

# Octadecylsilane-modified silicas prepared by grafting and sol–gel methods

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## Abstract

Silica bearing octadecylsilane groups were synthesized by grafting and the sol–gel method. In the former, commercial silica was chemically modified with octadecyltrimethoxysilane (ODS), while in the latter, it was produced by reacting tetraethoxysilane and ODS in alkaline milieu. Carbon content was much lower in the case of grafting reaction (1.2 and 3.5 wt.%) in comparison to that achieved with the sol–gel method (2.5–68.6 wt.%). Hybrid silicas were characterized by X-ray photoelectronic spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR), <sup>13</sup>C resonance nuclear magnetic spectroscopy (NMR), laser scattering and scanning electronic microscopy (SEM). Alkyl chain conformation was shown to depend on the preparation route. Grafting yields hybrid silica having a liquid-like conformation, while in silica prepared by the sol–gel method, the C18 chains present a more ordered and crystalline conformation. The presence of alkyl chains increases the particle size distribution for hybrid silicas prepared by the grafting method.

*Keywords:* Hybrid silica; Sol–gel; Grafting; Octadecylsilane; ODS

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## 1. Introduction

Organically functionalized hybrid silicas have attracted attention since a longtime ago. The covalent modification of silica surface is a powerful approach to control the level of solid–liquid or solid–vapor interactions.

Organosilanes with the general formula  $R_nSiX_{4-n}$ , where X is a reactive leaving group (H, Cl,  $-N(CH_3)_2$ ,  $-OCH_3$ , for instance) and R an organic side group, are available coupling agents, which allow the preparation of a large variety of organosilicon monolayers and thin films by reacting them with supports, such as inorganic oxides. The surface modification can be carried out by grafting reaction between the reactive leaving group of the organosilane and surface OH groups, for example.

In the case of sol–gel materials, hybrid silicas can be obtained from the hydrolysis and co-codensation of tetraethyl orthosilicate (TEOS) with other organosiloxanes ( $R_xSi(OR)_{4-x}$ , where R is an alkyl group). In these materials, TEOS functions as building

blocks to construct the framework while the organosiloxanes with non-hydrolysable organic groups contribute both to the framework silica units and to organic surface functional groups.

Among the employed organosilanes, octadecyltrimethoxysilane (ODS) and octadecyltrichlorosilane (OTS) have been largely used for surface chemical modification. Examples of application of such reactions can be found in the development of self-assembled monolayer [1–4], of chromatographic phases [5], of hydrophobic coatings [6], of supported enzymes [7], and of adsorbents [8], for instance.

In such materials, mostly prepared by grafting, the conformation order of octadecyl chains, as well as surface coverage are variable. The influence of solvents [9] and of synthetic route [10] on the conformational order of C18 alkyl modified silica gels were investigated in the literature. The effect of surface coverage on the conformational order of these alkyl chains was also evaluated in the case of materials based on carbon clad zirconia supports [11]. The large number of different experimental parameters employed in the preparation of such systems hardly allows a comparison among materials.

In the present study, we investigated the influence of the synthetic route in the development of ODS-modified silica sur-

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faces on the surface coverage, on the conformational order of octadecyl chains, on the texture and on the morphological characteristics. ODS-modified silica were prepared by both grafting and sol-gel route and resulting solids were characterized by a series of complementary techniques, namely, X-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FT-IR),  $^{13}\text{C}$  resonance nuclear magnetic spectroscopy (NMR), laser scattering and scanning electronic microscopy (SEM).

## 2. Experimental

### 2.1. Materials

Silica Wacker (HDK N20) was activated under vacuum ( $P < 10^{-5}$  bar) for 16 h at different temperatures in the 100–450 °C range. Octadecyltrimethoxysilane (ODS) (Acros), octadecyltrichlorosilane (OTS) (Aldrich) and tetraethylorthosilicate (TEOS) (Merck) were used without further purification. Pure grade toluene (Nuclear), ethanol (Merck) and dichloromethane (Nuclear) were deoxygenated and dried by standard techniques before use. Ammonium hydroxide (Merck) was purchased as a 25% solution.

### 2.2. Synthesis of xerogel by hydrolytic alkaline route

Xerogels were synthesized in accordance of Stöber synthesis [12]. In a typical preparation, 20 mL of ammonia solution was diluted in 100 mL of ethanol in a two-neck flask equipped with a mechanical stirrer. 5 mL of a TEOS ethanol solution (1:4, v/v) was added to that solution. The mixture was kept under stirring for 2 h. Then, the organosilane (ODS), 2.10 mmol diluted in ethanol (4 mL) was added drop-wise to the solution. The addition time lasted roughly 1 h, 45 min. After addition, the mixture was kept under stirring for more 2 h. The silica was then dried under vacuum and washed with  $5 \times 10$  mL of ethanol and finally dried under vacuum for 16 h.

### 2.3. Synthesis of grafted silica

All the chemicals were manipulated under inert atmosphere using the Schlenk technique. ODS (or OTS solution) (1.57 mmol diluted in 10 mL of toluene) was added to thermally activated silica (ca. 2.0 g) and kept stirring for 1 h. The slurry was then heated to 80 °C, under reflux, for 2 h. The slurry was then filtered, and washed with  $12 \times 2$  mL of toluene. The solid was finally dried under vacuum for 16 h.

## 2.4. Characterization of silicas

### 2.4.1. Elemental analysis (CHN)

Carbon content was determined in a Perkin-Elmer M-CHNSO/2400 analyzer.

### 2.4.2. Surface coverage concentration

Surface coverage concentration ( $\Gamma = \mu\text{mol m}^{-2}$ ) was calculated using the model proposed by Amati and Kováts [13],

employing data from elemental analysis (carbon content) and by nitrogen adsorption (specific surface area), according to Eq. (1):

$$\Gamma = \frac{10^6}{S_{\text{BET}}} \left( \frac{1201 \times n\text{C}}{\%C_{\text{CHN}}} - M_{\text{SUB}} + \delta \right)^{-1} \quad (1)$$

where  $S_{\text{BET}}$  ( $\text{m}^2 \text{g}^{-1}$ ) is the specific surface area of the untreated silica,  $n\text{C}$  the number of atoms of carbon of the surface coverage substituent,  $M_{\text{SUB}}$  the molecular mass of the substituent (in this case, the supported metallocene), and  $\delta$  is the correction for desorbed water and the proton substituted during reaction. In the present study,  $\delta = 1$ .

### 2.4.3. X-ray photoelectron spectroscopy (XPS)

XPS measurements were performed at room temperature using a Physical Electronics 1257 system with a hemispherical analyzer and non-monochromated radiation (Al  $K\alpha$ , 1486.6 eV) operating at 200 W. The pass energy was set to 50 eV. The powder was supported with double sided copper tape. The analysis area was approximately  $0.4 \text{ cm}^2$ . The surface charging effects (ca. 0.5 eV) were corrected by using the Si 2p from  $\text{SiO}_2$  at 103.3 eV. Numerical analysis of the peaks was performed using the MULTIPACK software for data analysis, from Physical Electronics, Inc., which evaluates the peak area and uses tables of sensitivity factors for quantitative calculation.

### 2.4.4. Fourier transform infrared spectroscopy (FT-IR)

Samples were analyzed as pellets, diluted in KBr, by transmission FTIR, using a BOMEM FTIR spectrophotometer (MB-102) at 25 °C coadding 32 scans at a resolution of  $4 \text{ cm}^{-1}$ . The measurements were restricted to the  $4000\text{--}1000 \text{ cm}^{-1}$  region.

### 2.4.5. $^{13}\text{C}$ Magic angle spin nuclear magnetic resonance ( $^{13}\text{C}$ MAS-NMR)

Solid-state NMR measurements were performed on a Chemagnetics CMX-300 (Varian, USA). Samples were transferred to zirconia rotors. Measurements were performed at 75.3 MHz for  $^{13}\text{C}$ . The number of scans was 5000 for  $^{13}\text{C}$ . NMR parameters for  $^{13}\text{C}$ , the contact time and a recycle time were chosen 2 ms of 1 s, respectively.

### 2.4.6. Nitrogen adsorption-desorption isotherms

Samples were previously degassed ( $10^{-1}$  bar) at 100 °C for 48 h. Adsorption-desorption nitrogen isotherms were measured at  $-196$  °C in a Micromeritics ASAP 20 surface area and porosity analyzer. Specific surface area ( $S_{\text{BET}}$ ) was determined by the Brunauer-Emmett-Teller equation ( $P/P_0 = 0.05\text{--}0.35$ ). The mesopore size and distribution were calculated by the Barrett-Joyner-Halenda (BJH method) using the Halsey standards. Micropore volumes were calculated by the  $t$ -plot method, using the Harkins and Jura standard isotherm.

### 2.4.7. Particle size analyzer

The size distribution was measured by light scattering using a Malvern Mastersize 2000 coupled to a Hydro 2000 UM (A) accessory. Samples were diluted in parafine (ca. 0.1016%).

Table 1  
Carbon content for different systems

System	Carbon content (wt.%)
GR450	1.2
GR200	1.9
GR100	3.5
SG100	2.5
SG20	10.8
SG10	19.9
SG5	37.7
SG2	53.4
SG0	68.6
Zorbax C18 <sup>a</sup>	15.0
Partisil 10 ODS 1 <sup>a</sup>	5.0
Partisil 10 ODS 2 <sup>a</sup>	15.0
Resolve C18 <sup>a</sup>	12.0
Partisil-40 <sup>b</sup>	18.7
S-C18 <sup>c</sup>	20.5

<sup>a</sup> Ref. [14].

<sup>b</sup> Ref. [15].

<sup>c</sup> Ref. [16].

#### 2.4.8. Scanning electron microscopy (SEM)

SEM experiments were carried out on a JEOL JSM/6060 and JEOL JSM/5800, respectively. The catalysts were initially fixed on a carbon tape and then coated with gold by conventional sputtering techniques. The employed accelerating voltage was 10 kV for SEM.

### 3. Results

Table 1 reports the grafted carbon content for the silicas obtained by both methods. In Table 1, GR refers to “grafting” procedure, the number refers to the pretreatment temperature. For instance, GR 450 means silica which was treated under vacuum at 450 °C prior to organosilane grafting. SG means silica obtained by the sol–gel method. The number refers to ODS to TEOS ratio, i.e., 0, 2, 5 and 10 means 1:0; 1:2; 1:5 and 1:10. For comparative reasons, data from the literature were also included.

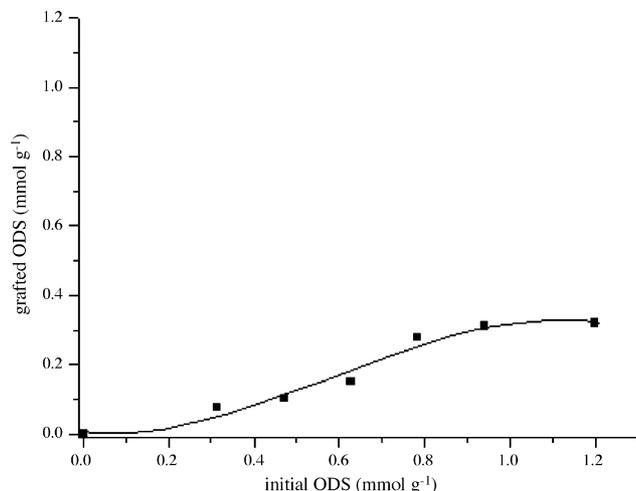


Fig. 1. Adsorption isotherm of ODS on silica surface.

Fig. 1 shows the adsorption isotherm of ODS on silica treated at 100 °C. Grafted content was calculated based on C content measurement.

According to Fig. 1, the saturation level for the silica surface is achieved at 0.3 mmol g<sup>-1</sup>. The surface reaction between silanol groups and alkoxyde from ODS is not a strong interaction, since all the grafted concentration are much lower than that available in solution. For instance, less than 65% of the ODS amount present in solution was immobilized in the case of the concentration 0.8 mmol g<sup>-1</sup>. Such behavior could be in part consequence of the low reactivity between ethoxyde and silanol groups. Nevertheless, the reaction between C<sub>18</sub>H<sub>35</sub>SiCl<sub>3</sub> and silanol groups, using more reactive ligands (chloride) did not provide a significant increase in grafted content: 0.24 mmol g<sup>-1</sup> versus 0.20 (in the case of C<sub>18</sub>H<sub>35</sub>Si(OEt)<sub>3</sub>). It is very likely that the steric effect played by the C18-alkyl chain might be preponderant during the surface reaction.

In order to determine the organosilane content in terms of Si, routine techniques such as absorption or emission atomic spectroscopy do not allow to distinguish Si of the matrix (SiO<sub>2</sub>) from that of the organosilane moieties (RSi). X-ray photoelectron spectroscopy (XPS) can potentially distinguish and quantify silica atoms from the surface (roughly 3 nm in depth) in different chemical environments [17]. Therefore, in the present work, XPS was employed to quantify the organosilane content in terms of Si in some samples.

The typical survey spectrum of chemically modified silica showed the elements which constitute the uttermost external surface, namely, O, C and Si. High-resolution spectra were recorded in the regions of C (1s), O (1s) and Si (2p) allowing the atomic percentual determination. Table 2 reports these data.

The carbon content present in Table 2 is not directly comparable to the values obtained by elemental analysis, since in the case of XPS, the outermost external surface is analyzed, while in the case of elemental analysis, the entire volume of the sample is evaluated. Besides, the main part of the 18.9 at.% of GR450 is probably associated with adventitious carbon.

Nevertheless, the same trend is observed here: samples prepared by the sol–gel method present a much higher carbon content, roughly three times higher, than those obtained by grafting. Besides, in the GR series, the same trend is also observed: As the number of silanol is reduced by thermal treatment, the carbon content decreases.

Fig. 2 shows a typical high-resolution spectrum in the Si 2p region. The deconvolution of the measured signal suggests the presence of two components: one centered at 103.3 eV, attributed

Table 2  
Atomic percentual of C, O and Si of hybrid silicas, determined by XPS

System	C (at.%)	O (at.%)	Si (at.%) <sup>a</sup>	Si <sub>102</sub> (at.%) <sup>b</sup>
GR100	27.4	55.0	17.6	1.3
GR200	20.3	50.2	21.4	1.2
GR450	18.9	66.0	15.0	0.5
SG2	72.5	21.0	6.5	1.3

<sup>a</sup> Total Si content.

<sup>b</sup> Component fraction at 102.0 eV.

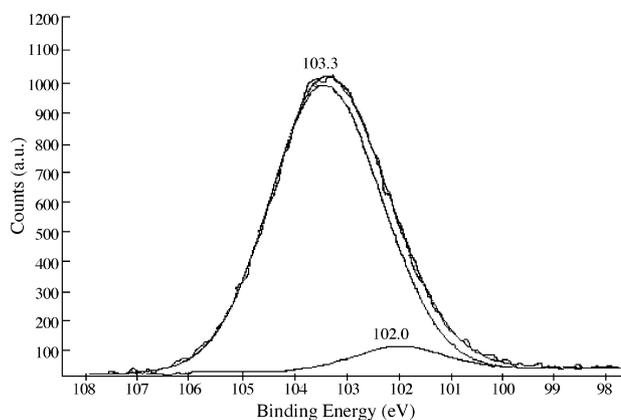


Fig. 2. High-resolution XPS spectrum in the Si (2p) region of hybrid silica of sample SG2.

to Si (2p) from SiO<sub>2</sub>, and another one, centered at 102.0 eV, which can be assigned to the Si (2p) from the organosilicon moieties [18].

Table 2 also presents the fraction of Si 2p peak from the species centered at 102.03 eV, assigned to the organosilane derivative. Values remained between 0.5 and 1.4 at.%.

Table 3 shows the ODS loading for the silicas prepared by grafting, determined in accordance with Amati and Kováts model [13]. Silicas treated at this temperature range (100–450 °C) afford solid phases bearing 0.23–0.80 μmol m<sup>-2</sup> of ODS.

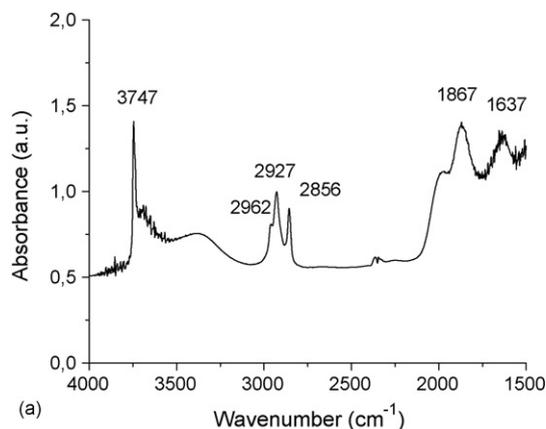
Table 3 also reports the percentage of silanol groups (P) replaced by organic phase. Thus, it is assumed that four OH groups per 100 Å<sup>2</sup> (1 nm<sup>2</sup>) are available for the reaction. Besides, it is assumed that roughly 70–80% of the total number of OH groups are capable to react with the organosilane [19]. For the P determination, it was taken into account the number of silanol groups as function of the pretreatment temperature [20].

The hybrid silicas were further analyzed by infrared (IR) spectroscopy. Fig. 3 shows transmission FT-IR spectra of two phases prepared by grafting and by the sol-gel method. It is worth noting that for the commercial silica (grafting procedure), FT-IR measurements were performed down to 1500 cm<sup>-1</sup> due to the strong absorption of Si–O–Si stretching (below 1200 cm<sup>-1</sup>). In the case of the solid produced by the sol-gel method, the detected region were as far as 500 cm<sup>-1</sup>, in order to confirm the formation of silica by the observation of a strong band at 1100 cm<sup>-1</sup>. The presence of alkyl groups can be observed in the region of C–H stretching, which assignments are reported in Table 4 [21] and Table 5.

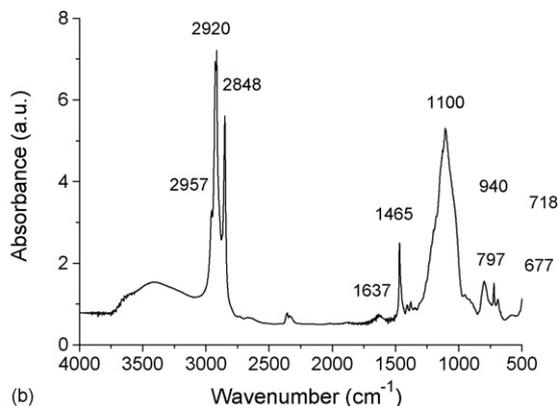
Under the condition of magic angle spinning and dipolar coupling of protons, the chemical shift of methylene groups in <sup>13</sup>C

Table 3  
Surface coverage of hybrid silicas prepared by grafting determined by the Kováts model

System	$\Gamma$ (μmol m <sup>-2</sup> )	P (%)
GR100	0.80	33
GR200	0.38	26
GR450	0.23	23



(a)



(b)

Fig. 3. FT-IR spectra of hybrid silica prepared by: (a) grafting (GR450) and (b) the sol-gel method (SG2).

CP/MAS NMR spectroscopy depends largely on the conformation of octadecyl chains. For each central carbon atom in a C18 chain with the *trans* conformation, a chemical shift of about 33 ppm is expected. On the other hand for conformation with rapid changes between *gauche* and *trans*, a chemical shift of about 30 ppm is expected [10,11,22,23].

Fig. 4 shows solid-state <sup>13</sup>C CP/MAS NMR spectra obtained from GR100 and SG10 systems.

The NMR signal for the main (CH<sub>2</sub>)<sub>n</sub> group for the GR100 system occurs at 30.4 ppm corresponding to *trans-gauche* con-

Table 4  
Assignment of infrared bands in spectra of hybrid silicas

Wavenumber (cm <sup>-1</sup> )	Assignment
3414	Interactions of OH groups
2956	CH <sub>3</sub> ν(C–H) <sub>as</sub>
2913	CH <sub>2</sub> ν(C–H) <sub>as</sub>
2848	CH <sub>2</sub> ν(C–H) <sub>s</sub>
1867	Si–O–Si overtone
1637	H <sub>2</sub> O δ(O–H)
1465	CH <sub>2</sub> δ(C–H)
1100	Si–O–Si ν(Si–O) <sub>as</sub>
940	Si–OEt ν(Si–O) <sub>as</sub>
797	ν(Si–O) <sub>s</sub> Si–O–Si
718	Si–OEt overtone
677	Si–OEt overtone

as, asymmetric; s, symmetric.

Table 5  
Peak positions in the  $\nu(\text{C-H})$  region for hybrid silicas

Group	$\nu(\text{C-H})$	ODS <sup>a</sup>	GR100	GR200	GR450	SG0	SG2	SG10	Crys. <sup>b</sup>	Liq. <sup>b</sup>
-CH <sub>2</sub> -	$\nu_a$	2924	2929	2927	2927	2918	2920	2920	2920	2928
	$\nu_s$	2854	2855	2855	2856	2849	2848	2850	2850	2856
CH <sub>3</sub> -	$\nu_a$	2962	2963	2964	2962	2957	2957	2957	2958	-

as, asymmetric; s, symmetric.

<sup>a</sup> Film of octadecyltrimethoxysilane on KBr window.

<sup>b</sup> Ref. [24].

formations and a small shoulder at 32.7 ppm is observed (Fig. 4a). This corresponds to a large fraction of *trans-gauche* conformations and indicates small order of octadecyl chains. In case of SG10 system, the main (CH<sub>2</sub>)<sub>n</sub> resonance appears at 33.5 ppm corresponding to crystalline-like *trans* conformations and a small shoulder at 31.0 ppm is observed (Fig. 4b). This corresponds to a large fraction of crystalline-like *trans* conformations and indicates high order of octadecyl chains.

Particle size distribution was monitored by laser scattering as shown in Fig. 5.

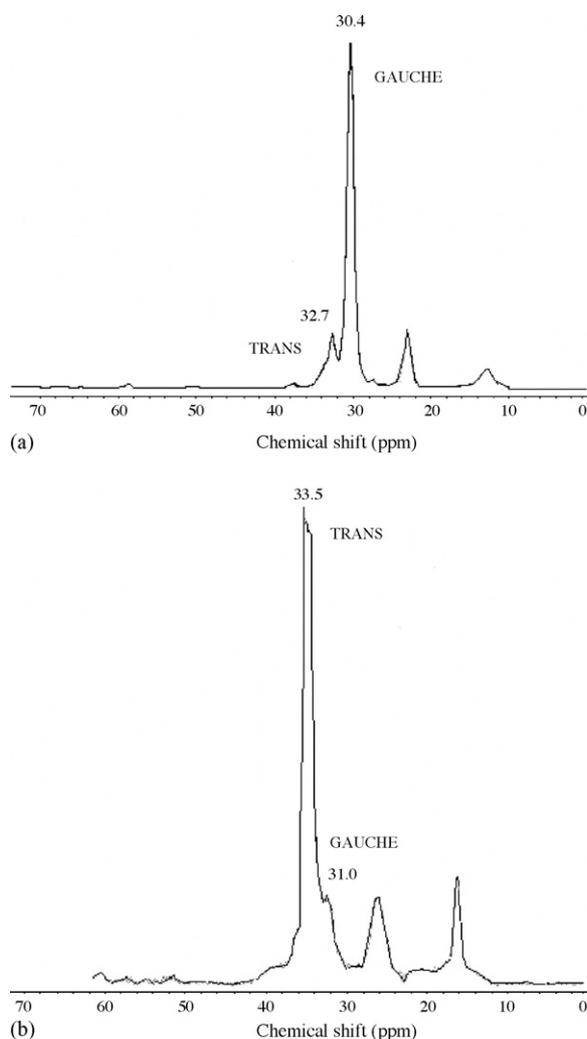


Fig. 4. <sup>13</sup>C MAS NMR spectra of hybrid silica prepared by: (a) grafting (GR100) and (b) the sol-gel method (SG10).

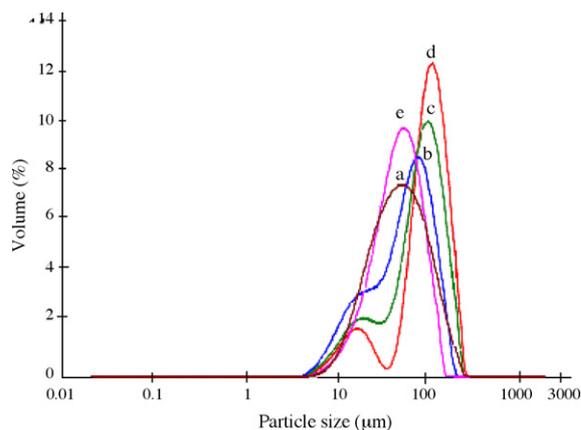


Fig. 5. Particle size distribution for silicas: (a) SiO<sub>2</sub> (Wacker); (b) GR100; (c) GR200; (d) GR450; (e) GR450M.

According to Fig. 5, for the systems prepared by grafting, there is a narrowing in size distribution of the hybrid silica in comparison to the modified ones. Besides, in the case of GR450, a bimodal distribution can be observed. Table 6 presents the particle size distribution expressed in terms of  $d_{10}$ ,  $d_{50}$  and  $d_{90}$  ( $\mu\text{m}$ ). It is worth noting that the terms  $d_{10}$ ,  $d_{50}$  and  $d_{90}$  corresponds, respectively, to the cumulative frequencies of 10, 50 and 90%. For instance,  $d_{50}$  means that 50% of the particles possess a diameter less than a given value.

Chemical modification with ODS increased the particle mean diameter ( $d_{50}$ ), as shown in Table 6. Particle size distribution for hybrid silica produced by the sol-gel method revealed smaller particles in the range of 10–30  $\mu\text{m}$ .

Fig. 6 shows micrographies of hybrid silica prepared by grafting (GR100) and by the sol-gel method (SG10). In the case of

Table 6  
Mean size distribution of silica particles expressed in terms of  $d_{10}$ ,  $d_{50}$  and  $d_{90}$  ( $\mu\text{m}$ ), determined by laser scattering

Silica	$d_{10}$	$d_{50}$	$d_{90}$
SiO <sub>2</sub> (Wacker <sup>®</sup> )	18.5	49.8	121.9
GR100	14.6	58.6	122.9
GR200	18.1	83.7	160.2
GR450	22.3	102.5	177.5
GR450M <sup>a</sup>	20.3	46.4	97.2
SG100	4.1	14.3	39.7
SG10	4.3	30.0	60.9
SG2	6.7	13.5	24.7
SG0	11.3	20.6	35.9

<sup>a</sup> Silica modified with (CH<sub>3</sub>)<sub>3</sub>SiCl.

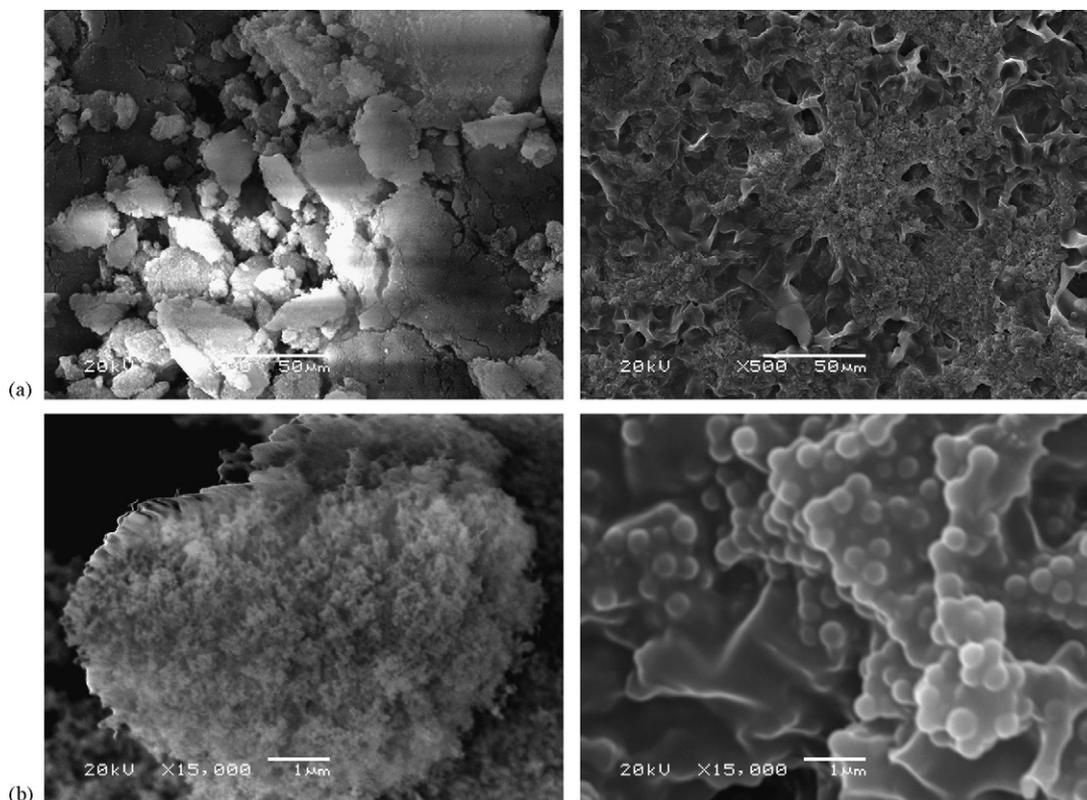


Fig. 6. SEM micrographs of hybrid silicas: (a) GR100 and (b) SG10 (magnification of 500 $\times$  and 15,000 $\times$ ).

GR100 (Fig. 6a), no particular morphology is observed, while in the case of SG10 (Fig. 6b), a combination of spherical silica and lamellar pattern is observed.

#### 4. Discussion

Silicas modified with octadecylsilane (ODS) were obtained by grafting and by the sol-gel method. In the first case, a commercial silica, pretreated at different temperatures, was reacted with  $(C_{18}H_{35}Si(OEt)_3)$ , while in the latter, the same organosilane was reacted with  $Si(OEt)_4$  at alkaline pH.

According to Table 1, carbon content in the silica prepared by the grafting method is very low, between 1.2 and 3.5 wt.%. Grafting reaction depends on the surface reaction between silanol groups from the silica with the alkoxy groups from the organosilane compound. Therefore, the grafted content is dictated by the number of silanol groups, which in turn depends on the thermal treatment, and on the availability of the remaining surface silanol on the silica surface, which might be partially covered by the alkyl chain of the grafted species. According to Table 1, as the silica treatment temperature increases, the carbon content reduces. This is totally coherent with the findings that the number of silanol groups which is reduced from 4.5 to 1.5 OH nm<sup>-2</sup> when the thermal treatment temperature is increased from 100 to 450 °C [20].

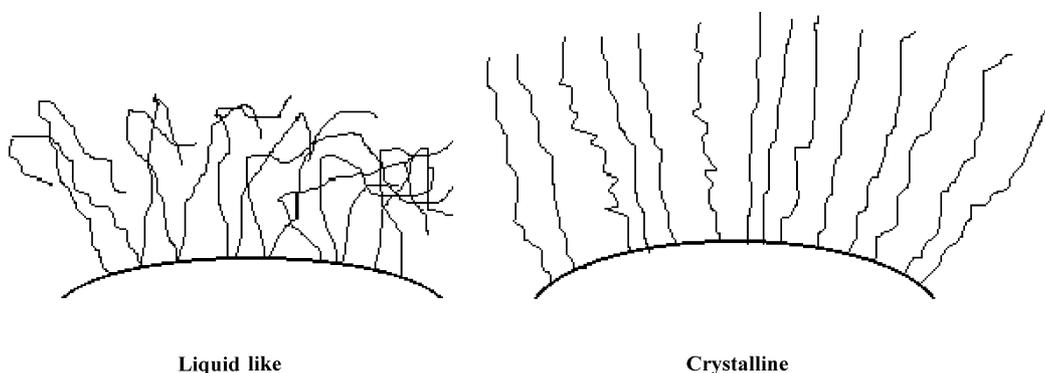
Silica prepared by the sol-gel method does not depend on the availability of surface silanol groups but on the amount and on the reactivity between the reagents. According to Table 1, the carbon content is much higher than those observed in the

case of grafted systems. Besides, the highest carbon content was achieved in the case of pure ODS (SG0), while the lower, in the case of quasi pure TEOS (SG100). For the systems resulting from the cohydrolysis between ODS and TEOS, the higher the ODS content in the reaction milieu, higher the carbon content in the resulting silica. For instance, an increase of 170% was observed when the ratio between ODS and TEOS increased from 1:10 to 1:2.

According to Table 1, commercial reversed-phase chromatographic phases present carbon content which is intermediate between the values obtained in the present work for the silicas prepared by grafting and by the sol-gel method. Most of the commercial phases present roughly 15% of carbon content. In some cases, the values are very close to those obtained by the sol-gel method. For instance, S-C18 has 18.72 wt.% C, using a commercial silica (344 m<sup>2</sup> g<sup>-1</sup>) as support, which was reacted with octadecyltrichlorosilane [16]. Similar results, remained between 15.9 and 22.3 wt.% C were reported in the literature for commercial silicas chemically modified by octadecyltrichlorosilane [18]. Such values are very low in comparison to those reported for commercial phases. For instance, silica chemically modified with octadecildimethylsilane presents 3.6  $\mu\text{mol m}^{-2}$  [25].

XPS deconvolution of 2p signal suggests that the fraction of organosilanes moieties is very close to that obtained for the sol-gel in the case of SG2. Thus, even in the case of sol-gel, the amount of the organic counterpart on the support surface is low under these preparative conditions.

According to Table 3, the *P*-values are between 33 and 23%, suggesting that a large number of silanol groups are not reached



Scheme 1.

under these conditions. In the literature, in the case of a silica with  $400 \text{ m}^2 \text{ g}^{-1}$ , it is reported that 23% of the surface was recovered by ODS groups, i.e., a value close to that observed in the present study. It is very likely that octadecyl groups are playing a steric effect during the surface reaction in both methods.

According to Fig. 3a, the band at  $3737 \text{ cm}^{-1}$  is attributed to isolated silanol groups. The presence of these groups suggest that grafting maximum content is not a question of available silanol groups, but more likely a problem of steric effect played by the octadecyl groups already grafted on silica surface, which render difficult the access of ODS molecules in solution to residual silanol groups. The large band below  $3500 \text{ cm}^{-1}$  is typical of silanol groups which are interacting through hydrogen bonds [14]. The intensity of C–H stretching bands is proportional to carbon content, in accordance with elemental analysis, since SG2 contains much more carbon percentage than GR450. In the spectrum of SG2 (Fig. 4b), the skeletal Si–O–Si vibration can be observed in  $1100 \text{ cm}^{-1}$  [26]. Besides, additional bands resulting from residual ethoxide can also be seen. It is worth noting that in the case of silica produced by the sol–gel method, isolated silanol groups are not observed. Silanol groups might be interacting by hydrogen bond among themselves, in the form of vicinal or geminal silanol groups, or with residual ethoxide groups.

Infrared analysis in the stretching region has been employed for the evaluation of polymethylene chain conformation. Table 5 presents data concerning  $\nu(\text{C–H})$  from the literature and observed in the present study. The proposed models consider crystalline-state positions in which the long-chain are fully extended with all-*trans* conformation and liquid-state, in which the chains are randomly oriented. The  $\nu_s(\text{CH}_2)$ ,  $\nu_{as}(\text{CH}_2)$  and  $\nu_{as}(\text{CH}_3)$  are selected for structural interpretation owing to the minimal overlap of their absorption bands with those of other modes. The position of these peak frequencies provides insight into the intermolecular environment of the alkyl chains in these assemblies, i.e., the location of these peaks are sensitive indicators for the extent of the lateral interactions between long *n*-alkyl and polymethylene chains. For instance, according to Ref. [27], the peak position for the  $\nu_{as}(\text{CH}_2)$  mode of a crystalline polymethylene chain ( $2920 \text{ cm}^{-1}$ ) is  $8 \text{ cm}^{-1}$  lower than that for the liquid state ( $2928 \text{ cm}^{-1}$ ). Similar trends have been reported for hybrid films produced by alkylmethoxysilanes [28]. Then, according to these models, it seems that in the case of

grafted system, the alkyl tails are less ordered, closer to a liquid state, whereas for the phase prepared by the sol–gel method, it seems that the alkyl tails are fully extended in a crystalline-like conformation. Similar results were observed by NMR analysis. Scheme 1 represents these two possible configurations.

Long chains are prone to interweave [29]. It seems that the modification of silica with ODS is causing an aggregation among particles. In order to verify this possibility, silica was modified with a very short alkyl chain,  $(\text{CH}_3)_3\text{SiCl}$ . The resulting hybrid silica (GR450M) has a particle size distribution close to that observed in the case of bare silica. Therefore, it might be very likely that the alkyl chain are interweaving, generating larger particles.

## 5. Conclusions

Chemical and textural characteristics of chemically modified silica bearing octadecylsilane groups are influenced by the preparation route. Grafting yields very low carbon content, since it depends on the availability of silanol groups both in terms of quantity as of accessibility, due to steric effect played by the grafted species on silica surface. The C18 alkyl ligands are in a liquid-like conformation, which are capable to interweaving, leading to an increase in particle size distribution. On the other hand, the sol–gel method allow the production of higher carbon content in hybrid silica, which is dependent on the ODS quantity in the synthesis milieu. In this case, C18 alkyl chains assume a more crystalline and organized conformation. The resulting morphology is shown to combine spherical and lamellar patterns, while mean particle size laid in the range of  $10 \mu\text{m}$ .

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