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THERMOGRAVIMETRY AS A RELIABLE TOOL TO ESTIMATE THE DENSITY OF SILANOLS ON A SILICA GEL SURFACE

R. F. de Farias[*] *and C. Airoldi*

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083-970
Campinas, São Paulo, Brasil

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Abstract

A method was developed to estimate the density of the silanol groups attached to silica gel surfaces from thermogravimetric data. Depending on the mechanism of condensation of silanol groups during heating, after removing physically adsorbed water, the results obtained ranged from 4.3 to 6.7 OH nm^{-2} for a series of silicas. The data are in good agreement with those obtained by other techniques. Thermogravimetry proved to be a reliable tool for this kind of study, with the great advantage of being a simple, quick and inexpensive method requiring only a few mg of the silica sample.

Keywords: density of silanol, silanol group, silica surface, thermogravimetry

Introduction

The amorphous inorganic polymer silica gel can be described as an oxide composed of siloxane groups (Si–O–Si), forming the internal part of the inorganic backbone of the polymer, which is normally coated by silanol groups (Si–OH), distributed on all the surface [1]. The permanent dipole on the silanol groups causes hydrogen bond formation with any basic centres, as expected, with water present in the atmosphere. To improve the reactivity of this group, an activation is required [1].

A very important property connected to the surface of silica gel is related to the density of silanol groups in a given unit area (nm^{-2}), since these groups are responsible for the reactivity of the silica surface. For this purpose a series of silylating agents can be covalently bonded to the activated silanol groups. In this

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[*] Permanent address: Departamento de Química, Universidade Federal de Roraima, Av. Venezuela s/n, 60310-270 Boa Vista, Roraima, Brasil

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process a change occurs in the chemical or physical characteristics of the original surface, whose properties can be utilized in a lot of applications, such as stationary phases for chromatography [2], supports for catalysts [3], pre-concentration of sorbents [4, 5], ion exchange [6] or biotechnology [7].

In attempting to quantify the silanol groups on a silica surface, a number of techniques and approaches have been employed [1, 8–19], of which some of the more sophisticated methods range from deuterium-exchange processes coupled with mass spectrometric analysis and CPMAS NMR to infrared spectroscopy. The amount of silanols established by these techniques varied from 2.0 to 9.5 OH groups per nm^{-2}. However, the current value accepted for most purposes is a mean value of 5.0 OH nm^{-2}.

In an extensive study [8] involving one hundred different samples of amorphous dispersed silicas, having specific areas varying from 9.5 to 950 $m^2 g^{-1}$, the author concluded that the density of the silanol groups may be considered as 5.0 OH groups nm^{-2}, independently of the origin and the diverse characteristics such as the specific surface area and type and size distribution of the pores, particle packing density and structure of the SiO_2 skeleton. In this treatment, the density of silanol groups is considered as a physicochemical constant. In this connection, these groups characterize the behaviour of the reactivity on the surface for amorphous silicas.

The understanding of many features connected to a silica surface requires in many cases, the use of thermal analysis techniques, which are very useful to follow the thermal behaviour of the groups bonded to the surface. In this context, the physicochemical properties of water films have been studied recently by means of thermoanalytical techniques [20] and also the thermal desorption of liquids from various mesopores or micropores in silica gel samples [21].

The aim of this publication is to prove thermogravimetry to be a useful and reliable tool to study silica gel. Some data from thermogravimetric curves obtained in our laboratory were compared with those already reported in the literature [22–25], in an attempt to develop a new quick and inexpensive method to estimate the density of silanol groups on silica gel surfaces.

Experimental

Silica gel (Merck) having a surface area of 354 $m^2 g^{-1}$ was used in samples 4, 8 and 9, as listed in Table 1. Sample 4 was treated with a 9:1 (v/v) mixture of 2.0 mol dm^{-3} solutions of nitric and sulphuric acids and then washed with twice distilled water to pH 7. After this treatment the sample was dried in vacuum at 425 K for 12 h. Sample 8 (Merck) with the same surface area of 9 received the same previous treatment. Samples 7 and 9 (Merck) with surface areas of 300 and 354 m^2/g, respectively, were used without any treatment.

The thermogravimetric curves were obtained on a DuPont model 1090B instrument coupled with a model 951 thermobalance with an inert atmosphere of argon. The samples were heated at a rate of $8.3\cdot10^{-2}$ K s^{-1}. In all cases only the second mass loss step was considered, due to the fact that the first one is related to physically adsorbed water [1].

Results and discussions

The results obtained for all the samples are summarized in Table 1, in which the surface area, initial mass and mass loss in the respective interval of temperature are shown. The mass lost during heating is related to the presence of the exposed silanol groups on the surface and from these data the respective silanol densities were calculated.

The same procedure of calculation was used for all the samples. To illustrate the method employed, an example is considered with the selected sample 3. In this case, 9.55 mg is the initial mass and, from the thermogravimetric curve a mass loss of 0.25 mg is detected during heating, which is due to the condensation of silanol groups to produce water. 0.25 mg of water contains $8.36\cdot10^{18}$ molecules of water which were originally distributed on a surface area of 503 m^{2}g^{-1}, expressed also as 4.81 m^2 or $4.81\cdot10^{18}$ nm^2.

In considering an extension of the silica sample, the accepted model to describe the distribution of the silanol groups on this kind of material establishes that the inorganic surface is covered by free and hydrogen bonded silanols at low temperature. On heating to higher temperatures, from 543 to 1243 K in the present case, the formation of water can be detected with a loss of 0.25 mg. The mechanism proposed for the appearance of water is due to the condensation of all the kind of silanol groups and the possible scheme is as follows [11, 17 and 18]:

This scheme shows that for each water molecule formed, the presence of two silanol groups on the silica surface is needed. In the mentioned sample the density of the silanol groups α_{OH} can be given by the quotient $2\cdot8.36\cdot10^{18}$ OH / $4.18\cdot10^{18}$=3.48 OH nm^{-2}. By applying the same procedure, the density of silanol groups was calculated for the samples examined. These values are included in Table 1.

The results obtained are in good agreement with those found by using other techniques and procedures [1, 8–19], showing the reliability of the procedure applied. The procedure proposed is based on a simple thermogravimetric curve and from the experimental point of view is quick, providing an easy method of analysis, which requires only a few milligrams of material.

In the present procedure of calculation considers the interval of temperature is considered where the silanol groups are condensed to form water. From the experimental point of view, all thermogravimetric curves must be referred to a standard temperature as a normal useful general method. Its application implies the use of any curve by extrapolating to a given temperature, at which the silanol groups are ideally absent. For this purpose, the final temperature of the experimental curve defines the increment to be added to the calculated value. In this connection, it is necessary to take into account that some silanol groups are still attached to the silica gel surface even near 1373 K, although this value is supposed to be less than 0.15 OH nm^{-2} [8]. In any case, a value corresponding to the remaining groups must be also added to the previously calculated one to correct the value, which is dependent on the number of uncondensed silanol groups still present above the range of temperature used [2, 16]. In this process, the total amount of bridged silanol groups is inevitably included, which are dominant at 773 K [16].

Table 1 Values of density of silanol groups α_{OH}/OH nm^{-2} calculated for some silica gel samples with different surface areas, S_{BET}/m^{2}g^{-1}, indicating the initial mass m_i/mg, mass loss m/%, and the interval of temperature ΔT/K considered

Sample	S_{BET}/m^{2}g^{-1}	m_i/mg	m/%	ΔT/K	α_{OH}/OH nm^{-2} calculated	α_{OH}/OH nm^{-2} corrected	Ref.
1	321	12.84	1.84	393– 824	3.84	5.54	22
2	503	19.10	2.5	593–1100	3.33	4.33	22
3	503	9.55	2.6	543–1243	3.48	3.78	23
4	354	9.27	3.2	583–1205	6.05	6.25	a
5	503	24.02	3.09	623– 923	4.11	5.52	24
6	270	6.00	2.27	653–1023	5.62	6.73	25
7	300	7.78	2.1	453–1103	4.68	5.38	a
8	354	8.92	2.4	413–1158	4.53	4.93	a
9	354	14.92	2.64	591– 862	5.00	6.60	a

[a] This work

As illustrated before, the chosen sample 3, Table 1, gave a density of silanol groups of 3.48 OH nm^{-2}. The additional increment to correct the final value was obtained by plotting the density of silanol group values against the respective temperatures of condensation [8], as is shown in Fig. 1. The resulting profile indicates a successive condensation of silanol groups on the surface during heating, this being more pronounced at lower temperature. Three main regions can be detected in this plot. The first one is characterized by a linear slope from 473 to 673 K, followed by another quasi-linear section from 673 to 1173 K and from this last temperature, the density of silanol groups decreases monotonously to zero. Then, to correct the assayed value an increment of 0.30 OH nm^{-2} must be inferred to give 3.78 OH nm^{-2}, which is derived from the profile of Fig. 1. For all samples this kind of correction was used and the values are listed in a column in Table 1.

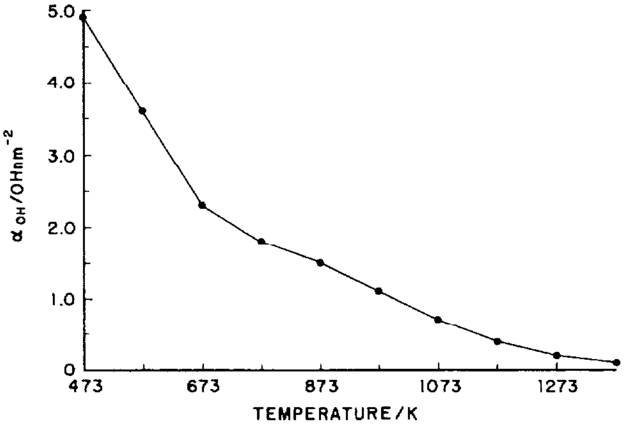

Fig. 1 Density of silanol groups (α_{OH}/OH nm^{-2}) as a function of the temperature (*T*/K) for a series of silicas

In examining the density of silanol groups in Table 1, the mean value is near to five, which confirms its practical use for many purposes for indistinct silicas. On the other hand, the present method of calculation provides a more specific value for a given silica by using a simple thermogravimetric curve run.

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References

1 R. K. Iler, The Chemistry of Silica, Wiley and Sons, New York 1979.
2 G. R. Bogart, D. E. Leyden, T. M. Wade, W. Schafer and P. W. Carr, J. Chromatogr., 483 (1989) 209.
3 Y. Kurusu, J. Macromol. Sci. Chem., A 27 (1990) 117.
4 N. Simonzadeh and A. A. Schilt, J. Coord. Chem., 20 (1989) 117.
5 C. Airoldi and E. F. C. Alcântara, Colloids Surf., 39 (1989) 219.
6 G. V. Kudryavtsev, S. Z. Bernardyuc and G. V. Lisichkin, Russ. Chem. Rev., 58 (1989) 406.
7 K. M. R. Kallury, W. E. Lee and M. Thompson, Anal. Chem., 65 (1993) 2459.
8 L. T. Zhuravlev, Langmuir, 3 (1987) 316.
9 T. Ishikawa, M. Matsuda, A. Yasukawa, K. Kandori, S. Inagaki, T. Fukushima and S. Kondo, J. Chem. Soc.. Faraday Trans., 92 (1996) 1985.
10 V. Y. Davidov, A. V. Kiselev and L. T. Zhuravlev, Trans. Faraday Soc., 60 (1964) 2254.

11 D. W. Sindorf and G. E. Maciel, J. Am. Chem. Soc., 105 (1983) 1487.
12 G. Curthoys, V. Y. Davidov, A. V. Kiselev, S. A. Kiselev and B. V. Kustetesav, J. Colloid Interface Sci., 48 (1974) 58.
13 J. B. Pery and A. L. Hensley Jr., J. Phys. Chem., 72 (1968) 2926.
14 I. Gillis-D'Hamers, I. Cornelissens, P. Van der Voort, K. C. Vrancken, E. F. Vansant and F. Daelemans, J. Chem. Soc. Faraday Trans., 88 (1992) 723.
15 D. W. Sindorf and G. E. Maciel, J. Phys. Chem., 87 (1983) 5516.
16 P. Van Der Voort, I. Gillis-D'Hamers and E. F. Vansant, J. Chem. Soc. Faraday Trans., 86 (1990).
17 C. H. Lochmuller and M. T. Hersey, Langmuir, 4 (1988) 572.
18 P. Van Der Voort, I. Gillis-D'Hamers, K. C. Vrancken and E. F. Vansant, J. Chem. Soc. Faraday Trans., 87 (1991) 3899.
19 I. Gillis-D'Hamers, J. Philipaerts, P. Van Der Voort and E. F. Vansant, J. Chem. Soc. Faraday Trans., 86 (1990) 3747.
20 P. Staszczuk, M. Jaroniec and R. K. Gilpin, Thermochim. Acta, 287 (1996) 225.
21 J. Goworek and W. Stefaniak, Thermochim. Acta, 286 (1996) 199.
22 A. R. Cestari and C. Airoldi, J. Thermal Anal., 44 (1995) 79.
23 E. F. C. Alcântara and C. Airoldi, Thermochim. Acta, 259 (1995) 95.
24 E. F. C. Alcântara and C. Airoldi, J. Chem. Thermodynamics, 27 (1995) 623.
25 A. R. Cestari and C. Airoldi, J. Braz. Chem. Soc., 6 (1995) 291.