11th Fall Rubber
Colloquium

INFRARED STUDY OF THE SILICA/SILANE REACTION

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Abstract

The silica-silane system is used in modern tire tread compounds to improve wet grip and rolling resistance. An efficient silica / silane coupling during the mixing process is necessary to achieve the required in-rubber-properties. In order to understand this coupling reaction in detail, the silanol group density of the silica was characterized in depth. Furthermore, the reaction of a mercapto silane (Si 263®) with two different silicas was studied with special infrared (IR) techniques. The infrared spectrum of the ν(SiOH) region shows the behavior of SiOH groups during the reaction and contributes to clarify their role in the silane grafting reaction.

Introduction

One of the key ways to improve the fuel consumption of a car is to reduce the rolling resistance of its tires[i]. The new EU tire labeling came into force in November 2012 and classifies tires due to their rolling resistance, wet traction behavior and noise.

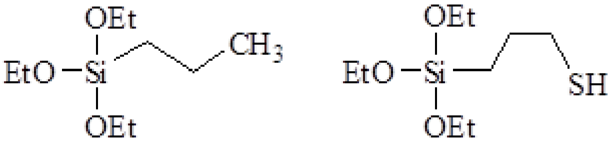
A good classification in the EU tire labeling can today only be reached by using a modern silica/silane system in the tire tread instead of the former used carbon black according to present knowledge. The bifunctional organosilane is able to react with the silica surface as well as with the polymer. One functional group is responsible for the coupling to the hydrophilic silica surface, the other one for the linkage to the hydrophobic polymer matrix.[ii,iii] An example for a modern silica / silane system in a passenger car tire tread formulation is the usage of a highly dispersible silica like ULTRASIL® 7000 GR in combination with a mercaptosilane like VP Si 363® in a S-SBR / BR matrix. A deep understanding about the silica / silane coupling reaction is essential to accomplish the best in-rubber properties.

In a previous work, the reaction between the conventional silica ULTRASIL® VN3 GR and the monofunctional silane triethoxypropylsilane (Dynasylan® PTEO) was analysed with a special operando technique[4]. It was shown that the adsorption of the silane on the silica surface determines the rate of reaction.

In the present work, the reaction of silica with mercaptosilane is investigated. Therefore, firstly the silanol groups on the silica surface were characterized by using another special IR technique. Two different silicas were investigated: the conventional silica ULTRASIL® VN3 GR and the highly dispersible silica ULTRASIL® 7000 GR (Table 1). Both silicas were specially produced in order to have the same BET and CTAB surface area. Secondly, the reaction of both silicas with Si 263® (3-(mercaptopropyl)triethoxysilane, the most simple structured mercaptosilane) (Scheme 1) was evaluated with the above mentioned operando IR technique. Comparing these results of the bifunctional mercaptosilane (which can couple not only to the silica but also to the polymer) with that one of the previous study with the monofunctional silane (which can couple only to the silica but not to the polymer) allows comparing the reactivity of the grafting reaction of silanes on the silica surface and investigating the role of the “S-H” function in this reaction. Other effects like the influence of different conformations of the molecules were not taken into account. The extinction coefficient of the ν(SH) vibration band was determined. It allows the quantification of the silane content in the case of an absence of interaction between the thiol-function and the silica surface silanol groups.

Table 1. Analytical properties of ULTRASIL® VN3 GR and ULTRASIL® 7000 GR

	ULTRASIL® VN3 GR	ULTRASIL® 7000 GR
BET / m²/g	170	170
CTAB / m²/g	160	160
DOA / ml/100g	185	205
Moisture content / %	5.5	5.2



Scheme 1: Chemical structure of Dynasylan® PTEO (left) and Si 263® (right)

Furthermore, the temperature dependence of the mercaptosilane / silica reaction was studied using the *operando*-IR and in-situ IR technique. The thermal stability of the silane on the silica surface has been investigated as well using temperature programmed desorption analysis (TPD analysis).

Experimental part

Grafting of silane on the silica samples

The grafting reaction of Si 263® on the silica samples was performed under air in a glass reactor placed in an oil bath. 3 g of silica have been dried under stirring (with a magnetic bar) at 120°C for 2 h in order to eliminate the water adsorbed on the surface. Then, ~0.5 ml Si 263® (0.6 g; ~20 wt.%) have been injected via a septum. The mixture was heated at 120°C for 2 h under atmospheric conditions. Finally, the powder was used for further characterization without any filtration. The experiment was repeated two to three times to calculate the repeatability.

In situ FTIR-analysis

A static IR-cell was used to detect the changes of hydroxyl groups and silanes on the silica surface during heating under vacuum conditions. Powders were pressed (~10^7 Pa) into self-supported discs (2 cm^2 area, 7-15 mg/cm^2). They were placed in a cell equipped with KBr windows (Figure 1).[iv] A moveable quartz sample holder allows placing the pellet in the infrared beam for recording spectra and moving it into a furnace at the top of the cell for outgassing. The cell was connected to a vacuum line for evacuation ($P_{residual}$~10^{-5} torr). A Nicolet Nexus 5700 FT-IR spectrometer (64 scans/spectrum) equipped with a MCT detector (Mercury Cadmium Telluride, HgCdTe) and an extended-KBr beam splitter was used for the acquisition of spectra recorded in the 400-5500 cm^{-1} range. Spectra were recorded at 2 cm^{-1}. 128 scans were co-added for each spectrum. In order to test the repeatability, each measurement has been done twice. The error has been estimated to be less than 20%. All of the results have been normalized to the same mass of pellet (20 mg).

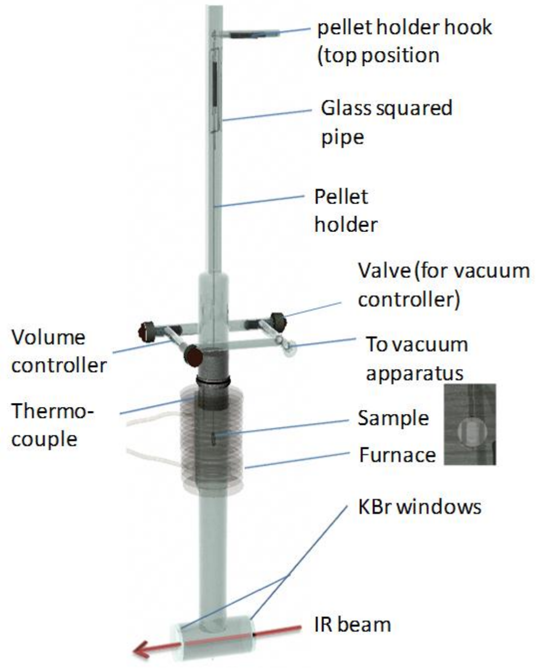


Figure 1. In-situ IR cell

Determination of the accessibility of Si-OH groups

H/D exchange using reactants of various sizes allows estimating the SiOH accessibility at molecular level and consequently the potential of the materials for the grafting of functionalized molecules. The H/D exchange process can be followed by IR spectroscopy due to the sensitivity of this technique to isotopic substitution: the SiOH > SiOD exchange shifts the stretching mode downwards from 3750-3500 cm^{-1} (νSiOH) to 2760-2600 cm^{-1} (νSiOD).[ii,v]

First, all accessible silanol groups were exchanged with heavy water vapor (by reagent excess, followed by evacuation). An IR spectrum was recorded, and the process was repeated until there was no difference between two consecutive spectra. Then different ROH probes (3-ethylpentan-3-ol, 2-methylpropan-2-ol, propan-2-ol, methanol) were successively adsorbed on deuterated silicas to re-exchange SiOD groups to SiOH groups. A small alcohol will be able to reach most of SiOD groups and exchange them back to SiOH, while a big alcohol molecule will only reach easily accessible SiOD groups. The global concentration of Si-OH groups before and after the re-exchange was estimated from the area of the ($\nu+\delta$) SiOH band at 4570 cm^{-1}.[v] All experiments were conducted at room temperature.

Operando FTIR-analysis

Firstly, the possible grafting reaction of the mercapto-function was evaluated. Therefore, methanethiol was selected in order to detect its reactivity towards a silanol group of the silica using

IR technique. The powder of the selected silica was pressed into self-supported wafers (Ø = 16 mm, m~10 mg/cm^2). IR spectra were again collected with a Nicolet Nexus 5700 FT-IR spectrometer equipped with a MCT detector. The *operando* system (Figure 2) is connected to a flow set-up. Gases are introduced into the lines (heated at 60°C) by mass flow controllers. The two gas mixtures, so called “activation” and “reaction” flows, can be prepared and sent independently to the reactor cell. The “Sandwich” reactor-cell used in this study is an evolution of the *operando* cell developed by Saussey et al.[vi], which has proven its reliability over many years of *operando* studies.[vii,viii]

A low partial pressure of CH_3SH was established in this equipment using diluted CH_3SH (1000 ppm CH_3SH /Ar) at atmospheric pressure. The gas mixture composition was then fixed at 400 ppm in O_2/Ar (ratio of 20% O_2 to 79.9% Ar) and the total flow was adjusted to 20 cm^3/min. The analysis of the outlet gases was performed by IR spectroscopy using a gas microcell where the gas phase of the reaction is collected.

Secondly, the grafting reaction of Si 263® on silica was monitored by *operando*-IR spectroscopy under the following conditions: A nitrogen gas stream is diverted to a saturator, filled with the silane, maintained at a constant temperature (35°C); the resulting vapor mixture feeds the reactor/IR cell (activation and reaction conditions: 120°C, total flow 20 cm^3/min). The lines are heated at about 60°C to prevent condensation of any silane into the capillaries.

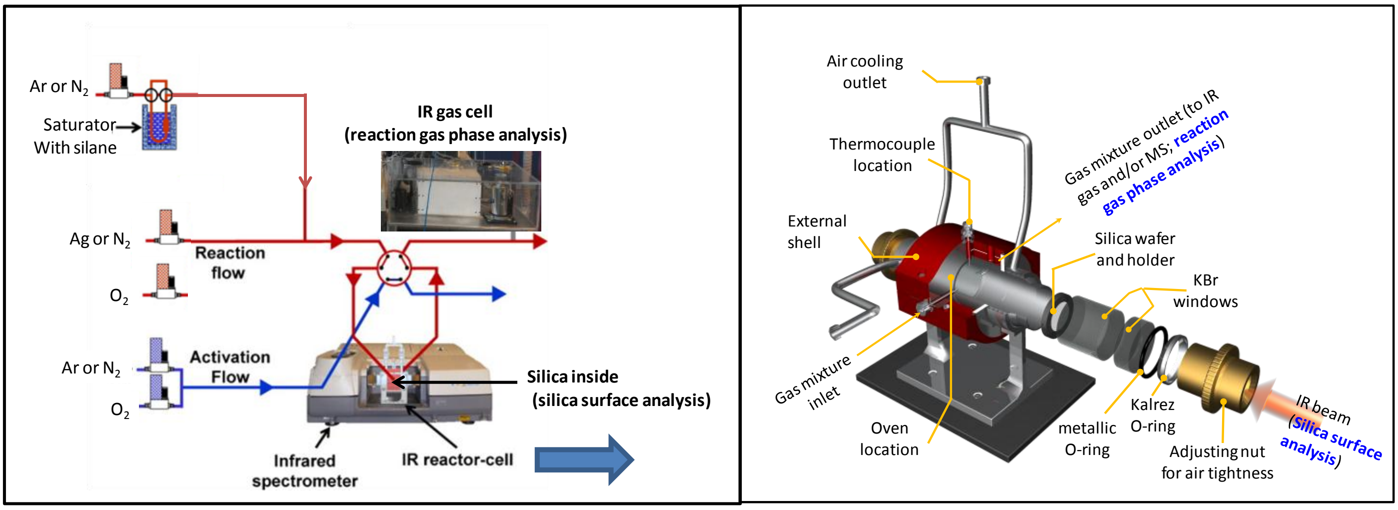


Figure 2. Scheme of the IR operando equipment (for the study of the grafting reaction of the silane on the silica surface)

Molecular modelling

The molecular modelling consists of calculating the most stable configuration of the molecule that corresponds to the lowest energy. It allows to present the molecule in the most probable spatial configuration and to determine different parameters such as bond energy dissociation, atomic charges and bond lengths. The method that has been used in this work is the semi-empirical method PM3[ix,x]. PM3, or Parameterized Model number 3, is used for the quantum calculation of molecular electronic structure and is based on the Neglect of Differential Diatomic Overlap (NDDO)[xi] integral approximation. PM3 uses two Gaussian functions for the core repulsion function between a charge distribution on one centre and a charge distribution on another centre. The one- and two-centered integrals are evaluated approximately or parameterized based on the experimental data while the three- and four-centered integrals vanish. Usually, only the valence electrons are treated quantum mechanically while the role of core electrons is to reduce the nuclear charge. Therefore, the parameter values are treated as optimizable values. PM3 method included parameters for H, C, O, S and Si elements, needed in the present work.

The calculations have been carried out by Hyperchem 7.0 software. A silica cluster $[(OH)_3Si\text{-}O\text{-}Si(OH)_3]$ and a silane grafted on that silica cluster has been used as model to estimate the bond lengths and the spatial orientation of the silane.

Results and discussions

Infrared characterization of Silica samples: Determination of the water and silanol contents

The water content of the silica samples was calculated under atmospheric conditions by integration of the surface areas of the bands at 5260 cm^{-1} and at 1630 cm^{-1} (Figure 3) that correspond to $(\nu+\delta)$ H_2O and (δ) H_2O, respectively, according to the reference[v]. The silanol content was also calculated after activating the samples at 150 °C under vacuum for 1 h by integrating the surface area of the band at 4570 cm^{-1} assigned to $(\nu+\delta)$ SiOH. From their integrated molar absorption coefficients (1.53, 0.22 and 0.16 cm/µmol for $(\nu+\delta)$ H_2O, (δ) H_2O and $(\nu+\delta)$ SiOH respectively)[v], the relation given by the Lambert-Beer law allows to determine the water concentration for all samples.[v] The spectrum of the dried sample presents a narrow band at 3740 cm^{-1} characterizing isolated silanol groups[ii]. The band of inner hydroxy groups occurs at about 3670 cm^{-1},[ii,v] the band of H-bonded hydroxy groups at about 3520 cm^{-1} (broad band) [ii,v]. The quantification of the latter is not possible due to the overlapping of their IR bands.

The isolated silanol sites in silica samples have been estimated using the IR intensity of the band situated at 3740 cm^{-1} and using ULTRASIL® 7000 GR silica sample as reference. The error values are estimated to be less than 3%. The detailed results are reported in Table 2.

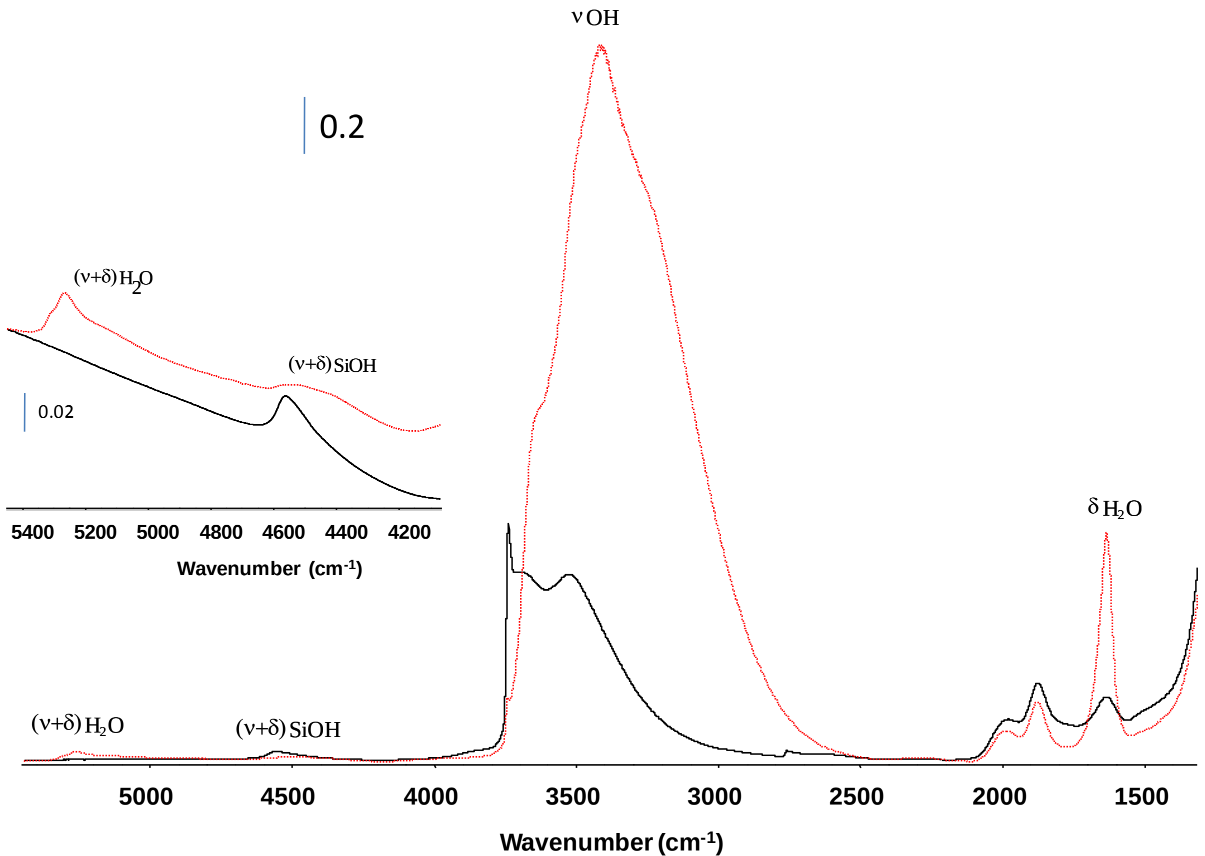


Figure 3. Example of an IR spectra of silica in the 1500-5500 cm^{-1} range.
Dotted red line: spectrum recorded under atmosphere conditions.
Solid black line: spectrum recorded after outgassing

Table 2. Properties of ULTRASIL® 7000 GR and ULTRASIL® VN3 GR

Sample	S_{BET} (m^2/g)	N_{H2O} /nm^2	$N_{SiOH(total)}$ /nm^2	% $N_{SiOH(isolated)}$
ULTRASIL®7000 GR	170	7.4	10.8	100
ULTRASIL® VN3 GR	170	9.9	12.3	80

N_{H2O}: water molecules number per nm^2 of silica surface
N_{SiOH}: Silanol sites number per nm^2 of silica surface
% $N_{SiOH(isolated)}$: relative values (in %) of the IR band intensity of isolated silanol sites estimated using ULTRASIL® 7000 GR as reference.

ULTRASIL® 7000 GR and ULTRASIL® VN3 GR have the same amount of N_2-adsorption (measured by BET method) but different DOA values (see Table 1) which is a hint for the significantly improved dispersion behavior of ULTRASIL® 7000 GR. It is known from the previous study[iv] that the isolated (and also the geminal) silanol groups are the reactive ones. ULTRASIL® 7000 GR has a lower absolute content of SiOH-groups per nm² in comparison to ULTRASIL® VN3 GR but has a higher content of isolated silanol groups.

Accessibility of SiOH groups

The H/D exchange process can be followed by IR spectroscopy since this technique is very sensitive to the isotopic substitution: the (OH → OD) exchange shifts the stretching mode from 3750-3500 cm^{-1} ν(OH) downward to 2760-2600 cm^{-1} ν(OD). The comparison of IR spectra for the dehydrated silicas before and after D_2O treatment (Figure 4) shows a strong decrease of intensity in the (ν) SiOH range of 3500-3750 cm^{-1} and concomitant formation of a (ν) SiOD band (at 2760-2600 cm^{-1}); a broad maximum centered at 3660 cm^{-1} remains, its intensity varying according to the sample. This band characterizes SiOH groups which are not accessible to water molecules and can be assigned to perturbed SiOH groups, located on the interparticle surface or/and inner surface; they are often called inner or bulk silanol groups or even referred as the structurally bound water.

In order to estimate silanol accessibility to reactants bigger than water molecule, ROH probes from the bulkier to the smaller were then successively adsorbed on deuterated silicas. The addition of these alcohol probes led to a back exchange of the accessible deuterated silanol sites (SiOD→SiOH) as could be observed in figure 4. Therefore, the silanols accessibility is determined from the residual intensity of the combination band (ν+δ) SiOH, at around 4570 cm^{-1} after each exchange (see experimental part). The results are summarized in Table 3.

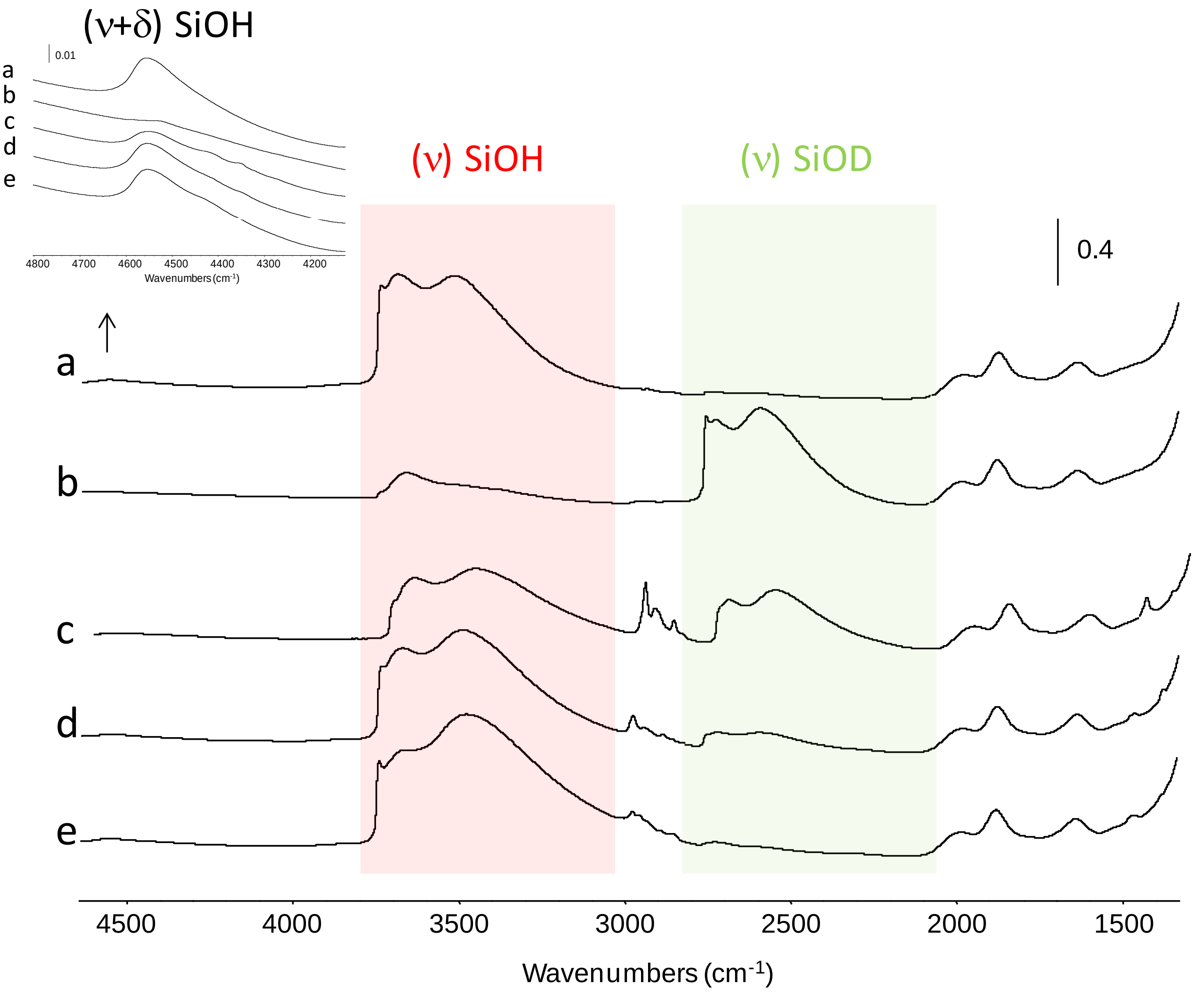


Figure 4. IR spectra of dried silica sample before (a) and after successive addition (followed by an evacuation under vacuum) of heavy water (b) 3-ethylpentan-3-ol (c) 2-methylpropan-2-ol (d) and methanol (e). Insert: evolution of (ν+δ) SiOH IR band.

For each sample, the same trend is observed: the bigger the reactant molecules, the lower the quantity of accessible silanol. This shows that the silica surface is rough and the silanol groups are accessed differently.

Table 3. Accessibility of silanol sites to probe molecules of increasing size

Samples	$N_{SiOH(total)}$ /nm^2	SiOH accessibility									
		3-ethylpentan-3-ol (0.410 nm^2)*		2-methylpropan-2-ol (0.316 nm^2)*		propan-2-ol (0.276 nm^2)*		Methanol (0.180 nm^2)*		D_2O (0.106 nm^2)*	
		%	/nm^2	%	/nm^2	%	/nm^2	%	/nm^2	%	/nm^2
ULTRASIL®7000 GR	10.8	26	2.8	57	6.2	63	6.8	70	7.6	84	9.1
ULTRASIL® VN3 GR	12.3	29	3.5	62	7.6	68	8.4	74	9.1	81	10.2

(*projected molecular area)

From the difference of the number of total silanol sites and that which are not accessible to D_2O ($N_{SiOH(total)}$- N_{SiOH} accessible to D_2O), we can observe that both silicas have a content of internal SiOH groups of ca. 2 OH/nm^2. Except to 3-ethylpentan-3-ol and D_2O, the difference between the total Si-OH content of ULTRASIL® VN3 GR and ULTRASIL® 7000 GR of 1.5 SiOH/nm² remains constant by using different probe molecules. Therefore, the size of the probe molecule determines how many SiOH groups can be reached for reaction.

IR-Operando study of the grafting reaction with Si 263$^{®}$

In order to study the grafting reaction of Si 263$^{®}$ on ULTRASIL$^{®}$ 7000 GR, the reaction has been realized under *operando* conditions as mentioned above in the experimental part. After the grafting reaction, the *operando* cell was flushed with dry N_2 at the grafting temperature in order to remove the silane weakly physisorbed on the silica surface. Therefore, it can be assumed that the remaining silane is chemically bonded to the silica surface (activation). Figure 5 presents the IR spectra evolution of ULTRASIL$^{®}$ 7000 GR surface during the reaction with Si 263$^{®}$ at 120°C. It shows a significant decrease of isolated SiOH (at 3740 cm^{-1}) with the increase of the silane amount shown by an increase of the CH-IR band intensity at 3000-2800 cm^{-1}. The increase of the hydrogen bonding silanol band intensity at ~3525 cm^{-1} is probably due to the adsorption of silane on the SiOH site.

In addition the SH band of Si 263$^{®}$ could clearly be followed at ~2580 cm^{-1}. An increase of this band versus the increase of the CH band is observed.

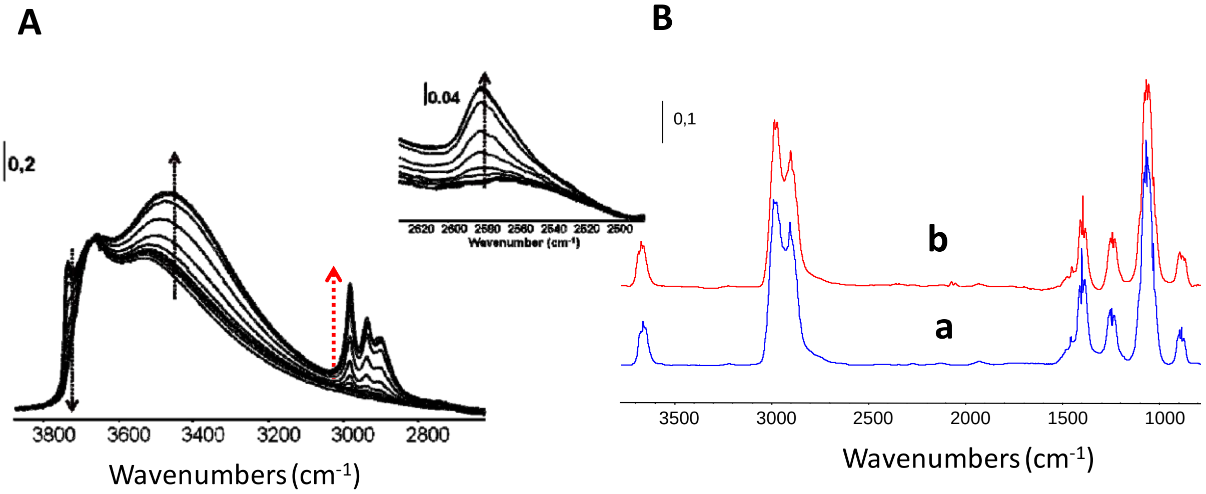


Figure 5. A) IR spectra of ULTRASIL$^{®}$ 7000 GR during the grafting reaction of Si 263$^{®}$ at 120°C. Insert : Evolution of ν(SH) IR-band.
B) Reference-IR spectra of ethanol (a) and the grafting reaction of Si 263$^{®}$ on ULTRASIL$^{®}$ 7000 GR (b) at 120°C

The IR spectrum of the grafting reaction gas phase is presented in Figure 5B (b). The comparison with the reference spectrum of pure ethanols (Figure 5B (a)) shows that the resulting reaction gas is indeed ethanol since the spectra are identical. Such a result confirms that Si 263$^{®}$ is chemically bonded to the silanol groups by evolution of ethanol.

Grafting reaction of CH_3SH on ULTRASIL$^{®}$ 7000 GR

In order to determine if any interaction between SH function of Si 263$^{®}$ and silanol sites of silica surface occurs, an IR *operando* study of the grafting reaction of methane thiol has been carried out under the same conditions of flow and temperature which are used for the grafting of silica (see experimental part). After flushing of CH_3SH, a very weak adsorption of CH_3SH on the silica surface could be observed. This low adsorption lead to a low decrease of the IR intensity of isolated SiOH band accompanied with a low increase of the IR intensity of the hydrogen bonding silanol band (3525 cm^{-1}), SH band (2580 cm^{-1}) and CH bands (3000-2800 cm^{-1}) (Figure 6A). In order to investigate if the temperature favors the condensation of Si-OH of silica with the SH-group of methanethiol (comparable to the ethoxy groups of the silanes) the grafting has been also realized at 120°C. Contrary to the case of Si 263$^{®}$ (Figure 5), no grafting has been observed even at high temperature (Figure 6A). The increase of the temperature leads to a rapid desorption of these weakly adsorbed methanethiol molecules: A complete desorption has been noted for T>70°C which confirms that methane thiol molecules are weakly physisorbed on silica surface contrary to Si263® molecules (Figure S1 in supplementary information section). In addition, the IR spectra of the gas phase of the grafting reaction shows the stability of the CH_3SH molecule for temperature lower than 200°C because only CH_3SH has been detected in the gas phase (Figure 6B). These results show no chemisorption (or strong interaction) of the thiol function on the silanol sites of the silica surface and also show a high stability of the SH-function for T<200°C. Therefore, it is possible to quantify the silane grafted (or adsorbed) on the silica surface and Si 263® could be used as probe molecule.

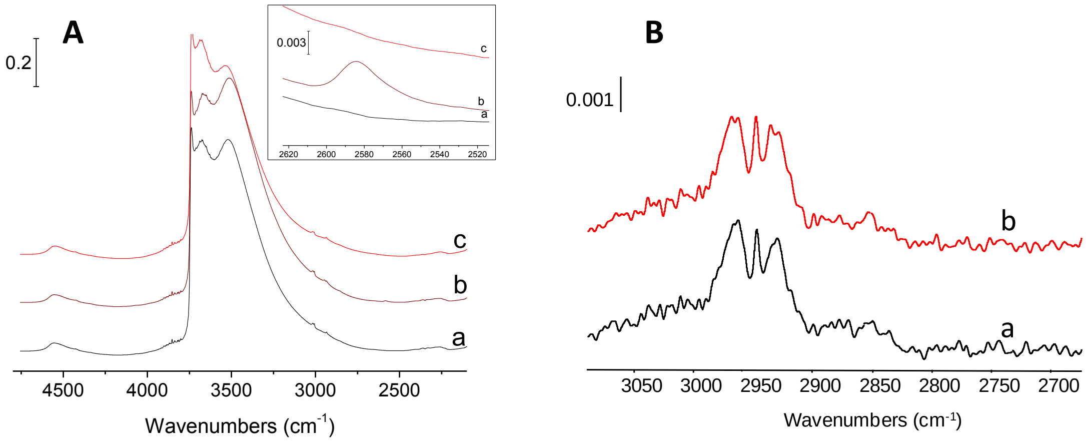


Figure 6. A: IR spectra at RT before (a) and after (b) CH_3SH adsorption and after 1h at 120°C under CH_3SH flow (c) (insert: thiol function vibration band).
B: reaction gas phase at RT (a) and at 200° (b).

Determination of the extinction coefficient of SH band of Si 263®

The extinction coefficient of SH function (ε_{SH}) adsorbed on the silica surface has been calculated using the mass of adsorbed silane on the silica surface and the area of the SH band at 2580 cm^{-1} of the IR spectra of the grafted pellet. The mass of silane has been calculated using the mass of the pellet before and after the grafting reaction at 120°C with an excess of silane.

In order to calculate the silane mass, the water mass has been calculated using the area of the band of water at ~5300cm^{-1} after recording the IR spectrum of the pellet under air at RT. By considering the mass of silane adsorbed and the area surface of the SH band, the ε_{SH} is calculated. After that, the pellet has been activated at 200°C under vacuum (~10^{-5} torr) in order to calculate the chemisorbed silane remaining on the silica surface. This difference of the mass of the pellet (Δm) corresponds to the mass of silane and water adsorbed on the sample. In order to calculate the error on the ε_{SH} value, this experiment has been repeated three times. A $\varepsilon_{SH} = 0.14 \pm 0.03$ cm/µmol has been determined.

Characterization of the grafted Silica samples (Grafted-"X")

ULTRASIL® 7000 GR grafted with Si 263® was characterized at different temperatures via IR spectra in order to analyze the stability of the grafting reaction (Figure 7). The IR spectra shows a decrease of CH and SH bands versus the temperature. The slow decrease in the low temperature range of RT up to 200 °C can be explained by desorption of the physisorbed silane of approximately 20-30%.

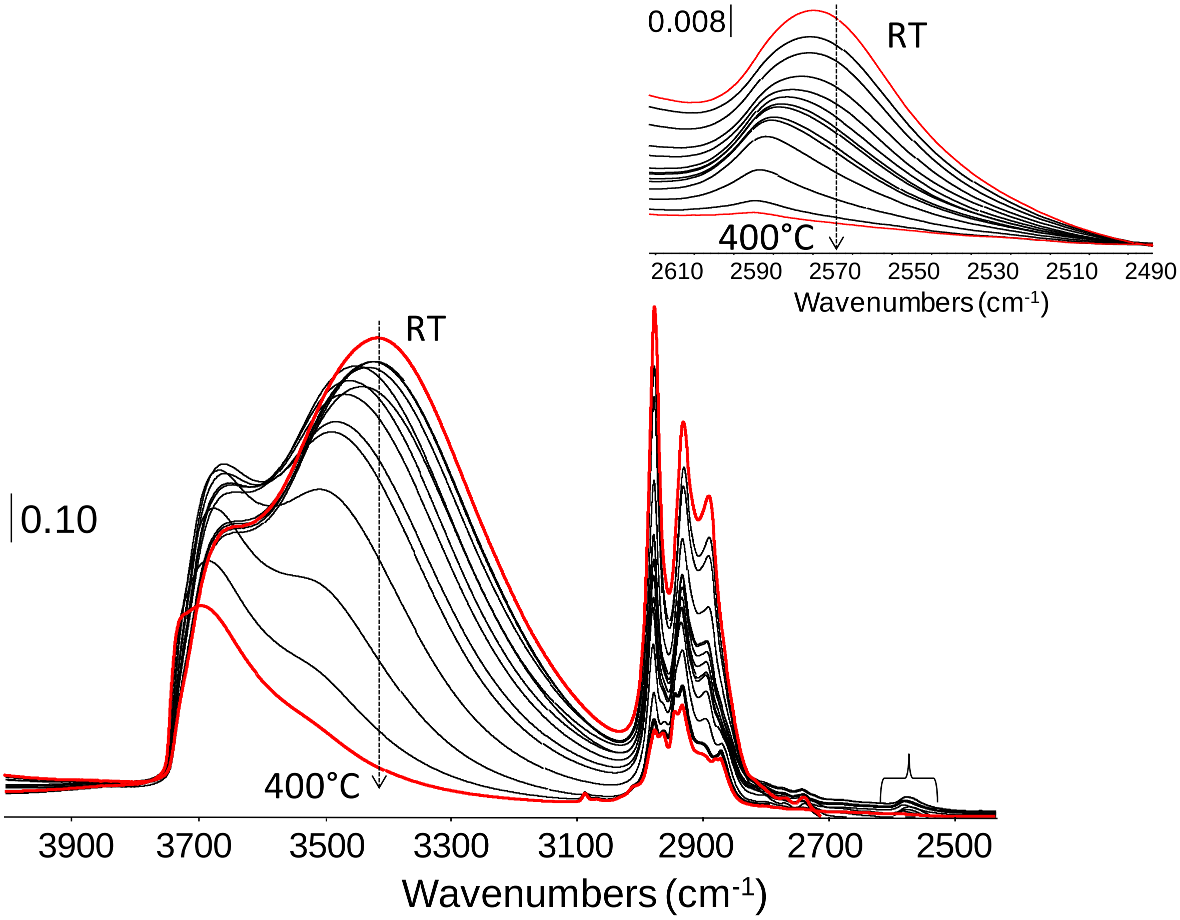


Figure 7. A) IR spectra of grafted ULTRASIL® 7000 GR after evacuation under vacuum (10^{-5} torr) at different temperatures.

For a temperature higher than 200°C, a significant decrease of SH bands has been observed. This can be assigned to the degradation of SH functions at higher temperatures and the formation of C=S groups. This result is reproducible for both grafted silicas. The area of the SH band has been calculated using the average of the SH band area (2650-2480 cm^{-1}) at 140°C≤T≤200°C (Figure 8 and Figure S2). The decrease of CH IR-band intensity is not accompanied with an increase of the isolated silanol IR-band intensity (at 3740cm^{-1}). Such result shows that all isolated silanol groups were consumed by the chemisorption of silane contrarily to methanethiol (see Figure 6). The decrease of the SiOH band intensity (3500 – 3000 cm^{-1}) at high temperatures (>150°C), especially for the hydrogen bonding silanol band, can be explained by the condensation reaction between two neighbor silanols ($2\ SiOH \rightarrow Si\text{-}O\text{-}Si + H_2O$). Table 4 summarizes the properties of the silica samples after the grafting reaction with Si 263® under the conditions cited in the experimental part.

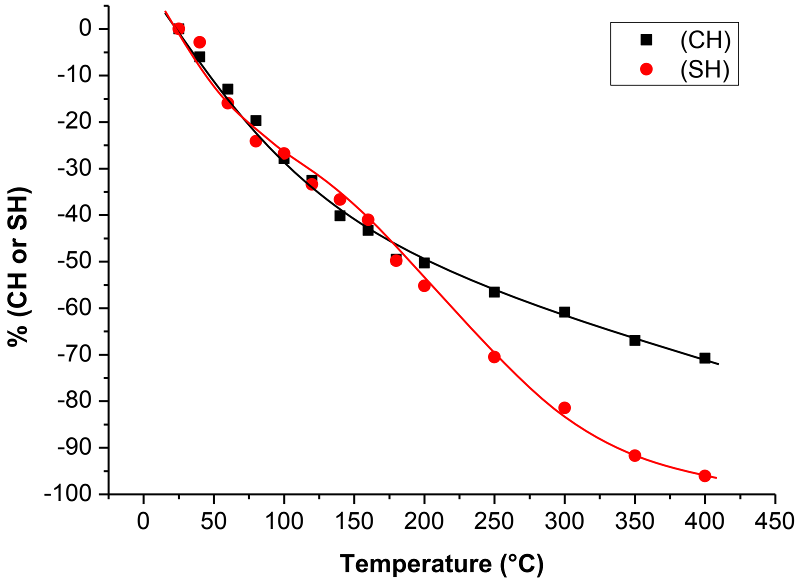


Figure 8. Evolution of “CH” and “SH” IR bands versus temperature

Table 4. Properties of grafted samples evacuated under vacuum at RT and at 200°C. N_{silane} corresponds to the average values of three experiments for each sample.

Sample	Evacuation Temperature [°C]	SH band area (cm^{-1})	Species/nm^2			
			N_{H2O}[a]	N_{H2O}[b]	N_{SH}=N_{silane}	N_{silane}-physisobed
grafted ULTRASIL® 7000 GR	RT	0.84	7.4	4.2	2.2	0.9
	~200	0.5			1.3	
grafted ULTRASIL® VN3 GR	RT	0.61	9.9	4.1	1.6	0.6
	~200	0.4			1.0	

N_{H2O}: water molecules number per nm^2 of silica surface before (a) and after silane grafting (b)
N_{SH}: thiol function number per nm^2 of silica surface which corresponds to silane number N_{silane}
N_{silane}-$_{physisobed}$: number of physisorbed silane calculated from the difference of the silane number in the sample evacuated at RT and that evacuated at 200°C.

As shown in Table 4, a significant decrease of the water content has been observed after the grafting with silane. This is assigned to the increase of the hydrophobicity of the silica due to the presence of silane and the decrease of silanol sites. The difference in N_{SH} at RT and at 200 °C can be correlated to the amount of physisorbed silane.

The number of silanes for the grafted ULTRASIL® 7000 GR, estimated in this work after evacuation under vacuum at 200°C (1.3 silanes/nm^2) corresponds to the chemisorbed silane and is in agreement with the results obtained above in the *operando* conditions (1.15 ± 0.25 silanes/nm^2).

The relative silane content per gram (SH band area) is higher for the grafted ULTRASIL® 7000 GR than for the grafted ULTRASIL® VN3 GR. The same tendency can be seen by evaluating the numbers of silanes (or numbers of SH) per nm^2: The grafted ULTRASIL® 7000 GR has a higher number of silanes per nm^2 than the grafted ULTRASIL® VN3 GR. The ranking of “relative silane content” in both samples is in good agreement with the ranking of the amount of isolated silanol sites: ULTRASIL® 7000 GR has a higher number of isolated silanol sites per area than ULTRASIL® VN3 GR (see Table 2 and Figure 9). Both silicas can therefore react with the mercaptosilane but the reaction of ULTRASIL® 7000 GR is more efficient. These results confirm the key role of the isolated silanol sites on the silane grafting reaction.

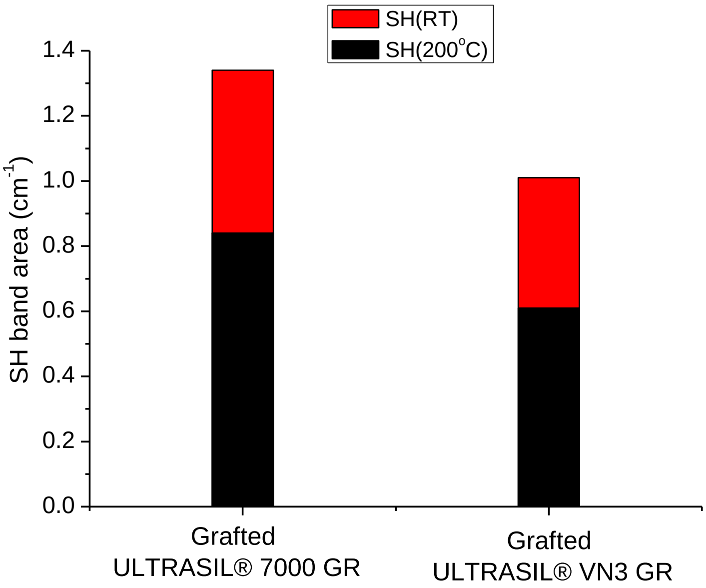


Figure 9. Evolution of the SH band area in grafted ULTRASIL® 7000 GR and grafted ULTRASIL® VN3 GR after evacuation at RT (red) and at ~200°C (black). (m_{pellet}= 20 mg)

Molecular Modelling

Molecular modelling has been used in order to understand the relationship between the isolated silanols and the number of silanes (or the surface area). Figure 10A shows the optimized structure of a $(HO)_3Si\text{-}O\text{-}Si(OH)_3$ molecule, used as a cluster for amorphous silica The structure with the highest stability contains a hydrogen bond between two adjacent silanol groups according to the modelling. The distance of this bond (~2.5 Å) represents the maximum distance for vicinal silanols. For $d_{SiOH\text{-}SiOH}$ >> 2.5 Å, the silanol groups are isolated. Figure 10B represents the optimized structure of silane Si 263®, grafted on a silica cluster. It shows that the distance between the grafting center and the $-CH_3$ of the ethoxy group is about ~4 Å. Thus, to have a grafting reaction on adjacent isolated silanol sites, the distance ($d_{SiOH\text{-}SiOH}$) is estimated to be >4 Å in order to have an accessible silanol site for silane.

This parameter ($d_{SiOH\text{-}SiOH}$) takes into account the relationship between isolated silanol groups and “numbers of silanes” and could explain the results obtained. As a conclusion, the number of silanes on the grafted samples depends not only on the number of isolated silanol sites, but also on the distance that separates these silanol sites.

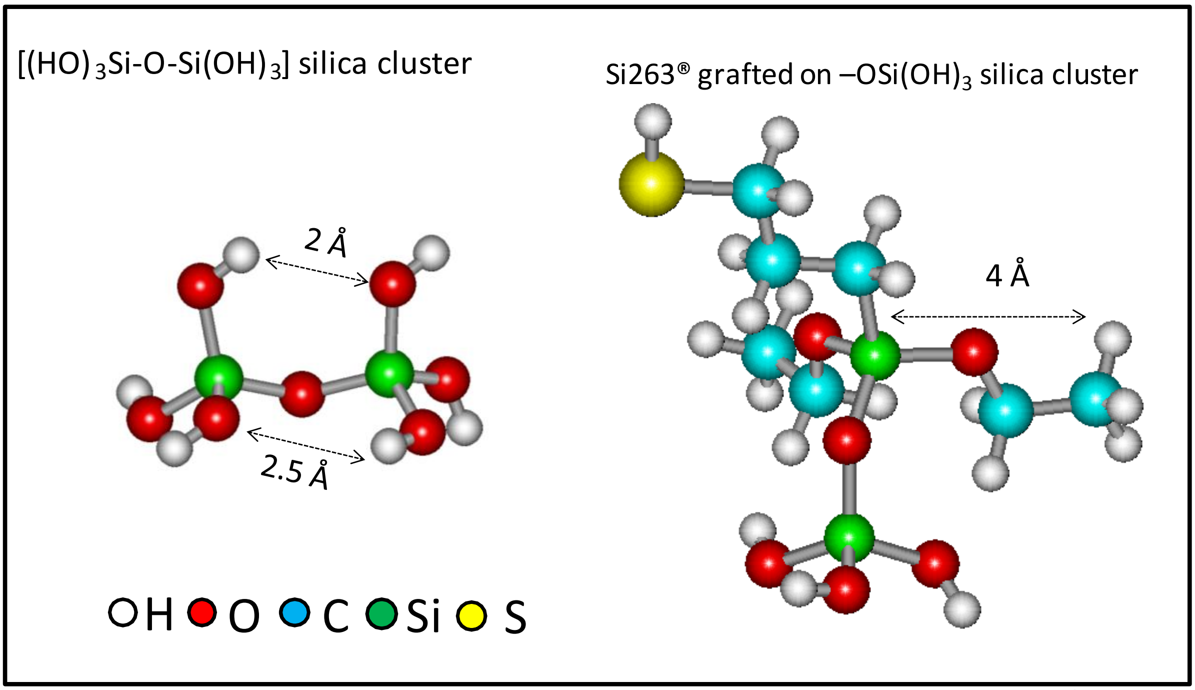


Figure 10. Structure modeling of $(HO)_3Si\text{-}O\text{-}Si(OH)_3$ cluster (A) and of silane Si263® grafted on $\text{-}OSi(OH)_3$ silica cluster (B).

Conclusion

This work presents an advanced study of the silane grafting on the silica surface and contributes to the role of the silanol sites in the silane grafting. Isolated silanol sites show a high activity in the chemisorption of silanes while only reversible physisorption could be observed for hydrogen bonded silanol sites. In order to highlight the role of isolated silanol sites in the silane grafting, the grafting reaction of the mercaptosilane Si 263® has been realized on two different silica samples. These samples present different amounts of isolated silanols sites. The results show that the hydrophobicity of the grafted silica surface increases with an increase in the amount of isolated silanol groups on the silica surface. This can be related to the amount of the silane chemisorbed on the silica surface exclusively via isolated silanol site.

The molecular modeling shows that the distance between two neighbor silanols ($d_{SiOH\text{-}SiOH}$) should be higher than 1.8 Å for isolated silanol sites. Therefore, the length of the alkoxy groups of silane plays an important role in the grafting reaction: two Si 263® molecules can only react to adjacent silanol groups if the internal distance ($d_{SiOH\text{-}SiOH}$) is higher than 4 Å. This means that the number of silanes on the grafted samples depends not only on the isolated silanol number but also on the distance that separates these silanol sites.

Supplementary Information

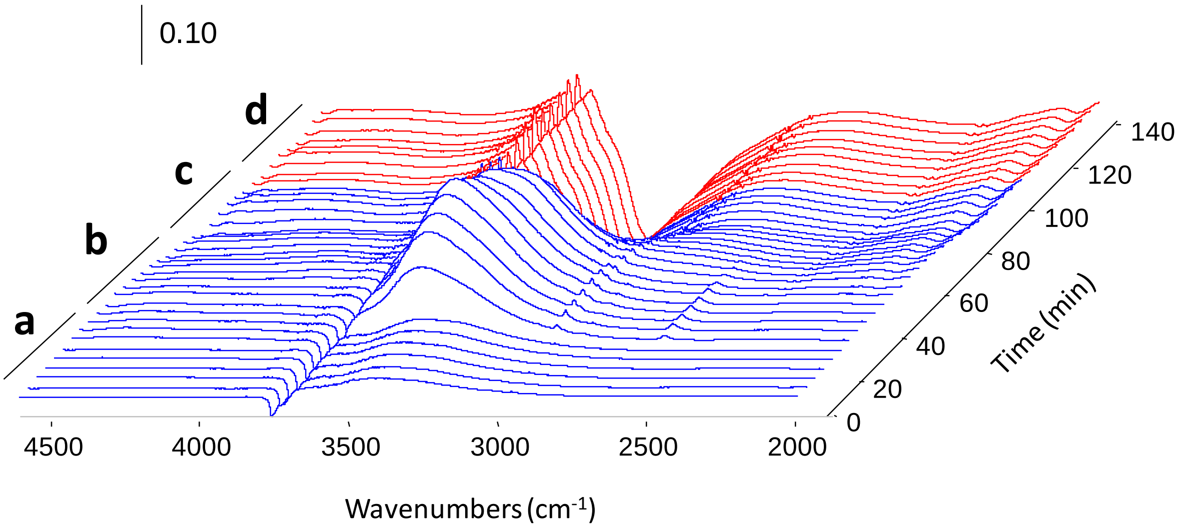


Figure S1. IR spectra of Silica during the grafting reaction of CH_3SH (400 ppm in synthetic air, flow=20 cm^3/min) subtracted from the IR spectrum of Silica after activation at 150°C: a) before reaction at RT b) during the CH_3SH adsorption at RT, c) heating from RT to 120^{O}C (5^{o}C/min) and d) during the reaction at 120^{o}C. (one spectrum / four minutes).

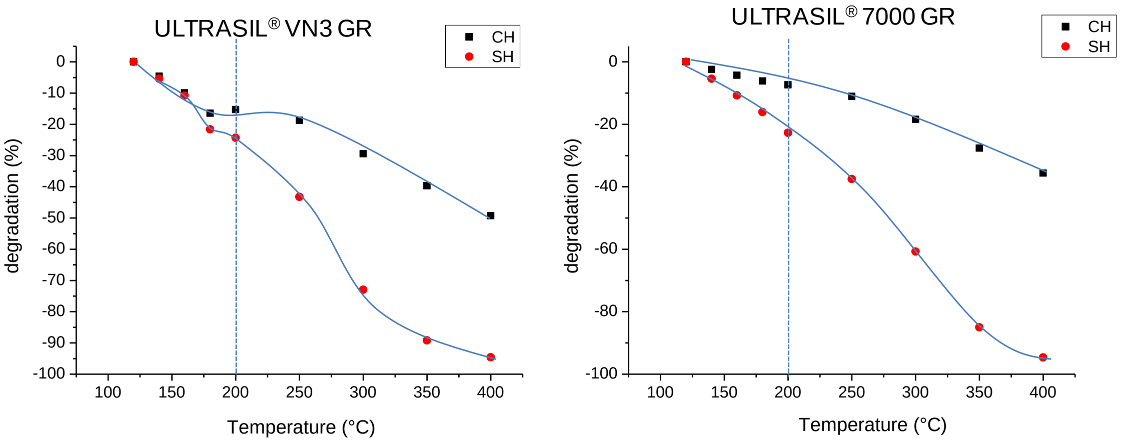


Figure S2 Evolution of CH (squares) and SH (circles) band areas of the different samples versus the temperature of evacuation (100°C-400°C) under vacuum conditions.

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