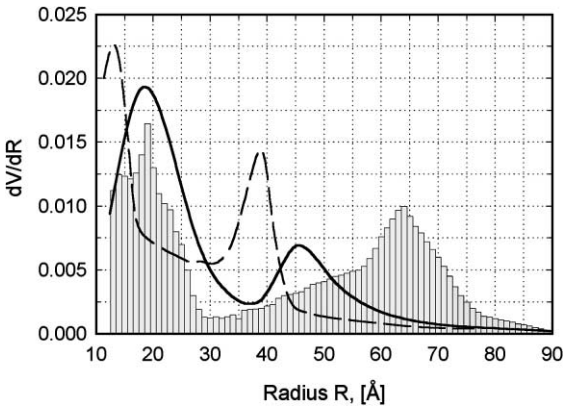

Fig. 5. PSDs for silica gel Si-40/100. Histogram: nitrogen method; lines: desorption of water; solid line: PSD derived from the experimental TG curve; broken line: PSD derived from the composite TG curve.

higher temperature range for pure Si-40 silica represents the mass loss by emptying of a narrow pores. For mixed silica sample at lower temperatures, when larger pores are evacuated, the loss of mass is increased by a partial desorption of liquid from a part of pores of silica Si-40 and its external surface.

The above described effect is pronounced for water and it practically disappears in the case of *n*-hexane. This points to the multimolecular surface layer as a source of some destortion of the desorption process in the case of solid characterised by a very wide range of pore dimensions.

PSD curves derived from TG curves using Kelvin equation in the manner described previously [7] are shown in Figs. 5 and 6. The histograms represent the PSDs obtained from the nitrogen method. The solid line is the PSD from the TG method. The broken line plotted for illustrative purposes, represents the PSD derived from the composite desorption curves. The comparison of these results enables one to admit that strong interactions of the adsorbate molecules with the silica surface and the formation of a stable surface film deformate the desorption curves in the TG experiment and consequently, provide incorrect PSD curves. In

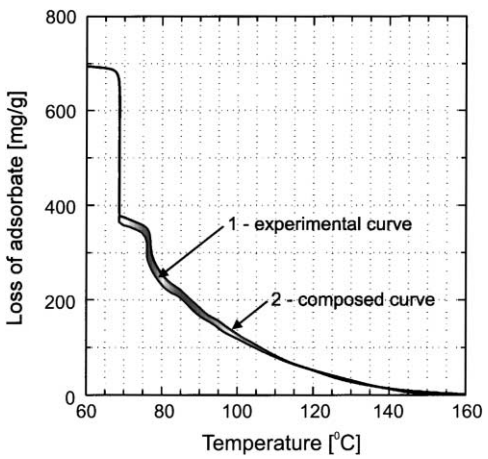

Fig. 4. Thermodesorption curves of *n*-hexane onto mixed Si-40/100 silica sample.

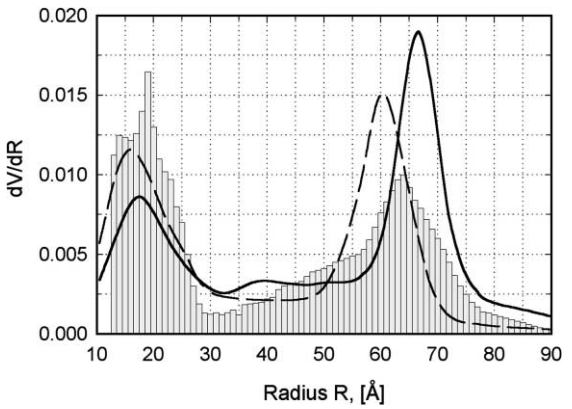

Fig. 6. PSDs for silica gel Si-40/100. Histogram: nitrogen method; lines: desorption of *n*-hexane; solid line: PSD derived from the experimental TG curve; broken line: PSD derived from the composite TG curve.

Table 1
Parameters characterising the porous structure of the adsorbents investigated

Adsorbent	Nitrogen method			TG method			
	S_{BET} (m^2/g)	V_p (cm^3/g)	R_p (Å)	Water		*n*-Hexane	
				V_p (cm^3/g)	R_p (Å)	V_p (cm^3/g)	R_p (Å)
Si-40	842	0.56	19	0.59	<12	0.50	17.3
Si-100	322	1.1	66	1.02	42	1.03	57.2
Si-40/100	645	0.71	20, 65	0.58	17.6, 44	0.59	17.8, 67

the case of hydrocarbon weakly interacting with the silica surface, the PSDs obtained by using various techniques are quite similar.

The numerical values of the porosity parameters are collected in Table 1. The mean pore radii obtained by using nitrogen method and thermogravimetry are similar only in the case of *n*-hexane as a wetting liquid. However, the total pore volumes are similar in respective of the technique and the adsorbate used. A limiting weight loss of adsorptives within the temperature range from boiling point of liquid to end of desorption is an approximate measure of the pore volume of mesoporous or microporous silicas.

4. Conclusions

Thermogravimetric technique is suitable for estimation of the porosity parameters of solids. The results obtained depend on the nature of the adsorbate and its affinity for the sorbent. It is evident that the fairly good agreement between parameters determined by using various techniques may be obtained using similar adsorptive molecules and presuming the real equilibrium conditions. Thus, comparison of the results from the TG measurements with those from the nitrogen method is given for illustrative purposes only.

Hydrocarbons are the most suitable wetting liquids to be used in the TG experiment. Water, due to formation of a stable, strongly held surface film is inadequate for determination of the pore dimensions in silica gels.

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