Thermoanalytical studies of water films on porous silicas at subambient and elevated temperatures

P. Staszczuk [1], M. Jaroniec *, R.K. Gilpin

Department of Chemistry, Kent State University, Kent, Ohio 44242, USA

Abstract

Physicochemical properties of water films formed on the surfaces of porous silicas were studied by high-resolution thermogravimetry (TGA) and differential scanning calorimetry (DSC) over a temperature range from -70°C to 250°C. Silica samples were exposed to water under different conditions in order to prepare surface films of variable thickness. It was shown that TGA and DSC measurements are useful for investigating the physicochemical properties of surface water films and the sorption properties of silica supports.

Keywords: Adsorbed water; Calorimetry; Porosity; Silica; Thermogravimetry

1. Introduction

The surface activity and sorption properties of hydrophilic porous solids,e.g. silica, alumina, zeolites, exposed to air can change significantly because a hygroscopic film is formed due to the presence of water molecules. The thickness of this film depends on the humidity of the air and the temperature. Thus,the application of hydrophilic porous solids in sorption-based separation processes often requires a special pre-treatment in order to control surface hydrophilicity.

The physicochemical properties of surface water differ significantly from those observed for bulk water because of strong interactions between water molecules and the surface active sites. These properties change with distance [1–3]and approach

---

* Corresponding author.

[1] Permanent address: Department of Physical Chemistry, M. Curie-Sklodowska University, 20031 Lublin, Poland.

those of bulk water at relatively long range. The water layer adjacent to the solid surface (so-called vicinal water) has ice-like structure [4,5]. It has been shown elsewhere [6–9]that in addition to surface effects, temperature changes may influence strongly the structural properties of water films.

In spite of extensive studies, the structure of water films formed on various solid surfaces is not completely underestood. At present, the increasing activity in this field is due to recent developments in the methodology for studying solid surfaces. One of many examples is high-resolution thermal analysis, which is widely used to study the thermal stability and structural properties of surface films [1–3]. The present paper demonstrates the utility of two thermoanalytical methods, high-resolution thermogravimetry (HR TGA) and differential scanning calorimetry (DSC),to study the physicochemical properties of water films formed on porous silicas as well as to characterize the surface and structural properties of these solids. It is shown that modern thermoanalytical methods are extremely useful to study liquid/solid interfaces in general and particularly the water/silica interface.

2. Experimental

2.1. Systems studied

Two types of silica gel, Kieselgel MN-60 (Machery Nagel, Germany) and Schuchardt SG(Germany), were studied by high-resolution thermogravimetry and differential scanning calorimetry. Silica samples were exposed to water molecules in three different ways: (i) by exposing silica to air of a given humidity, (ii) by saturating silica samples with water vapor, and (iii) by immersing silica in deionized water.

2.2. Thermogravimetric measurements

Thermodesorption of water molecules from the silica surface was measured in a nitrogen atmosphere using a TA Instruments, Inc. (New Castle, DE,USA) model TGA 2950 high-resolution thermogravimetric analyzer. The instrument was equipped with an open platinum pan and an automatically programmed temperature controller.

The thermogravimetric (TGA) curves, which give the dependence of the weight loss of a sample as a function of temperature or time, were measured over a temperature range from 20 to 250°C. The heating rate was regulated automatically by the instrument in order to maintain a constant temperature during a given thermal event. The maximum heating rate between thermal events was $10 \, K \, min^{-1}$. The resolution and sensitivity parameters were 4 and 6, respectively. These parameters were established experimentally in order to provide the optimal heating rate for thermodesorption [10,11].

2.3. Calorimetric measurements

Calorimetric measurements were carried out for hydrated silica samples using a model DSC 2910 equipped with a standard DSC cell and subambient accessories

from TA Instruments, Inc. (New Castle, DE). This instrument can cover a temperature range from $-150°C$ to $725°C$. The DSC measurements were performed as follows: first, the hydrated sample of silica was cooled to about $-70°C$ under controlled conditions, and then it was gradually heated in a nitrogen atmosphere up to 250°C. A slow (1°C min^{-1}) scan rate was used as suggested elsewhere [12,13]. The resulting DSC curve has a complex shape with peaks related to freezing and melting of different types of surface water at subambient temperatures as well as to the thermodesorption of physically adsorbed water molecules from the pores of the silica and from its surface at elevated temperatures. The DSC data at elevated temperatures can be correlated with thermogravimetric measurements.

3. Results and discussion

The DTG curves, which are differential curves of the thermogravimetric weight-loss (TGA) scans, are shown in Fig. 1 for the silica samples exposed to air. Under these conditions, about 65% of the silica surface was covered by physically adsorbed water. This value was estimated by assuming a single occupation of active sites by water molecules and 0.125 nm^2 of the surface area occupied per molecule [14]. For each silica sample studied in the temperature range from 20 to 250°C, the DTG curve has a distinct peak with a maximum at about 60°C and a shoulder at higher temperatures. In comparison to the MN sample, the peak for the SG sample is more narrow and has a small shoulder (I) about 90°C. Since for the MN silica the shoulder (I) is quite distinct and located at a temperature about 25°C higher than the SG silica, this sample shows greater surface heterogeneity. The observed shape of the DTG curves indicates the existence of at least two types of active sites, which strongly adsorb water molecules. The first group of sites (which account for 68% of the occupied sites) corresponds to the
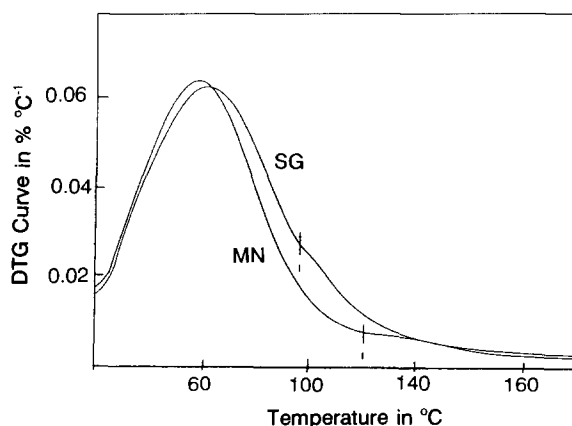

Fig. 1. The DTG curves for the MN and SG silica samples exposed to air. The inflection point I denotes the beginning of thermodesorption of water molecules from the high-energy active sites.

weight loss measured up to the inflection point I, whereas the second group of sites relates to the weight loss between the temperature of point I and 250°C. A similar distribution of active sites was reported for other silicas [15].

Fig. 2 shows the DTG curves for silica samples exposed to the saturated water vapor. The total amount of adsorbed water under these conditions defines the overall adsorption capacity, which in the case of porous solids is a measure of the total porosity [10,11]. The values of the total amount adsorbed for the samples studied are given in Table 1. In addition, each DTG curve plotted as a function of time shows a distinct inflection point II, which is a measure of vicinal water, i.e., water adsorbed on active sites. The amount of water determined by this point relates to the amount adsorbed by exposing a given silica to air (see Table 1).

Finally, the DTG curves for the silica samples immersed in water are shown in Fig. 3. The DTG curves plotted as a function of time possess a distinct minimum (III) which, extended to the end of the run, determines the overall adsorption capacity. Note that at the point III, the value of the retained water on the silica sample is close to the total amount adsorbed by exposing silica to saturated water vapor (see Table 1). Up to the point III, the excess of the bulk water is evaporated and then the thermodesorption of water molecules from the porous structure of silica and its surface begins. Since for fully immersed silica samples the weight loss of the bulk water (which is not adsorbed on silica) is often much greater than the amount of adsorbed water, the TGA data measured for these samples are less useful in evaluating the amount of hygroscopic water (which is marked by point II in Fig. 2).

The characteristic quantities (see Table 1) evaluated on the basis of the TGA data shown in Figs. 1, 2 and 3 suggest the following mechanism for formation of the water film on the silica surface. First, the high-energy active sites are occupied by water molecules. The amount of these sites can be estimated by the inflection point I on the DTG curves for silica samples exposed to air of a given humidity (see Fig. 1) and
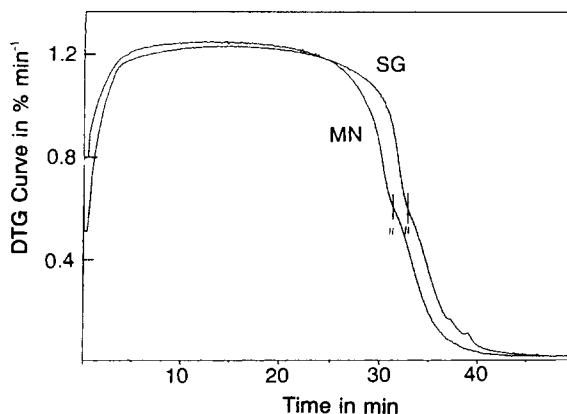

Fig. 2. The DTG curves for the MN and SG silica samples exposed to saturated water vapor at room temperature. The inflection point II denotes the beginning of thermodesorption of water from active sites of the silica surface.

Table 1
The characteristic amounts of adsorbed water on the porous silicas studied evaluated from the TGA measurements for samples exposed to water vapor and immersed in water

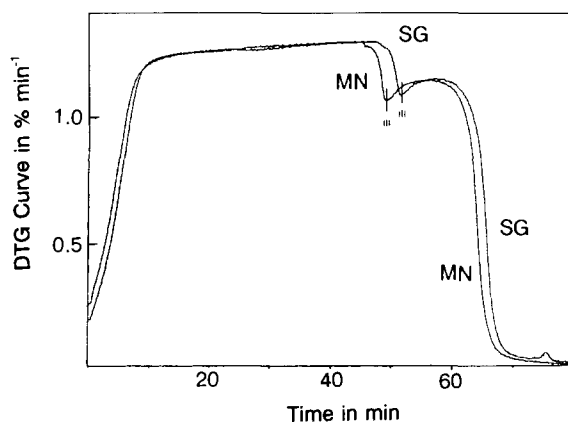| Silica | BET surface area/$m^2 g^{-1}$ | Characteristic amounts of adsorbed water from the TGA data/$m\,mol\,g^{-1}$ | | | | |
		Silica exposed to air		Silica exposed to saturated vapor		Silica immersed in water
		Total	Point I	Total	Point II	Point III
MN	340	2.46	0.78	36.5	2.41	36.3
SG	275	2.15	0.53	37.8	2.09	38.3

Fig. 3. The DTG curves for the MN and SG silica samples fully immersed in water. The point III denotes the beginning of thermodesorption of water from pores.

exposed to the saturated water vapor (see Fig. 2). This process is followed by adsorption of water molecules on the active sites of lower adsorption energy. For the samples studied, about 2/3 of the silica surface is covered with these sites. The total amount of adsorbed water by silica exposed to humid air is a crude estimation of the total amount of surface sites (see Fig. 1). A more accurate estimation of these sites is given by the inflection point II on the DTG curves for silica samples exposed to the saturated water vapor (see Fig. 2). Finally, when all surface sites are occupied, multilayer adsorption and capillary condensation occur in the porous structure of silica. The total amount adsorbed by silica exposed to the saturated vapor measures the overall adsorption capacity of the sample (see Fig. 2). Also, this adsorption capacity is evaluated by the point III on the TGA curves measured for the silica samples immersed in water (see Fig. 3). In the case of the immersed samples, excess non-adsorbed (bulk) water is present, which evaporates at temperatures before that marked by the point III. The

process of evaporation of the bulk water differs significantly from the process of thermodesorption of water molecules from pores, which is manifested by a distinct minimum on the DTG curves for the immersed samples (see Fig. 3).

In addition to the TGA measurements, the hydrated silica samples were studied by differential scanning calorimetry (DSC). First, the DSC studies were carried out for samples which were prepared under the same conditions as those used to measure the TGA curves shown in Fig. 2, i.e., the silica samples were exposed to the saturated water vapor at room temperature. The amounts of adsorbed water on the MN and SG silica samples were equal to 36.5 and 37.8, respectively. The DSC curves for these samples are shown in Fig. 4 for the temperature range from − 70 °C to 250 °C. The DSC curves shown in Fig. 4 have a series of peaks associated with: freezing (1) and melting (2) of adsorbed water in pores at subambient temperatures, and thermodesorption of water
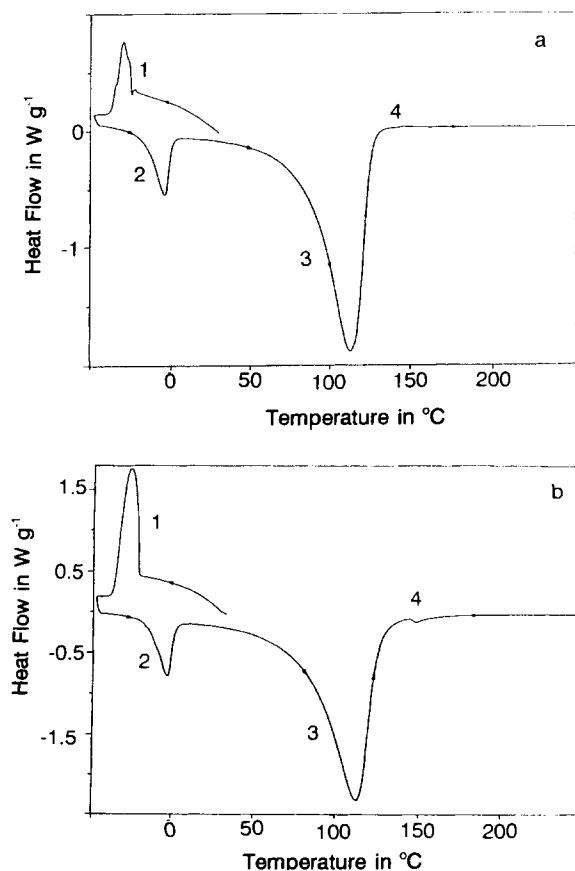

Fig. 4. The DSC curves for the MN (a) and SG (b) silica samples exposed to saturated water vapor; successive peaks represent freezing (1) and melting (2) of water adsorbed in pores, and thermodesorption of water molecules from pores (3) and from active sites (4).

molecules from the pores (3) and from the surface (4) at elevated temperatures. The shapes of the DSC peaks depend on type of sample and can be used to obtain information about the surface and structural properties of the silica studied. As can be seen in Fig. 4, the freezing of water present in the pores occurs at temperatures between −20 and −40°C, which are much below 0°C. The freezing process occurs in a relatively wide temperature range and is often represented by an irregular peak, the shape of which provides information about the heterogeneity of the porous structure of the sample studied. According to Refs. [16–20], the "freezing" peak relates to the pore-size distribution. The modified Laplace equation, which relates the freezing temperature to the pore width, can be used to convert the "freezing" peak to the pore-size distribution. Since for each silica the "freezing" part of the DSC curve has the shape of a single peak, the pore-size distributions for both samples appear to be single-modal distributions. In contrast to the freezing process, which due to the relation between the freezing temperature and the pore width has a stepwise character, the melting process (peak 2) is less sensitive to the sructural changes of the solid. For the samples studied the "melting" peaks appear in the temperature range above −20°C and show less details than the "freezing" peaks.

The heat effect associated with thermodesorption of water molecules from pores is represented by peak 3 on the DSC curve (see Fig. 4). This process is followed by thermodesorption of water molecules adsorbed strongly on surface sites of a given silica (see peak 4, which is much smaller than peak 3). For the silicas studied, peak 4 appears over a temperature range of about 150°C because relatively high temperatures are required to remove water molecules adsorbed strongly on active sites [21,22].

The DSC curves for the silica samples fully immersed in water are shown in Fig. 5. For these samples, double peaks were obtained for the freezing, melting and pore
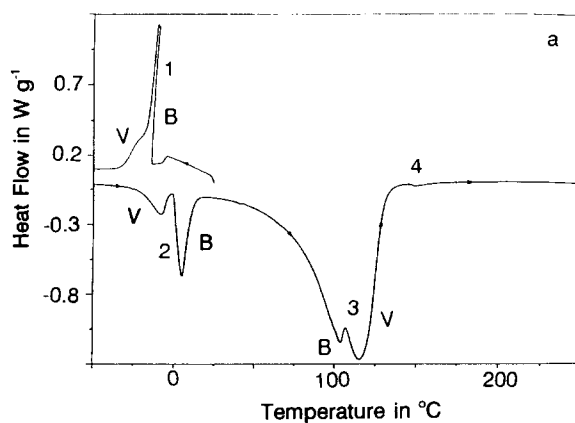

Fig. 5. The DSC curves for the MN (a) and SG (b) silica samples fully immersed in water; successive double peaks represent freezing (1) and melting (2) of water adsorbed in pores, and thermodesorption of water molecules from pores (3) and from active sites (4). The symbols B and V refer to the non-adsorbed (bulk) water and adsorbed water, respectively.
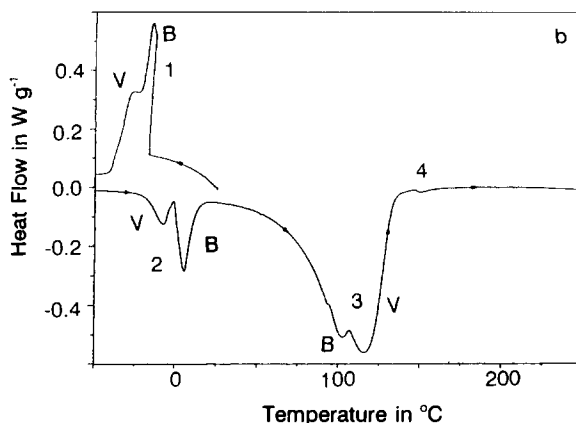
Fig. 5. (Continued.)

thermodesorption processes. Additional peaks denoted by "B" represent freezing, melting and evaporation of non-adsorbed (bulk) water, which was added in excess during the immersion process. The remaining peaks (denoted by "V") are analogous to those observed for the silica samples exposed to the saturated vapor (see Fig. 4). Fig. 5 illustrates that physicochemical properties of the bulk water and adsorbed water differ significantly, and therefore the observed phase transitions occur in different temperature ranges. These results are in good agreement with earlier studies of surface water [13,21,22].

4. Conclusions

The present paper shows the utility of the TGA and DSC measurements to study physicochemical properties of water films on porous silicas. Comparative TGA studies of the silica samples exposed to air, saturated water vapor, and immersed in water provided information about the mechanism of hydration of silica and permitted characterization of the sample studied in terms of the total adsorption capacity (which in the case of porous silicas is a measure of the total pore volume) and the amount of water adsorbed on active sites. The DSC studies of these samples under conditions analogous to the TGA experiments provided information about heat effects associated with thermodesorption of water molecules contained in pores and adsorbed on active sites. In addition, the DSC measurements at subambient temperatures were useful to study the influence of porous structure on the freezing and melting transitions of adsorbed water. For silica samples fully immersed in water, the TGA and DSC measurements demonstrated that the phase transitions such as freezing, melting and evaporation occur at different temperature ranges for the bulk water and adsorbed water. This result illustrates clearly that the physicochemical properties of the bulk and surface water are significantly different.

References

[1] P. Staszczuk, R. Dobrowolski and M. Jaroniec, Langmuir, 5 (1992) 229.
[2] P. Staszczuk, M. Jaroniec and R.K. Gilpin, Anal. Chim. Acta, 269 (1992) 157.
[3] P. Staszczuk and M. Jaroniec, J. Therm. Anal., 38 (1992) 2041.
[4] F.M. Etzler, Langmuir, 4 (1988) 878.
[5] F.M. Etzler, R.F. Ross and R.A. Halcomb, Physica A, 172 (1991) 161.
[6] F.M. Etzler and W. Drost-Hansen, Croatica Chim. Acta, 56 (1983) 563.
[7] G. Peschel and K.H. Adlfinger, J. Colloid Interface Sci., 34 (1970) 505.
[8] F.M. Etzler, J. Colloid Interface Sci., 92 (1983) 43.
[9] W. Drost-Hansen, Ind. Eng. Chem., 61 (1969) 10.
[10] M. Jaroniec, R.K. Gilpin, J. Ramler and J. Choma, Thermochim. Acta, 272 (1995) 1.
[11] M. Jaroniec, R.K. Gilpin, P. Staszczuk and J. Choma, in J. Rouquerol, F. Reinoso-Rodriguez, K.S.W. Singh and K.K. Unger (Eds.), Characterization of Porous Solids III, Elsevier, Amsterdam, 1994, pp. 613–622.
[12] M. Brun, A. Lallemand, J.F. Quinson and C. Eyraud, Thermochim. Acta, 21 (1977) 59.
[13] K. Ishikiriyama and M. Todoki, Thermochim. Acta, 256 (1995) 213.
[14] A.L. McClellan and H.F. Harnsberger, J. Colloid Interface Sci., 23 (1967) 577.
[15] M. Jaroniec and R. Madey, Physical Adsorption on Heterogeneous Solids, Elsevier, Amsterdam, 1988.
[16] G.G. Litvan, J. Colloid Interface Sci., 38 (1972) 75.
[17] L.G. Homshaw, J. Therm. Anal., 19 (1980) 215.
[18] L.G. Homshaw, J. Colloid Interface Sci., 84 (1981) 127.
[20] L.G. Homshaw, J. Colloid Interface Sci., 84 (1981) 141.
[20] M. Sasthav, W.R.P. Raj and M. Cheung, J. Colloid Interface Sci., 151 (1992) 376.
[21] R.P.W. Scott and S. Traiman, J. Chromatogr., 196(1980) 193.
[22] R.P.W. Scott, Adv. Chromatogr., 20 (1982) 167.