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Revisiting alkoxysilane assembly on silica surfaces: grafting *vs.* homo-condensation in solution

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Abstract: Silica surface functionalization is mandatory for a large variety of applications. This step is often done through the condensation of functional silanes on silanol, silica surfaces' terminal groups. Among these silanes, aminopropyltriethoxysilane (APTES) is widely used due to its assumed high reactivity with silanols, kinetically promoted by the catalytic action of the terminal amine function. Here, we revisit, based on a quantitative analysis by solid state ^{29}Si NMR, the assembly of this silane on silica surface to investigate whether its presence result from grafting, i.e. hetero-condensation with silanol groups or from homo-condensation of silane molecules in solution leading to polycondensates physisorbed on the surface. We investigate the interaction of APTES with a crystalline layered silicate, the ilerite and with amorphous non-porous silica. We also studied the assembly on these materials of a second silane, cyanopropyltrichlorosilane (CPTCS), which exhibit a similar reactivity towards silanol groups but without the input of a terminal amine as it ends with a nitrile group. Unlike the classical characterization techniques, solid state ^{29}Si NMR, when used in quantitative conditions allows for the discrimination of grafted silanes from those homo-condensed in solution and physisorbed on the surface. Our results undoubtably prove that while CPTCS is grafted on the silica surface, the presence of APTES on silica and silicate materials is only marginally associated to silanols consumption. The analysis of the signal related to silicon atoms from silanes (T^n species) and those from silica (Q^n species) allowed for the accurate estimation of the extent of homo-condensation vs grafting based on the ratio T-O-T/Q-O-T siloxanes bridges. These findings deeply question the well-established certainties on APTES assembly on silica that should no longer be seen as grafting of alkoxysilane by hetero-condensation with silanol groups but more accurately as a homo-condensed network of silanes, predominantly physisorbed on the surface but including some sparse anchoring points to the surface involving less than 6 % of the overall silanols groups.

Keywords: surface functionalization; silane assembly; grafting; condensation; APTES; ^{29}Si NMR; ilerite; silica

1. *Introduction*

Few materials are as important and ubiquitous as silica and silicates in modern technological applications. In addition to being an important material in its own right, silica serves as a prototype for understanding the wide variety of oxides, native oxide layers, and glasses that have widespread applications such as catalysis, biosensing, drug delivery, and molecular electronic.[1-4] The functionalization of these materials is a necessary prerequisite to endow them with the appropriate activity, and this is reflected in the considerable interest devoted to their surface chemistry in the scientific community. [5-10] Silane assembly on silica and silicates materials is universally acknowledged to be the most efficient way to achieve their surface functionalization; it is, incidentally, the first referenced example of molecules assembly on surfaces [11] which initiated the field of Self Assembled Monolayers. [9, 12] The silanes are expected to react with the silica surfaces' terminal groups, silanol (Si-OH) and undergo hetero-condensation reactions leading to their grafting *via* the formation of solid covalent siloxane bridges (Si-O-Si). Among these silanes, 3-Aminopropyl(triethoxysilane) (APTES) is one of the most widely used agent due to its commercial availability and to the presence of -NH_2 end groups on the surface as it allows other moieties to be attached in a simple way. [13-21] In addition, the amine function catalytically promotes the condensation reactions [22] which may facilitate the silane attachment to the surface. The assembly of APTES, and other aminosilanes, on silica surfaces was widely studied, especially on planar surfaces using techniques such as XPS [23] or IR[24] and the experimental variables allowing to optimize the silane coverage, were thoroughly explored in numerous studies that pointed out the major influence of parameters such as chains lengths, temperature, hydration rate, and contact time. [5-9] Yet, when compared to other silanes, the films formed from aminosilanes assembly are often less ordered. [25] The main reason for this lack of organization is that amine functions not only promote the hetero-condensation reactions between silanols and silanes, i.e. silane grafting, but they also strongly favor the homo-condensation reactions between silanes molecules at the solid-liquid interface leading to aggregates formation.[21, 26-28] These homo or poly-condensation reactions, have worse consequences that the above mentioned disorder as they may lead to unstable layers subject to desorption and leaching when immersed in complex media.[21, 29, 30] As a consequence, distinguishing grafting from silanes homo-condensation became a challenge for the community of surface chemists exploring silica and silicates functionalization. [31] As it turns out, most surface characterization techniques inform on the presence of silane on the surface but without differentiating the physisorbed from the covalently attached silanes. IR spectroscopy analysis of the longitudinal optical (LO) phonon mode of thin SiO_2 films and transverse optical (TO) makes it possible to qualitatively assess the newly formed Si−O bonds at the interface but again, without any formal quantification of the extent of homo-condensation and aggregates formation compared to hetero-condensation and direct grafting to the surface. [31]

^{29}Si MAS NMR (Magic Angle Spinning Nuclear Magnetic Resonance) is probably the most powerful tool currently available for investigating silane grafting on silica. Not only does ^{29}Si NMR make it possible to distinguish Si atoms in silica (Q^n units: $Si(OSi)_n(OH)_{4-n}$; chemical shift range: from -75 to -120 ppm) from Si atoms in the functionalized silanes (T^n units: $Si(OSi)_n(OH)_{3-n}R$; chemical shift range, from -45 to -65 ppm) or (D^n units: $Si(OSi)_n(OH)_{2-n}R_2$; chemical shift range, from 0 to -20 ppm) but it can also differentiate, within the Q, T, and D domains, the degree of condensation of the species, n, for Q^n (Q^2 $\delta \approx$-90 ppm, Q^3 $\delta \approx$-100 ppm, Q^4 $\delta \approx$-110 ppm) and for T^n species (T^1, $\delta \approx$-45 to -50 ppm, T^2, $\delta \approx$-55 to -60 ppm , T^3, $\delta \approx$-65 ppm). [32] The main drawback of this technique is that it is time consuming, and the collection of a spectra, in direct polarization which allows to access quantitative data, requires several days of acquisition as it is necessary to wait enough time between each scan for the system to fully relax (approx. 100s). [33] In addition, while the chemical shift of D^n units is modified when grafted to the surface, T^n units, as present for APTES, keep the same signal upon grafting which impedes the differentiation between homo and hetero-condensation. [34] In numerous reports, ^{1}H-^{29}Si cross polarization (CP) MAS NMR is used to establish whether grafting of the silane has occurred on the silica surface. The reason is that, compared to ^{29}Si DP (Direct Polarization) MAS NMR, ^{1}H-^{29}Si CP MAS NMR sequence considerably reduces the time required to collect a spectrum (ca. 1 hour, compared to 48 hours for DP measurements), and is therefore useful for quickly determining the presence of certain silica sites, as well as their chemical shifts. [35] These measurements, however, are not quantitative: in cross-polarization, the response of each site is modulated by the number of neighboring protons and their distance, two parameters that vary from one Si to another and significantly enhances the response of some of the silicon atoms considering the average density of 5 SiOH/nm² for most amorphous silicas[36] and the presence of hydrogen atoms in the alkyl chains of silanes.

We undertook here to revisit and quantitatively investigate the condensation processes upon APTES assembly on silica surfaces relying on quantitative, albeit time-consuming, ^{29}Si DP MAS NMR measurements. In addition to amorphous silica we explored the assembly of APTES on structured layered silicates which are synthetic or naturally occurring materials made up of stacks of nanometer-thick silicate sheets separated by cations. This family of materials has already led to major applications in the polymer industry.[37] By simple cation exchange, the spacing between two consecutive sheets can be set to a specific length, with accuracy on the order of 1 Å.[38] This controlled spacing allowed us to also explore the effect of porosity and confinement on the assembly. APTES assembly was performed on amorphous silica surface and on two well-known layered silicates, ilerite (also known as octosilicate, or RUB-18), first synthesized by Iler [39], bearing an extremely high density of silanol groups (50 % of the silicon species) [33], and magadiite, a naturally occurring material first discovered in Magadi lake, Kenya.[40] In addition to APTES we explored for comparison the assembly of a second silane cyanopropyltrichlorosilane (CPTCS), which differs in the terminal group, nitrile instead of amine in the case of APTES. We combine several characterization techniques, and strongly rely on an in-depth exploitation of ^{29}Si DP MAS NMR data to draw a comprehensive picture of the assembly process, and to quantitatively describe the extent of grafting versus homo-condensation.

2. *Materials and methods*

2.1. Synthesis protocols

2.1.1. Silicate synthesis

The sodium-intercalated ilerite ($Na_2H_2Si_8O_{20}$, nH_2O), denoted here as Na-Iler, was synthesized through a hydrothermal process already described in the literature [41]. A colloidal suspension of silica (Ludox HS-40, Sigma-Aldrich) was combined with sodium hydroxide and milliQ water, with the molar composition 1:0.5:7, in a Teflon-lined, stainless steel autoclave. This mixture was heated to 398 K for 9 days. The resulting white solid was dispersed in water at pH 9 (to minimize exchange of Na^+ by protons) and centrifuged at 5000 rpm for 5 minutes. This washing process was repeated three times, followed by drying in air at 313 K.

The synthesis procedure of sodium-intercalated magadiite, Na-Mag, is similar. The initial molar composition is SiO_2:NaOH:H_2O – 9:2:75 [42]. The mixture was heated to 423 K for 72h. The product was then washed with milliQ water and centrifuged following the same steps as for Na-Iler.

The hexadecyltrimethylammonium ($C_{16}TMA^+$) intercalated silicates are denoted C_{16}-Iler and C_{16}-Mag. These materials were obtained by dispersing 12 g of Na-Iler or Na-Mag in 400 mL of a 0.1 M solution of $C_{16}TMA^+$, Cl^-. The solution was stirred for 24 hours, then centrifuged at 5000 rpm for five minutes.

This entire process was repeated three times. The final product was washed with milliQ water and dried in air at 313 K.

2.1.2. Silanes assembly

Aminopropyltriethoxysilane (APTES) and cyanopropyltrichlorosilane (CPTCS) assembly on the intercalated layered silicates was performed applying a protocol optimized on glass slides and silicon wafers [14, 21, 32, 43]. Prior to silane assembly, 1 g of the CTMA exchanged silicate (C_{16}-Iler) was dried in air, along with the glassware, at 398 K for one hour to remove water traces. then quickly dispersed in silane solution. Silane solutions containing $6.3\text{x}10^{-3}$ mol of silane (APTES or CPTCS) in 50 mL anhydrous toluene were freshly prepared for the assembly then the mixture (silicate + silane solution) was quickly covered with the refrigerant to launch the reaction and the reflux. As the chemical formula for C_{16}-Iler is $CTMA_2H_2Si_8O_{20}$ (for a complete exchange of the sodium by $CTMA^+$ cations), this corresponds to an excess of silane with regards to silanols/silanolates (about 1.8 silane per silanol/silanolate). This mixture was refluxed at 363 K for 48 h. The relatively high temperature is expected to favor the grafting of the silane at the expense of homo-condensation [21]. Finally, the product was centrifuged at 5000 rpm for 5 minutes, and washed in toluene three times. The resulting powder was dried under vacuum at 363 K for one hour. Silane-modified samples are noted C_{16}-Iler (or Mag)-APTES and C_{16}-Iler (or Mag)-CPTCS.

The same procedures were applied to fumed silica nanoparticles (Aerosil 200, Degussa, ≈ 12 nm in diameter). For these samples also, the silanes are introduced in excess with regards to the density of silanols (Based on the literature, the surface density of silanols on silica is about 5 $OH.nm^{-2}$. [44, 45] considering the surface area of Aerosil 200, this corresponds to a density of silanols of 1.66 $mmol.g^{-1}$ and to a silane to silanol ratio of about 3.8).

2.2. Characterization

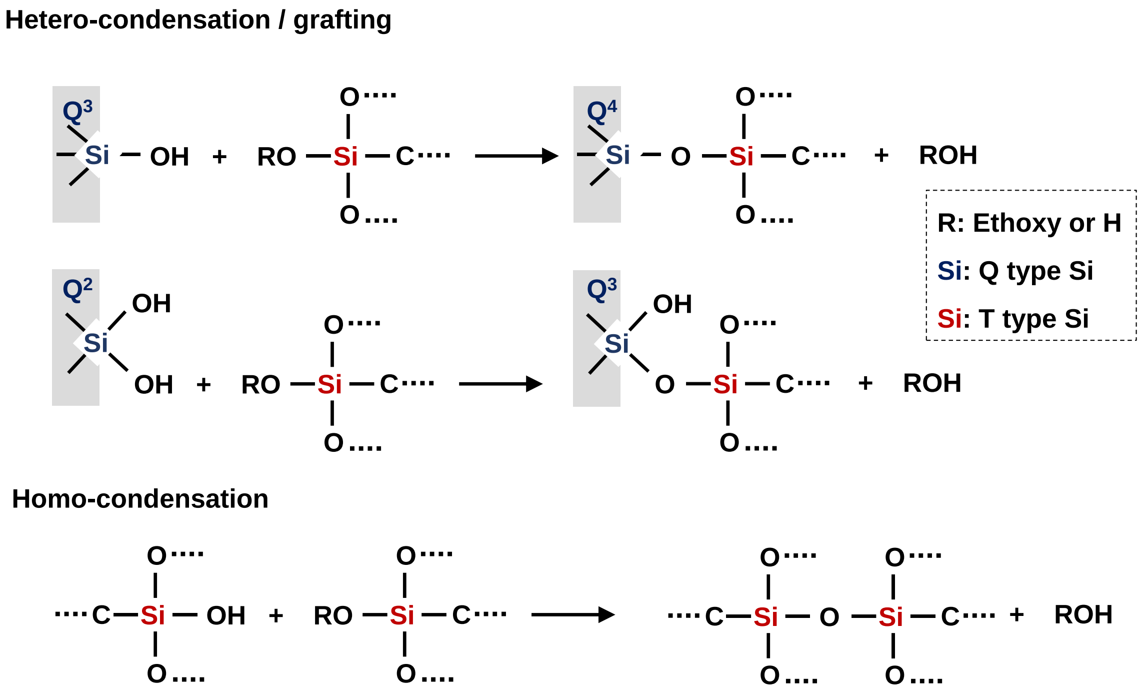
X-Ray Diffraction (XRD) measurements were carried out using a $\theta-\theta$ D8 Advance (Bruker) powder diffractometer working with Cu-Kα radiation (λ=1.54 Å) and equipped with a 1D LynxEye detector. In order to suppress the signal of incident beam at low angle, a shield was mounted on the primary beam side with the knife-edge of the shield at a close distance to the sample surface. The LynxEye detector opening was set to 3°. The diffractograms are reported without baseline correction.

Sample morphologies were investigated with a high-resolution Ultra 55 Zeiss FEG scanning electron microscope (SEM). DRIFT, diffuse reflection IR spectroscopy, measurements were performed with a Bruker Invenio S spectrometer using a DRIFT accessory Spectratech collector II, equipped with a DTGS detector (resolution 4 cm^{-1}, 128 scans per spectrum, spectral range 4000 – 500 cm^{-1}). Prior to IR analysis, the samples were dried at 363 K for one hour to remove the adsorbed water. The spectra were then recorded within a chamber purged with dry air.

^{29}Si MAS NMR spectra were recorded with a Bruker Avance spectrometer at 99.4 MHz using 7 mm zirconia rotors. The chemical shifts of silicon were measured by reference to tetramethylsilane (0 ppm). For magic angle spinning direct polarization measurements (DP MAS), the measurement conditions allowing for quantification were as follows: pulse duration 3 μs, recycle delay 100 s, number of accumulations 864 and spinning rate 5 kHz; for magic angle spinning ^{1}H-^{29}Si NMR cross polarization (CP MAS): 3-(trimethylsilyl)-1-propanosulfonic sodium was used for setting the Hartmann-Hahn conditions, proton pulse duration was set at 2.5 μs (π/2), contact time 4 ms, recycle delay 5s, number of accumulations 2024 and spinning rate 5 kHz.

3. *Results and discussion*

The grafting of aminopropyltriethoxysilane (APTES) on silica or silicate surfaces occurs when the alkoxy groups of this silane undergo hetero-condensation reactions with silanols, the reactive terminal groups present on silica surface (see Scheme 1). In what follows we investigate the assembly of this silane, and compare it to that of a second silane cyanopropyltrichlorosilane (CPTCS), which differs in the terminal group, nitrile instead of amine in the case of APTES. CPTCS also differs from APTES in the departing group, chlorine vs ethoxy and is expected to exhibit show a higher activity than cyanopropyltriethoxysilane (CPTES).[46] Indeed, under the conditions used for the assembly, and with the precautions taken to limit as much as possible the contribution of water, the amount of CPTES adsorbed on silica surface was too small to allow meaningful comparison (see SI Figure S1 and section 1: Reactivity of CPTES). Two other materials are also explored and compared to ilerite, a second layered silicate with thicker sheets but similar basal spacing, the magadiite and an amorphous fumed silica, Aerosil. The two layered silicates materials were prepared “in house” while the amorphous silica was commercial. Therefore, prior to the study of silanes interaction with these surfaces we undertook a deep characterization of the prepared silicates.



Scheme 1: Reaction of hetero-condensation (grafting) of silane with silanol groups and homo-condensation between ethoxysilanes following the hydrolysis of one or more ethoxy groups in presence of water and the removal of one or more R. The Q type and T type silicon atoms are depicted in Figure 3.

3.1. Structural and morphological characterization of ilerite

The structures of the initial, sodium-intercalated ilerite, referred to as Na-Iler, was confirmed by XRD, as shown in Figure 1-a. Peak positions match those found in the literature, with the lowest-angle peaks at 8.0°, indicating a basal spacing of 1.1 nm.[41] The formation of the material is further confirmed by SEM images, which show sheet-like rectangular particles several micrometers across, and several hundreds of nanometers thick (Figure 1-a) [33] . The same measurements for magadiite are shown in the SI section, Figures S1. XRD confirms the formation of Na-magadiite, whereas SEM images show thinner and more loosely arranged in rosette-like stacks particles, consistently with previous observations.

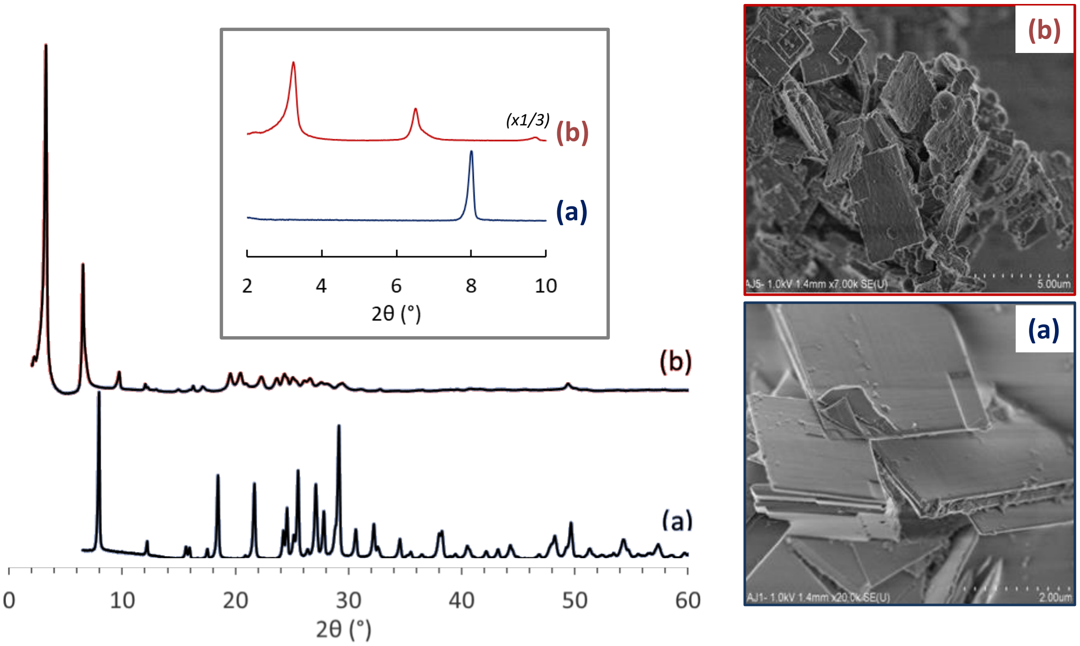


Figure 1: XRD patterns, small angle XRD patterns, and SEM images of (a) Na-Iler and, (b) C_{16}-Iler, the interlayer space expands from 1.1 nm to 2.72 nm after exchanging Na^+ with $C_{16}TMA^+$.

The first step toward the functionalization of layered silicates is the insertion of an intercalating agent whose role is to push the individual layers apart. This is necessary because the space between the silicate sheets in ilerite is too small to allow efficient interlayer diffusion of the silane.[40] Intercalation was achieved by placing the material in solution containing a large excess of $C_{16}TMA^+$, Cl^-, in order to form the swollen materials referred to as C_{16}-Iler. The ability of bulky $C_{16}TMA^+$ molecules to diffuse into the narrow interlayer space, which is inaccessible to smaller molecules such as silanes, is likely driven by the electrostatic interaction between these positively charged moieties and the negatively charged silica surface.

Figure 1 shows low-angle XRD measurements of both the sodium and the intercalated forms of ilerite. The shift in the position of the lowest-angle peak from 8° to 3.24°, resulting from the intercalation, corresponds to an increase in the basal spacing from 1.1 nm to 2.72 nm, in agreement with previously reported values. [41] Likewise, the basal spacing in magadiite increases from 1.55 nm to 3.20 nm after intercalation (Figure S1), consistently with the literature values.[47] SEM characterization of C_{16}-Iler (Figure 1-b) confirms that the sheet structure is preserved. In the case of C_{16}-Mag (Figure S1b), the sheet structure is also preserved but the particles are no longer stacked in rosette-like arrangements. This is likely due to the large expansion of the interlayer space upon ion-exchange of Na^+ by $CTMA^+$. Additional characterization of the intercalation step was done by IR spectroscopy. The main modification in the spectra, shown in Figure S2, is the presence of intense bands at 2920 and 2850 cm^{-1} and another band at 1470 cm^{-1}, attributed to the stretching and scissoring vibrations of methylene groups, present in large numbers because of the long carbon chains on the intercalation agent, C_{16}TMA. The shape of the bands corresponding to the OH groups is also modified; the bands are sharper due to less H-bonds between silica sheets [39]. Once the intercalation agent is in place, the silicate surface can be functionalized.

3.2. IR investigation of silane assembly

Alkoxysilanes are known to undergo hetero-condensation reactions with silanol groups, allowing for their grafting on silica surface as depicted in Scheme 1. The two silanes used for this process, aminopropyltriethoxysilane (APTES) and cyanopropyltrichlorosilane (CPTCS), have relatively small sizes and are commercially available. In addition, in the case of APTES, the amine function has been shown to act as a catalyst in the condensation reaction which made this silane the most used molecule for chemical modification of silica-like surfaces.[48] Silane grafting on the intercalated layered silicates was firstly investigated by IR in diffuse reflectance mode.

Figure 2 shows the infrared spectra for Na-Iler, and for the same material after the intercalation and grafting steps, referred to here as C_{16}-Iler-APTES and C_{16}-Iler-CPTCS.

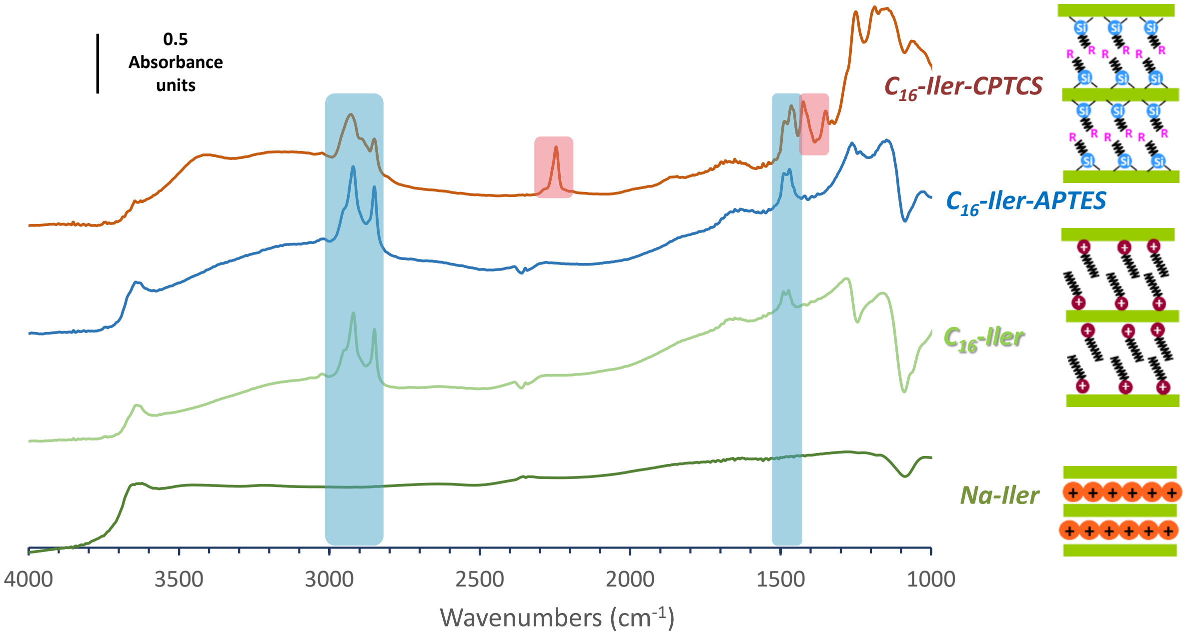


Figure 2: FTIR spectra of Na-Iler, C_{16}-Iler, C_{16}-Iler-APTES, and C_{16}-Iler-CPTCS. Methylene peaks from the swelling agent C_{16}TMA are highlighted in blue for C_{16}-Iler-APTES and C_{16}-Iler-CPTCS, and the nitrile peak from CPTCS is highlighted in red. Markers for APTES are absent from the C_{16}-Iler-APTES spectrum.

The methylene groups signature (highlighted in blue in Figure 2) that is often used to evidence the presence of silane on materials surfaces, is not relevant here as $C_{16}TMA^+$ intercalation led to the presence of the same groups. For an account on silane presence, we have to rely on the signature of the terminal groups, i.e. amine and nitrile groups for APTES and CPTCS, respectively. For C_{16}-Iler-CPTCS, an additional band ascribable to nitrile group of CPTCS (highlighted in red in Figure 2) is clearly observable at 2250 cm^{-1}. In addition to this band, there is a significant drop in the intensity of the band ascribed to silanol groups at 3650 cm^{-1}, pointing out a decrease in SiOH number, which would be expected if they were involved in hetero-condensation reactions with silanes to form siloxane bridges. Therefore, the IR spectrum of C_{16}-Iler-CPTCS shows that the nitrile terminated silane is present on the surface and that it is likely grafted on it. The IR signature obtained upon reaction with the amine-terminated silane, C_{16}-Iler-APTES, is less informative and the presence of silanes is more uncertain. Indeed, the infrared spectrum for C_{16}-Iler-APTES shows no peak in the 3400-3500 cm^{-1} region which would normally indicate the presence of a primary amine function. Additionally, unlike when CPTCS is grafted, no significant drop in intensity of the silanol band at 3650 cm^{-1} is noticeable. This result is quite surprising as APTES is known to easily functionalize silica surface and to benefit from the catalytic action of the terminal amine function [21, 28]. The absence of bands related to APTES in the IR spectrum suggests that no adsorption nor grafting - or very minor ones - occurred for this silane. The same experiments were conducted on the second layered silicate, magadiite. The IR spectra obtained for C_{16}-Mag-APTES and C_{16}-Mag-CPTCS are very similar to those recorded for ilerite (Figure S3): CPTCS grafting is evidenced by the presence of nitrile bands concomitantly with a decrease in silanol bands intensity while no straightforward conclusion could be drawn on the possible presence of APTES from the IR spectrum. The apparent lack of APTES adsorption on silicates is therefore not solely related to ilerite.

On the other hand, observing a silane signature the IR spectrum proves its presence on the surface but is not sufficient to confirm that the grafting reaction, i.e; hetero-condensation with silanol groups, has occurred. Indeed, as depicted in Scheme 1, silanes undergo homo-condensation reactions, especially if trace amounts of water are present, which could be the case in most protocols, including the protocol we have selected here and despite the use of anhydrous toluene. [21, 26, 27] The resulting poly-condensate particles may be partially grafted onto the silicate's outer surface or even simply physisorbed strongly enough to remain on the surface after washing and centrifugation along with the functionalized silicate. In the case of CPTCS, there's a bundle of evidences towards grafting as the nitrile groups signature comes with a decrease in the intensity of silanols band. To further investigate the mechanism of interaction of both silanes with ilerite surface and better explore the nature of the bonds between the silane and the surface, we utilized ^{29}Si NMR.

3.3. ^{29}Si MAS NMR investigation of silane assembly

^{29}Si MAS DP NMR measurements were performed to determine the extent of both grafting – hetero-condensation - and homo-condensation of silanes in the ilerite samples. Figure 3 shows ^{29}Si DP NMR spectra for C_{16}-Iler, C_{16}-Iler-APTES, and C_{16}-Iler-CPTCS. C_{16}-Iler produces a spectrum with two major peaks at -102 and-113 ppm. These peaks can be assigned to Q^3 (i.e. $Si[(OSi)_3(OH)]$) and Q^4 (i.e. $Si[(OSi)_4]$) environments, respectively, as is typically found in the literature and in agreement with the two main chemical environments of silicon in ilerite layers. [33]

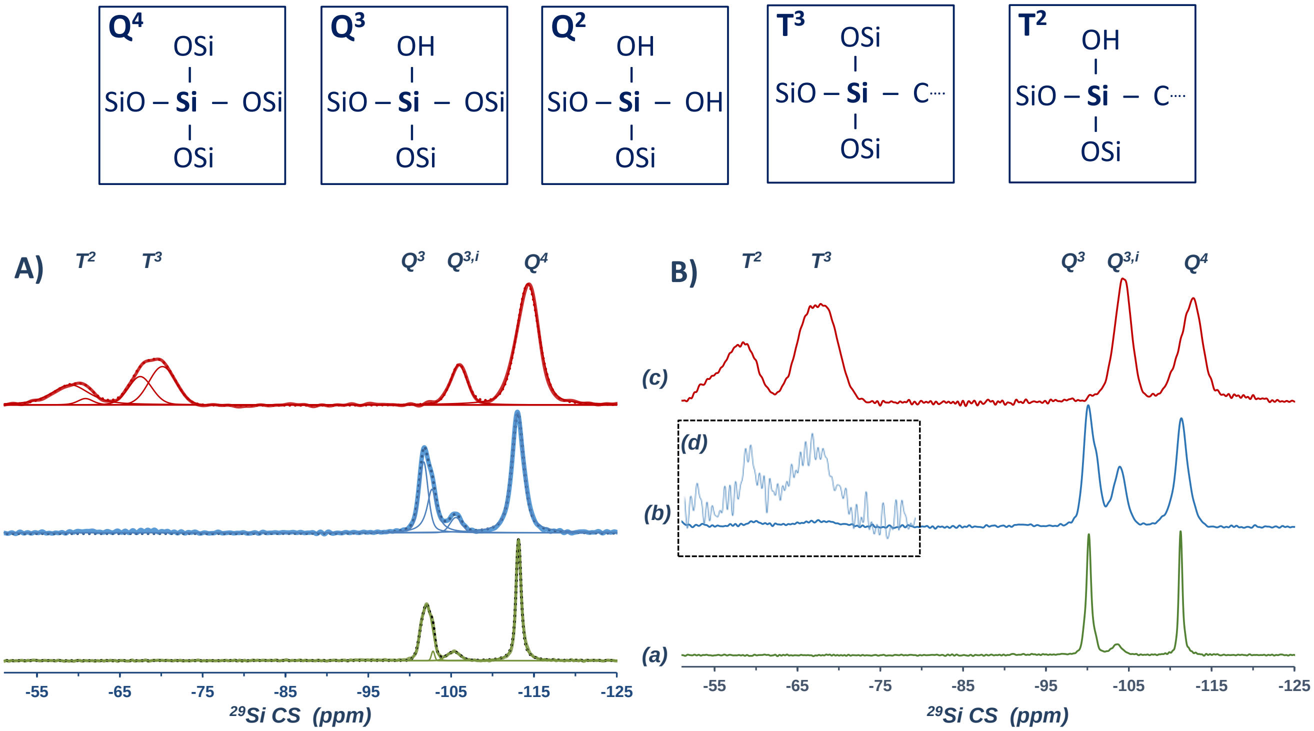


Figure 3: ^{29}Si DP (A) and ^{1}H-^{29}Si CP (B) NMR spectra for ilerite before (a) and after reaction with APTES (b) and CPTCS (c) silanes and the chemical environment of silicon in the utilized nomenclature. (d) Zoom between -50 and -75 ppm of the ^{1}H-^{29}Si CP spectrum. The reaction with CPTCS leads to the appearance of two peaks in the T^n region, and noticeable decrease in the intensity of the Q^3 peak visible in C_{16}-Iler. No such changes occur after the reaction with APTES.

The integration of these two peaks (see Table 1) indicates that they have the same area, which is also consistent with the ilerite structure.[33] This is an extra confirmation that the conditions we used - in particular, the recycle delay - for the acquisition of the ^{29}Si DP NMR spectra are appropriate for a quantitative analysis of the spectra. [33]

A smaller, additional peak is observed at -105 ppm and attributed to internal silanols ($Q^{3,i}$). Based on other examples in the literature, the same peak seems to be present for proton-intercalated ilerite, H-Iler, which may partially form through ion exchange of sodium with protons in solution. [49, 50] Upon reaction with silanes, this $Q^{3,i}$ peak remains unchanged on the ^{29}Si NMR spectra, also shown in Figure 3-A, which further confirms the assignment to internal silanols located in area where the interlayer space is too small to allow the insertion of APTES or CPTCS, consistently with its association to H-Iler domains. Based on the intensity of this NMR peak, as well as the absence of the characteristic peaks of H-ilerite on the diffractogram, the portion of the material associated with this additional peak likely accounts for only a small fraction of the sample.

In the ^{29}Si NMR spectra in Figure 3-A, upon reaction of C_{16}-Iler with CPTCS, two peaks appear at -60.2 and -68.5 ppm, attributable to the presence of T^2 (i.e. $Si[(OSi)_3(R)]$) and T^3 (i.e. $Si[(OSi)_2(OR')(R)]$) type Si on the silicate. These peaks further confirm the presence of CPTCS in the ilerite previously demonstrated by IR analysis. In addition, the intensity of silanols peak, Q^3 at -102 ppm, dropped significantly, which indicates that an important portion of these Si-OH groups were hetero-condensed with the alkoxy groups upon CPTCS grafting on the surface. Indeed, when the silicon atoms from silane (T type Si) are condensed with silanols (Q^3 type Si) the environment of these Q^3 silicon atoms changes into Q^4 as the H is replaced by a fourth silicon second neighbor (see Scheme 1). This change will have two additional consequences on the ^{29}Si NMR spectra: first, an important decrease in the ratio Q^3/Q^4 as, simultaneously, the proportion of Q^3 type Si decreases while that of Q^4 type Si increases, and second, a broadening of the Q^4 peak as the new Q^4 type Si (ex Q^3 type Si + T) have C atoms as third neighbors and therefore a different chemical environments than the original Q^4 type Si (only oxygens as third neighbors). This induced global heterogeneity in Q^4 type Si environment leads to the broadening of their NMR signal. These two consequences are clearly observable on C_{16}-Iler-CPTCS ^{29}Si NMR data assembled in Table 1: The full width at half maximum, (FWHM) of Q^4 peak, originally 73 Hz for C_{16}-Iler increases to 314 Hz (4.3-fold higher) for C_{16}-Iler-CPTCS. All the same, the Q^3/Q^4 ratio strongly decreases from 0.95 to 0.24 (~75 % decrease) upon CPTCS adsorption. Therefore, based on ^{29}Si NMR, CPTCS assembly on ilerite is realized through hetero-condensation with silanol groups and this silane is, to a large extent, grafted to the silicate surface.

Table 1: ^{29}Si DP MAS NMR data for ilerite and Aerosil before and after reaction with APTES and CPTCS. The amounts of Q and T species are expressed per 100 Q units (100 Si atoms of the starting silica or silicate).

Materials	Q^4	FWHM Q^4 (Hz)	Q^3	Q^2	T^3	T^2	Q^3/Q^4 [a]
C_{16}-Iler	51.2	73	48.8	0.0	__	__	0.95
C_{16}-Iler-APTES	54.2	165	45.8	0.0	< 0.1	< 0.1	0.85
C_{16}-Iler-CPTCS	80.5	314	19.5	0.0	44.2	27.1	0.24
Aerosil	86.6	__	12.6	0.8	__	__	0.16
Aerosil-APTES	86.6	__	13.4	0.0	21.8	8.0	0.15
Aerosil-CPTCS	92.5	__	7.5	0.0	7.8	12.3	0.08

[a] This value is obtained considering the Q^2 silanols when present $\left(\frac{Q^3+2\cdot Q^2}{Q^4}\right)$.

The observations are completely different for C_{16}-Iler-APTES. Indeed, the NMR spectrum of C_{16}-Iler-APTES in Figure 3-A shows no sign of T^2 or T^3 peaks, no perceptible change in Q^3 type Si peak, and, consequently, no presence nor grafting of APTES on the ilerite - at least within the limit of detection of the spectrometers - consistently with the absence of amine bands in the IR spectrum. A deeper look at the previously discussed parameters (Table 1) reveals small modifications: The Q^3/Q^4 ratio slightly decreases by 11 % (*vs* 75 % for CPTCS) and the FWHM of Q^4 peak is 2.3-folds higher than the C_{16}-Iler (vs 4.3-fold higher for C_{16}-Iler-CPTCS). These small changes may result from the grafting of some APTES molecules on the ilerite surface, in proportions lower than the limit of detection. To validate this hypothesis and better observe whether APTES is present in small amounts, we collected the ^{1}H-^{29}Si cross-polarization (CP) MAS NMR spectra for both silanes on ilerite, shown in Figure 3-B. In the CP sequence, the response of each site is modulated by the neighboring protons and their distance, which enhances the responses of silicon atoms bearing an OH group (silanol) or CH groups (silanes) and provides a useful method for quickly determining the presence and the chemical shifts of these species. The main drawback is that these measurements are not quantitative because of this amplification, unlike the direct polarization sequence utilized previously as can be seen in the^{1}H-^{29}Si CP spectra of ilerite where the Q^3 signal appears much higher than the Q^4 one. The collected spectra for C_{16}-Iler-CPTCS and C_{16}-Iler-APTES in Figure 3 confirm the presence of some APTES molecules. The ^{1}H-^{29}Si CP MAS NMR show a strong amplification of silane signal for C_{16}-Iler-CPTCS and the presence of a small signal of T^3 silicon atoms (and even smaller signal for T^2 ones) for C_{16}-Iler-APTES. This observation is consistent with the slight changes recorded for Q^3/Q^4 ratio and for the FWHM of Q^4 peak upon APTES adsorption and confirms the attachment of a barely detectable portion of APTES to the ilerite surface.

APTES is widely used because of the presumed facility of its attachment to the silica surface, the absence of reaction of APTES with layered silicates is very surprising at first and questions these established certainties regarding its attachment to the silica. As mentioned above, APTES molecules undergo homo-condensation reactions, kinetically promoted due to the catalytic activation by the amine functions.[21, 26-28] The kinetics of these homo-condensation reactions can lead to the rapid formation of APTES aggregates in solution. One plausible explanation to the absence of APTES in C_{16}-Iler-APTES is a restricted diffusion within the interlayer space, that can not be encountered for molecular APTES but would be an obstacle for the aggregates formed upon homo-condensation of APTES molecules. Once these aggregates formed, they may attach to available silanol groups on silica surfaces, as long as they can diffuse and access these silanols, which is not the case for layered silicates. The mechanism is likely different for CPTCS molecules where the hydrolysis/condensation reactions are not catalyzed by amines, and single molecules can diffuse within the interlayer space and hetero-condensate with the available silanols. The reaction with the ilerite silanol might even benefit from the confinement within the interlayer space. To further explore this mechanistic hypothesis, we performed the same NMR experiments on fumed silica nanoparticles (Aerosil 200, spherical particles with an average diameter of 12 nm), exhibiting similar surface sites but on a freely accessible surface rather than inside a layered structure.

Figure 4-A shows ^{29}Si DP MAS NMR spectra of Aerosil silica before and after reaction with APTES and CPTCS. Aerosil silica displays Q^3 and Q^4 peaks similar to layered silicates, though much broader due to its amorphous nature and to the high heterogeneity of silicon environment. [45] A small contribution of Q^2 is also present. Unlike for ilerite, there is a strong overlap of the peaks associated with Q^n type silicon atoms, which impacts the precision of the data compared to the well-resolved spectra of ilerite. A detailed decomposition of the ^{29}Si NMR spectra was made and is included in Table 1.

As expected, T^2 and T^3 peaks are clearly present after reaction with both APTES and CPTCS, confirming the presence of the silanes in both cases. The overall intensity of T^n peaks is higher for APTES than CPTCS, which, at a preliminary examination, may be mistaken for a better “grafting” of APTES on the silica surface. The relative intensities of T^n peaks are different with predominance of T^3 for APTES and T^2 for CPTCS. The same differences in relative intensities were observed by Kobayashi, Slowing and coworkers in their ^{1}H-^{29}Si CP MAS NMR kinetical study of the grafting, on mesoporous silicas, of two silanes having the same size and the same terminal groups than APTES and CPTCS, i.e. APTMS (aminopropyltrimethoxysilane) and CPTMS (cyanopropyltrimethoxysilane), respectively.[51] The higher T^3 fraction for amine terminated-silanes indicates a higher rate of condensation than for nitrile-terminated silanes.

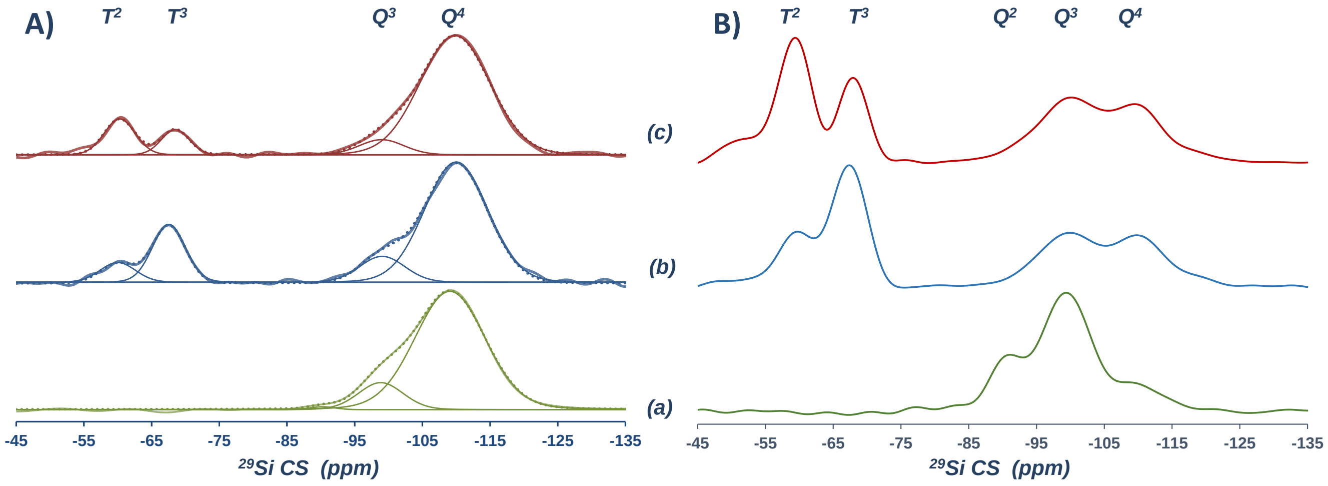


Figure 4: ^{29}Si DP (A) and ^{1}H-^{29}Si CP (B) NMR spectra of Aerosil before (a) and after APTES (b) and CPTCS (c) assembly. The CP spectra significantly overestimate the reduction in Q^3 peak intensity and increase in T^n intensity after reaction with silanes, as compared to the quantitative DP measurements.

Going back to ^{29}Si DP MAS NMR spectra in Figure 4-A and to the corresponding data in Table 1, the presence of silane for Aerosil-CPTCS is associated with a noticeable decrease in the intensity of silanols signal (Q^3 and Q^2) an a drop in Q^3/Q^4 ratio from 0.16 to 0.08 (50 % decrease), which indicates the grafting through the hetero-condensation of alkoxy groups with the silica surface silanols to form Si-O-Si bridges. As for the case of ilerite, the observations are different upon APTES addition: The silanols signal is barely modified, except from the disappearance of Q^2 signal (possibly changed into Q^3, see Scheme 1) and the ratio Q^3/Q^4 - calculated by considering Q^2 species – remains almost unchanged (~ 6% diminution). On the light of these data it becomes certain that **the presence of APTES signal on Aerosil silica nanoparticles is not resulting from hetero-condensation with silanols** and that **the T^n species originate mainly from the homo-condensation of APTES molecules in solution**. These findings deeply question the widely established certainties regarding APTES assembly on silica and/or silicate surfaces.

To quantitatively estimate the extent of grafting vs homo-condensation, we further analyzed the ^{29}Si DP MAS NMR data in what follows.

3.4. Quantitative estimation of the extent of hetero vs homo-condensation

As discussed in the previous section, quantitative data can only be obtained based on the analysis of ^{29}Si DP MAS NMR and not^{1}H-^{29}Si CP MAS NMR. Indeed, even if CP sequence has numerous advantages, especially reducing considerably the time required to collect a spectrum (ca. 1 hour, vs 24-48 hours for DP), and allowing for quickly determining the presence and the chemical shifts of silicon sites, Q and T, one of its main drawbacks is that the signal intensity is modulated by the neighboring protons and therefore can not be used quantitatively, at risk of greatly overestimating the proportions of some sites. The spectra collected for Aerosil silica prior to its interaction with silane in Figure 4-B, shows how the cross-polarization mode of acquisition can be misleading when it comes to quantification as Q^3 and Q^2 signal appears dominating in CP sequence while these sites only account for 13.4 % of silicon sites in the quantitative conditions of direct polarization (Table 1). The simple comparison of the shape and intensity of Q^3 and Q^4 peaks in CP before and after reaction with silanes also impedes drawing qualitative conclusions regarding silane assembly, as the spectra obtained for Aerosil-APTES and Aerosil CPTCS look similar unlike the DP data where the shoulder of Q^3 is no longer visible in the Aerosil-CPTCS spectrum. In summary, CP-NMR is quite convenient for obtaining a rapid but crude understanding of the surface species but should be interpreted with care. In what follows we rely on the quantitative analysis of the ^{29}Si DP NMR spectra to estimate the extent of homo and hetero-condensation.

Upon silane grafting on the silica surface, a hetero-condensation with silanols occurs and these silanols consumed during condensation change into Q^4 when a Q^3 - or Q^3 when a Q^2 (see Scheme 1). Therefore, the first and simplest method to estimate the extent of grafting is the calculation of the percentage of consumed silanols as follows:

$SiOH_{cons}(\%) = 100\left(\frac{n(SiOH)_i - n(SiOH)_f}{n(SiOH)_i}\right) = 100\left(\frac{(Q_i^3+2Q_i^2)-(Q_f^3+2Q_f^2)}{(Q_i^3+2Q_i^2)}\right)$, with i referring to the initial fraction of Q and f to the final ones, after reaction with silane

In addition, using NMR nomenclature, the siloxane bridge, Si-O-Si, formed upon hetero-condensation of silane with silanols will be a T-O-Q as depicted in Scheme 1 and Scheme 2. Therefore T-O-Q bridges account for grafting. While when silanes undergo homo-condensation reactions, the formed Si-O-Si bridges are T-O-T and are not associated to any consumption of surface silanols. T-O-T bridges account for homo-condensation. Note that a T-O-T bridge can be close to the surface and have a T-O-Q as neighbor or result from separate aggregates in solution (see Scheme 2). The number of T-O-Q bridges can be estimated from number of consumed silanes:

$$\text{n(T-O-Q) per 100 Q} = \text{n(Si-OH)}_i - \text{n(Si-OH)}_f = Q_i^3 + 2 \cdot Q_i^2 - Q_f^3 - 2 \cdot Q_f^2$$

A T^n Si has n silicon atoms as second neighbors but these silicon atoms can be either T or Q. As only T^2 and T^3 sites are observed, the number of T-O-T bridges can be calculated as a weighted sum of T^2 and T^3 sites minus the previously calculated T-O-Q as follows:

$$\text{n(T-O-T) per 100 Q} = 3/2 \cdot T^3 + 2/2 \cdot T^2 - 1/2 \cdot \text{(Q-O-T)}$$

The results obtained by applying these equations to ^{29}Si DP NMR data collected upon APTES and CPTCS interaction with Aerosil and ilerite silicas are reported in Table 2.

Table 2: Quantitative estimation of the extent of grafting and condensation from ^{29}Si DP MAS NMR data reported in Table 1. Q-O-T refers to the number of O atoms bound to a T^n and a Q silicon atoms and accounts for grafting, T-O-T refers to O atoms bound to two T^n sites, and accounts for homo-condensation. Q-O-T and T-O-Q are calculated per 100 Q.

Materials	% SiOH$_{cons}$ [a]	Q-O-T [b]	T-O-T [c]	T-O-T/Q-O-T
C$_{16}$-Iler-**APTES**	6.1	3.0	< 0.1	< 0.3
Aerosil-**APTES**	5.9	0.8	40.3	48.4
C$_{16}$-Iler-**CPTCS**	60.0	29.3	78.7	2.7
Aerosil-**CPTCS**	47.2	6.7	20.6	3.1

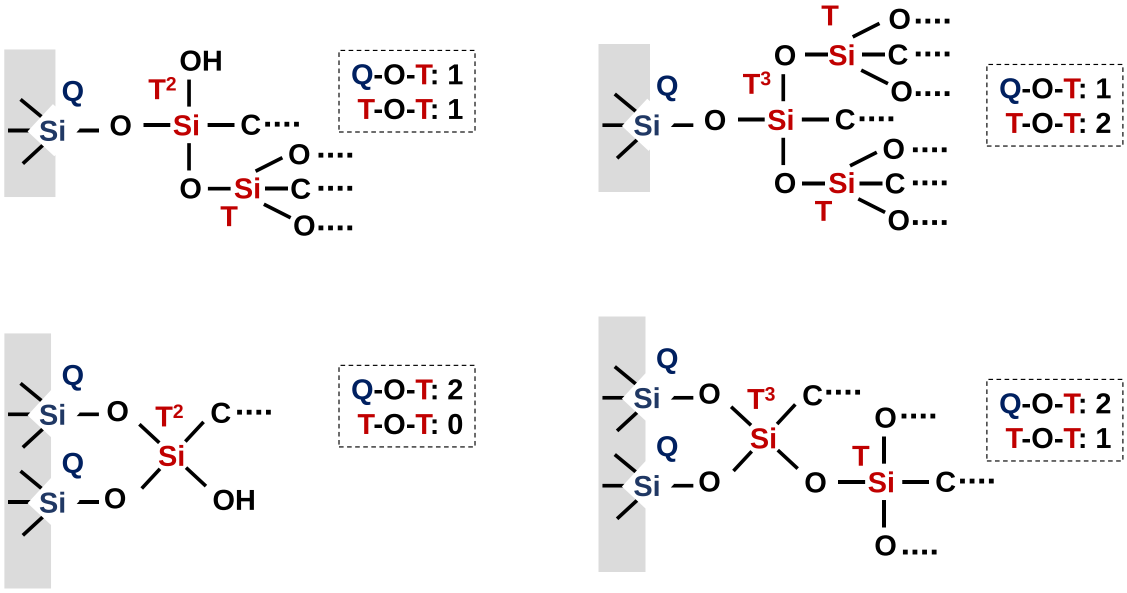
[a] SiOH$_{cons}$ is the % of consumed Si-OH= $100\left(\frac{(Q_i^3+2Q_i^2)-(Q_f^3+2Q_f^2)}{(Q_i^3+2Q_i^2)}\right)$, with i referring to the initial Q and f to the final Q, after reaction with silane

[b] Q-O-T (per 100 Q)= $Q_i^3 + 2 \cdot Q_i^2 - Q_f^3 - 2 \cdot Q_f^2$

[c] T-O-T (per 100 Q)= $3/2 \cdot T^3 + 2/2 \cdot T^2 - 1/2 \cdot$(Q-O-T)

The first observation that can be made from Table 2 is that the percentage of consumed silanols when APTES is used to functionalize silica, whether ilerite or Aerosil, is extremely low, which corroborates the conclusions drawn on the qualitative examination of the DP MAS NMR spectra. Interestingly the value is quite similar for both ilerite and Aerosil silica, ~ 6 % despite the huge difference in terms of amounts of T species (see Table 1). CPTCS assembly on both surfaces induces greater consumption of silanols, up to 60 % for ilerite but a very high value on Aerosil as well with approx. 47 % of silanols consumed. Therefore, if we focus on CPTCS assembly, the difference in crystallinity between the amorphous fumed silica and the crystalline ilerite does not seem to play a significant role in the adsorption process, a result consistent with earlier observations.[52]

The estimated Q-O-T fraction per 100 Q unit, which also accounts for silanols consumption upon grafting, point out a higher number of Q-O-T bridges for ilerite, consistently with its structure containing 50 silanols per 100 Q compared to 14.2 for Aerosil (see Table 1). T-O-T bridges account for homo-condensation, therefore we calculated the ratio T-O-T/Q-O-T to quantitatively assess the extent of homo- versus hetero-condensation. Note that for C_{16}-Iler-APTES, T species were seen on the ^{1}H-^{29}Si CP MAS NMR spectrum (Figure 3) but were below the limit of detection of the ^{29}Si DP MAS NMR, approx. 0.1 per 100 Q. These T species can account for T-O-T or Q-O-T bridges, consequently the ratio T-O-T/Q-O-T is, in all configurations, lower than 0.1/3, i.e. < 0.3.



Scheme 2: Possible configurations for a T^2 or T^3 silicon atom involved in hetero-condensation reactions with silanols together with the corresponding amount of Q-O-T and T-O-T bridges surrounding this atom. The extremely unlikely grafting of a silane via 3 Q-O-T bridges and no T-O-T ones is not represented.

To better visualize the ratio T-O-T/Q-O-T in the context of silane grafting, the possible configurations resulting from a hetero-condensation of alkoxysilanes with silanols are depicted in Scheme 2 together with the corresponding number of T-O-T and Q-O-T bridges. As can be seen in this scheme, the ratio T-

O-T/Q-O-T related to a hetero-condensation ranges between a minimum of 0 (full grafting) and a maximum of 2, when a T^3 is grafted via a unique siloxane bridge. Therefore, any value of T-O-T/Q-O-T significantly higher than 2 accounts for silanes molecules not condensed with silanols but homo-condensed with other silanes. The ratio calculated upon CPTCS assembly on ilerite and on Aerosil silica, 2.7 and 3.1, respectively, are quite consistent with silane grafting on silanols. The small excess of T species possibly results from second-condensed silanes, i.e silane homo-condensed with a silane hetero-condensed with surface silanols, similar to those depicted in the top left part of Scheme 2. In the case of APTES assembly on silica, the T-O-T/Q-O-T ratio, 48.4, is 24-fold higher than the maximum value possible when silane adsorption is related to a hetero-condensation. This is an **unquestionable evidence that APTES is not grafted on the silica surface** but its presence is due to **a new network of homo-condensed silanes**, mainly physisorbed, but with some sparse anchoring points accounting for approx. 5 % of the formed siloxane bridges.

The most plausible explanation for the lack of hetero-condensation of APTES with silanols is the presence of the terminal amine function that catalytically activates the homo-condensation (as well as the hetero-condensation, but the solution's entropy favors the condensation reactions compared to those at the solid interfaces). One main consequence is that the new network of poly-condensed silanes forms very quickly and leads to aggregates formation as previously evidenced by AFM, [21] aggregates that could not penetrate the interlamellar space of the intercalated ilerite which explains the lack of T signal compared to when APTES is assembled on amorphous Aerosil silica. The in-situ kinetical study of T^n species formation by ^{1}H-^{29}Si CP MAS NMR by Kobayashi, Slowing and coworkers showed that, unlike the other silanes, among which nitrile-terminated one, in the case of APTMS no T^1 species are observed including at the very first stages of the interaction, and the total concentration of T^n sites reaches its saturation level within the first 3.5 hours while it takes up to 80 hours for the other silanes. [51] In addition, in the same study, they observed for APTMS that even if the total amount of T^n sites stabilizes within 3.5 hours, the conversion of T^2 into T^3 species continue until approx. 24 hours, this may result from the anchoring of some T^2 sites to silanols by hetero-condensation and could provide a plausible explanation to the dominant proportion of T^3 observed solely for APTES and APTMS compared to other alkoxysilane. Of course, due to the long acquisition time required for ^{29}Si DP MAS NMR, such a kinetic study can not be performed to quantitively estimate the extent of grafting vs condensation. Nevertheless, the quantitative data collected here clearly state that upon APTES interaction with amorphous silica **only one siloxane bridge among 50 comes from hetero-condensation or grafting on silica surface, and**

that ~ 95 % of siloxanes formed during the adsorption of silanes originate from homo-condensation of silanes in solution.

4. Conclusion

We used here ^{29}Si DP MAS NMR to quantitatively revisit the assembly of silanes on silica surface. We selected the most commonly used silane, aminopropyltriethoxysilane (APTES) and also studied a second silane with similar reactivity but without the catalytic input of the terminal amine function of APTES, for instance, cyanopropyltrichlorosilane (CPTCS). In a first part of the study, we used ilerite, a lamellar crystalline silicate, which structure includes 0.5 silanol per silicon atom. The results showed that APTES was not grafted on this silicate, unlike CPTCS. The same results were observed for these two silanes upon interaction with a second layered silicate, magadiite. The data collected using cross-polarized ^{1}H-^{29}Si CP MAS NMR for ilerite, allowed for the amplification of silane species signal at the expense of the quantitative analysis of the data and showed that APTES molecules were present but in amounts below the detection limit of the direct polarization measurement. Upon interaction with a non-porous amorphous silica (fumed silica), and unlike the results obtained for lamellar silicates, both silanes were present on the surface. Nevertheless, the quantitative data collected using ^{29}Si DP MAS NMR undoubtably prove that APTES presence on the amorphous silica surface is the result of homo-condensation between silane molecules and is not related to a hetero-condensation with silanol groups, i.e. grafting, as assumed within the community working on silica and silicate surfaces functionalization. A large bundle of evidences suggests that APTES molecules quickly undergo homo-condensation reactions in solution leading to aggregates formation, whose size prevents them from penetrating the interlayer space of layered silicates such as ilerite or magadiite but does not prevent them from attaching to the amorphous silica surface through physisorption or even, in some extent, through hetero-condensation reactions with silanols that would take place in a second timescale, and remain limited to approx. 5% of the siloxane bridges formed upon APTES interaction with silica. The data collected using cross-polarized ^{1}H-^{29}Si CP MAS NMR was quite convenient for obtaining a crude understanding of how the silica and silicate surfaces have reacted. However, if used quantitatively, it can greatly overstate the extent of grafting that has occurred. In the light of these data, APTES assembly on silica should no longer be seen as grafting of alkoxysilane by hetero-condensation with silanol groups but more accurately as a homo-condensed network of silanes, predominantly physisorbed on the surface but including some sparse anchoring points to the surface accounting involving less than 6 % of the overall silanols groups.

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Supporting Information. XRD, FTIR and SEM data obtained using magadiite as starting silicate and CP-MAS characterization of silanes condensation on Ilerite.

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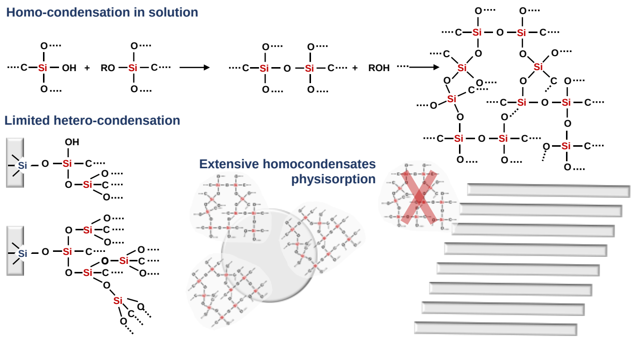

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