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A NEW ELEMENTAL ANALYSIS METHOD BASED ON THERMOGRAVIMETRIC DATA AND APPLIED TO ALKOXYSILANE IMMOBILIZED ON SILICAS

A. R. Cestari and C. Airoldi

Instituto de Química, Universidade Estadual de Campinas, Caixa Postal 6154, 13083–970
Campinas, Sao Paulo, Brazil

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Abstract

A new analytical method based on thermogravimetry and applied to chemically functionalized surfaces is proposed. The mass losses of surfaces modified with alkoxysilane reagents, Sup-$CH_2CH_2CH_2$-R (*Sup* = support and *R* = Cl, SH, NH_2, $NHCONH_2$, $NHNHCOCH_3$ or $(CH_2)_4NH$), are interpreted by considering the physically adsorbed water, the silanol groups and the organic moiety. The elemental analyses calculated from these data are in agreement with those obtained by classical elemental analysis. The method is quick and reproducible, and requires the use of only a few milligrams of material.

Keywords: alkoxysilane immobilization, elemental analysis, thermogravimetry

Introduction

The reactivity of silica gel has been very well explored, due to the fact that a great number of molecules can be chemically bonded to its surface [1]. Normally, in this process ligands bearing trimethoxy or triethoxy groups are the most commonly used. The advantage of this kind of reagent is related to the high thermal and hydrolytic stabilities of the product [2].

The adsorption of metallic cations from dilute ethanolic and acetonic solutions onto molecules anchored on silica gel surfaces has been studied in our laboratory [3, 4]. Several other applications of these chemically modified surfaces are as stationary phases for chromatography [5], ion-exchange [6] and biotechnology [7], use in the glass industry [8] and also as supports for catalysis [9].

Thermogravimetric analysis is a useful technique, which reveals the loss in mass of a given substance during the heating process [10]. The mass losses derived from the thermogravimetric curves can be correlated with the various

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stages of decomposition. As concerns a molecule covalently bonded to a silica surface, the main molecule bonded to the surface and also the silanol groups bonded to the matrix can be quantitatively determined during the disruption process, since the anchored molecule is known. However, this procedure has not been well explored for characterizing functionalized surfaces. Increased use of this technique could be of considerable importance in the following of all immobilization processes [3]. In that case, elemental analysis is required to establish the degree of functionalization of the surface.

The objective of this publication is to propose a new quantitative elemental analysis of is organofunctionalized silicas with alkoxysilanes, by means of thermogravimetric data. This is a quick and reproducible method, which avoids the use of complex instrumentation and reagents. The results obtained through the thermogravimetric data are compared with the respective elemental analyses of the surfaces.

Experimental

Silica gel reagents

Two different samples of silica gel (Merck) had organic molecules anchored on their surfaces, for which the main characteristics were: i) Silica I: a surface area of 321 $m^2 \cdot g^{-1}$ and a particle size of 70–230 mesh. ii) Silica II: a surface area of 503 $m^2 \cdot g^{-1}$ and a particle size of 80–170 mesh. The samples were initially degassed at 423 K for 8 h under vacuum.

All solvents were of reagent grade and were used after purification. The alkoxysilanes (Aldrich) 3-mercaptopropyltrimethoxysilane (mts), 3-aminopropyltriethoxysilane (ats) and 3-chloropropyltrimethoxysilane (cts) were used without further purification.

Immobilization and characterization of silica gel surface

Samples of activated silica gel were reacted with mts, ats or cts to produce the following modified surfaces: Sil–SH [11], Sil–NH_2 [12] or Sil–Cl [3], respectively. Following reaction of the precursor Sil–Cl with acetylhydrazine piperazine or urea, the new surfaces Sil–A [3], Sil–P [4] or Sil–U [13] were isolated. The origins of the silicas used and the final prepared surfaces are detailed in Table 1.

The organic groups anchored on the surfaces were detected via the infrared spectra of self-supported disks. The degree of functionalization was determined through chloride (Sil–Cl), nitrogen (Sil–NH_2, Sil–A, Sil–P and Sil–U) or sulphur (Sil–SH) elemental analysis [3, 14]. Thermogravimetric curves were ob-

Table 1 Silicas (Sil I, II) used and the respective immobilized surfaces (Sil–X)

Silica	Sil-X	Reference
Sil–I	Sil–Cl	[3]
Sil–II	Sil–A	[3]
Sil–II	Sil–P	[4]
Sil–I	Sil–SH	[11]
Sil–II	Sil–NH_2	[12]
Sil–I	Sil–U	[13]

tained on a DuPont thermogravimetric analyser mode 9900 in a dynamic atmosphere, using a dry nitrogen or argon flux. At least two samples with immobilized surfaces, with masses varying between 10 and 25 mg, were heated from ambient temperature up to 1073 K at a heating rate of 0.17 deg·s^{-1} or 0.083 deg·s^{-1}. These curves proved to be completely reproducible.

Results and discussion

Six different molecules were anchored covalently on the silica gel surface, half of them by one-step immobilization (Sil–SH, Sil–NH_2 and Sil–Cl), while the other three surfaces were obtained by treating the molecule of interest with the precursor Sil–Cl. With the exception of Sil–NH_2, which was bonded to the surface in the triethoxy form, all surfaces involved the trimethoxysilane compound.

All surfaces were submitted under identical conditions to thermogravimetric measurements and the curves were analysed on the basis of the respective silica gel used in the immobilization process. Thermogravimetric curves for some silicas were also assayed in both inert atmospheres and at different heating rates. The curves proved reproducible in both atmospheres and at different heating rates. However, a nitrogen flux and a heating rate of 0.17 deg·s^{-1} were selected, since i) this cheap inert gas is more commonly used in this technique, ii) the same steps of decomposition were observed in both atmospheres, iii) this heating rate gave the curves quickly, and iv) elemental analysis calculations involving different heating rates and inert atmospheres gave the same results.

The activated silica gel Sil–I was used to immobilize the chloro group (Sil–Cl), the thiol group (Sil–SH) and urea (Sil–U). Figure 1 presents thermogravimetric curves of the activated and the modified silicas. The respective percentage mass losses are presented in Table 2.

The set of thermogravimetric curves associated with the amino group (Sil–NH_2), acetylhydrazine (Sil–A) and piperazine (Sil–P), with activated Sil–II as precursor, are shown in Fig. 2. The percentage mass losses for all these silicas are also included in Table 2.

The activated silica gel exhibited two distinct decomposition steps during heating, as shown in Figs 1 and 2. In the first step, the physically adsorbed water on the surface was lost at a low temperature. On increase of the temperature, the water produced by condensation of surface silanol groups was continuously lost, as shown in the second step, and a plateau was attained at high temperature.

The functionalized surfaces showed a loss in mass of physically adsorbed water in the first step, near the same range as observed for the original silica. An abrupt loss in mass was detected in the second step, which included the anchored molecule and also the condensed water from the surface silanol groups. This general behaviour is outlined in all thermogravimetric curves for the immobilized surfaces shown in Figs 1 and 2.

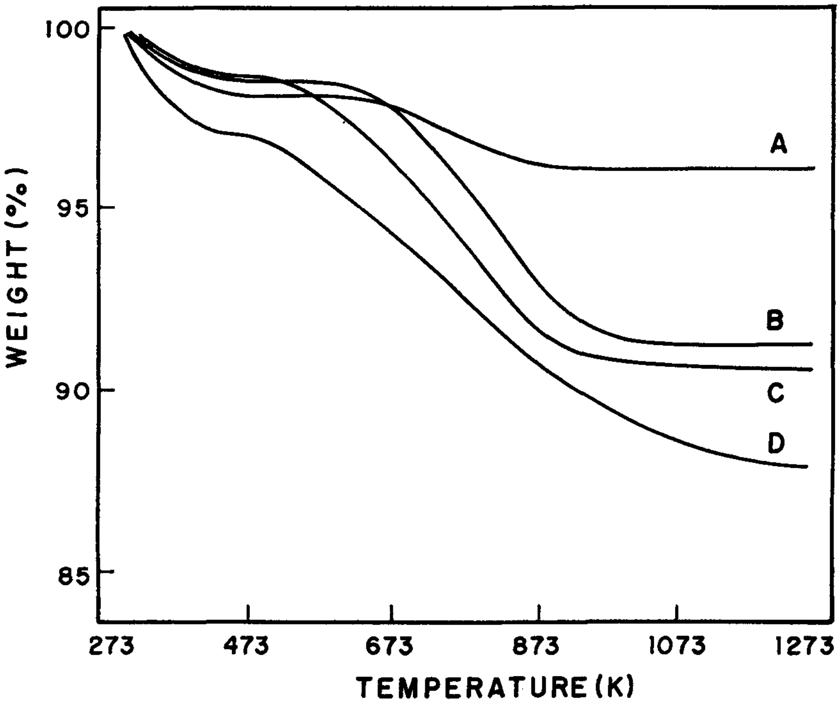


Fig. 1 Thermogravimetric curves of A) activated silica gel (Sil–I), B) chloro group (Sil–Cl), C) thiol group (Sil–SH), and D) urea (Si–U)

The mass lost in the second step of decomposition for each chemically modified surface can be related to the amount of the anchored molecule. These results can be related to the elemental analysis of a particular element of the

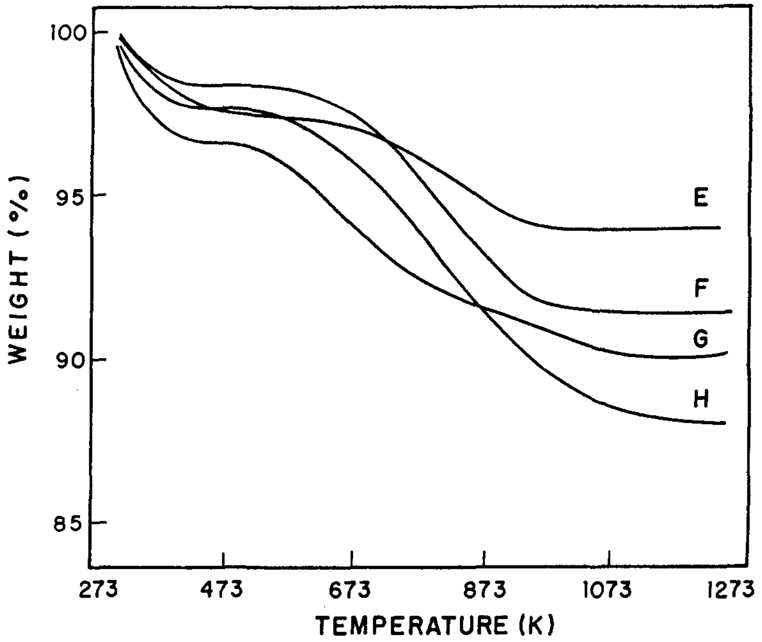


Fig. 2 Thermogravimetric curves of E) activated silica gel (Sil–II), F) piperazine (Sil–P), G) acetylhydrazine (Sil–A), and H) amino group (Sil–NH_2)

surface. For this purpose, an example involving activated Sil–I and Sil–SH surfaces (Fig. 1) has been used and the following procedure may be considered:

1. The number of silanol groups per gram of pure silica should be known. Equation (1) is used for this [3, 15]:

$$\alpha_{OH} = S_{BET}\,\beta_{OH} \qquad (1)$$

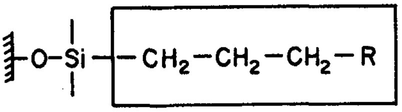
where α_{OH}, S_{BET} and β_{OH} are the number of silanol groups per gram of silica, the surface area ($m^2 \cdot g^{-1}$) and the number of silanol groups per nm^2, respectively. The latter value for silicas with a surface area in the interval 300–500 $m^2 \cdot g^{-1}$ is in the range of 4 to 5 silanol groups per nm^2 [15]. In this case, a mean value of 4.5 is used in all calculations. Since the surface area of Sil–I is 321 $m^2 \cdot g^{-1}$ and 1 nm^2 corresponds to 1.0×10^{-18} m^2, we have $\alpha_{OH} = 1.44\times10^{21}$ OH groups per nm^{-2}. Via Avogadro's number, the number of moles of silanol groups on the silica is $\alpha_{OH} = 2.39\times10^{-3}$ mole OH g^{-1}.

2. The major loss in mass of the organofunctionalized surfaces should be due to the carbon chain bonded to the silica. However, the water formed by unreacted silanol groups is also included in the 9.10% loss. Thus, the net organic loss should be corrected [3, 16].

Table 2 Initial mass (m_i), percentage of mass loss (m%) and temperature range (K) for original and chemically modified surfaces

Surface	m_i /mg	m / %	T / K
Sil–I	12.84	1.88	316.2–352.0
		1.84	393.0–824.3
Sil–II	19.10	2.50	293.0–413.0
		2.50	593.0–1100.0
Sil–A	10.09	3.50	293.0–443.0
		6.10	493.0–1000.0
Sil–Cl	21.40	1.48	308.0–400.0
		6.49	673.0–1073.0
Sil–P	17.85	1.50	293.0–393.0
		6.50	493.0–993.0
Sil–U	21.36	3.09	310.0–324.3
		11.59	330.0–1100.0
Sil–NH_2	26.18	2.37	320.0–337.0
		6.25	523.0–1073.0
Sil–SH	20.34	0.97	318.3–523.0
		9.10	824.0–1000.0

From the general behaviour involving methoxy- and ethoxysilanes with low carbon chains in several syntheses, it was established a mean proportion of 45% of the silanol groups were used in the reaction [17]. An amount of 55% of the free silanol groups condensed during the heating gives 1.31×10^{-3} mole OH g^{-1} support, which value corresponds to a certain percentage of the remaining loss of silanol groups from the Sil–SH surface. This calculated percentage was obtained by relating the number of silanol groups and the respective mass of the surface after the removal of the physical water. Thus, after losing 1.88% of its mass in the first step, 12.60 mg of Sil–I suffers a new loss of 1.84% in the second step, through the removal of water of condensation of silanol groups. In the second step, 20.14 mg of Sil–SH surface lost both organic material and water of condensation. Presuming the same behaviour for activated and immobilized silica, the contribution of water corresponds to 2.94%. Since this percentage relates to the total silanol groups on the surface (2.39×10^{-3} mole), 55% of them gives 1.31×10^{-3} mole, which causes a loss of 1.61% of the remaining silanol groups. In conclusion, 20.14 mg of this surface lost 9.10% in this step, where 7.49% corresponds to 1.50 mg or organic material.



$R = -Cl, -SH, -NH_2, -N(H)C(O)NH_2, -N(H)N(H)C(O)CH_3, -N(CH_2)_4NH$

Scheme

3. All molecules chemically immobilized on the silica gel surface are shown in the Scheme.

During the heating, the Si–O–Si bonds on the surface remain unchanged due to their thermal stability (2). However, the organic moiety indicated in the closed box in the Scheme is prone to decomposition.

For R = SH, the organic portion is C_3H_7S, with a molecular mass of 75 g, with 32 g due to sulphur. The thermogravimetric curve for this surface indicated a mass loss of 1.50×10^{-3} g, where 6.40×10^{-4} g corresponds to sulphur, giving 2.00×10^{-5} mole. From this value, the amount of sulphur is 0.98 mmole g^{-1} sample. This value is coincident with that obtained by elemental analysis.

This same procedure was used for all six thermogravimetric curves and the results were compared with those of the conventional elemental analyses for chloride (Sil–Cl), sulphur (Sil–SH) or nitrogen (Sil–A, Sil–P, Sil–U and Sil–NH_2). These values are listed in Table 3.

Table 3 Analytical elemental analyses (X_E) and those (X_T) derived from thermogravimetric curves ($mmol\cdot g^{-1}$) for all chemically immobilized surfaces

Surface (element)		X_E	X_T
Sil–SH	(X = S)	0.98±0.01	0.98±0.05
Sil–Cl	(X = Cl)	0.54±0.02	0.60±0.03
Sil–A	(X = N)	0.36±0.01	0.39±0.01
Sil–P	(X = N)	0.47±0.01	0.42±0.02
Sil–U	(X = N)	0.92±0.03	0.99±0.05
Sil–NH_2	(X = N)	0.65±0.02	0.70±0.04

The deviations obtained for the elemental analysis values X_E are inherent to the self-experimental determination, while for the X_T values a high deviation of 5% was assumed in all calculations. This deviation was attributed by taking into account the chosen position on each plateau in the calculated value X_T. However, this deviation caused an error of less than 0.05 $mmole\cdot g^{-1}$ for each determination, as shown in Table 3. A coincident analytical result was observed for the Sil–SH surface. However, with the exception of Sil–P, all X_T values were higher than the X_E values. In the experimental elemental determinations, the crude material was digested to liberate the desired element prior to analysis, when the final result can be affected by possible sources of errors such as incomplete digestion, transference of digested material and the titration.

The method based on thermogravimetric curves led to reasonable results being obtained for these surfaces, as listed in Table 3, with the advantage of the element being determined directly in the solid sample. This suggests that thermogravimetry is a useful technique for calculation of a given elemental content in an immobilized molecule, in spite of the high deviation of the X_T values. Extension to other chemically immobilized surfaces is desirable, since the characteristics of the activated silica used in the synthesis are known.

Conclusions

This method permits a quick calculation of the degree of functionalization of a silica surface without a knowledge of the elemental analysis, which in practice requires very carefully interpretations. For example, hydrogen and carbon elemental analyses for this sort of material give results with lower confidence levels due to the presence of water (or silanol groups) and at least one methoxy (or ethoxy) group on the surface, with distortion of the results to high values. On the other hand, the reproducibility of the thermogravimetry curves is easily confirmed by reproducing the experiment, only a few milligrams of material being involved in each run.

Another positive feature of this method is the simple condition of checking the possible interference of the surface in each step of a series of experiments. For example, immobilized molecules can be liquidated in inadequate media, as happens in catalysis studies at high temperature and pressure [18], or in very concentrated eluent solutions, during pre-concentration and chromatographic separations [19].

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Zusammenfassung — Es wird eine neue, auf der Thermogravimetrie basierende und an chemisch funktionierten Oberflächen angewendete analytische Methode vorgeschlagen. Unter Inbetrachtnahme physisch adsorbierten Wassers, der Silanolgruppen und der organischen Anteile wurde der Massenverlust von Oberflächen interpretiert, die mit den Alkoxysilanreagenzien Sup-$CH_2CH_2CH_2$–R (*Sup* = Träger, *R* = Cl, SH, NH_2, $NHCONH_2$, $NHNHCOCH_3$ oder $(CH_2)_4NH$) modifiziert wurden. Die anhand dieser Angaben berechneten Elementaranalysen stehen in Übereinstimmung mit denen aus klassischer Elementaranalyse. Die Methode ist schnell und reproduzierbar durchführbar und bedarf nur einiger Milligramm der fraglichen Substanz.