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Dependence of surface properties of silylated silica on the length of silane arms

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Abstract Amorphous precipitated Zeosil 1165 MP silica was silylated with low grafting degrees of organosilicons bearing different alkoxy and hydrocarbon tails, like monomethoxy(dimethyl)octadecylsilane (DMODMS), monomethoxytrimethylsilane (TMMS), trimethoxymercaptopropylsilane (MPTS), and 3-octanoylthio-1-propyltriethoxysilane (NXT®). Thermogravimetry and Elemental Analysis were used to determine the degree of silane grafting and the final number of free silanol OH groups/nm^2 on the modified Zeosil surface. Free energy, enthalpy and entropy of adsorption of hydrocarbon probes were determined by Inverse Gas Chromatography at infinite dilution and dispersive component, γ_s^d, and specific interaction parameter, I^{sp}, of the surface tension of the silica surface were calculated. Silylation changes the hydrophilic character of Zeosil silica to the hydrophobic one, on increasing the grafting degree and, mainly, the length of hydrocarbon tail of the silane molecule (DMODMS and NXT®). The long hydrocarbon tails practically shield the silica particle surface and the adsorbed probes preferentially interact with them. In the case of TMMS-Zeosil the adsorbed probes practically interact with the silica surface, with loss of entropy well above that of the bare silica, while being equal the values of the enthalpy of adsorption. All the other modified silicas show loss of entropy lower than that of bare silica. Steric hindrance, played by the presence of methyl groups of TMMS, is suggested to reduce the freedom of translational and rotational movements of the adsorbed probe.

Keywords Zeosil silica · Silylation · Structure of silanes · Surface properties

1 Introduction

Chemical modification of surface of oxide powders by covalent attachment of organosilanes is a versatile technique to tune surface properties, on the ground of different requirements and specific applications of the oxide powders: basic catalysts, solids with significant Brønsted acidity, polymer fillers, and so on (Vansant et al. 1995; Beck et al. 1992; Vartuli et al. 1994; Koyano et al. 1997; Jaroniec et al. 1998; Brunel et al. 1995; O'Brain et al. 1997; Subba Rao et al. 1997; Van Der Voort et al. 1999). In the polymer field such a modification plays an important role in promoting adhesion between powder and polymer, in improving the disperdibility of oxide powders into polymer matrix (Niedermeier et al. 2002; Kim and Vanderkooi 2002; Wang et al. 1991; Wang and Wolff 1992; Wolff et al. 1994a, 1994b; Evans and Waddell 1995; Wang 1998; Schuster et al. 1996; Costa et al. 2003; Castellano et al. 2005; Fröhlich et al. 2005; Hunsche et al. 1998; Ramier et al. 2007; Bertora et al. 2011).

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The grafting of alkoxysilanes onto silica particle surface occurs due to the presence of different types of silanol OH groups. These can be both on the surface and internal; the first ones exist as: free geminal; vicinal (free, or bridged through the hydrogen bond); isolated, also on dry silica. The internal silanol groups are located into very fine ultramicropores, with diameter less than 1 nm, and are accessible for small molecules, for example, water (Zhuravlev 2000; Zhuravlev and Potapov 2006; Iler 1979; Burneau and Gallas 1998).

Alkoxy groups of silane condense with free silanols, giving rise to Si-O-Si surface. The accessability and then the reactivity of silanols is probably not the same for all of them, and will also depend both on alkoxysilane molecule size and on the number of alkoxy groups present in the same silane molecule. Internal silanols, i.e. OH groups bound to internal atoms of silica particles, are not involved in surface process, then to study the active behaviour of silica surface only surface silanols have to be considered (Vidal and Papirer 1998; Iler 1979; Jaroniec et al. 1998; Vansant et al. 1995; Bergna 1994).

Several and different methods, such as Fourier transform infrared spectroscopy (FTIR), scanning and transmission electron microscopy (SEM, TEM), X-ray diffraction, inverse gas chromatography (IGC), etc., can be used to characterise the filler surfaces. Nowadays, IGC has been developed as a universal technique of surface characterization for solid materials because it permits to determine their surface forces or energies, i.e. the dispersive and polar surface energy components (Wang et al. 1991; Santos and Guthrie 2005; Wolff et al. 1994a; Corder and Young 1979; Glass and Larsen 1993; Castellano et al. 2002, 2005, 2007; Costa et al. 2003 Chenhang and Berg 2003).

For some years, we are involved in using IGC to study the changes of surface thermodynamic properties of silica modified with different alkoxysilanes. We showed that trialkoxysilanes, like bis(triethoxysilylpropyl)tetrasulfane (TESPT), octadecyltriethoxysilane (ODTES) and triethoxysilane (TES) and their mixtures, reduced the polarity of the silica surface and, consequently, reduced the tendency of silica particles to agglomerate in an elastomer matrix, according to the morphological findings by transmission electron microscopy (Castellano et al. 2002, 2005, 2007; Costa et al. 2003).

Furthermore, a previous our study by FTIR spectroscopy (Marrone et al. 2004) evidenced that, in the experimental conditions used, a trialkoxysilane molecule, like TESPT or TES, binds to the Zeosil by means of, on average, two Si-O-Silica siloxane bridges; it follows that one alkoxy group does not react.

The present investigation extends the previous study and aimed: (a) at determining the changes of the surface properties of precipitated amorphous silica as a function of the number of alkoxy groups and of the length of hydrocarbon arm of the modifiers; (b) at comparing the aforementioned changes induced by different silanes with those obtained by using the 3-octanoylthio-1-propyltriethoxysilane (NXT silane, by General Electric 2006), corrently used to modify silica in tire production. The interest in this silane is due to the fact that previous studies have shown that it offers more scorch safety compared to the well known TESPT (Yan et al. 2004a, 2004b) and it raises the tire performance bar with improved dynamic and physical properties. However, no thermodynamic studies have been reported in literature on the NXT-modified silica.

The ultimate object of our work is addressed to find new silane-based modifiers that, upon grafting of small quantities on silica particles are able to significantly modify the silica surface to use in preparing rubber-silica composites, in which silica is highly dispersed as required for the production of high performance tire. Employment of small quantities of silane in modifiyng silica is very important from the technical point of view as small grafting degree of silica means not only lower consumption of silane, but lower methanol evolvement during the silylation of silica, compared to what is happening today.

The degree of modification of the Zeosil silica surface was estimated using thermal gravimetric and elemental analyses; silylation with monomethoxytrimethylsilane (TMMS) was also investigated by FT-IR spectroscopy. Changes in surface thermodynamic properties of modified silicas were evaluated determining the components of surface free energy by inverse gas chromatography.

2 Experimental methods

2.1 Materials

The amorphous precipitated silica, used in the present study, was Zeosil 1165MP (Rhodia), with surface area of about 160 m^2/g and average pore diameter around 320 Å (Castellano et al. 2002), indicating that the silica surface is essentially characterized by mesopores. This Zeosil is mostly used in elastomer reinforcement and its main market is the tire industry.

Surface modification of silica with different silanes was performed in accordance with the procedure previously described for TESPT (Costa et al. 2003). Briefly, the modification procedure was performed by first immersing the silica micropearls in silane CH_2Cl_2 solution. After evaporation of the solvent, the silica physically covered with modifier was sealed in a vial, under Argon, and thermally treated at 120 °C for two hours. Thermal treatment was followed by soxhlet extraction with CH_2Cl_2 for six hours to eliminate the unreacted silane.

Different silanes were used as modifiers, like monomethoxydimethyloctadecylsilane (DMODMS), monomethoxytrimethylsilane (TMMS), trimethoxymercaptopropylsilane (MPTS), all the products purchased from Aldrich, and 3-octanoylthio-1-propyltriethoxysilane (NXT®). Silica and NXT® samples were kindly supplied by Pirelli Tyre S.p.A.

All the *n*-alkanes, alkenes and alkylated benzenes used in this work were analytical grade and were obtained from Aldrich.

2.2 Thermal gravimetry

The apparent grafting degree of the silanes onto silica particles was determined by thermal gravimetric analysis (TGA) carried out by a Perkin-Elmer TGA7 analyser, by operating with a heating rate of 20 °C/min in the range 25–700 °C under nitrogen atmosphere and then under air atmosphere up to 900 °C; flow rate 40 cm^3/min.

2.3 Elemental analysis

Carbon analysis (C wt%) of silane grafted onto silica was performed with a Carlo Erba Instruments Mod. Elemental Analysis (EA) 1110 CHNS apparatus, operating up to 1000 °C.

2.4 Inverse gas chromatography

Change of surface thermodynamic properties of modified silica was studied by inverse gas chromatography (IGC), at infinite dilution, by using modified silicas as the stationary phase; the silica particle size ranged from 150 to 250 µm. A stainless steel column with a length of 50 cm and inner diameter of 4 mm was filled with about 2 g of silica. Before the measurements, the column was conditioned for at least 40 hr in the gas chromatograph at 170 °C, with a carrier gas flow rate of 6–8 $cm^3\ min^{-1}$. Methane was used to determine the dead volumes.

n-alkanes (C_5–C_{10}), 1-alkenes (C_5–C_{10}), and alkylbenzenes (alkyl group C_1–C_4) were used as the probes.

Chromatographic experiments were carried out with a Dani GC 1000 gas chromatograph equipped with a flame ionization detector (FID) and operating under isothermal condition. Helium was used as the carrier gas and the column inlet and outlet pressure was measured using standard pressure gauges; the carrier gas flow rate was determined using a bubble flowmeter (20–30 $cm^3\ min^{-1}$). The solutes were injected in the form of vapor by using a 1 µL Hamilton syringe. To satisfy the condition of adsorption at infinite dilution and of gas chromatography linearity, the injected vapor volume was generally lower than 0.1 µL.

IGC experiments were performed in the 80–160 °C temperature range. Each value of retention time is an average of three injections.

2.5 Infrared spectroscopy

FTIR spectra were recorded on a Nicolet Nexus Fourier Transform instrument provided with a DTGS KBr detector: for each spectrum 100 scans in the range 4000–400 cm^{-1} were recorded, resolution 4 cm^{-1}. The self-supporting silica pressed disks were treated by outgassing in the IR cell. Spectra were collected after the pretreatment and after contact with the silane vapors, which were distilled under vacuum and then contacted with the sample surface through the ramp.

3 Results and discussion

3.1 Grafting degree

In Fig. 1 FTIR spectra of pure powder pressed disks of pristine silica and of TMMS-modified silica are reported in the OH stretching region, after outgassing at increasing temperature. It is evident that the spectrum of hydroxyl groups and of adsorbed water is significantly modified by the presence of TMMS. The overall absorbance of the OH stretching absorption (note that the Absorbance scales in the two sections of the Figure are different) is reduced to near 63 % of the original intensity, in excellent agreement with the grafting degree that will be discussed later. The pattern of adsorption due to H-bonded species is slightly modified. The position of the maximum of the free terminal silanols is markedly shifted down (3738 versus 3743 cm^{-1}, after outgassing at 400 °C, see the insert in Fig. 1) and its intensity is reduced, showing that the silanols characterized by the highest frequency disappeared because of their condensation with TMMS, while those responsible for the lowest frequency tail of the band did not. Previous spectroscopic studies performing with sterically hindered molecular probes provided

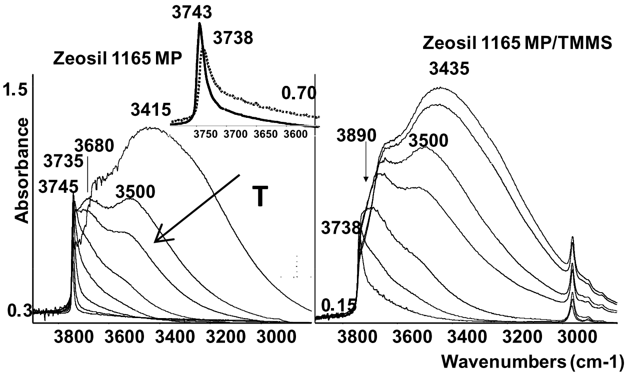


Fig. 1 FTIR spectra of (OH stretching region) of pure powder pressed disks of Zeosil silica (*left*) and of TMMS-modified silica (*right*) after outgassing at increasing temperatures from 25 °C to 500 °C (as shown by the *arrow*). In the *inset*: IR spectra of pure silica (*full line*) and of the modified silica (*point line*) after outgassing at 400 °C

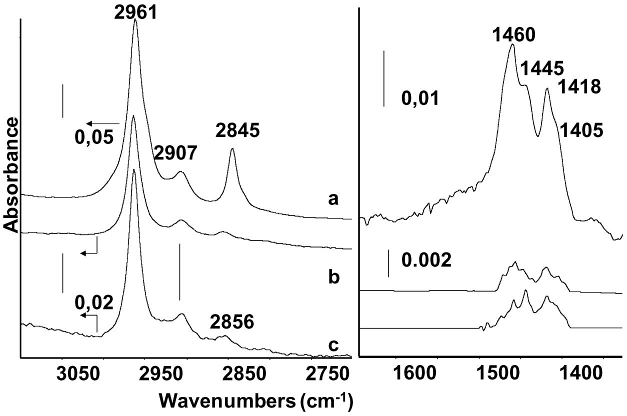


Fig. 2 FTIR spectra (CH stretching and deformation region) of the pure powder pressed disk of bare Zeosil silica (**a** and **b**) after activation by outgassing at 500 °C and adsorption from vapour phase of TMMS (**a**, gas spectrum subtracted) and following outgassing at 100 °C (**b**); (**c**) spectrum of TMMS-modified Zeosil silica after outgassing at 100 °C: (*left*) C-H stretching region; (*right*) CH deformation region

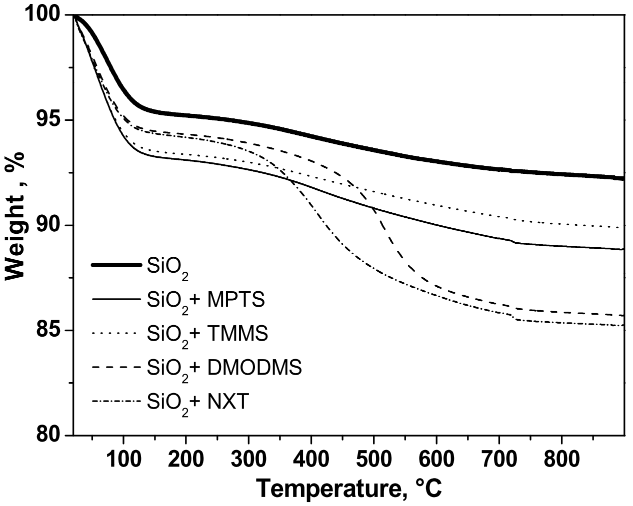


Fig. 3 TGA measurements of the loss mass of bare Zeosil and Zeosil silica modified with four different silanes

evidence for the nature of the silanol sites responsible such a lowest frequency component. They are due to silanol groups located in very small pores and are consequently unaccessible to large molecules (Busca 2012).

In Fig. 2 the FTIR spectrum in the CH stretching (left) and deformation (right) regions of the silica modified with TMMS (Fig. 2c) is compared with the spectra of physisorbed (Fig. 2a) and of chemisorbed TMMS (Fig. 2b) obtained after adsorption from vapor phase of TMMS on vacuum- activated silica. While the physisorbed TMMS species (whose spectrum is similar to that of liquid TMMS, White and Tripp 2000) disappears by outgassing at room temperature, chemisorbed TMMS species resist outgassing at 500 °C. Chemisorbed TMMS, whose spectrum is virtually identical to that of species present on TMMS-modified silica, is characterized by the disappearance of the CH_3 symmetric stretching mode of methoxy groups at 2845 cm^{-1}, confirming the condensation reaction with silanol groups and the likely complete disappearance of methoxy groups. These data confirm that on the TMMS-modified silica part of the OH groups irreversibly reacted with TMMS, giving rise to surface trimethylsilyloxy-species, TMS groups.

To determine the real grafting degree onto silica, the loss weight by TGA and the C wt% of grafted silane obtained by EA were considered. As before mentioned, the amorphous silica particles are characterized by the presence of OH silanol groups located at the surface, in the bulk and/or in ultramicropores. Therefore, such particles have a significant polar character which favours the physisorbtion of water (Iler 1979; Zhao and Lu 1998; Zhao et al. 1998). Then, upon heating, silica first losses physisorbed water and then water from dehydroxylation. These two processes do not overlap, as experimental TGA curves show in Fig. 3 (Iler 1979; Jaroniec et al. 1998; Zhuravlev 2000; Ligner et al. 1989).

As one can see, the physisorbed water loss is practically complete around 200 °C, where a plateau is observed, before the dehydroxylation process begins. During thermal gravimetric analysis of grafted silica the loss of material, in the range 200–900 °C, is due to decomposition of the grafted silane and to the water by dehydroxylation of OH residual silanol groups. Upon heating pure precipitated silica, water coming out by dehydroxylation of internal and surface OH silanol groups amounts to about 3 wt% (Zhuravlev and Potapov 2006). This water loss cannot be neglected in determining the number of grafted silane molecules and, then, the density of residual silanol OH groups.

TGA and EA results are collected in Table 1. The amount of silane burned (column 4) between 200–1000 °C was calculated using the %*C* by EA. The figure refers to the dry sample at 200 °C, deducible from the TGA data shown in column 2 (25–200 °C) of Table 1. The lower values of material loss calculated by EA respect to the ones obtained by TGA should be attributed to the water coming out by dehydroxylation in the 200–900 °C range. From the data reported in Table 1 we deduced that the concentration of the total (surface+bulk) OH/nm^2 was 12.5 of the dry Zeosil; the concentration of the unreacted OH/nm^2 for the modified-silicas ranged from about 55 to 90 %.

It was taken into account that the combustion of grafted silane leads to the formation of volatile carbon dioxide and water and solid SiO_2. The last compound goes with the preexistent silica to make up the residual solid phase. We underline that the grafting degree wt% refers to the alkylsiloxy residual group bond to silica surface, as sketched in Scheme 1.

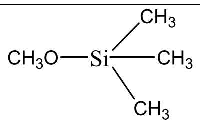
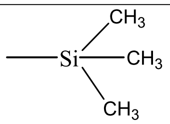
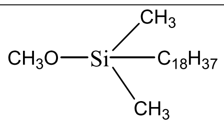
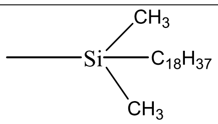
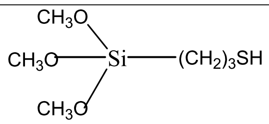
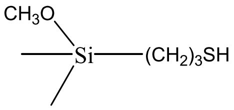
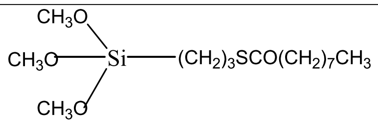
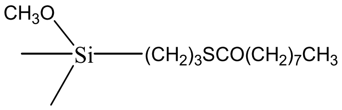
Table 1 Weight loss from thermal gravimetric and elemental analysis of bare and modified Zeosil 1165 MP silica

Sample	wt% loss from TGA		wt% loss calculated from EA[b]
	25–200 °C	200–900 °C	200–1000 °C
SiO_2[a]	4.8	3.0	–
SiO_2/ODTES[a]	5.1	5.8	4.1
SiO_2/TMMS	6.3	3.5	1.9
SiO_2/DMODMS	5.4	8.5	6.5
SiO_2/MPTS	6.7	4.1	1.9
SiO_2/NXT	5.4	8.8	7.0

[a] Castellano et al. (2007)

[b] Calculated by %*C*, from EA, due to the silane combustion of dry sample

Scheme 1 Silanes molecules and their alkylsiloxy residual groups

Acronym	**Silane molecule**	**Alkylsiloxy residual group**
TMMS		
DMODMS		
MPTS		
NXT		

The grafting density (number of grafted groups/nm^2) of the modifier monolayers, ρ, was calculated using the following formula (Plueddtemann 1991):

$$\rho = \frac{6 \cdot 10^5 (\%C)}{1200 \cdot n_C - MM(\%C)} \frac{1}{s} \tag{1}$$

where: $\%C$ is the carbon weight percentage of the modified silica, MM and n_c are the molecular mass and the number of carbon atoms of alkylsiloxy group, respectively, and s is the surface area of original Zeosil silica (160 m^2/g).

The values of reacted OH/nm^2 were calculated by assuming that a monoalkoxysilane molecule reacts evidently with one silanol OH group, while each trialkoxysilane molecule on the average would react with two OH groups, as before underlined (Marrone et al. 2004).

Values from 4.6 to 7.9 OH/nm^2 were calculated for surface with only either single or geminal sylanols (Peri and Hensley 1968). As a matter of fact Zhuravlev measured a mean value of 4.9 OH/nm^2 at 180–200 °C in vacuo, for 100 samples of totally hydroxylated amorphous silicas (Zhuravlev 1987, 2000; Zhuravlev and Potapov 2006). Following Zhuravlev, the percentage of residual OH groups on the modified silica surface was derived by assuming 4.9 OH/nm^2 present on the surface of the original Zeosil silica.

Table 2 shows data of grafted silane groups per nm^2 and the surface concentration of reacted and residual OH groups of all modified Zeosil specimens. As comparison, data referred to pristine and ODTES-modified silicas from our previous papers are reported (Castellano et al. 2007).

As one can see, different grafting degrees, for instance 4.6 and 7.2 wt% of ODTES and DMODMS, respectively, lead to the same percentage of residual OH groups (about 80 %), while the same grafting degree, for instance 7.2 and 7.8 wt% of DMODMS and NXT, respectively, leads to very different percentage of residual OH groups (80.9 and 52.3, respectively).

On the other hand, small amounts of silane at low molecular mass (TMMS, MPTS) are sufficient to neutralize a large number of OH silanol groups. Therefore, we expect that the effects of silylation on surface properties of silica depend both on amount and on type of silane grafted (molecular mass and number of alkoxy groups present), under the same conditions of graft.

Table 2 Surface concentration of silanol OH groups of bare and modified Zeosil silica, calculated from data of grafting degree of dry silica

Sample	Grafting degree, wt%	Grafted silane groups/nm^2	Reacted OH/nm^2 (surface)	Residual OH groups, % (surface)
SiO$_2$[a]	–	–	–	100
SiO$_2$/ODTES[b]	4.6	0.55	1.1	78.0
SiO$_2$/TMMS	3.0	1.6	1.6	67.1
SiO$_2$/DMODMS	7.2	0.9	0.9	80.9
SiO$_2$/MPTS	2.3	0.7	1.4	71.0
SiO$_2$/NXT	7.8	1.30	2.6	52.3

[a] 4.90 OH/nm^2 is assumed to be the density of OH groups at the surface of precipitated silica, according to Zhuravlev and Potapov (2006)

[b] Castellano et al. (2007)

Triethoxysilane (ODTES) and the monomethoxysilane (DMODMS), are characterized by the same molecular mass. According to that the grafting of 0.55 ODTES groups/nm^2 neutralizes 1.1 OH/nm^2; by grafting 7.2 wt% of the DMODMS neutralizes 0.9 OH/nm^2 (Table 2) , i.e., a value that is very close to that obtained by grafting 4.6 wt% of ODTES, amount almost half that of DMODMS. This confirms that a trialkoxysilane molecule on the average reacts with two OH groups, as previously shown by FTIR spectroscopic investigation (Marrone et al. 2004).

3.2 Adsorption thermodynamics

According to numerous recent papers, inverse gas chromatography (IGC) is one of the most reliable methods to study the filler surface, where the filler under investigation is the stationary phase and the solutes are appropriate low molecular weight compounds, with chemical nature similar to others interacting macromolecular or molecular species (Montes-Moran et al. 2002; Roshchina et al. 2001).

Application of IGC for studying adsorption processes is based on the assumption that the solute equilibrium conditions are achieved between the mobile and stationary phases. Such a condition is satisfied at the zero coverage of the surface, i.e. operating at infinite dilution. Under such conditions the adsorbate can be considered as ideal gas, both in gaseous phase and on the adsorbent surface, the interaction between the adsorbed probes is negligible, and the Henry's law can be applied.

From the measured retention time, t_r, and then the neat retention volume, V_n, IGC allows to calculate several standard thermodynamic quantities, such as the free energy ΔG^0, the enthalpy ΔH^0, and the entropy ΔS^0 for probe adsorption at infinite dilution (Castellano et al. 2007; James and Martin 1952; Wang and Wolff 1992; Adam 1968):

$$V_n = D \cdot j \cdot (t_r - t_d)\left(1 - \frac{P_w}{P_a}\right)\frac{T_c}{T_f} \tag{2}$$

where: D is the flow rate, j is the James-Martin factor for the correction of gas compressibility (James and Martin 1952), t_r and t_d are the retention times measured with a specific probe and a non adsorbing probe (such as methane), respectively, P_w is the vapour pressure of pure water at the flow meter temperature (T_f), P_a is the pressure at the flow meter and T_c is the column temperature.

At infinite dilution, the surface state is essentially two-dimensional and a given 'surface pressure', π_0, must substitute the usual gaseous pressure, as discussed in detail by N.K. Adam in his classical book (Adam 1968).

Thus the adsorption refers to the following process: ideal vapour phase (at $P_0 = 1.013 \times 10^6$ dynes/cm^2, and at a given T) to ideal adsorbed phase (in two-dimensions, at $\pi_0 =$ the surface pressure dyne/cm, and a given T).

Therefore, the energy associated to the process is $\Delta G = \Delta G^0$. In other words, the adsorption free energy for one mole of solute vapour from a reference gaseous state (considered as an ideal gas), defined by the pressure P_0, to a reference adsorbed state, defined by the spreading pressure π_0, is given by:

$$\Delta G^0 = -RT\left[\ln V_n + \ln(P_0/s \cdot g \cdot \pi_0)\right] \tag{3}$$

where: T is the column temperature in K, R is the gas constant, s is the specific surface area of silica, and g is the mass of the filler in the column.

The value of π_0 depends on the chosen reference state. There are two frequently used states, which serve to illustrate the arbitrariness of choice: the Kemball-Rideal (Kemball and Riedeal 1946) and the de Boer (DeBoer 1953) standard surface states. de Boer standard surface state assumes that the adsorbed molecules are at the same distance apart as they are in the 1 atm gas state at 0 °C. In this state $\pi_0 = 0.338$ dyne/cm and the ratio $P_0/\pi_0 = 2.99 \times 10^8\ \mathrm{m}^{-1}$, is the well known de Boer constant C.

Therefore, one can write the equation:

$$\Delta G^0 = -RT \ln\left(\frac{C \cdot V_n}{s \cdot g}\right) \tag{4}$$

The value of ΔG^0 clearly depends on the choice of surface standard state.

For the same standard process to which refers ΔG^0, the adsorption enthalpy can be calculated from the Gibbs-

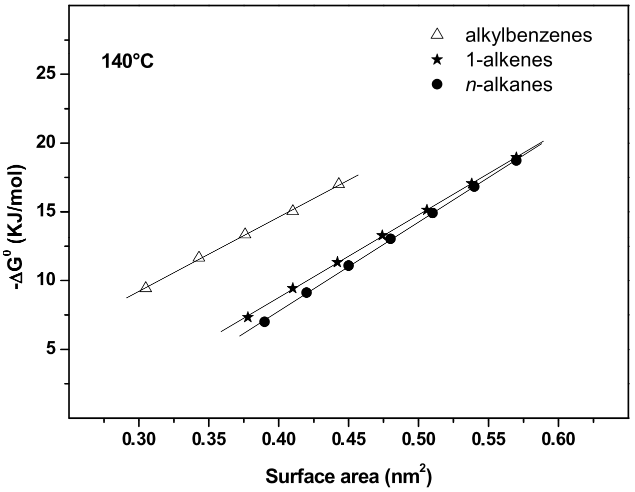


Fig. 4 Typical trends of adsorption free energy versus surface area of probe on NXT-modified Zeosil silica

Helmholtz equation, given the temperature dependence of V_n:

$$\Delta H^0 = \left[\frac{\partial(-\Delta G^0/T)}{\partial(1/T)}\right]p = -R\frac{d\ln V_n}{d(1/T)} \tag{5}$$

ΔH^0 is usually assumed to be independent of temperature.

Finally, the entropy change in the adsorption process is given by:

$$\Delta S^0 = \frac{\Delta H^0 - \Delta G^0}{T} \tag{6}$$

Equation (5) indicates that ΔH^0 does not depend on choice of the surface standard state, whereas (6) shows that ΔS^0 is affected by such a choice.

According to (4)–(6) by injecting several families of probes, free energies, enthalpies and entropies of adsorption were calculated at different temperatures for different stationary phases.

When plotting $-\Delta G^0$ versus the surface area (or number of C atoms) for a series of n-alkanes, 1-alkenes and alkylbenzenes, linear relations are commonly observed, as previously reported for several systems (Wang et al. 1991; Wolff et al. 1994a; Roshchina et al. 1999; Montes-Moran et al. 2002; Castellano et al. 2002). As an example, the $-\Delta G^0$ of different probes, determined at $T = 140$ °C for the stationary phase NXT-modified SiO_2, as a function of the surface area of the probes, is given in Fig. 4. Interaction force between stationary phase and eluates increases as follows: n-alkanes < 1-alkenes < alkylbenzenes. Furthermore, it is interesting to observe that the slope of the straight line of the alkanes is always higher than those of 1-alkenes and alkylated benzenes. These trends are shown by pristine precipitated silica and by all the modified silicas analyzed in the present and in previous works (Castellano et al. 2002, 2005, 2007).

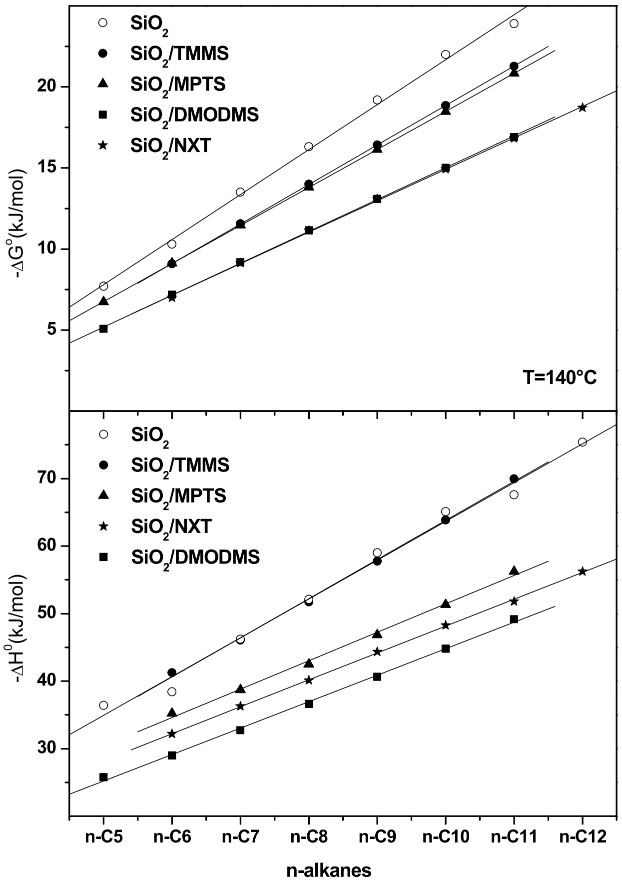


Fig. 5 Adsorption free energy and enthalpy versus carbon atoms number of n-alkanes for modified Zeosil silicas

The behaviors of $-\Delta G^0$, and $-\Delta H^0$ of adsorption as a function of number of C atoms, n_C, for bare silica (Castellano et al. 2002) and for silicas modified with different silanes, are given in Figs. 5, 6 and 7 for n-alkanes, 1-alkenes and alkylbenzenes, respectively.

As far as the n-alkanes are concerned (Fig. 5), the highest $-\Delta G^0$ values are determined with bare silica and then they decrease, on modifying the silica, as follows: SiO_2 > SiO_2-TMMS = SiO_2-MPTS > SiO_2-DMODMS = SiO_2-NXT.

The $-\Delta H^0$ values (Fig. 5) change as follows: SiO_2 = SiO_2-TMMS > SiO_2-MPTS > SiO_2-NXT > SiO_2-DMODMS. The lowest values are observed with the modifiers NXT and DMODMS that have a long alkane tail, even if the residual OH percentage is 80.9 for SiO_2-DMODMS and 52.3 for SiO_2-NXT systems.

Similar trends are observed upon adsorption of 1-alkenes and alkylbenzenes on the same modified silicas, with one exception: in the case of alkylbenzenes, $-\Delta G^0$ and $-\Delta H^0$ related to the system SiO_2-NXT are surprisingly lower than the ones of the system SiO_2-DMODMS.

In all the cases, the values of $-\Delta G^0$ and $-\Delta H^0$ increase going from n-alkanes to alkenes (Fig. 6) and to aromatics (Fig. 7), due to increasing contribution of specific interactions between silanol OH groups and the double bonds of alkenes and aromatic rings of alkylbenzenes.

To try to deeply understand the origin of the adsorption phenomenon, let us consider $-\Delta H^0$ data determined for bare silica and silica modified with TMMS. Contrary to what is expected on the basis of reacted silanol groups (1.6 OH/nm^2) (Table 2), the adsorption enthalpy values of SiO_2-TMMS system are practically the same to those of unmodified silica (4.9 OH/nm^2). Such a chemical modification reduces only slightly the polar character of the surface, as data of the specific interaction parameter show (see later Table 3). This finding agrees with what reported in literature that hydrophobic properties of the silica surface are achieved only with high values (80–90 %) of the degree of silylation with trymethylchlorosilane (Zhao and Lu 1998), with dimethyldichlorosilane (Ridaoui et al. 2008) or by replacing a H atom of silanol group with an alkyl group (Kimura et al. 1998). However, on grafting MPTS and DMODMS, bearing an alkyl tail longer than a methyl group, $-\Delta H^0$ decreases, even if the grafting degree is lower than the aforementioned systems. This result suggest that the tail acts as shield around silica particles, hindering interaction between the probe and the polar group of the silica surface. The lowest ΔH^0 values of NXT-modified silica observed using alkenes and alkyl-

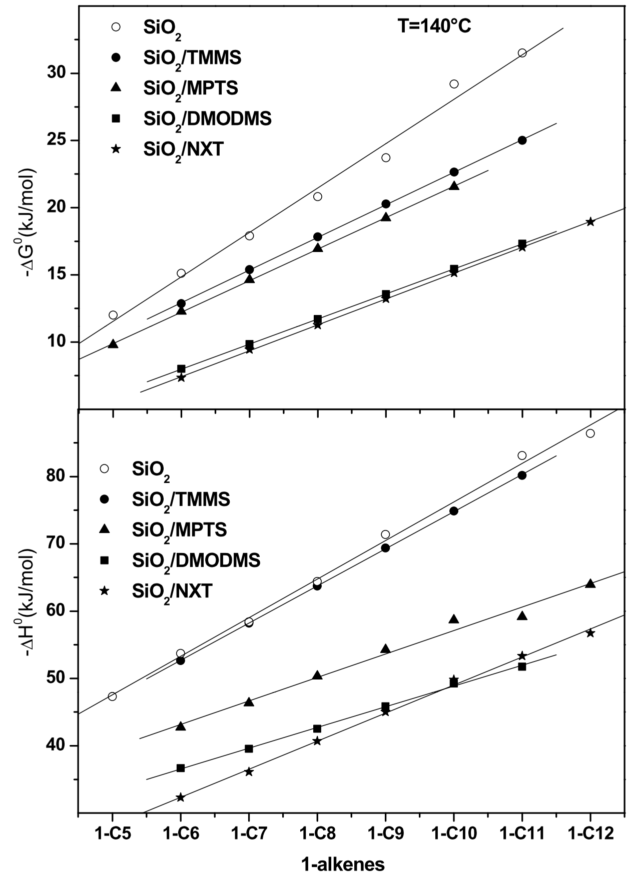


Fig. 6 Adsorption free energy and enthalpy versus carbon atoms number of 1-alkenes for modified Zeosil silicas

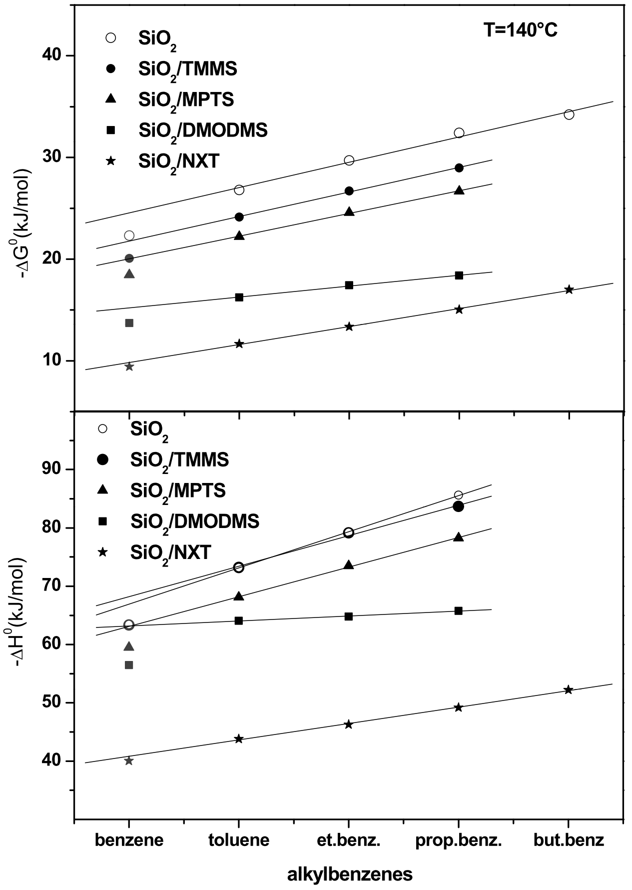


Fig. 7 Adsorption free energy and enthalpy versus carbon atoms number of alkylbenzenes for modified Zeosil silicas

Table 3 Dispersive component and specific interaction parameter at 20 °C of modified and unmodified Zeosil silica with different residual OH groups

Sample	Residual (free) OH/nm^2	γ_s^d (mJ/m^2)$_{20\,°C}$	I^{sp} (mJ/m^2)$_{20\,°C}$
SiO_2[a]	4.9	86.7	142.6
SiO_2/ODTES[b]	3.82	38.6	110.4
SiO_2/TMMS	3.29	70.6	135.6
SiO_2/DMODMS	3.96	37.5	110.7
SiO_2/MPTS	3.48	53.6	109.5
SiO_2/NXT	2.56	39.2	64.9

[a] Costa et al. (2003)

[b] Castellano et al. (2007)

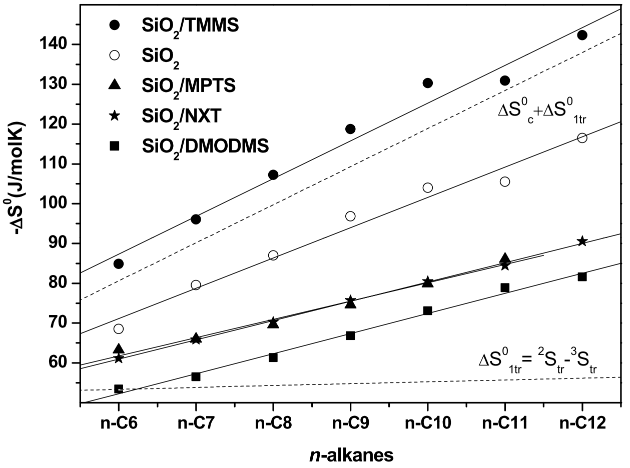


Fig. 8 Entropy of adsorption versus carbon atoms number of *n*-alkanes for modified Zeosil silicas; comparison with calculated entropy losses $-\Delta S^0_{1tr}$ and $-\Delta S^0_{1tr+c}$ (see text)

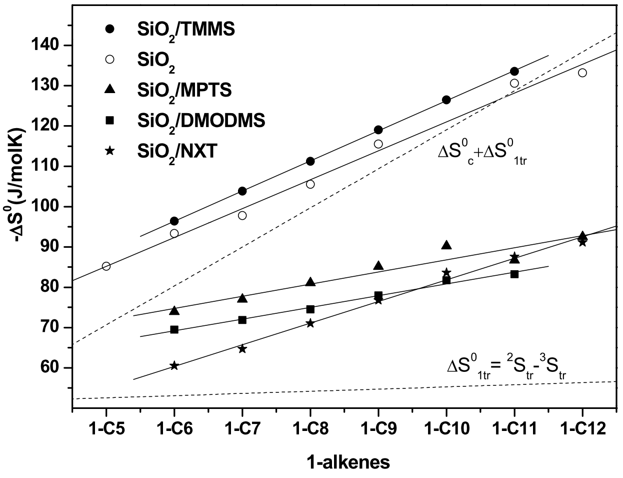


Fig. 9 Entropy of adsorption versus carbon atoms number of 1-alkenes for modified Zeosil silicas; comparison with calculated entropy losses $-\Delta S^0_{1tr}$ and $-\Delta S^0_{1tr+c}$ (see text)

benzenes as the probes, are ascribable to the higher number of reacted OH silanol groups (about 50 %). The loss of hydrophylicity due to the decrease of the number of silanol groups is not counterbalanced by the presence of the –SCO groups of the NXT molecules.

All our data suggest that the hydrophylicity or hydrophobicity of the modified silicas may change according to not only the chemical characteristics, the size of the modifier molecule and its extent of grafting, but even the size and chemical nature of the molecule used as the probe to test such properties. Particularly significant and interesting is the trend of the adsorption entropy for the same modified silica . In fact, $-\Delta S^0$ experimental values of all the families of hydrocarbons adsorbed on different modified Zeosil 1165MP silicas increase with increasing the length of hydrocarbon molecule (Figs. 8, 9 and 10). This is in agreement with data

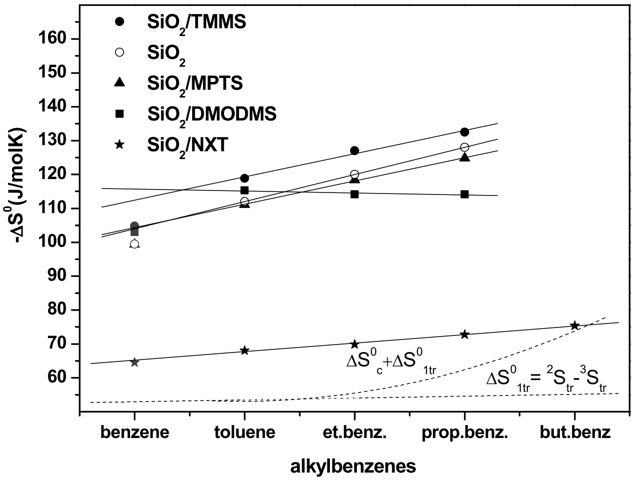


Fig. 10 Entropy of adsorption versus carbon atoms number of alkylbenzenes for modified Zeosil silicas; comparison with calculated entropy losses $-\Delta S^0_{1tr}$ and $-\Delta S^0_{1tr+c}$ (see text)

in literature (Vukov and Gray 1988; Roshchina et al. 1999; Montes-Moran et al. 2002; Wang et al. 1991; Choudhary and Mantri 2000; Castellano et al. 2005). In our case, moreover, we observe that $-\Delta S^0$ values of TMMS-modified silica are higher than those of bare silica, while all other modified silicas show $-\Delta S^0$ values lower than those of bare silica. This confirms our previous finding obtained on modifying the same silica with TES (Castellano et al. 2007). Similar $-\Delta S^0$ trend was reported in literature (Roshchina et al. 1999) on bare and phenyltrichlorosilane-modified Silichrome C-120 silicas, where, however, $-\Delta H^0$ values of *n*-alkanes adsorbed on such modified silica were much higher (about 25 %) than those of bare silica.

To try to explain the causes of such a behaviour, it is useful to examine the several entropy contributions which characterize the transfer of a molecule from the gas phase to adsorbate phase.

According to the experimental conditions used in the gas chromatographic measurements (at infinite dilution), it is generally assumed that the adsorption occurs from the ideal vapour phase to an ideal adsorbed phase, associated with loss of one translational degree of freedom, $-\Delta S^0_{1tr}$ (Kemball 1950).

Theoretical values of standard $-\Delta S^0_{1tr}$ can be calculate as a difference between the three-dimensional translational entropy of the adsorbate as an ideal gas by DeBoer (1953):

$$ {}_gS^0_{tr} = R\ln\left(M^{3/2}T^{5/2}\right) - 9.2 \tag{7}$$

and the entropy of the adsorbate as an ideal two-dimensional gas by Kemball (1950)

$$ {}_aS^0_{tr} = 0.667\,{}_gS^0_{tr} + 2.76\ln T - 12.71 \tag{8}$$

$$ -\Delta S^0_{1tr} = {}_aS^0_{tr} - {}_gS^0_{tr} \tag{9}$$

where: M is the molar mass and T is the temperature. The entropies are expressed in J/K mol.

In Fig. 8 it can be noted that the estimated $-\Delta S^0_{1tr}$ values are practically independent of the length of hydrocarbon molecules, while the experimental ones increase with the mass of probe. Furthermore, the experimental values are more negative than the theoretical ones. This different behaviour must be ascribed to kind of hydrocarbon molecules. Unlike an ideal gas, hydrocarbons here examined have many more ways to arrange them in the space (3D) than in a plane (2D). Therefore, going from 3D to 2D such molecules will be accompanied by rotational and conformational entropy losses.

Vukov and Gray (1988) calculated rotational entropy loss upon adsorption from 3D gas to 2D gas of n-C_8/n-C_{13} n-alkanes and put into evidence that such a contribution, ranging from about 6 to about 10 J/K mol, is still not large enough to account for the additional entropy loss.

In our previous work (Castellano et al. 2002), we suggested that the rotational isomerism would give the main contribution to the entropy loss upon adsorption, so as to justify its dependence on molecular mass. In this paper, we present the values of the rotational isomerism contribution to the entropy of hydrocarbons with more than three C atoms. Upon adsorption, the number of spatial conformations comes down more or less according to the interaction forces with the modifier and/or the active sites of silica surface. By considering that the actual number of bonds which are effective in increasing the number of conformations is $n-2$, with $n =$ number of bonds of the molecule, conformational entropy, ΔS^0_c, from the simplest possible model, i.e., a freely rotating chain without excluded volume and with three possibilities for each bond (g^+, g^- and t), is given by:

$$\Delta S^0_c = R \ln 3^{(n-2)} \tag{10}$$

where: R is the gas constant.

By considering that the thermodynamic quantities increase linearly with the molecular mass, we may assume that on adsorption the probe interacts in the totally flat position , i.e., in the planar zig-zag conformation.

In Fig. 8, trends of the experimental $-\Delta S^0$ values, as a function of molecular length of n-alkanes, are compared with those calculated by $-\Delta S^0_{1tr+c} = -(\Delta S^0_c + \Delta S^0_{1tr})$. As one can see, the calculated $(-\Delta S^0_{1tr+c})$ values are higher of about 20 % than the experimental $-\Delta S^0$'s determined for bare Zeosil 1165 MP silica, in the all range of molecular mass considered. However, the calculated values are lower by about 6 % than the ones obtained for the TMMS-silica system, despite taking into account the loss of conformational entropy well above that of the real molecular chain (i.e., not freely rotating chain and with excluded volume). All this shows that on adsorption the n-alkanes lose one degree of freedom and a number of conformations depending on the chain length of the hydrocarbon molecule with respect to the pore configuration of silica (Eder and Lercher 1997; Daems et al. 2007). In the crystalline zeolites the straight and sinusoidal pore segments are narrow and impose stretching of the alkylchains along the pore axis, and then significant loss of entropy (Denayer et al. 2003). In such a case, however, strong interactions with the pore walls implies high adsorption enthalpy too.

Since, in the case of TMMS-modified silica, the grafting degree of TMMS was about 30 % and the mean pore diameter of Zeosil 1165 MP was 320 Å, one may deduce that the pore configuration as well as the kind of interactions with active sites of silica were not affected by the silylation process. However, the adsorption would force the entire molecule in a totally flat position, and probably some of the rotational degrees of freedom around its centre would be lost too. Then, two main phenomena could be invoked: (a) weak specific interactions between the n-alkanes probes and the surface active sites, like free OH and Si-O-Si$(CH_3)_3$ groups. This is not surprising because it is well known that hydrogen bonding also occurs between "unpolar" molecules, such as alkanes, and silanol groups (Herl and Hair 1968; Ghiotti et al. 1979; Trombetta et al. 2000; Eder and Lercher 1997); (b) steric hindrance played by the presence of methyl groups of silane grafted, which reduces the freedom of movements of the adsorbed probe.

The lowest experimental values of entropy loss are obtained on Zeosil silica surface modified with NXT or DMODMS. As first suggested, the long paraffinic tail would tend to prevent the interaction between the probe and the active centres of silica surface. Therefore, the probes adsorbed on these surfaces would maintain a given mobility for weaker interaction forces (mainly dispersive forces) between the probe and essentially the grafted modifier.

The same comments may practically be made by using 1-alkenes as probes (Fig. 9). The main difference with respect to n-alkanes is due to a greater experimental loss of entropy, due the presence of the double bond in the probe, capable of establishing specific interactions with silica surface. On increasing the molecular mass, the behaviour of 1-alkene molecule tends to be that of n-alkane molecule of equal molecular mass.

The entropy loss values of adsorbed alkylbenzenes as a function of molecular mass are shown in Fig. 10. First of all, we underline that the values of benzene are slightly lower than those of other alkylbenzenes, as the aromatic rings of the latters are richer in electrons because of the attached electron donating alkyl groups. Three main aspects distinguish these compounds from the n-alkane and 1-akenes: (i) higher values of entropy loss; (ii) less dependence on the molecular mass; (iii) experimental values higher than the calculated $-\Delta S^0_{1tr+c}$. The first phenomenon indicates stronger interactions between the aromatic compounds and silica surface, in agreement with the results reported on fully silylation of MCM-41 with trimethylchlorosilane (Zhao and

Lu 1998); the second suggests that the aromatic ring practically determines the overall interaction with the adsorbent surface; the third one suggests that, on adsorption, the two dimensional translational motion, parallel to the surface, is itself somewhat restricted and again, due to the steric hindrance of the grafted TMS group, the rotational freedom of benzene molecule would restrict too. In fact, by considering that the calculated $-\Delta S^0_{1tr+c} = 51.5$ J/mol K, the entropy of benzene rotation $S_{\mathrm{rot}} = 87$ J/mol K (Dollimore et al. 1973) and the experimental $-\Delta S^0 = 103$ J/mol K, one may deduce that, without taking into account the torsional vibrations with respect to the principal axes, at least two rotational degrees of freedom of benzene are lost upon adsorption.

3.3 Surface energy of modified silicas

A measure of interaction between a solid and the medium, like solid, liquid or gas, is given by the surface energy, γ_s. It could be split into two terms: the dispersive, γ_s^d, and the specific, γ_s^{sp}, component.

γ_s^d can be calculated from the free energy of adsorption of a CH$_2$ group, $\Delta G^0_{\mathrm{CH2}}$, on the base of the following equation (Dorris and Gray 1979):

$$\gamma_s^d = \left(\Delta G^0\right)^2_{\mathrm{CH2}} / \left(4N^2\alpha^2_{\mathrm{CH2}}\gamma_{\mathrm{CH2}}\right) \qquad (11)$$

where: N is the Avogadro number, a_{CH2} is the area covered by a CH$_2$ group, γ_{CH2} is the surface tension of a surface constituted only by tightly packed methylene groups (Gaines 1972; Aveyard 1975) and has given by:

$$\gamma_{\mathrm{CH2}} = 35.6 + 0.058(20 - t) \qquad (12)$$

where t is the experimental temperature in °C.

The direct measurement of the specific component of the surface energy cannot be easily carried out. In our studies, the method proposed by Donnet et al. (1991) and Wang et al. (1991), Wolff et al. (1994a) was adopted, by evaluation of the specific interaction parameter, I^{sp}, which relates to specific interaction established between the filler and a polar probe. I^{sp} is given by the difference in adsorption energy, $-\Delta\Delta G^0$, between a polar probe and a hypothetical or real saturated hydrocarbon with the same surface area (Donnet et al. 1991):

$$I^{sp} = -\frac{\Delta\Delta G^0}{a \cdot N} \qquad (13)$$

where: a is the surface area occupied by the polar probe.

Following such an approach, benzene was used as the probe able to realize an electron donor-acceptor complex with the OH groups present on the silica surface. Benzene, in other words, is capable of specific interaction with silica surface via the electronic localization of the π-bond system.

The values of γ_s^d and I^{sp} as a function of the temperature (Figs. 11 and 12) were calculated through (11) and (13) for all the modified silicas. As a comparison, in the same plots our previous data of pristine silica (Costa et al. 2003) are reported.

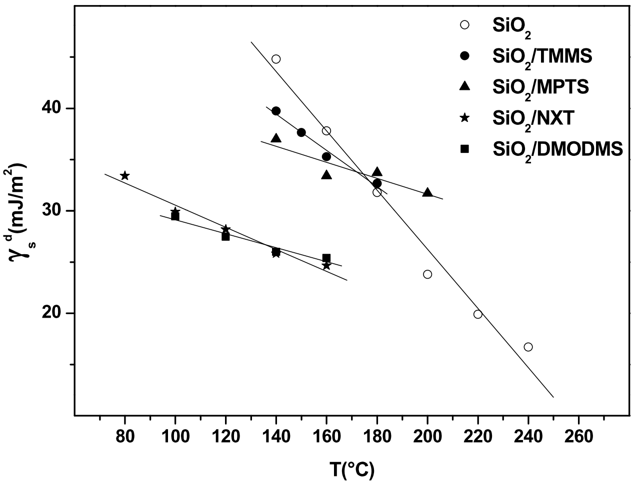


Fig. 11 Dispersive component of surface energy as a function of temperature for bare and modified Zeosil silicas

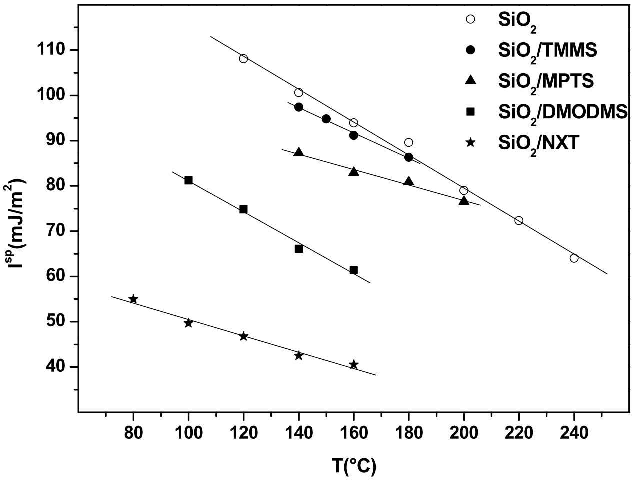


Fig. 12 Specific interaction parameter as a function of temperature for bare and modified Zeosil silicas

It is interesting to underline that silylation affects both the dependence of surface activity on temperature, as expected, and the polar character of the silica surface. On increasing the temperature, γ_s^d values of modified Zeosil 1165 MP silicas show smaller change than unmodified one, while I^{sp} practically shows a similar dependence on T for all specimens examined. Silylation of this silica reduces the hydrophilic character of its surface more or less sharply, depending on the type and amount of grafted modifier.

The role of different silanes is evidenced by the values of the specific interaction parameter. To better understand this effect, in Table 3 the values of γ_s^d and I^{sp}, extrapolated at 20 °C, are collected with free silanol OH groups of each modified silica.

DMODMS- and ODTES-modified silica, having about the same density of free silanol OH groups /nm^2 (3.96 and 3.82, respectively), are characterized by equal values of both γ_s^d and I^{sp}. On the other hand, these two modified silicas result less hydrophilic (average values $\gamma_s^d \approx 38$ mJ/m^2 and $I^{sp} \approx 110$ mJ/m^2) than the one modified with TMMS ($\gamma_s^d = 70.6$ mJ/m^2 and $I^{sp} = 135.6$ mJ/m^2), even if the first two have a slightly higher density of free silanol OH groups than the second one (3.29 OH/nm^2).

Since both the silanes TMMS and DMODMS have only one alkoxygroup, the less hydrophilic character of DMODMS- and ODTES-modified silicas again supports that long paraffinic tails screens the free silanol OH groups. As a consequence, the probes mainly interact with the silane through weak dispersive forces. On decreasing the length of alkane group of silane, γ_s^d increases, as shown by the values in Table 3 for TMMS-silica and MPTS-silica.

In the case of NXT-modified silica, the low density of residual OH groups and the long paraffinic tail of silane lead to smaller values of both the components of the surface free energy.

4 Conclusions

The surface thermodynamic properties of the precipitated amorphous Zeosil 1165MP silica modified by grafting of a silane significantly depends on the degree of grafting, as expected, and on the chemical structure of the modifier, in a complex way.

Thermogravimetric and elemental analyses were combined, in determining the real grafting degree of the silica for each silane used and, then, the final concentration of the free silanol OH groups after silylation. The dispersive component, γ_s^d, of the surface tension of Zeosil silica and the specific interaction parameter, I^{sp}, determined via IGC, are reduced by modification.

The values of both the parameters do not strictly depend on the residual silanol OH groups present on the modified Zeosil surface. The replacement of one hydrogen atom of the silanol OH group with $–Si(CH_3)_3$ group, see silica/TMMS system, reduces γ_s^d of about 20 % and I^{sp} of about only 5 %. When a tail of the silane is a long hydrocarbon group, see silanes ODTES, DMODMS and MPTS, the apparent hydrophylicity of Zeosil surface (I^{sp}) is reduced more than 20 %, even if the concentration of the free OH groups is higher than that of silica-TMMS system. This result must be attributed to the shielding action of the long arm of the grafted silane, that does not permit to the probe molecules to directly interact with the OH groups still present on the silica surface and/or with the new Si-O-silane bonds. In general, we observed that, upon low degree of silylation, γ_s^d is much more reduced than I^{sp}.

Furthermore, we found that free energies of adsorption of n-alkanes, 1-alkenes, and alkylbenzenes mainly depend on the entropy loss on adsorption. This loss, in turn, is due to the loss of one translational degree of freedom, and mainly to the conformational and rotational entropies losses of hydrocarbon on adsorption. Entity of these losses depends both on the amount of the silane grafted on the silica surface and, surprisingly, on the length of the hydrocarbon tails of the silane used. In other words, on increasing the length of the tail the entropy loss of adsorbed probes decreases: the adsorbed molecules are hindered to contact the surface sites of the silica and weaker interactions mainly occur between the hydrocarbon molecule and the tail of the silane.

However, in the case of silane with very short arms, like TMMS, the adsorbed molecules have a more limited mobility than in the cases of bare and modified silicas, probably not only for the active site-probe interaction but also for the steric hindrance of the methyl groups of TMMS.

Type of dependence of the entropy loss upon adsorption is very interesting and deserves to be analyzed thoroughly. Therefore, in a next paper, we intend to extend our study on investigating the structure and the coordination geometry of adsorbed hydrocarbons, trying to correlate them with the loss of entropy.

Finally, our thermodynamic data of the surface of the modified Zeosil 1165 MP silica suggest that to avoid agglomeration of its particles and then to increase their disperdibility into a rubber matrix, it is enough a low degree of silylation (about 5 wt%) of a silane with a long (probably at least 10 carbon atoms) hydrocarbon tail.

This result is very important from the technological point of view, because small grafting degree means not only lower consumption of silane but also lower methanol evolvement during the silylation of silica compared to what is happening today.

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References

Adam, N.K.: The Physical and Chemistry of Surfaces. Dover, New York (1968)

Aveyard, R.J.: Application of Fowkes' theory to alkane-water interfaces. J. Colloid Interface Sci. **52**, 621–622 (1975)

Beck, J.S., Vartuli, J.C., Roth, W.J., Leonowicz, M.E., Kresge, C.T., Schmitt, K.D., Chu, C.T.-W., Olson, D.H., Sheppard, E.W., McCullen, S.B., Higging, J.B., Schlenker, J.L.: A new family of mesoporous molecular sieves prepared with liquid crystal templates. J. Am. Chem. Soc. **114**, 10834–10843 (1992)

Bergna, H.E.: The Colloid Chemistry of Silica. Advances in Chemistry Series, vol. 234. American Chemical Society, Washington (1994)

Bertora, A., Castellano, M., Marsano, E., Alessi, M., Conzatti, L., Stagnaro, P., Colucci, G., Priola, A., Turturro, A.: A new modifier for silica in reinforcing SBR elastomers for the tyre industry. Macromol. Mater. Eng. **296**, 455–464 (2011)

Brunel, D., Cauvel, A., Fajula, F., Di Renzo, F.: MCM-41 type silicas as supports for immobilized catalysts. Stud. Surf. Sci. Catal. **97**, 173–180 (1995)

Burneau, A., Gallas, J.P.: Vibrational spectoscopies. In: The Surface Properties of Silicas. Wiley, Chichester (1998)

Busca, G.: Location and accessibility of hydroxy groups in silico-aluminate porous materials as studied by IR spectroscopy. Curr. Phys. Chem. **2**, 136–150 (2012)

Castellano, M., Conzatti, L., Costa, G., Falqui, L., Turturro, A., Valenti, B., Negroni, F.: Surface modification of silica, 1: thermodynamic aspects and effect on elastomer reinforcement. Polymer **46**, 695–703 (2005)

Castellano, M., Conzatti, L., Turturro, A., Costa, G., Busca, G.: Influence of silane modifier on the surface thermodynamic characteristics and dispersion of the silica into elastomer compounds. J. Phys. Chem. B **111**, 4495–4502 (2007)

Castellano, M., Falqui, L., Costa, G., Turturro, A., Valenti, B., Castello, G.: Investigation on elastomer-silica interaction by inverse gas chromatography and image analysis aided trasmission electron microscopy. J. Macromol. Sci. Phys. B **41**, 451–471 (2002)

Chenhang, S., Berg, J.C.: A review of the different techniques for solid surface acid-base characterization. Adv. Colloid Interface Sci. **105**, 151–175 (2003)

Choudhary, V.R., Mantri, K.: Adsorption of aromatic hydrocarbons on highly siliceous MCM-41. Langmuir **16**, 7031–7037 (2000)

Corder, J.R., Young, C.L.: Physical-Chemical Measurements by Gas Chromatography. Wiley, New York (1979)

Costa, G., Dondero, G., Falqui, L., Castellano, M., Turturro, A., Valenti, B.: Investigation into the interactions between filler and elastomers used for tyre production. Macromol. Symp. **193**, 195–207 (2003)

Daems, I., Baron, G.V., Punnathanam, S., Snurr, R.Q., Denaye, J.F.M.: Molecular cage nestling in the liquid-phase adsorption of N-alkanes in 5A zeolite. J. Phys. Chem. C **111**, 2191–2197 (2007)

DeBoer, J.H.: The Dynamical Character of Adsorption. Oxford University Press, London (1953)

Denayer, J.F.M., De Meyer, K., Martens, J.A., Baron, G.V.: Molecular competition effects in liquid-phase adsorption of long-chain n-alkane mixtures in ZSM-5 zeolite pores. Angew. Chem. **42**, 2774–2777 (2003)

Dollimore, D., Heal, G.R., Martin, D.R.: Thermodynamics of adsorption of a series of related organic molecules on graphite and on a carbon black, part 2: entropies of adsorption. J. Chem. Soc. Faraday Trans. **1**(69), 1784–1796 (1973)

Donnet, J.B., Park, S.I., Ballard, H.: Evaluation of specific interactions of solid surfaces by inverse gas chromatography. A new approach based on polarizability of the probes. Chromatographia **31**, 434–440 (1991)

Dorris, G.M., Gray, D.G.: Adsorption, spreading pressure, and London force interactions of hydrocarbons on cellulose and wood fiber surfaces. J. Colloid Interface Sci. **71**, 93–106 (1979)

Eder, F., Lercher, J.A.: On the role of the pore size and tortuosity for sorption of alkanes in molecular sieves. J. Phys. Chem. B **101**, 1273–1278 (1997)

Evans, L.R., Waddell, W.H.: Ultra-high reinforcing precipitated silica for tire and rubber applications. Kautsch. Gummi Kunstst. **48**, 718–723 (1995)

Fröhlich, J., Niedermeier, W., Luginsland, H.D.: The effect of filler-filler and filler-elastromer interactions on rubber reinforcement. Composites, Part A, Appl. Sci. Manuf. **36**, 449–460 (2005)

Gaines, G.L.: Surface and interfacial tension of polymer liquids—a review. Polym. Eng. Sci. **12**, 1–11 (1972)

General Electric: GE extends NXT silane coupling agent family. Addit. Polym. **2006**(10), 3–4 (2006)

Ghiotti, G., Garrone, E., Morterra, C., Boccuzzi, F.: Infrared study of low temperature adsorption. 1. Carbon monoxide on aerosil. An interpretation of the hydrated silica spectrum. J. Phys. Chem. **83**, 2863–2869 (1979)

Glass, A.S., Larsen, J.W.: Inverse gas chromatography of glassy polymer surfaces. Macromolecules **26**, 6354–6358 (1993)

Herl, W., Hair, M.L.: Hydrogen bonding between adsorbed gases and surface hydroxyl groups on silica. J. Phys. Chem. **72**, 4676–4682 (1968)

Hunsche, A., Görl, U., Koban, H.G., Lehmann, T.: Investigations on the reaction silica/organosilane and organosilane/polymer, part 2: kinetic aspects of the silica-organosilane reaction. Kautsch. Gummi Kunstst. **51**, 525–533 (1998)

Iler, R.K.: Chemistry of Silica—Solubility, Polymerization, Colloid and Surface Properties and Biochemistry. Wiley, New York (1979)

James, A.T., Martin, A.J.P.: Gas-liquid partition chromatography: the separation and micro-estimation of volatile fatty acids from formic acid to dodecanoic acid. Biochem. J. **50**, 679–690 (1952)

Jaroniec, C.P., Kruk, M., Jaroniec, M.: Tailoring surface and structural properties of MCM-41 silicas by bonding organosilanes. J. Phys. Chem. B **102**, 5503–5510 (1998)

Kemball, C.: Entropy of adsorption. Adv. Catal. **2**, 233–250 (1950)

Kemball, C., Riedeal, E.K.: The adsorption of vapours on mercury, I: non-polar substances. Proc. R. Soc. Lond. A **187**, 53–73 (1946)

Kim, K.J., Vanderkooi, J.: TESPT and treated silica compounds on TESPD rhelogical property and silica breack down in natural rubber. Kautsch. Gummi Kunstst. **55**, 518–528 (2002)

Kimura, T., Kuroda, K., Sugahara, Y., Kuroda, K.: Esterification of the silanol groups in the mesoporous silica derived from kanemite. J. Porous Mater. **5**, 127–132 (1998)

Koyano, K.A., Tatsumi, T., Tanaka, Y., Nakata, S.: Stabilization of mesoporous molecular sieves by trimethylsilylation. J. Phys. Chem. B **101**(46), 9436–9440 (1997)

Ligner, G., Vidal, A., Balard, H., Parirer, E.: Variation of the specific interaction capacity of heat-treated amorphous and crystalline silicas. J. Colloid Interface Sci. **134**(2), 486–496 (1989)

Marrone, M., Montanari, T., Busca, G., Conzatti, L., Costa, G., Castellano, M., Turturro, A.: A Fourier transform infrared (FT-IR) study of the reaction of triethoxysilane (TES) and Bis[3-triethoxysilylpropyl-]tetrasulfane (TESPT) with the surface of amorphous silica. J. Phys. Chem. B **108**, 3563–3572 (2004)

Montes-Moran, E.P., Paredes, J.I., Martinez-Alonso, A., Tascòn, J.M.D.: Adsorption of n-alkanes on plasma-oxidized high-strength carbon fibers. J. Colloid Interface Sci. **247**, 290–302 (2002)

Niedermeier, W., Fröhlich, J., Luginsland, H.D.: Reinforcement mechanism in the rubber matrix by active fillers. Kautsch. Gummi Kunstst. **55**(7–8), 356–366 (2002)

O'Brain, S., Tudor, J., Barlow, S., Drewitt, M.J., Heyes, S.J., O'Hare, D.: Modification of MCM-41 via ring opening of a strained [1]ferrocenophane. Chem. Commun. **6**, 641–642 (1997)

Peri, J.B., Hensley, A.L.-J.: The surface structure of silica gel. J. Phys. Chem. **72**(8), 2926–2933 (1968)

Plueddtemann, E.P.: Silane Coupling Agents, 2nd edn. Plenum, New York (1991)

Ramier, J., Gauthier, C., Chazeau, L., Stelandre, L., Guy, L.: Payne effect in silica-filled styrene-butadiene rubber: influence of surface treatment. J. Polym. Sci., Part B, Polym. Phys. **45**, 286–298 (2007)

Ridaoui, H., Donnet, J.B., Balard, H., Kellou, H., Hamdi, B., Barthel, H., Gottschalk-Gaudig, T., Legrand, A.P.: Silane modified fumed silicas and their behaviour in water: influence of grafting ratio in temperature. Colloids Surf. A, Physicochem. Eng. Asp. **330**, 80–85 (2008)

Roshchina, T.M., Gurevich, K.B., Fadeev, A.Y., Astakhov, A.L., Lisichkin, G.V.: Gas chromatography study of retension of organic compounds on silica with an attached layer of hydrophobic groups. J. Chromatogr. A **844**, 225–237 (1999)

Roshchina, T.M., Shonia, N.K., Kazmina, A.A., Gurevich, K.B., Fadeev, A.Y.: Adsorption study of alkyl-silicas and methylsiloxy-silicas. J. Chromatogr. A **931**, 119–127 (2001)

Santos, J.M.R.C.A., Guthrie, J.T.: Analysis of interactions in multicomponent polymeric systems: the key-role of inverse gas chromatography. Mater. Sci. Eng. **50**, 79–107 (2005)

Schuster, R.H., Issel, H.M., Peterseim, V.: Selective interactions in elastomers, a base on compatibility and plymer-filler interactions. Rubber Chem. Technol. **69**, 769–780 (1996)

Subba Rao, Y.V., De Vos, D.E., Jacobs, P.A.: 1,5,7-Triazabicyclo[4.4.0]dec-5-ene immobilized in MCM-41: a strongly basic porous catalyst. Angew. Chem., Int. Ed. Engl. **36**(23), 2661–2663 (1997)

Trombetta, M., Armaroli, T., Gutiérrez-Alejandre, A., Ramirez, J., Busca, G.: An FT-IR study of the internal and external surfaces of HZSM5 zeolite. Appl. Catal. A, Gen. **192**, 125–136 (2000)

Van Der Voort, P., Baltes, M., Vansant, E.F.: Synthesis of stable, hydrophobic MCM-48/VOx catalysts using alkylchlorosilanes as coupling agents for the molecular designed dispersion of VO(acac)2. J. Phys. Chem. B **103**, 10102–10108 (1999)

Vansant, E.F., Van Der Voort, P., Vrancken, K.C.: Characterization and Modification of the Silica Surface. Elsevier, Amsterdam (1995)

Vartuli, J.C., Schmitt, K.D., Kresge, C.T., Roth, W.J., Leonowicz, M.E., McCullen, S.B., Hellring, S.D., Beck, J.S., Schlenker, J.L., Olson, D.H., Sheppard, E.W.: Effect of surfactant/silica molar ratios on the formation of mesoporous molecular sieves: inorganic mimicry of surfactant liquid-crystal phases and mechanistic implications. Chem. Mater. **6**(12), 2317–2326 (1994)

Vidal, A., Papirer, E.: Chemical reactivity. In: The Surface Properties of Silicas. Wiley, Chichester (1998)

Vukov, A.J., Gray, D.G.: Adsorption of n-alkanes on carbon fibers at zero surface coverage. Langmuir **4**, 743–748 (1988)

Wang, M.J.: Effect of polymer-filler and filler-filler interactions on dynamic properties of filled vulcanizates. Rubber Chem. Technol. **71**, 520–589 (1998)

Wang, M.J., Wolff, S.: Filler-elastomer interactions, part V: investigation of the surface energies of silane-modified silicas rubber. Chem. Technol. **65**, 715–735 (1992)

Wang, M.J., Wolff, S., Donnet, J.B.: Filler-elastomer interactions, part I: silica surface energies and interactions with model compounds rubber. Chem. Technol. **64**, 559–576 (1991)

White, L.D., Tripp, C.P.: An infrared study of the amine-catalyzed reaction of methoxymethylsilanes with silica. J. Colloid Interface Sci. **227**, 237–243 (2000)

Wolff, S., Wang, H.C., Tan, E.H.: Surface energy of fillers and its effect on rubber reinforcement, part 1. Kautsch. Gummi Kunstst. **47**, 780–798 (1994a)

Wolff, S., Wang, M.J., Tan, E.H.: Surface energy of fillers and its effect on rubber reinforcement, part 2. Kautsch. Gummi Kunstst. **47**, 873–884 (1994b)

Yan, H., Sun, K., Zhang, Y., Zhang, Y.: Effects of mixing conditions on the reaction of 3-octanoylthio-1-propyltriethoxysilane during mixing with silica filler and natural rubber. J. Appl. Polym. Sci. **94**, 2295–2301 (2004a)

Yan, H., Sun, K., Zhang, Y., Zhang, Y., Fan, Y.: Effects of silane coupling agents on the vulcanization characteristics of natural rubber. J. Appl. Polym. Sci. **94**, 1511–1518 (2004b)

Zhao, D., Feng, J., Huo, Q., Melosh, N., Fredrickson, G.H., Chmelka, B.F., Stucky, G.D.: Triblock copolymer syntheses of mesoporous silica with periodic 50 to 300 angstrom pores. Science **279**, 548–552 (1998)

Zhao, X.S., Lu, G.Q.: Modification of MCM-41 by surface silylation with trymethylchlorosilane and adsorption study. J. Phys. Chem. B **102**, 1556–1561 (1998)

Zhuravlev, L.T.: Concentration of hydroxyl groups on the surface of amorphous silicas. Langmuir **3**, 316–318 (1987)

Zhuravlev, L.T.: The surface chemistry of amorphous silica. Zhuravlev model. Colloids Surf. A, Physicochem. Eng. Asp. **173**, 1–38 (2000)

Zhuravlev, L.T., Potapov, V.V.: Density of silanol groups on the surface of silica precipitated from a hydrothermal solution. Russ. J. Phys. Chem. **80**(7), 1119–1128 (2006)