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STUDIES OF BENZENE ADSORPTION LAYERS ON SILICA GELS BY THERMAL ANALYSIS AND McBAIN BALANCE METHODS

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Abstract

The Q-TG mass loss and first derivative Q-DTG mass loss accompanying benzene thermodesorption from silica gel samples under quasi-isothermal conditions were studied with a Derivatograph Q-1500 D (MOM, Hungary). The isotherms of adsorption–desorption of benzene vapour on different porous silica gels were measured gravimetrically by using a McBain balance. The benzene mass loss in the adsorption region, obtained from the Q-TG curves, and the adsorption capacity, established gravimetrically, exhibited a satisfactory correlation.

Keywords: adsorption–desorption, benzene, Q-DTG, silica gel, thermogravimetry

Introduction

The methods of characterization of adsorption film layers and the heterogeneous properties of solid surfaces are usually based on adsorption studies [1]. Both types of investigations are most often evaluated from the adsorption isotherms obtained by using a McBain balance, a sorption apparatus, or sorptometric, porosimetric or chromatographic methods. These procedures are time-consuming and the calculations involved in them are arduous. Although the above methods are useful for the characterization of materials, they have become less and less popular. For this reason, it is necessary to develop other simple and quick methods to obtain adsorption and heterogeneity parameters.

A special mode of thermal analysis has recently been adopted for the study of liquid/solid systems [2–4]. The main idea of such studies as compared with the traditional methods is to use and register the effects taking place in the processes comprising the reverse of adsorption, i.e. the programmed thermodesorption of liquids from solid surfaces. This method utilizes mass loss Q-TG and the first derivatives of the Q-DTG curves with respect to temperature and time. On the basis of experiments involving the simple and quick liquid thermodesorption from a studied sample, it is possible to obtain important information concerning liquid adsorbed films, liquid–solid interactions and heterogeneous properties of solid surfaces.

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This paper reports on measurements of the thermodesorption of benzene from silica gel samples under quasi-isothermal conditions, using a Hungarian Q-1500 D derivatograph. The data obtained were correlated with the adsorption–desorption of benzene on silica gel samples by means of a vacuum apparatus with a McBain balance.

Experimental

Apparatus

Measurements of the programmed thermodesorption of benzene from a silica gel surface under quasi-isothermal conditions were made with a simultaneous derivatograph Q-1500 D (MOM, Budapest, Hungary). The apparatus is connected with a computer via the interface and equipped with the Derivat program for calculation of the first derivatives of the mass loss Q-DTG curves with respect to temperature and time. The mass loss Q-TG and differential Q-DTG curves were measured under quasi-isothermal conditions over the temperature range 20–300°C, using an analyzer equipped with an automatic ultraslow heating device and a special crucible, capable of maintaining quasi-isothermal conditions to increase the resolution of thermal analysis. The Q-TG and Q-DTG curves were registered and printed with the help of the computer system. As compared with studies carried out under classical 'dynamic' conditions, the quasi-isothermal method has some advantages, including a broader applicability and much greater selectivity. This method is more reliable in the investigations of transformations involving overlapping processes [5].

The adsorption and desorption of benzene vapour on silica gel samples were measured gravimetrically in an apparatus with a McBain microbalance. The silica gel was dried at 200°C for 4 h before use. The benzene (pure for analysis) was dried with A4 molecular sieve, which had been dried previously for 6 h at 500°C. More information on the method, experimental mode and apparatus are given in an earlier paper [6].

Materials

The studies were carried out on silica gel surfaces with various heterogeneous properties: Si-40 (specific surface area 793 $m^2 g^{-1}$, fraction with grain size 0.062–0.2 mm), Si-60 (specific surface area 522 $m^2 g^{-1}$ fraction with grain size 0.2–0.5 mm) and Si-100 (specific surface area 343 $m^2 g^{-1}$, fraction with grain size 0.2–0.5 mm), with mesopore radii 40, 60 and 100 Å (Merck, Darmstadt, Germany), respectively. Before thermal analysis measurements, the samples were completely immersed in benzene.

Results and discussion

Figures 1, 2 and 3 present mass loss Q-TG and differential Q-DTG curves with respect to temperature for the thermodesorption of benzene from completely immersed Si-40, Si-60 and Si-100 silica gel samples, respectively, under quasi-isothermal conditions. The Q-TG curves are characterized by numerous inflections, segments parallel to the ordinate (e.g. AB) and abscissa, forming ‘steps’, which result from the evaporation of bulk benzene, intergranular and capillary benzene films, benzene present in the mesopores and benzene adsorbed on the active sites of the silica surface. At least three inflections are found in the liquid thermodesorption Q-TG curves of the completely immersed samples under investigation. These result from the discontinuous properties of the adsorbed layers, disruption of the adsorbate–adsorbate and adsorbate–adsorbent bonds, and the desorption of benzene in different energetic states in the sample [7]. The benzene adsorption energies result from dispersive interactions. Benzene undergoes π-electron interactions with the silica gel surface.

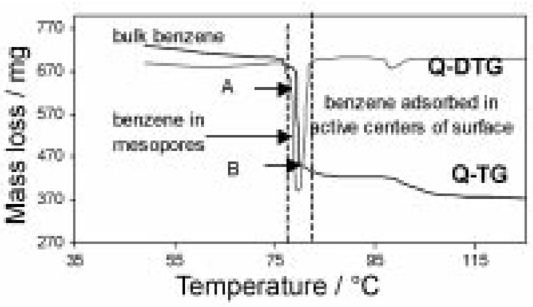

Fig. 1 Mass loss Q-TG and differential Q-DTG curves with respect to temperature for the thermodesorption of benzene from completely immersed silica gel Si-40 under quasi-isothermal conditions

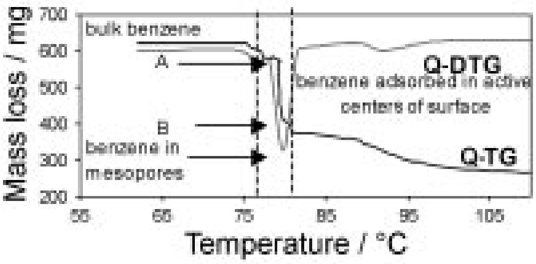

Fig. 2 Mass loss Q-TG and differential Q-DTG curves with respect to temperature for the thermodesorption of benzene from completely immersed silica gel Si-60 under quasi-isothermal conditions

The mechanism and kinetics of the controlled thermodesorption of the controlled thermodesorption of benzene from solid surfaces are influenced by the interactions between the benzene molecules in the adsorption layers (lateral interactions) and the solid surface [7]. The energy of the interactions depends on the polarity of the benzene molecule, the nature of the active sites and the surface porosity.

The above-mentioned parameters affect the properties of adsorbed benzene films (their thickness and structure), but the programmed thermodesorption process reveals the state of the layers on the studied surface in the form of the Q-TG mass loss curves obtained. The Q-TG curves presented in Figs 1–3 allow determination of the

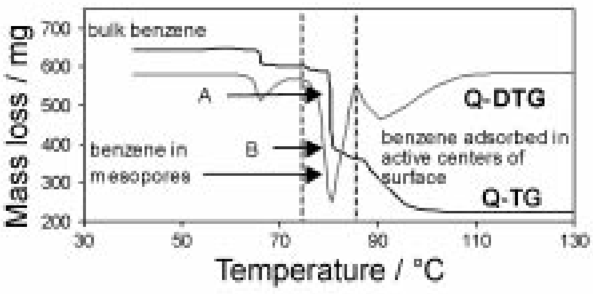

Fig. 3 Mass loss Q-TG and differential Q-DTG curves with respect to temperature for the thermodesorption of benzene from completely immersed silica gel Si-100 under quasi-isothermal conditions

adsorption capacity of the studied silica gel sample, the volume of mesopores present on the surface and the amount of benzene bonded with the surface.

Accurate determination of the inflection points in the Q-TG curves relating to the various forms of benzene desorbed is a very difficult, but important problem. The first derivatives of the mass loss Q-DTG curves with respect to temperature and time are interesting and useful. For precise determination of the inflection points in the Q-TG curves, the differential Q-DTG curves with respect to temperature and time are used. The studies carried out so far indicate that the differential Q-DTG curves with respect to time are more useful, because they allow study of the kinetics and mechanism of the process of thermodesorption of the liquid, and the energetic heterogeneity of the solid surface [8–10].

Figures 4–6 present the mass loss Q-TG and differential Q-DTG curves with respect to time for the same process of benzene evaporation from the silica gel samples given in Figs 1–3. It follows from Figs 4–6 that the evaporation of benzene from the mesopores is preceded by the desorption of molecules from the intergranular space of the silica gel grains and also from the capillary tubes present on the surface. Benzene from the inside mesopores is evaporated first, then that adsorbed on the mesopore surface, and finally the

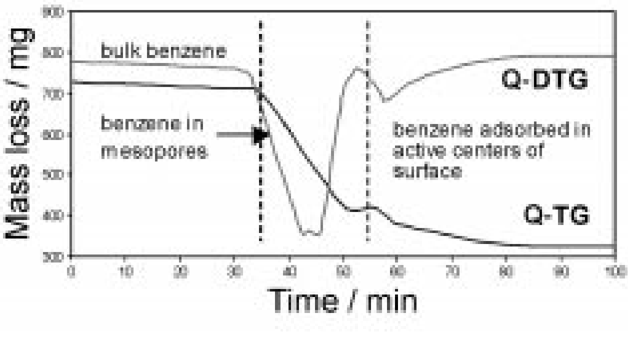

Fig. 4 Mass loss Q-TG and differential Q-DTG curves with respect to time for the thermodesorption of benzene from completely immersed silica gel Si-40

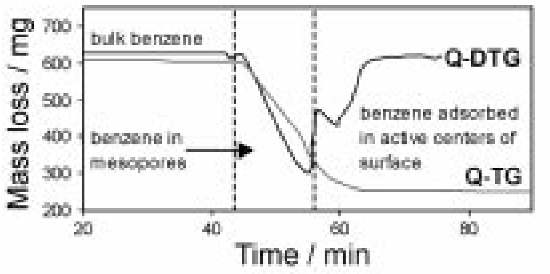

Fig. 5 Mass loss Q-TG and differential Q-DTG curves with respect to time for the thermodesorption of benzene from completely immersed silica gel Si-60

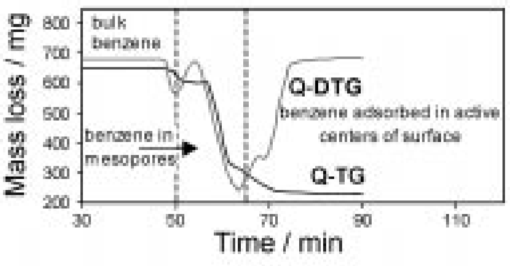

Fig. 6 Mass loss Q-TG and differential Q-DTG curves with respect to time for the thermodesorption of benzene from completely immersed silica gel Si-100

molecules most strongly bonded with the active sites of the silica gel surface. The data reveal that the shapes of the Q-TG and Q-DTG curves obtained during the recording of the sample mass loss in time (Figs 4–6) are quite different from those obtained during the registration of the sample mass loss with change of temperature (Figs 1–3).

The Q-TG curves in Figs 4–6 do not display characteristic 'steps' and the corresponding segment AB parallel to the ordinate, but are inclined to the ordinate at an angle. The differential Q-DTG curve with respect to time is therefore different from the analogous Q-DTG curve with respect to temperature. It is noteworthy that the Q-DTG curves presented in Figs 4–6 are characterized by a high selectivity and resolving power distribution. This can be regarded as a certain type of 'spectrum' of the thermodesorption process, describing the energy state of the benzene molecules on the silica gel samples, and reflects the energy distribution function of desorption of the liquid from the studied surface [8–10].

As mentioned above, the thermodesorption process under quasi-isothermal conditions reflects the energy state of the benzene films adsorbed on the studied surface. Numerous parameters influence the shapes of the Q-TG and Q-DTG curves, but particularly the natures of the liquid and surface studied, the liquid–solid interactions, the heating rate, the decomposition rate, the types of apparatus and crucible, the experimental data registration program used and some parameters of the kinetic process of desorption [5, 7].

Figures 7–9 illustrate the benzene adsorption and desorption isotherms on Si-40, Si-60 and Si-100 silica gels, obtained by means of the static method with a McBain balance. The points show the stages of the benzene vapour adsorption process. Each point of the adsorption branch was obtained by dosing appropriate established earlier) quantities of benzene vapour into the weighing space. This process was driven to obtain a pressure p/p_s=1 in the weighing space. In the first part of the adsorption process, the benzene adsorbs on the surface of the active centers on the silica gel where the adsorption energy is greatest. In the next stage, the benzene adsorbs on the silica gel surface and in the micropores. At p/p_s=0.9, we can observe a marked increase in the adsorbed liquid.

It may be seen in Fig. 7 that the desorption curve for benzene (dark symbols) on narrow-pore Si-40 silica gel nearly coincides with the adsorption isotherm. Such a situation indicates that the adsorption on this adsorbent proceeds similarly to that on a flat surface.

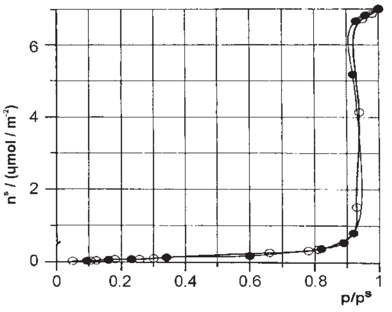

Fig. 7 Isotherms of adsorption (o) and desorption (•) of benzene on silica gel Si-40

The points denote the desorption branch obtained by stepwise pressure reduction. Analogously as in the adsorption process, there is a mass decrease in response to the equilibrium pressure. The first stage involves the desorption of the benzene condensed in the capillaries of the mesoporous silica gel sample. As the pressure is successively diminished, the benzene is desorbed from the mesopores. In the last stage, the benzene is desorbed from the active silica gel centers. Figures 7–9 depict the characteristic hysteresis loop of the adsorption and desorption curves, resulting from the different values of the adsorbent–desorbate and adsorbate–adsorbate interactions as a

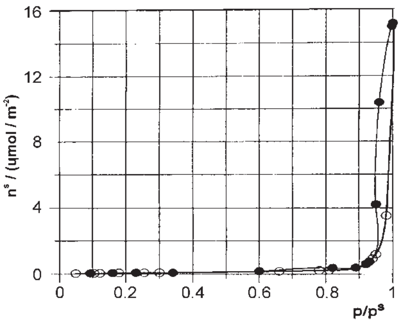

Fig. 8 Isotherms of adsorption (o) and desorption (•) of benzene on silica gel Si-60

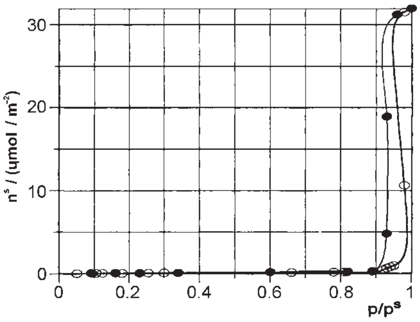

Fig. 9 Isotherms of adsorption (○) and desorption (●) of benzene on silica gel Si-100

consequence of the capillary condensation of benzene. According to De Boer’s [11] theorem, such a shape of the hysteresis loop in adsorption–desorption isotherms arises from open capillaries with various cross-sectional configurations (circular, triangular, square and so on). In such capillaries, condensation sometimes initially occurs along their internal angles until a cylindrical meniscus, the result of the joining of angular meniscuses, appears. Further condensation takes place until the filling-up of the pores is completed, slightly changing the relative pressure.

Assuming that such a process of capillary condensation is correct, the narrow hysteresis loop presented in Figs 8 and 9 may be explained in the following way. When the angle meniscuses join, the capillaries are filled with liquid benzene. Capillary condensation in liquid circular capillaries plays only a minimal part in the process.

Table 1 Adsorption capacity of silica gel samples

Silica gel	Sorption of benzene	Thermodesorption of benzene
	a^s/µmol m^{-2}	
	McBain balance	Derivatograph
Si-40	7.0	6.4
Si-60	15.2	15.9
Si-100	33.9	24.1

Table 1 presents the results of measurements of the adsorption capacity of silica gel samples with a McBain balance and the mass loss accompanying benzene thermodesorption from the samples, corresponding to the adsorption region in the Q-TG curves. The agreement can be stated to be good.

Conclusions

The measurements made during the programmed thermodesorption of benzene under quasi-isothermal conditions from surfaces of silica gel were correlated with those made with a McBain balance.

The sorption of benzene on silica gel, measured with a McBain balance, corresponds to the inflection point obtained in the adsorption region of the Q-TG curves during the thermodesorption of benzene from samples fully immersed in liquid. The results presented above demonstrate that the method of programmed thermodesorption is useful in studies of the adsorption processes on different samples. The technique is a good alternative to the traditional methods because of its speed (1–2 h; McBain balance: a few days) and accuracy in obtaining data and the simplicity of the experimental operation.

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