

STUDY OF HETEROGENEOUS PROPERTIES OF SOLIDS BY MEANS OF A SPECIAL THERMAL ANALYSIS TECHNIQUE

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Abstract

Thermogravimetry (TG) was successfully applied in order to study the heterogeneous properties of solid surfaces and adsorbed liquid films. The method utilized the thermogravimetric mass-loss Q-TG and differential Q-DTG curves with respect to temperature and time for the desorption of liquidus from solid surfaces under quasi-isothermal conditions. Evaluation of the experimental data revealed the heterogeneous properties of the tested samples. It appears that this modern special TG technique is very useful for the study of liquid/solid systems and can be competitive with traditional techniques because of the speed and accuracy with which the data are obtained and the simplicity of the experimental operations.

Keywords: heterogeneity of solids, quasi-isothermal technique, thermodesorption of liquids

Introduction

Real solid surfaces are geometrically and energetically heterogeneous. This property is generally considered to be a main characteristic of almost all materials. Convincing arguments have been put forward that heterogeneous properties are important parameters influencing the nature and extent of interactions at liquid/solid interfaces. The heterogeneous properties of solid surfaces have been described through the use of experimental and theoretical methods, illustrated by computer simulations of crystal growth, kinetics and selectivity of catalysis, and explained by means of amorphous structure formation theories [1, 2].

Solid geometrical heterogeneity is seen as surface irregularities, cracks, roughness and porosity. This property can be divided into structural heterogeneity (specific surface area, size and volumes of pores, and pore distribution functions) and surface heterogeneity (nature and number of active centres, and adsorption and desorption energy distribution functions). In most cases, energetic heterogeneity is a direct consequence of geometric heterogeneity, i.e. it results

from crystal lattice 'errors', such as the lack of individual atoms or their aggregates, or the presence of various atoms and impurities. The phenomenon of energetic heterogeneity occurs when the energy of the adsorbate-adsorbent system changes during the relocation of the molecule on the surface and depends on its position on the surface. The sites causing energetic heterogeneity constitute active centres on which the processes of physical and chemical adsorption and catalysis take place, affecting the magnitude of the adsorption potential, its distribution, and functions of adsorption and desorption energy distribution. The above-mentioned parameters determine mainly the thickness and structure of adsorbed liquid films.

Heterogeneous properties of solids are determined by using classical adsorption, calorimetric, chromatographic and porosimetric methods. They involve estimation of:

- i. the adsorption abilities of various substances and adsorption capacities (determination of adsorption isotherms and the extent of adsorption at $p/p_0=1$),
- ii. the energetic effects accompanying adsorption processes (heats of adsorption and desorption, heat of immersion, adsorption potential distribution functions, and adsorption and desorption energy distribution functions),
- iii. the porosities of solids (specific surface area, radii and volumes of pores, and pore distribution functions).

Determination of the above parameters requires complicated research apparatus [1]. The experiments are often difficult and time-consuming, and the computations of the individual parameters are arduous and complicated. It is necessary, therefore, to find new, simpler and faster research techniques. For this reason, thermal analysis was adopted to study the properties of liquid/solid systems (the surface heterogeneity, the properties of the adsorption layers, and the nature of the adsorbate-adsorbent interactions). Programmed thermodesorption of liquids from solid surfaces was applied (under quasi-isothermal conditions), in which the parameters accompanying the desorption process are measured [3–6]. This paper presents the results of a special application of the Q-1500D Derivatograph (MOM, Hungary) for study of the heterogeneous properties of solid surfaces.

Apparatus and measuring methods

Measurements of the programmed thermodesorption of liquids from solid surfaces under quasi-isothermal conditions were carried out with a Q-1500D derivatograph (MOM, Budapest, Hungary). The apparatus was connected to a computer (via an interface) equipped with a suitable program (Derivat) in order to register the sample mass loss, depending on temperature and time, to determine the differential Q-DTG curves with respect to temperature and time, and to

integrate corresponding areas on the DTA curves during classical measurements. The sample mass loss Q-TG and the differential Q-DTG curves were registered and printed with respect to temperature and time under the quasi-isothermal conditions, using the computer system.

The studies were made by using various solid samples with respect to their heterogeneous properties. The paper reports the results on water and butanol thermodesorption from porous adsorbents of silica gel type, Si-40, Si-60 and Si-100 (Merck, Germany), with mesopore radii of 40, 60 and 100 Å, and also oxidized samples of active carbon from Merck (Germany) and Norit (The Netherlands).

In the studies of the controlled-rate thermodesorption of liquids, the samples were prepared as follows. To obtain different thicknesses of liquid adsorption films on the solid surfaces, the samples were wetted with water and butanol up to complete saturation, and/or saturated with water vapour in a vacuum desiccator at $p/p_0=1$.

Results and discussion

Application

Thermal analysis carried out under quasi-equilibrium condition was developed by Paulik, Paulik [7] at the beginning of the sixties. In the eighties, the quasi-isothermal technique was improved in the Q-1500D Derivatograph and the computerized Derivatograph-C (MOM, Budapest, Hungary) [8]. The analysers are equipped with an automatic ultra-show heating program and a crucible with a bayonet socket [9] and are capable of maintaining quasi-isothermal conditions in order to increase the resolution of thermal analysis. Figure 1 presents the special Paulik crucible for carrying out reactions in a self-generated atmosphere. As compared to measurements carried out under classical dynamic conditions [10–12], the quasi-isothermal method has certain advantages, including wider application and much higher selectivity. This method is more reliable for the study of overlapping processes. The quasi-isothermal method enables precise determination of, for example, the amount of crystalline water released from the chemical compound under investigation at a given temperature, and/or the mechanism of the decomposition process. The Q-TG curves relating to the decomposition of chemical compounds are characterized by inflections and 'steps' resulting from chemical bond disruption and the evolution of a concrete type and amount of crystalline water from the sample at the temperature of the transformation [8].

This method was successfully applied in the study of physical bonds present in various kinds of liquid films adsorbed on solid surfaces [4–6]. During the evaporation of liquids from powdered materials, several steps are observed in the

Q-TG curves [6]. Figure 2 presents the Q-TG curves for the thermodesorption of water from completely wetted, oxidized samples of active carbons from Merck (curve M) and Norit (curve N). The Q-TG curves registered with a commercial recorder are characterized by numerous segments parallel to the axes (e.g. AB), forming 'steps' which result from the evaporation of bulk water, intergranular and capillary water, water present in the macro-, meso-, micro- and submicropores, and water adsorbed on the active centres of the surface. They result from the discontinuous properties of the adsorbed water layers, the disruption of hydrogen-bonds and the gradual desorption of water in different energetic states in the sample. The characteristic inflections indicate the evaporation of bulk water from intergranular spaces and capillary tubes, as well as that bonded in pores and on the active centres of the surface of the studied material.

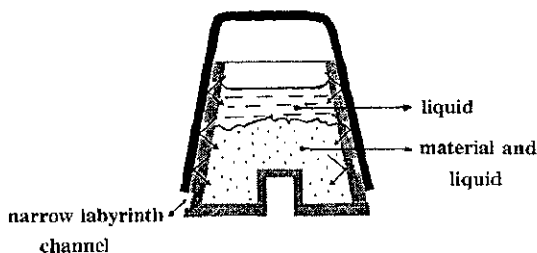


Fig. 1 Paulik's platinum crucible with bayonet socket for the attainment of a self-generated atmosphere [8, 9]

The most interesting results were obtained in the study of the water/adsorbent systems with well-developed specific surface areas. It was found that the liquid desorption corresponding to the individual steps in the Q-TG curves correlates to the amount adsorbed from the gas phase at 20°C, the adsorption capacity, the total porosity and the specific surface area of the studied sample [6]. The above parameters can be calculated from the Q-TG curves. For the precise determination of inflection points in Q-TG curves, differential Q-DTG curves are used. The dependence of the thickness of the water layer on the surface and the volume of the micropores was pointed out for active carbon [13], and for the value of the desorption and the total porosity of aluminium oxide [14]. Moreover, it is possible to determine the specific surface area of an unknown silica gel from the calibration curve. A correlation was found between the thickness of the adsorption film and the polar component of the free energy for an aluminium oxide surface [6].

Interpretation of the curves. Possibilities and limitations of the method

The method consists mainly in measuring the liquid mass lost from the sample during the thermodesorption process carried out under quasi-isothermal conditions [4, 5]. During the measurements, the Q-TG and Q-DTG curves are regis-

tered as a function of temperature and/or time; these are characterized by inflections showing the individual stages of liquid desorption from the samples.

The original 'step' shape of the Q-TG curves results primarily from the special program for the steering of the thermodesorption process and from the application of a special platinum crucible (Fig. 1) [7-9] which allows stepwise evaporation of the liquid from the sample under quasi-isothermal conditions [6]. It is worthy of note that the quasi-isothermal apparatus program (patented in [7]), the special platinum crucible (patented in [8, 9]) and the method for measuring the thermodesorption of liquids from solid surfaces under quasi-isothermal conditions [4, 5] were not developed by the authors, as was suggested in the papers [15, 16].

It follows from the studies that the kinetics of the controlled thermodesorption of liquids from solid surfaces is influenced by the interactions of the adsorbate molecules in the adsorption layers (due to lateral interactions) and liquid molecules with the solid surface [6]. The energy of the interactions depends on the properties of the adsorbate molecules (e.g. their polarity) and also the heterogeneous properties of the surface (nature and number of the active centres and the porosity). The above parameters affect the properties of liquid adsorption films (mainly their thickness and structure), but the programmed thermodesorption process shows the state of the layers on the studied surface in the form of the type of mass loss curves obtained. It follows from the experimental data that many factors influence the shape of the thermogravimetric Q-TG and Q-DTG curves obtained during the thermodesorption of liquids from solid surfaces under quasi-isothermal conditions. The most important of them are:

- i. the natures of the solid and the wetting liquid,
- ii. the amount of liquid present in the sample (the thickness of the adsorbed surface layer and the mode of surface immersion),
- iii. the apparatus parameters governing the kinetics of desorption (e.g. the heating rate and the evaporation rate),
- iv. the kind of program used in the apparatus permitting quasi-isothermal conditions, the type of the crucible, the manner of data registration and the kind of program for calculation of the derivative Q-DTG curves with respect to temperature and time.

At least 3 inflections are found in the liquid thermodesorption Q-TG curves from the surface of the completely immersed studied samples. With increase in the porosity and specific surface area of such adsorbents as aluminium oxide, silica gel and active carbon, the number of inflections in the Q-TG curves increases during the thermodesorption, and the selectivity and the resolving power distribution of the method improve (more distinct inflections are obtained) [6]. In the case of active carbon, various active centres and pores (macro-, meso-, micro- and even submicropores) are present, which determine both the extent of the surface forces, i.e. the number of adsorbed liquid layers and the extent of structur-

ing. As stated above, the Q-TG curves in Fig. 2 allow determination of the adsorption capacity of the studied sample, the total volume of pores present on the surface and the amount of water bound on the surface. In order to determine the inflection points in the Q-TG curves, the differential Q-DTG curves with respect to temperature and time [6]. We found that the differential Q-DTG curves with respect to time are more useful because they permit studies of the kinetics and mechanism of the thermodesorption process. According to the Polanyi-Wigner equation and the Tronconi-Forzatti model of liquid thermodesorption, the rate of desorption r_d is described by the following equation [17, 18]:

$$r_d/\alpha = -d\Theta/dT = k_n\Theta^n/\alpha = \pi^2 D_n k_d \Theta/\alpha R^2 v_m k_a \quad (1)$$

where Θ is the average degree of coverage, α is the heating rate, R is the radius of the studied material grain, D_n is the effective diffusion coefficient, k_d is the desorption rate constant, k_a is the adsorption rate constant, v_m is the initial concentration of the probe molecule adsorbed, k_n is the effective desorption rate constant, n is the reaction order, and T is the temperature.

The temperature dependence of r_d is given by the Arrhenius equation [17, 18]:

$$r_d = -d\Theta/dt = A(\Theta) \exp[-E_d(\Theta)/RT]\Theta^n \quad (2)$$

where E_d is the activation energy of desorption, A is the pre-exponential coefficient, n is the reaction order, t is the time of desorption, and R is the gas constant.

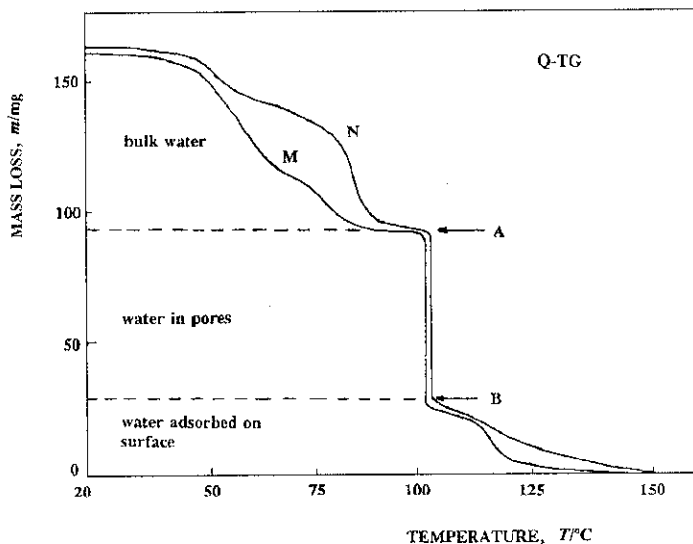


Fig. 2 Q-TG curves of water thermodesorption from completely immersed samples of active carbon from Merck (curve M) and Norit (curve N)

The differential Q-DTG curves describe the desorption energy distribution function, i.e. they characterize the energetic heterogeneity of the adsorbent corresponding to various active centres on the surface. Thus, it is impossible to determine the geometrical heterogeneity (i.e. the pore size distribution function) directly from the Kelvin equation and the Q-TG and Q-DTG curves as was mentioned in papers [15, 16, 19–25]. Without any proof, the authors attributed the shape of the differential Q-DTG curve with respect to temperature to the shape of the pore size distribution function $\{dV/dr=f(r)$, where V is the pore volume and r is the pore radius}. Moreover, use was also made of the Kelvin equation:

$$\ln(p/p_0) = -2\gamma V_m/rRT \quad (3)$$

where p/p_0 is the relative vapour pressure, γ is the surface tension, V_m is the molar volume of the liquid, and r is the pore radius, which has limited applicability for pore radius calculations.

In practice, Eq. (3) is used for calculations on cylindrical pores in systems under static conditions, because it does not include parameters that take into account the kinetics of the process and the diffusion of molecules during the thermodesorption of liquid from the solid surface (e.g. the change in the relative equilibrium vapour pressure with temperature). The Kelvin equation does not take into account the changes in molar volume and surface tension of the liquid with the variation of temperature, the changes in thickness of the adsorption film on the surface and of the pore radii, or the changes in liquid properties with the variation in distance from the surface during the evaporation of liquid in the special crucible of the derivatograph. As mentioned earlier, many other parameters (including the instrumental factors) influence the shapes of the Q-TG and Q-DTG curves, and neglect of these leads to results different from those obtained by using other measuring techniques. Tests were made on the thermodesorption of six different liquids (benzene, octane, decane, methanol, propanol and pentanol) from the surface of silica gel Si-60 with a mesopore radius of 60 Å (Merck, Germany), using the Q-1500D derivatograph under quasi-isothermal conditions. According to the suggestion of the authors of [15, 16, 19–25], an attempt was made to calculate the pore radii by using the Kelvin equation. The results obtained were more than 10 times smaller than those expected. The mesopore radii calculated from the peak maximum in the Q-DTG curves corresponding to the thermodesorption of the individual liquids are (in Å): 5.32 (benzene), 4.21 (octane), 4.30 (decane), 4.12 (methanol), 4.05 (propanol) and 5.29 (pentanol) [26, 27]. Therefore, the Kelvin equation does not 'work' and is not suitable for investigation of the above systems by using the method of thermal desorption of liquids under quasi-isothermal conditions.

The above limitations of the quasi-isothermal method for the determination of pore size distribution functions also follow from the individual parts of the Q-TG curves. Figure 3 presents the Q-TG curve and differential Q-DTG curve with

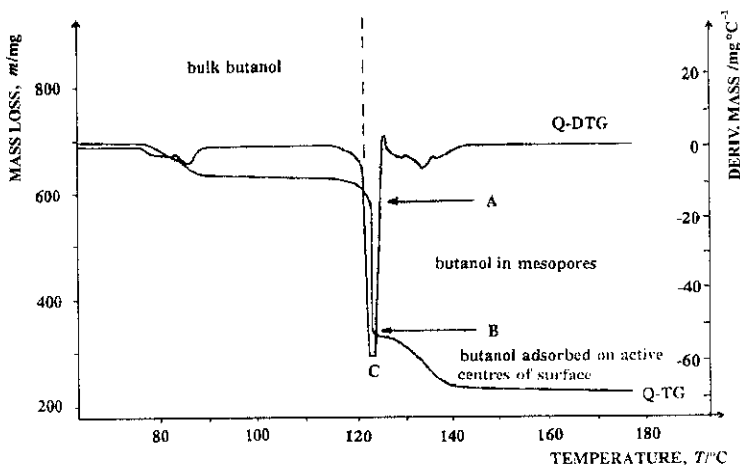


Fig. 3 Q-TG and differential Q-DTG curves of butanol desorption from completely immersed silica gel Si-60, plotted vs. temperature. Mass of silica gel: 225 mg

respect to temperature obtained during the thermodesorption of butanol from completely wetted silica gel Si-60 under quasi-isothermal conditions. This Figure reveals 3 steps in the thermodesorption processes. The segment AB parallel to the ordinate corresponds to the evaporation of butanol from mesopores. Since the differential of segment AB is mathematically infinite, the Q-DTG curve at point C was numerically shortened ('cut') by the computer computation program for practical reasons. It is now impossible to calculate from the differential curve of segment AB (a straight line going to infinity) the mesopore distribution function curve, which assumes the shape of a Gaussian curve for most adsorbents. Thus, the Q-TG and differential Q-DTG curves with respect to temperature can not be useful for determination of the pore size distribution functions of the studied materials from the Kelvin equation and using the method described in papers [15, 16, 19–25].

Figure 4 presents the Q-TG and differential Q-DTG curves with respect to time, obtained during the same process of butanol evaporation from the silica gel sample given in Fig. 3. It follows from Fig. 4 that the evaporation of butanol from mesopores with a radius of 60 Å is preceded by the desorption of molecules from the intergranular spaces in the silica gel, and also from some capillary tubes present on its surface. First, the butanol from inside the mesopores is evaporated, then that adsorbed on its surface, and finally the molecules most strongly bound to the active centres of the silica gel surface. The data in Figs 3 and 4 reveal that the shape of the Q-DTG curve obtained during registration of the sample mass loss in time is quite different from the curve obtained during registration of the sample mass loss against temperature. In Fig. 4, the characteristic 'steps' are less separated and the corresponding segment AB is not parallel to the ordinate, but is

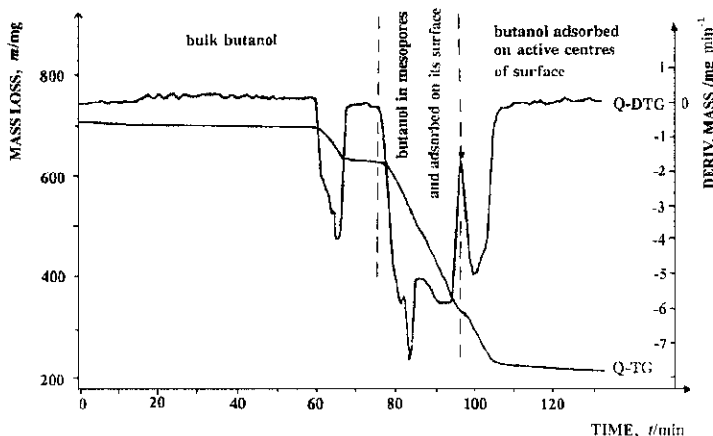


Fig. 4 Q-TG and differential Q-DTG curves of butanol desorption, plotted vs. time (same experiment as in Fig. 3)

inclined at an angle. It is noteworthy that the Q-DTG curve in Fig. 4 is characterized by high selectivity and resolving power distribution. It can be regarded as a type of 'spectrum' of the thermodesorption process describing an energetic state of butanol molecules on the silica gel surface sample because it reflects the distribution function of the desorption energy of the liquid on the studied surface.

Figure 5 depicts the Q-TG and Q-DTG curves with respect to the temperature of water desorption from completely wetted silica gel Si-60 under quasi-isothermal conditions. It follows from the data in this Figure that segment AB of the Q-

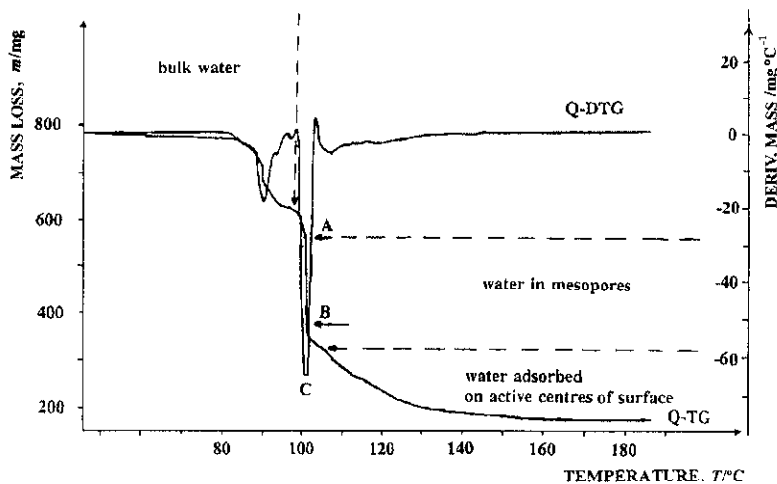


Fig. 5 Q-TG and differential Q-DTG curves of water desorption from completely immersed silica gel Si-60 plotted vs. temperature. Mass of silica gel: 175 mg

TG curve parallel to the ordinate corresponds to the process of water evaporation from the mesopores. For this reason, the differential of segment AB at point C was also numerically shortened. This is clearly seen in Fig. 6, in which an enlarged portion of the Q-TG and Q-DTG curves in the temperature range corresponding to water desorption from the mesopores is presented. From Fig. 6, it appears that the evaporation of water from the mesopores is also preceded by the desorption of water present in the intergranular spaces in the silica gel, and also in the capillary tubes on its surface. Next, the water is evaporated from the mesopores (3.18 statistical water monolayers, Q-TG curve, segment AB), then that adsorbed on their surface, and finally that most strongly bound to the active centres of the silica gel surface (4.62 statistical water monolayers, Q-TG curve, segment below point B).

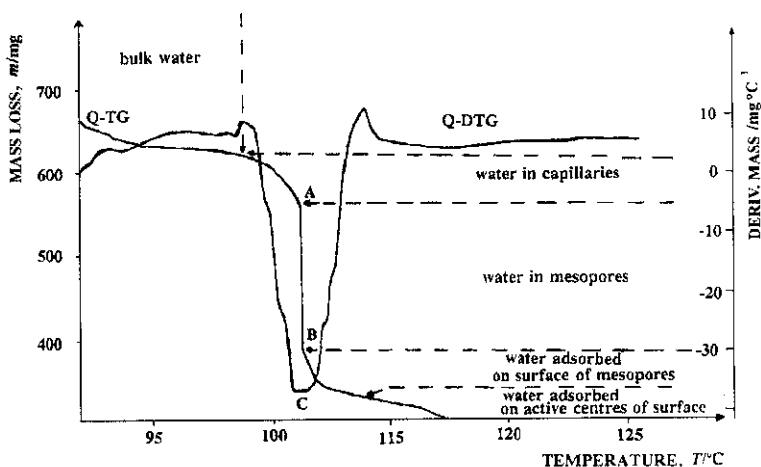


Fig. 6 Q-TG and differential Q-DTG curves of water desorption from mesopores of completely immersed silica gel Si-60 sample (an enlarged part of the curves in Fig. 5), plotted vs. temperature

Figure 7 presents the Q-TG and Q-DTG curves with respect to time of the same process of water evaporation from the silica gel sample which was presented in Fig. 5. It may be observed that the shape of the Q-TG curve obtained during the registration of the sample mass loss with respect to time is completely different from the analogous one obtained during registration of the sample mass loss with respect to temperature. The Q-TG curve in Fig. 7 does not display characteristic 'steps' and segment AB is not parallel to the ordinate, but is inclined at an angle. Therefore, the differential Q-DTG curve does not exhibit the numerically 'cut' segments and is characterized by high selectivity and resolving power similar to those in Fig. 4. For this reason, these curves were applied to study the mechanism and kinetics of solid surface wetting phenomena [26].

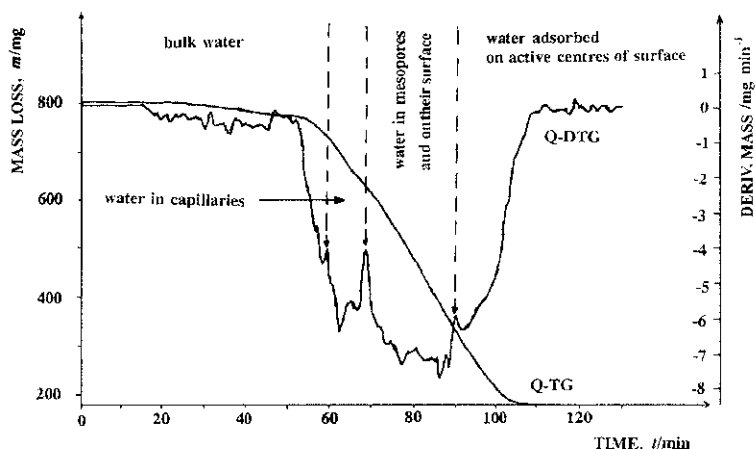


Fig. 7 Q-TG and differential Q-DTG curves of the water desorption process presented in Fig. 5, plotted vs. time

To obtain correct and useful results from programmed thermodesorption, it is necessary to prepare suitable samples before measuring (deposition of liquid films of an appropriate thickness) and to determine the exact experimental quasi-isothermal conditions in the measuring instrument. Each liquid/solid system studied by means of the above method should therefore be considered individually and the results should be compared with analogous ones obtained by means of other measuring techniques and interpreted with regard to current knowledge in this field.

Application

The application of adsorbents and/or catalysts requires a knowledge of many surface physicochemical parameters: mainly adsorption properties and porosity, but also selectivity, catalytic activity and properties of active centres on the surface. For estimation of the nature, quantity, localization and energy of active centre interactions (of Lewis or Brønsted acid type), adsorption and microcalorimetric methods are most frequently used. The experimental studies have shown that the programmed thermodesorption of water can be successfully applied to estimate the nature and number of active centres (particularly hydroxy groups) on the silica gel surface [27]. The shapes of the Q-TG and Q-DTG curves reveal the character of the interactions between the molecules and the energetically different active centres localized on the adsorbent surface. Surface wetting phenomena depend on the amount and nature of the active surface sites and the porosity [27, 28]. It follows from the studies carried out so far that the presence of a large number of liquid molecules on the sample surface diminishes the resolving

power distribution and selectivity of the thermodesorption process, as a consequence of the lateral interactions of the liquid molecules, which diminishes the bonding energy of the molecules adsorbed on the active centres of the surface. The thicknesses of liquid layers adsorbed on surfaces can be controlled by immersion of solid samples. In the study of liquid films adsorbed on active centres, however, the samples of adsorbents were saturated with saturated vapour in the vacuum desiccator, where $p/p_0=1$. During the above preparation, all the surface forces of the tested solids were blocked. The samples prepared in this way did not include an excess of bulk liquid whose presence influenced the thermodesorption kinetics and mechanism ('screening' of the surface).

Figure 8 presents the Q-TG and Q-DTG curves with respect to time obtained during the evaporation of water from silica gels Si-40, Si-60 and Si-100 saturated

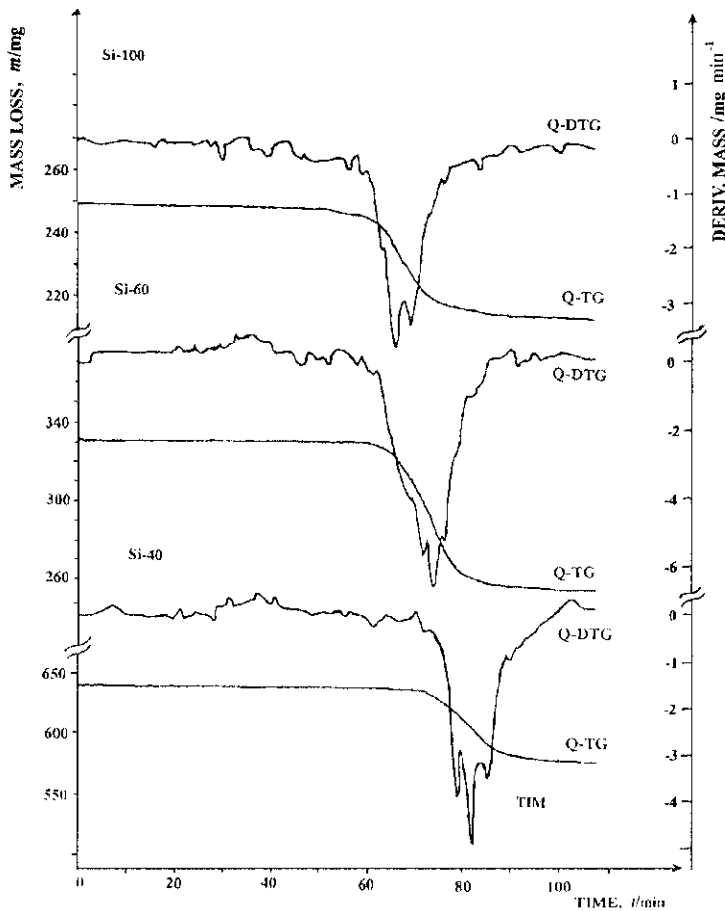


Fig. 8 Q-TG and differential Q-DTG curves of water desorption from Si-40, Si-60 and Si-100 silica gel saturated with water vapour in a desiccator, plotted vs. time

with water vapour in a desiccator. It corresponds to the lower part of the Q-TG curve presented in Fig. 5, which is a result of sample wetting by immersion. It follows from Fig. 8 that the Q-DTG curves are characterized by peaks and inflections resulting from the presence of mesopores and various active centres on the sample surfaces. Figure 8 shows that the desorption of water from sample Si-40 is the slowest; this is due to a large bonding energy in the ice-like structures formed in the range of surface forces (a higher degree of water structuring in the smaller pores with a radius of 40 Å). As mentioned above, the differential Q-DTG curve with respect to time (the 'spectrum' curve of the thermodesorption process) reflects an energetic state of water molecules on the surface of silica gel with various heterogeneous properties. In Fig. 8, two-three stages can be distinguished in the differential Q-DTG curve. The first stage is the evaporation of the adsorbed water film from the mesopore surfaces and the low-energetic sites of the silica gel surfaces. During the next stages, the thermodesorption of water takes place from various active centres and the flat part of the silica gel surface. Peaks resulting from the presence of three energetic different types of hydroxyl groups on the surfaces are observed in the above Q-DTG curves. It is possible to calculate the numbers of individual hydroxyl groups present on the surfaces of various types of silica gel and to compare their hydrophilicities from the sample mass losses from the Q-TG curves. From the data obtained by means of the thermogravimetric method, the number of hydroxyl groups was calculated and good agreement was obtained with the analogous data obtained by reduction of the complex $(\text{CH}_3)_2\text{Zn-TfH}$ from the active centres of the silica gel [26].

On the other hand, the liquid thermodesorption process under quasi-isothermal conditions describes the evaporation of the molecules from the pores, surfaces and finally various active centres with different energies. The desorption part of the activation energy distribution function E_d can be determined on the basis of liquid thermodesorption measurements. For energetically heterogeneous surfaces of solids, the distribution function $f(E_d)$ is calculated from the equation [17]:

$$r_d = -(d\Theta/dt)_n = (A/\alpha) \int_{E_{d,\min}}^{E_{d,\max}} \Theta(E_d, T)^n \exp(-E_d/RT) f(E_d) dE_d \quad (4)$$

Only a few examples of the practical application of Eq. (4) for estimation of the energetic heterogeneity of solid surfaces are reported in the literature. The differential Q-DTG curves with respect to time in Fig. 8 show the course of the distribution function of water desorption activation energy on the silica gel surface. They can be applied to estimate the energetic heterogeneity of the studied sample surface. During the 27th International Vacuum Microbalance Techniques Conference (July 16–18, 1997, Lublin, Poland), a new method for energetic and geometrical (e. g. total) heterogeneity studies of solid surfaces was proposed. On the basis of the desorption activation energy data calculated from Eq. (2), the mesopore radius was evaluated from the equation [29]:

$$E_d = Q_{vp} = Q_{vp}^0 + a/r_k \quad (5)$$

where Q_{vp} is the vaporization heat in the mesopores, Q_{vp}^0 is the vaporization heat of the pure liquid, a is a constant for a liquid and r_k is the mesopore radius.

Moreover, the energy distribution of the desorption process and the mesopore size distribution functions of butanol on a silica gel surface are calculated on the basis of one experimental thermal analysis experiment under quasi-isothermal conditions.

Conclusions

From the above studies, it can be stated that the method of programmed thermodesorption of liquids from sample surfaces under quasi-isothermal conditions can be successfully applied to estimate heterogeneous properties of solids. Samples wetted in different ways before measurement are heated under suitable quasi-isothermal conditions of temperature increase in the derivatograph, using a special platinum chamber in order to evaporate liquids from the surface. For calculations of the mass loss, Q-TG curves and derivative Q-DTG curves are used with respect to temperature and time. From the experimental data, it is possible in a simple and quick way to obtain important information about the properties of solid surfaces as concerns:

1. Energetic heterogeneity: the distribution function of the desorption activation energy, and determination of the nature of the active centres, and the hydrophilicity and hydrophobicity of the surface.
2. Geometrical heterogeneity of solids: estimation of the specific surface area, total porosity and pore size distribution function.
3. Adsorption properties and mechanism of surface wetting phenomena: determination of the adsorption capacity, adsorbed film thickness, range of surface forces, liquid structurization and discontinuous properties of adsorbed layers.

The above examples illustrate the great applicability of the methods described above, among others, due to the fact that it is possible to obtain many parameters characterizing the properties of liquid/solid systems in a single experimental run. From the obtained and presented data, it can be stated that the special thermodesorption technique of thermal analysis can be competitive as regards the traditional adsorption and calorimetric methods in studies of solid heterogeneous properties in consequence of the speed and accuracy of obtaining data and the simplicity of the experimental operations.

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